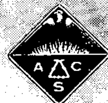


ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Information on Scientific Apparatus

ATTENTION of our readers is called to the existence of the Scientific Apparatus Information Service, a divisional activity of UNESCO.

From a practical viewpoint we believe that this service will be of more practical assistance to analytical chemists in countries other than the United States. Nevertheless, the history and scope of its activities will interest many of our readers.

During the Conference of Allied Ministers of Education in London, when many requests were received for information on scientific equipment, the idea of an international noncommercial Scientific Apparatus Information Bureau was conceived. The Science Commission of the Conference of Allied Ministers of Education responded to such requests as best it could and when the conference was liquidated, suggested that UNESCO organize a similar service to help scientists all over the world.

The first session of the general conference (Paris 1946) accepted this suggestion and authorized the secretariat to set up a Scientific Apparatus Information Service (SAIS) in 1947. The staff then available was entirely occupied with the urgent task of scientific reconstruction of war-devastated countries. Nevertheless, the second session of the general conference (Mexico City 1947) endorsed the previously approved activities of SAIS and included them in the program for 1948.

The scope of this service is deliberately limited to answering queries concerning scientific and technological equipment for education and research in the pure and applied sciences. It is also being equipped to satisfy the need among scientific workers for information on new materials and equipment developed in recent years.

The equipment of SAIS, rudimentary as yet, consists of:

1. Up-to-date catalogs of the principal scientific manufacturers of the world and information on the newest developments in the fields of instruments.
2. Important periodicals dealing with scientific instruments.
3. Technical journals published by the leading industrial concerns.
4. A card index of scientific instruments with cross references and related to a World Index of Scientific Manufacturers.

In order to enhance the efficiency of SAIS and extend the available services of information, assurances of close cooperation were obtained from sixteen representatives of scientific apparatus manufacturers in nine leading countries, at a specially convened meeting at UNESCO House in Paris in June 1948. Contacts are being extended to include universities, research associations, and international scientific unions.

In addition to providing technical assistance in operating the Science Credit Scheme for the purchase of equipment for the war-devastated countries, SAIS has been responding during the past year and a half to the queries from UNESCO's Science Cooperation Offices, science institutions, and individual scientists.

ANALYTICAL CHEMISTRY shortly will expand its services to readers in disseminating information about scientific apparatus and equipment. For several years Ralph H. Müller's column on Instrumentation has acquainted readers with the rapid strides being made in the development and use of instruments. We will introduce a section on industrial literature and manufacturers' announcements of new scientific apparatus, instruments, and materials of direct interest to the analyst.

The widespread use of comparable information in both *Chemical and Engineering News* and *Industrial and Engineering Chemistry* has demonstrated conclusively the value of such information to our readers. Each such item of information in *C.&E.N.* and *I.&E.C.* is carefully screened by our editorial staff to ensure that what does appear is important and new. A similar policy will be followed in ANALYTICAL CHEMISTRY.

The Analyst's Role in Increasing Crop Yields

THE scientific approach to the problem of increasing food yields to feed more adequately a constantly increasing world population is gaining acceptance at a highly satisfactory rate. Rule of thumb procedures are rapidly disappearing as scientists apply objective methods to provide truly scientific answers to questions which have long baffled those seeking to improve the quality and increase the quantity of foods the world over.

Robert M. Salter, chief of the U. S. Department of Agriculture's Bureau of Plant Industry, Soils, and Agricultural Engineering, speaking at the fourth annual convention of the American Plant Food Council at Bretton Woods last month, reported that while one improved method of crop production is beneficial, the advantages often pyramid when several good practices are used in the right combination. Recognition of this principle is spreading rapidly in research programs in this and other countries. Continuing, Dr. Salter stated:

> So far we have no more than scratched the surface with this combined approach to research. We have by no means exhausted the possibilities of still further increasing crop yields as we learn to combine in optimum degree the various factors of crop production under the diverse environments of soil and climate. We now recognize that past ideas of what constituted adequate facility must now be revised drastically upward if we are to strive for top yield through this combined approach.

The chemical analyst will continue to play a very important and significant role in soil science. Improved analytical methods are providing soil scientists with more accurate analysis of soils. In every step along the way to better food yields, the analyst is offered a challenging opportunity to extend present knowledge. As in most other fields of human endeavor, the analyst is essential to the successful conclusion of any program of uncovering the secrets of nature and the application of new knowledge to improving the material well-being of man.

Polarographic Studies of Organic Peroxides in Nonaqueous Solutions

W. R. LEWIS[1], F. W. QUACKENBUSH, AND THOMAS DE VRIES
Purdue University, Lafayette, Ind.

A procedure is outlined for the polarographic study of water-insoluble materials in nonaqueous solutions. Current-voltage curves for the peroxides of fats, ethers, and hydrocarbons are given. In early stages of autoxidation of fats, a linear relationship exists between wave height and peroxide number. In very advanced stages of autoxidation, the polarograph does not reduce all the substances that are reduced by iodides in acidic solution. Three waves appear in the current-voltage curves of fat peroxides in neutral solution.

IN A study of the oxidation of fats, it was desirable to distinguish between reactive and stable peroxides. Fat peroxides are a poorly defined group of compounds which are thought to vary appreciably in reactivity. However, the methods commonly used which are based on the oxidation of iodide or ferrous ions, offer little opportunity to distinguish between reactive and relatively stable peroxides. A study was made with the polarograph, and when suitable conditions were established, several waves were obtained for the autoxidation products of fats.

Procedures for the polarographic determination of a few organic peroxides in aqueous media have been described. Dobrinskaya and Neiman (*2*) determined methyl hydroperoxide in mixtures with aldehydes. Later Shtern and Pollyak (*5*) determined methyl hydroperoxide, ethyl hydroperoxide, ethyl peroxide, etc., in several aqueous electrolyte solutions. However, the peroxides of many larger relatively nonpolar molecules cannot be determined by similar procedures because of solubility limitations. In the present work nonaqueous media were used.

EQUIPMENT AND REAGENTS

The current-voltage curves were obtained with a Leeds & Northrop Electrochemograph. The m and t values for the capillary were determined at 25° C. with an open electrical circuit and the tip dipping into a 0.3 M solution of lithium chloride in a mixture of equal volumes of absolute methanol and benzene. The values of m and t were 2.76 mg. per second and 2.10 seconds, respectively. Therefore, $m^{2/3} t^{1/6}$ was 2.13 mg.$^{2/3}$ $t^{-1/2}$. At −0.70 volt with a closed circuit m and t were 2.10 mg. per second and 1.56 seconds. At this potential $m^{2/3} t^{1/6}$ was 1.77 mg.$^{2/3}$ $t^{-1/2}$. A short drop time was used because it completely eliminated oscillations in the polarograms recorded by the Electrochemograph.

Two types of electrolysis cells were used. One utilized a mercury pool anode approximately 6.2 sq. cm. in surface area. Results obtained with this cell were satisfactory only in a neutral supporting electrolyte solution because the potential of the pool did not remain constant in acidic or alkaline solutions. In the alkaline solutions the peroxides reacted with the mercury of the pool. The other cell was an H-cell of the type described by Lingane and Laitinen (*4*), which utilized an external saturated calomel half-cell. The H-cell gave reproducible curves in all three electrolytes over the entire range of voltage which could be used with these electrolytes. The H-cell was used for all data reported herein except those dealing with gasoline peroxides. The polarograms of gasoline peroxides were obtained with a mercury pool anode before it was learned that the H-cell gave more satisfactory results.

Solvents. The most suitable solvent investigated for use in studying autoxidation of fats was a solution of equal volumes of methanol and benzene. Mallinckrodt's analytical reagent absolute methanol was satisfactory without further purification. Barrett & Company's thiophene-free benzene was also satisfactory as received. Two other brands of thiophene-free benzene contained an impurity which interfered, but could be removed by vigorously shaking 1 liter of benzene with 100 ml. of concentrated sulfuric acid in a separatory funnel for 10 minutes at room temperature, drawing off the sulfuric acid, and distilling the unreacted benzene.

The effect of traces of water in the solvents has not been carefully investigated. However, addition of 1% of water to each of the three supporting electrolyte solutions had little effect on the current-voltage curves of oxidized lard except to alter somewhat the ratio of the height of the three waves obtained. Consequently, the electrolyte should be anhydrous if quantitative results are to be obtained. That the solvents used were essentially anhydrous was shown by placing a few particles of anhydrous copper sulfate and 5 ml. each of methanol and benzene in a stoppered test tube and shaking occasionally. After standing for a day, the copper sulfate was still white. However, in the case of the methyl hydrogen sulfate supporting electrolyte solution 3.6 grams of water per liter were formed by the reaction of methanol and sulfuric acid. This water was not removed.

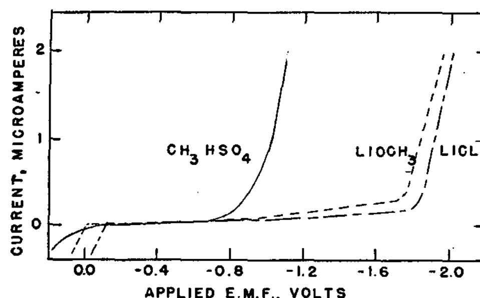


Figure 1. Residual Current Curves for Three Electrolytes
H-cell used for all three curves

Supporting Electrolytes. A supporting electrolyte solution must possess two properties if it is to be useful for the determination of fat peroxides. It must be capable of dissolving appreciable quantities of fat, and it must offer low electrical resistance, a property that was found very important for the production of polarographic waves with desirable characteristics. Solutions of high resistance gave waves which were drawn out over a considerable voltage range and usually had pronounced maxima. Reasonably satisfactory curves were not obtained with solutions which caused the minimum resistance of the unpolarized electrolysis cell appreciably to exceed 4000 ohms. A lower resistance is desirable. The resistance of the cells used was 3500 to 4000 ohms.

Three supporting electrolytes, which differed markedly in

[1] Present address, Research Laboratory, Kingan and Co., Indianapolis 6, Ind.

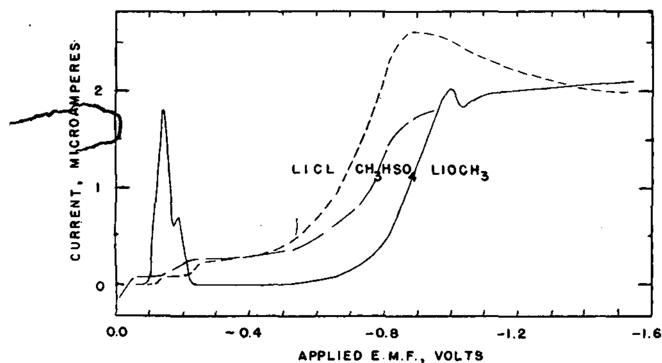


Figure 2. Reduction Curves of Lard Peroxides in Three Electrolytes
H-cell used for all three curves

acidity, gave information that was useful in studying the products of autoxidation of fats and related materials. Figure 1 shows the residual current curves for these supporting electrolyte solutions when a saturated calomel H-cell was used.

Methyl Hydrogen Sulfate Supporting Electrolyte Solution. The strongly acidic supporting electrolyte used was a 0.2 *M* solution of methyl hydrogen sulfate in equal volumes of absolute methanol and benzene. It was prepared by adding 0.2 mole of analytical reagent grade sulfuric acid to 500 ml. of methanol and 500 ml. of benzene in a flask and refluxing the resulting solution for 30 minutes or longer. Titration indicated that the sulfuric acid was quantitatively converted to methyl hydrogen sulfate by this procedure.

Lithium Chloride Supporting Electrolyte Solution. A satisfactory neutral supporting electrolyte was a solution of 0.3 *M* lithium chloride in equal volumes of absolute methanol and benzene. It was prepared by adding 12.72 grams of lithium chloride (C.P.) to a solution containing 500 ml. of methanol and 500 ml. of benzene. A study of various electrolyte concentrations showed that higher concentrations of lithium chloride decreased the resistance of the cell and somewhat improved the shape of the waves obtained. However, as the salt concentration was increased, the solubility of fat in the solution decreased. Because a 0.3 *M* solution of lithium chloride would dissolve only about 2% of fat, more highly concentrated electrolyte solutions were not found practicable.

Lithium Methoxide Supporting Electrolyte Solution. A 0.1 *M* solution of lithium methoxide was prepared by immersing a 1- to 2-gram piece of pure lithium metal in methanol until the surfaces became shiny, and then quickly transferring the metal to a flask containing about 400 ml. of methanol into which hydrogen was continuously bubbled. After the reaction was complete, an aliquot of the solution was diluted with water and titrated with standard hydrochloric acid. The lithium methoxide solution was then diluted to exactly 0.2 *M* with methanol. The 0.2 *M* solution was diluted with an equal volume of benzene.

Sodium methoxide and lithium methoxide electrolyte solutions gave similar reduction curves with rancid lard. When a 0.1 *M* solution of either electrolyte was used, half-wave potentials were identical and wave heights were only slightly different. However, the maximum which appeared at −1.0 volt with some samples of rancid lard was larger and more frequently present when the sodium methoxide electrolyte was used than when the lithium methoxide electrolyte was used (Figure 2). Therefore, a 0.1 *M* lithium methoxide electrolyte solution was used in this study.

A 0.1 *M* concentration of lithium methoxide was chosen because that concentration gave waves of desirable shape without excessive destruction of peroxides due to the high alkalinity of the solution. Lower concentrations resulted in cells of excessively high resistance. Higher concentrations decreased the height of the maximum which occurred at −0.1 to −0.2 volt and also of the small wave on which the maximum appeared (Figure 2).

PROCEDURE

Transfer 10 ml. of electrolyte solution to the cathode compartment of the H-cell. Bubble oxygen-free nitrogen through the solution for 1 minute, then add 20 to 200 mg. of oxidized fat, depending upon the peroxide content of the fat. Fit a cork on the capillary in the correct position to stopper the H-cell loosely when the capillary is lowered into the solution to be analyzed. Continue to bubble nitrogen through the solution for 2 minutes, then pass nitrogen over the surface of the solution during the remainder of the time required to obtain the polarogram. After the polarogram has been obtained, rinse the capillary and the H-cell with methanol. Connect the cathode compartment of the H-cell to a vacuum line and evacuate for at least 10 minutes. This step is essential if reproducible results are to be obtained. If the H-cell is not to be used again for several hours, fill the cathode compartment with aqueous potassium chloride solution.

The peroxide numbers given in this paper were determined by the Wheeler method (*6*), which is based on the oxidation of iodide ions in a chloroform-acetic acid solution. When the peroxide number of oxidized methyl linoleate was determined, the method was modified to exclude all oxygen from the reagents and the atmosphere over the reaction mixture, and the reaction time was extended to 30 minutes. The peroxide number as used in this paper is the number of millimoles of peroxide oxygen per kilogram of fat or per liter of gasoline or ether.

EXPERIMENTAL

Fat Peroxides. The oxidized fats used in these studies were prepared by weighing 10 grams of fat into a 6-cm. Petri dish and placing it in a 100° C. oven for a suitable length of time. The concentration of fat used in the electrolyte solutions was varied with the degree of oxidation of the fat. In early stages of oxidation, 2% of fat was dissolved in the electrolyte solution. At this concentration it was possible to obtain significant waves for autoxidation products before the peroxide number reached 1.0.

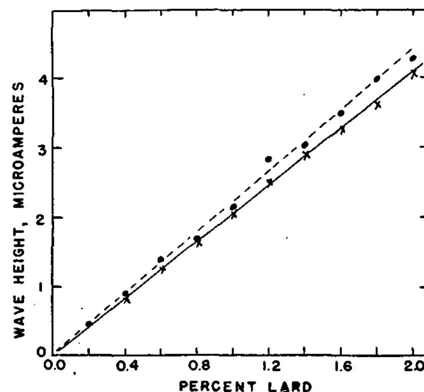


Figure 3. Relation between Wave Height and Concentration of Lard Oxidized to Peroxide Number 40

-·-·- Lithium methoxide supporting electrolyte. Wave height measured at −1.4 volts
-x-x Lithium chloride supporting electrolyte. Wave height measured at −1.7 volts

The height of the waves given by 0 to 2% of rancid lard in either the lithium chloride or the lithium methoxide electrolytes was directly proportional to the concentration of rancid lard when the wave height was measured at −1.7 and −1.4 volts, respectively (Figure 3). A similar relationship could not be accurately established in the methyl hydrogen sulfate electrolyte because when the wave at about −0.8 volt was large, it did not reach a plateau before the hydrogen wave began. However, wave height was roughly proportional to the concentration of rancid fat.

Solutions of oxidized fat in the electrolytes did not change significantly on standing 30 minutes at room temperature. However, the characteristics of the curves were appreciably altered if the solutions were allowed to stand for several hours. Consequently, solutions were always prepared immediately before the current-voltage curves were obtained. Solutions of oxidized

fat in the strongly alkaline lithium methoxide electrolyte were observed to change less rapidly than the neutral or acidic solutions. However, because only two waves were obtained from lard peroxides in the lithium methoxide solution, one type of peroxide may have been almost instantly destroyed in the alkaline medium. This seems possible in light of the fact that benzoyl peroxide gave no wave in the alkaline electrolyte solution but did give two waves in either neutral or acidic solution (Figure 6).

Typical current-voltage curves for oxidized lard in acidic, neutral, and alkaline supporting electrolyte solutions are shown in Figure 2. Each electrolyte solution contained 0.5% of lard oxidized to a peroxide number of 48. The curves have been corrected for the residual current obtained with the electrolyte alone. The curves of fresh fats did not differ significantly from the curves of the electrolyte alone. The potentials are referred to the saturated calomel electrode but are not corrected for the liquid junction potential. The potentials given elsewhere in this report, with the exception of the figure concerning gasoline peroxides, are also referred to the saturated calomel electrode and are uncorrected for the *IR* drop of the cell or liquid junction potentials. Reference to the residual current curves of Figure 1 will show that the correct position for the beginning of the first wave on each of the three curves is somewhat in doubt because in each case the curves for the electrolyte solution alone began to change rapidly at potentials which were more negative than the beginning of the wave for the peroxides. The small maximum at −0.19 volt which follows the large maximum in the curve obtained with the lithium methoxide electrolyte is due to the characteristics of the recording instrument and does not accurately represent current-voltage relationships on this portion of the curve.

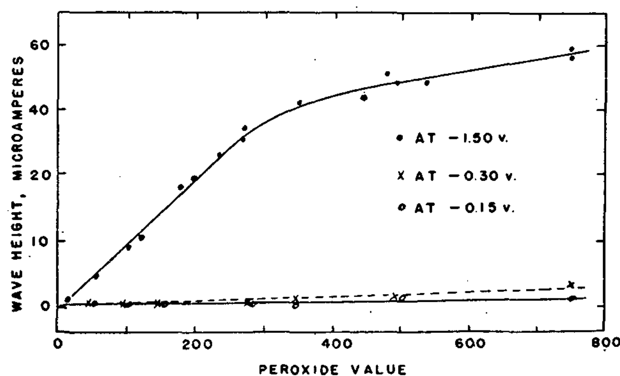


Figure 4. Relation between Peroxide Number and Wave Height

Data obtained from methyl linoleate oxidized at 40° C. Concentration of methyl linoleate in 0.3 *M* lithium chloride, 1%

Similar characteristic curves have been obtained with refined corn, cottonseed, soybean, peanut, and coconut oils. The method is currently being applied to the study of autoxidation of edible fats and related substances.

Relation of Peroxide Number to Wave Height. The relation that exists between peroxide number and wave height is shown in Figure 4. On the vertical axis is plotted the height of the waves obtained when 1% solutions of oxidized methyl linoleate in the lithium chloride supporting electrolyte were analyzed. The polarograms of the peroxides of methyl linoleate were similar to those of lard peroxides shown in Figure 2. If the polarographic and the chemical methods determined the same structures, a linear relation would exist. The lower line, which is nearly parallel to the horizontal axis of Figure 4, shows the relation between peroxide number and the height of the first small wave measured at −0.18 volt. The broken line indicates the height

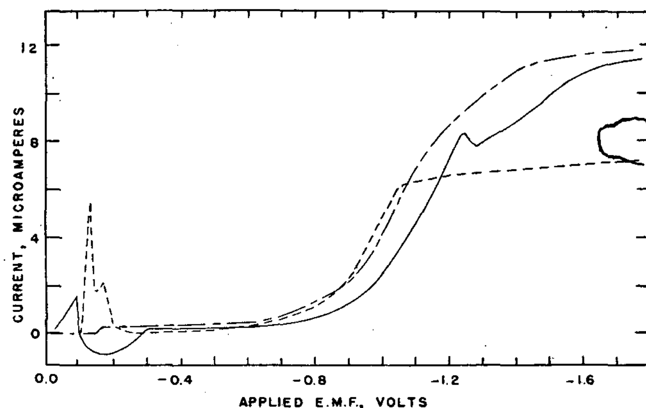


Figure 5. Ether Peroxides

--- Isopropyl ether, peroxide number 33, lithium chloride supporting electrolyte
—— Isopropyl ether, peroxide number 33, lithium methoxide supporting electrolyte
----- *n*-Butyl ether, peroxide number 13, lithium methoxide supporting electrolyte
Saturated calomel H-cell used for all three curves

of the second small wave measured at −0.30 volt. A linear relation appeared to exist between the height of these two small waves and peroxide value. However, the reproducibility of the height of these waves was only about ±20%. Consequently, deviations from linearity would not have been detected unless the deviations were rather large. A linear relation existed between the wave height measured at −1.50 volts and peroxide value until the peroxide value reached 275. Thereafter, the slope of the line decreased, indicating that the chemical method determined one or more structures which the polarographic method did not. The height of the large wave was reproducible to within ±5%.

Ether Peroxides. Peroxides were removed from samples of three ethers by the chromatographic technique described by Dasler and Bauer (*1*). Autoxidation was accelerated by bubbling air through the samples during refluxing. Before oxidation, the ethers gave no waves with any of the electrolytes. The methyl hydrogen sulfate electrolyte gave no useful wave with ethyl, isopropyl, or *n*-butyl ether peroxides. The lithium chloride and lithium methoxide electrolytes each gave waves with all these peroxide-containing ethers. The curve given by isopropyl ether peroxides in the alkaline electrolyte differs uniquely from all other peroxides which the authors have studied, in that a negative current was obtained between about −0.1 and −0.26 volt (Figure 5). This was observed on two occasions with isopropyl ether from different sources. No plausible explanation is offered for this anomalous result. The curve for *n*-butyl ether in lithium methoxide is included in Figure 5 to show the differences in these two ether peroxides. The general shape of the curve given by isopropyl ether peroxides in the lithium chloride electrolyte was also obtained with ethyl and *n*-butyl ethers.

Benzoyl Peroxide. Benzoyl peroxide was included in this study because it has been used for comparative purposes in fat autoxidation studies. Figure 6 shows the curves obtained from 0.001% benzoyl peroxide using three electrolytes. Apparently benzoyl peroxide was very rapidly destroyed in the alkaline electrolyte solution.

Gasoline Peroxide. A sample of gasoline was distilled to remove inhibitors. Autoxidation was accelerated by bubbling air slowly through the solution while it was refluxed. Peroxide numbers and current-voltage curves were obtained at intervals. Some of the curves are shown in Figure 7. The mercury pool was used as the anode and the potentials given are referred to it. Much gum formation occurred before the gasoline reached a peroxide number of 43. It is possible that these polymerization

products may have been responsible for the pronounced changes in the character of the curves which were obtained from the highly oxidized samples.

The three supporting electrolytes were not equally useful for polarography of gasoline peroxides. Unoxidized gasolines gave a wave when the methyl hydrogen sulfate electrolyte was used, and oxidized gasoline gave no additional useful waves. Unoxidized gasoline gave no wave with either the lithium methoxide or the lithium chloride supporting electrolytes, but gasoline peroxides gave waves in each of these electrolytes. When 10 ml. of gasoline were added to 100 ml. of the electrolyte, 0.1 millimole of peroxide oxygen per liter of gasoline could be detected.

The gasoline for which the curves are given was probably a high olefin gasoline. Another brand of gasoline which was much more stable toward autoxidation gave very different curves. No further work was done with gasoline peroxides, because the authors were interested principally in showing that the method constitutes a useful tool for the petroleum laboratory as well as for the fats laboratory.

DISCUSSION

The procedure and reagents used in this study frequently do not give polarograms in which the waves are as well defined and as regular in shape as those usually obtained in aqueous solutions. Consequently, no attempt has been made to give precise values for half-wave potentials. The values given have been corrected for residual current but not for the *IR* drop across the cells. Because the resistance of the cells used was approximately 4000 ohms, the *IR* drop would be approximately 4 millivolts per microampere.

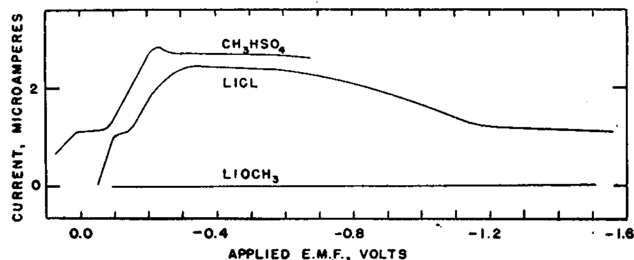


Figure 6. Benzoyl Peroxide in Three Electrolytes
H-cell used for all three curves

Several maximum suppressors were tried, but none was effective. Gelatin was not soluble to any appreciable extent in the electrolytes. Methyl red and methylene blue were completely ineffective. Salts such as aluminum acetate and trisodium phosphate were also ineffective.

The waves for fat peroxides which appeared at −0.12 and −0.23 volt in the lithium chloride electrolyte are too close together to provide good precision in measuring either wave. However, the sum of the heights of these two waves or the height of the third wave could be determined with a precision of ±5%, unless very low concentrations were to be determined.

The sensitivity of the method permits detection of less than 1 milliequivalent of peroxide per kilogram of fat. The solubility of gasoline or ethers in the electrolyte solutions is greater than the solubility of fats. Consequently, 0.1 milliequivalent of gasoline or ether peroxides per liter can be detected.

The lithium chloride supporting electrolyte solution has proved to be the most useful of the three that were used. It gives waves that appear to correspond to the waves obtained in the alkaline and acidic electrolytes without the interference of the hydrogen wave obtained in acidic solution or the large maximum and probably peroxide destruction obtained with the lithium methoxide solution.

The procedure outlined has been used for a more extensive study of oxidized fats and fatty esters (*3*). It is suggested that this technique may profitably be used in the study of reaction mechanisms, the mode of action of inhibitors, and the kinetics of autoxidations.

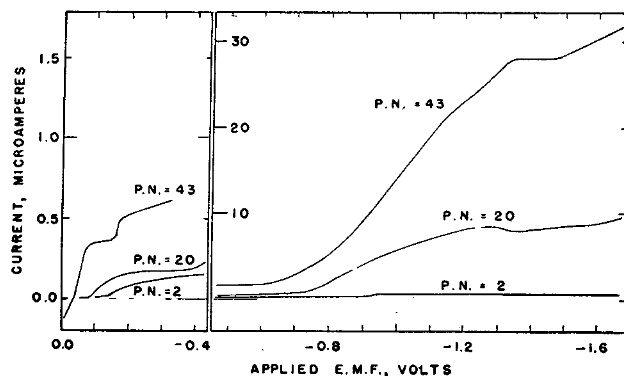


Figure 7. Gasoline Autoxidation Products
Lithium chloride supporting electrolyte. Mercury pool anode. P.N. = Peroxide number

SUMMARY

A polarographic procedure is outlined which permits polarographic study of water-insoluble peroxides, such as those which form in fats, ethers, and hydrocarbons. With each of these substances, more than one wave is obtained for the autoxidation products. The precision of measurement is within ±5% for fats with a peroxide number of 5 or higher. A linear relation exists between the peroxide number determined by a modification of the Wheeler method and wave heights until the peroxide number exceeds 250. Thereafter, wave heights do not increase as rapidly as peroxide numbers.

ACKNOWLEDGMENTS

The authors wish to acknowledge the many helpful suggestions which were made by James B. Martin of the Agricultural Chemistry Department, Purdue University, during the development of this method. They also thank H. A. Laitinen, of the Department of Chemistry, University of Illinois, for suggesting the use of a mixture of methanol and benzene as a solvent and for other helpful advice.

LITERATURE CITED

(1) Dasler, Waldemar, and Bauer, C. D., Ind. Eng. Chem., Anal. Ed., 18, 52 (1946).
(2) Dobrinskaya, A. A., and Neiman, M. B., *Zavodskaya Lab.*, **8**, 280 (1939).
(3) Lewis, W. R., and Quackenbush, F. W., *J. Am. Oil Chem. Soc.*, 26, 53 (1949).
(4) Lingane, J. J., and Laitinen, H. A., Ind. Eng. Chem., Anal. Ed., **11**, 504 (1939).
(5) Shtern, V., and Pollyak, S., *Acta Physicochim. U.R.S.S.*, **11**, 797 (1939).
(6) Wheeler, D. H., *Oil & Soap*, **9**, 89 (1932).

Received June 16, 1948. Journal Paper 354 of the Purdue University Agricultural Experiment Station. The subject matter of this paper was undertaken in cooperation with the Committee on Food Research of the Quartermaster Food & Container Institute for the Armed Forces. The opinions or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or endorsement of the War Department.

Determination of Water in Freon 12

W. A. PENNINGTON
Carrier Corporation, Syracuse, N. Y.

A modification of the phosphorus pentoxide absorption method for determining water in Freon 12 is suitable for use where an accuracy of 1 p.p.m. is desired. Such accuracy can be attained for moisture contents up to at least 35 p.p.m. The recommended technique requires from 18 to 24 hours for an analysis, but no more than 0.5 man-hour of actual work per analysis. The method is especially suitable for research investigations where no unusual speed is necessary.

REFRIGERANTS, particularly Freon 12, are analyzed for water content for at least two reasons: to find whether the material meets certain exacting specifications and to ascertain the dryness of a refrigerating system through an analysis of the refrigerant removed from it. This analysis may be especially useful on systems having a hermetic compressor and a permanent drier containing an adsorbent desiccant.

A technique developed in this laboratory can be relied upon for an accuracy of 1 p.p.m., where a sample of as much as 300 grams is used, even with a moisture content as high as 35 p.p.m.

In this determination as in no other known to the writer, obtaining check results cannot be accepted as proof of accuracy. Precise checks indicate only a uniform sample and a well defined, specific technique. Poor technique can "beget water"; it is possible to make an error of as much as 3 p.p.m. with checks that may be more than comforting to the analyst.

METHODS AVAILABLE

A search of the literature revealed only one method readily adaptable to the determination of water in refrigerants (*2*)—essentially that recommended by Kinetic Chemicals, Inc. (*3*).

In both cases phosphorus pentoxide, P_2O_5, is used as the absorbent. The phosphorus pentoxide is mixed with asbestos to provide adequate gas passage with a fairly low differential pressure. Griest (*2*) used Swartz tubes for the absorbent mixture; Kinetic Chemicals (*3*) recommended a tower. Both took the refrigerant sample in an open filter flask from which it was distilled through the gas train.

There are two serious objections to such procedure: The flow of refrigerant cannot be controlled adequately, and owing to fractionation, serious changes in moisture content occur from the time the sample is taken until it is analyzed.

A method recently described by Benning, Ebert, and Irwin (*1*) makes use of infrared spectrophotometry. The method was not available to this laboratory for the research that led to the method described here. The authors claim an accuracy of 1 p.p.m. where the moisture is not more than 10 p.p.m. They point out that several compounds interfere with the analysis of impure refrigerant samples, and suggest a preliminary distillation to eliminate oil interference.

Weaver and Riley (*4*) recently adapted electrical conduction in a thin film to the measurement of water in gases.

APPARATUS

Sample Cylinder. One of the first requirements was a cylinder that could be dried easily to hold the refrigerant, without leakage, until the technician was ready to carry out the analysis. The one shown in Figure 1 is made of copper and provided with two angle valves, one from the liquid and the other from the gas. The liquid-side valve is convenient in taking the sample; the gas-side serves as an outlet during the distillation.

Absorption Train. The working train shown in Figure 2 consists of three Nesbitt bulbs in series placed in a wooden box. Rubber bands hold the bulbs in place against a strip of steel down the center. A hinged top protects the bulbs from dirt and breakage. The gas is led into and out of the box through a short length of copper tubing which is rigidly fastened to the wood by means of a copper collar.

A mixture of equal volumes of phosphorus pentoxide and asbestos is held in the center portion of the bulbs by glass wool at top and bottom. The bulbs are connected by rubber tubing, in which glass inserts are placed to reduce to a minimum the contact area of rubber tubing to refrigerant.

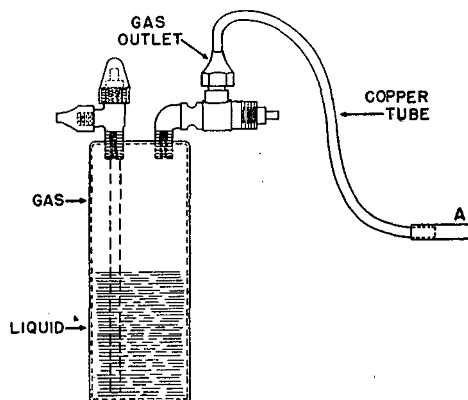


Figure 1. Sample Cylinder

With bulbs properly packed, all moisture will be absorbed in the first bulb within a short travel into the phosphorus pentoxide. The first, second, and third bulbs are in the order shown in Figure 2 from left to right. The gas enters the phosphorus pentoxide at the bottom and leaves at the top, going from bulb 1 to 2 and on to 3.

A Nesbitt bulb has much greater volume than brass weights; therefore its weight will change with different conditions, even though the mass is constant. With the same mass a difference in weight of 2 mg. with widely varying conditions is possible—about 7 p.p.m. on a 300-gram sample. As compensation for this, another bulb (No. 3 in the train) serves basically as a "tare" in weighing. The tare bulb should be the lighter in weight; brass weights will be needed on the right pan to achieve the final balance. The idea of the tare's being put in the train is to treat all bulbs alike, except that only the first has a chance to get the water.

Good analyses are possible with two bulbs, but extreme care is necessary—for example, the chemical balance must be examined thoroughly each time a weighing is made. To avoid such extreme care, a second bulb used between the first and third is the real protected standard. Bulbs 1 and 2 are weighed, using No. 3 as a tare, at the beginning and end of a run. The change in weight for bulb 2 (ΔW_2) may be due to a change in the balance or to something that has happened to bulb 3. The change in weight for bulb 1 (ΔW_1) includes not only this same change, but also another change due to moisture absorption. It follows that the weight of water absorbed (ΔW) may be given as

$$\Delta W = \Delta W_1 - \Delta W_2 \qquad (1)$$

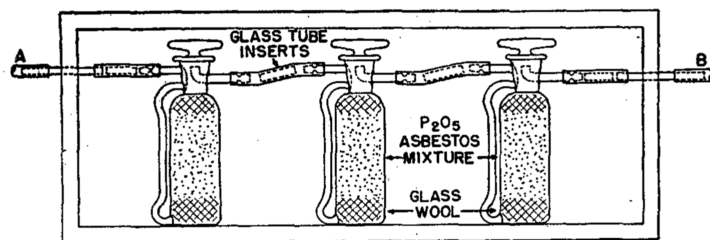


Figure 2. Absorption Train

Bulb 3 is also weighed with brass weights only, but this weight is not used to determine the moisture. When certain kinds of trouble prevail it becomes useful.

Dry Air Supply. A continuous supply of dry air is necessary, so the refrigerant can be flushed from the train at any time without fear of trouble. The assembly used is shown in Figure 3.

Two towers hold the phosphorus pentoxide, the second always being kept in excellent condition as a precaution. The safety trap prevents the build-up of a high pressure in the train if accidentally closed.

Before the spare Nesbitt bulb, shown on the end of the line, was used the air supply gave too much gain in the first bulb of the absorption train. The rubber stopper at the top of the second tower probably caused the trouble.

Air passes through the supply train constantly. At least once a month it is checked and, if not satisfactory, the rubber tubing is heated in an evacuated flask for about an hour at 175° F. The reassembled train is then checked again.

Until recently a sulfuric acid bubbler was used in the line immediately preceding the first tower to indicate the rate of air flow. As it was suspected of causing trouble under certain conditions, a temporary bubbler containing a concentrated water solution of lithium bromide (about 60%) is now used at the end of the air supply line to regulate the flow. A good rate is about 4 bubbles per second.

CHECKING THE ABSORPTION TRAIN

Before an analysis, the absorption train should be checked by passing dry air through it for a considerable length of time. Such precaution serves as a test both of the nature of the dry air and of the analyst.

The copper tube entering the box should be dried before air is allowed to flow through the bulbs. This drying can be accomplished with the passage of dry air for about an hour. It is practically possible never to expose the inside of the tube to anything except refrigerant and dry air. At this point, connections are made through the train with the stopcocks open. The lithium bromide bubbler is used on the end of the train to determine that the air is flowing through at a desirable rate.

If the air supply is really pure and dry, it can be passed through the train indefinitely without giving any change in ΔW. For this reason, a long air check (overnight) is made, to discover when impurities are causing trouble. These impurities may come from the air supply train or they may actually be in the absorption train. Reaction products from rubber and sulfuric acid mist could cause the former; entrained oil, the latter.

After the air sweep, the box may be disconnected and taken to the balance room, or, as in this laboratory, left connected to the dry air supply. The bulbs are left open, taken out of the box, wiped carefully with a clean, dry cloth, and allowed to stand for an hour. An electric blower may be used to free the bulbs of dust, while the air sweep is being made. Electrostatic charges are produced by wiping and under some conditions cause serious trouble.

At the expiration of the temperature and pressure equalization period, the bulbs are weighed while still in the open position, then returned to their box and dry air is allowed to pass through until they are needed again.

If contaminations in the laboratory air make it inadvisable to leave the bulbs open, the conventional procedure, in which the bulbs are closed, should be used in spite of its shortcomings. High concentrations of ammonia in the air should be avoided if the new technique is used. It is not necessary, however, to have constant conditions in the laboratory. Ordinary temperature changes, even with a considerable movement of air, will not cause the pickup of appreciable water in 2 hours.

Data given in Table I indicate the type of results expected on check runs involving the air sweep only. The limit for ΔW for a 16-hour sweep has been set at 0.0003 gram on the positive side; a value lower than -0.0001 has not been found.

CLEANING THE SAMPLE CYLINDER

A new sample cylinder (Figure 1), made through the use of silver solder, must be treated to remove flux or moisture-holding compounds. For this purpose, water is charged into the evacuated cylinder and boiled for 1 hour at 30 pounds per square inch gage (21,000 kg. per square meter). The water is poured out and the open cylinder is placed in an oven at 300° F. for an hour or more. While still hot, it is evacuated to a high degree of vacuum (as low as 30 microns).

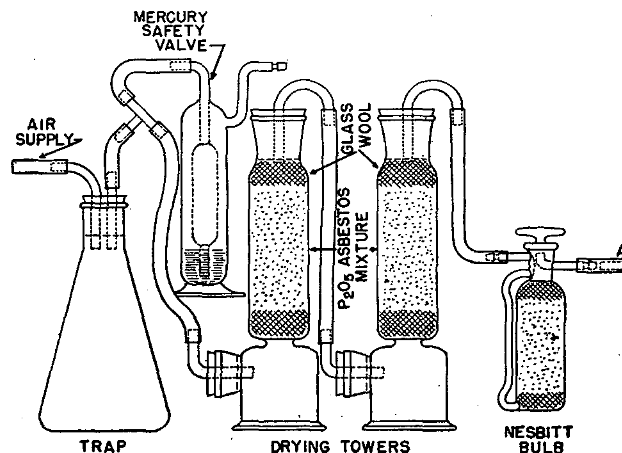


Figure 3. Train for Drying Air

Table I. Check on Absorption Trains

Time, Hours	ΔW_1	ΔW_2	ΔW
22	0.0000	0.0000	0.0000
64	0.0002	0.0000	0.0002
17	0.0001	0.0001	0.0000
18	0.0003	0.0002	0.0001
18	−0.0001	−0.0001	0.0000
16	−0.0005	−0.0007	0.0002
16	0.0000	−0.0001	0.0001

Once the sample cylinders have been used for refrigerant, they may contain oil. Because of this possibility they are washed with clean carbon tetrachloride, previously dried over calcium, and heated in the oven at 300° F. Carbon tetrachloride forms a heteroazeotrope with water and consequently will help dry the cylinders as it is boiled out.

SAMPLING

Sample, in the present discussion, refers to a representative portion of refrigerant taken from any closed container.

Analyses of Freon 12 were made for two up-ended 145-pound cylinders, which remained in this position until emptied. Ten

samples from cylinder E varied from 3.3 to 6.0 p.p.m. with an average of 4.8 p.p.m. and a maximum deviation of 1.5 p.p.m.; the average of seventeen samples for cylinder F was 5.1 with a maximum deviation of 2.8 p.p.m. (not satisfactory).

It was suspected that the difficulties were within the original cylinder containing the Freon 12, where fractionation pushed the water in greater proportions into the vapor space. Hot air flowing over the lower part of the cylinder will cause a continuous reflux, such that comparatively dry refrigerant liquid can exist under a layer of free liquid water.

To demonstrate that some such difficulty was causing the large deviations two supplies of refrigerant, each in a 25-pound cylinder, were analyzed. To avoid difficulty with fractionation, the cylinder was shaken thoroughly for 5 minutes before the sample was taken. The results in Table II indicate that the large cylinders also needed a good shaking. The data are far more precise than those for the large cylinders, even though the water content is much higher.

Table II. Water Content of Freon 12

Cylinder A		Cylinder B	
Sample No.	H_2O, p.p.m.	Sample No.	H_2O, p.p.m.
28	26.3	32	22.5
29	25.1	33	22.4
30	25.4	34	23.0
31	25.9	35	22.1
	Av. 25.7		22.5

Taking a sample from the liquid phase is fraught with difficulties, but taking one from the vapor is worse. To demonstrate this contention, two 500-gram samples were distilled so as to collect the distillate of each in three separate portions. Table III demonstrates clearly the concentration of water in the early fraction. The moisture content of the 500-gram sample cannot be predicted from the analysis of the first portion, unless the distillation is effected under a condition of practical equilibrium. Even so some involved mathematics is required.

For a representative sample all liquid must be evaporated. The experiments performed in this laboratory are convincing that the technician must have control of fractionation. It is entirely possible to take liquid samples that are just as unrepresentative as the vapor samples. If only a portion of the liquid is to be taken, one must make sure that the water is all in solution and that the liquid is homogeneous.

Table III. Fractionation in Freon 12–Water System

Cylinder A (25.7 P.P.M.)			Cylinder B (22.5 P.P.M.)		
Sample No.	Portion	P.p.m.	Sample No.	Portion	P.p.m.
36	1st	65.2	39	1st	58.4
37	2nd	12.3	40	2nd	11.9
38	3rd	3.6	41	3rd	6.2
	Av.	27.0			25.5

Because of the great tendency to fractionate, the final vapor left in the sample cylinder need not be swept through the train. It should not contain an appreciable amount of water.

MAKING THE ANALYSIS

Check the sample cylinder for valve leaks through the use of flare connections and glass tubing by holding the tubing under water to see if gas is escaping. Because of fractionation, a small leak may give a very large error.

Connect the absorption train box to the air supply at point *A*, with the first bulb not yet connected, to dry the copper tubing. Allow air to flow through for at least an hour.

Put the copper tubing connector (Figure 1) in the oven at 110° C. or higher for at least 10 minutes.

Take the hot tubes from oven, blow out with an electric blower, and connect to the gas outlet of the sample cylinder after the valve has been dried with the blower.

Have air passing through the absorption train, so that it may be known to be open.

Disconnect the absorption train from the air supply, and connect point *A* (Figure 1) to point *A* (Figure 2) and a bubbler at *B*.

With the train open and bubbler connected, open the valve at the gas outlet slightly until the desired flow of refrigerant is obtained.

Remove the bubbler and connect the exhaust into an exhaust manifold through which dry air is passing.

When the refrigerant has passed through the train, with the exception of vapor in the cylinder, disconnect the absorption train, connect to air supply, and pass dry air through for 20 minutes; longer will do no harm.

Remove dust with an electric blower while air sweep is being made, take open bulbs from box, and set them aside for an hour near the balance.

Once the weighings have been finished, return the bulbs to their boxes and allow dry air to pass through until needed for another analysis.

The final weights for one analysis become the initial weights for the next, except that the bulbs should be weighed on the day the analysis is started.

Where speed is not essential the flow of refrigerant is adjusted to a low rate. The analyses are started in the late afternoon and considered to be progressing satisfactorily if all the gas has passed through the train by morning—about 30 grams per hour. The air sweep is made immediately.

Experience will soon enable the analyst to detect certain difficulties that may arise—for example, if ΔW_2 is found to be a fairly large positive value ($> +0.0005$), the train may be badly contaminated. Oil can cause such trouble. It can be entrained and carried into all three bulbs; more stopping in No. 1. After such a refrigerant analysis, a long air sweep will give large negative values for ΔW_1. Fortunately, Freon 12, even from refrigeration units, can be handled without this difficulty. Large positive values for ΔW_2 cannot be tolerated where an analysis is being made; large negative values for ΔW_1 cannot be tolerated for either an analysis or an air check.

TYPICAL ANALYSES OF FREON 12

Table IV represents typical analyses obtained in this laboratory after due consideration was given to the sampling technique. The precision is satisfactory; the average range of variation is 1.1 p.p.m., and the average deviation from the average is not more than 0.55 p.p.m. However, the accuracy is not acceptable.

Attention may be called to the analyses of refrigerant from sources A, A′, B, and B′. In reality A and A′ are the same source; likewise, B and B′ are the same. However, the runs were made in triplicate 3 months apart. Consistent results were obtained for immediate checks, but the results at one time do not agree sufficiently well with those obtained at a wholly different time. The difficulty was finally traced to the rubber tubing connecting the sample cylinder with the absorption train. Sulfuric acid mist from the bubbler may have been reacting with the rubber.

This connecting tubing, at present, carries a glass insert permitting as little area of rubber as possible to come into contact with the refrigerant. The tubing is heated at 175° F. in an evacuated flask for an hour or more between uses. It is understood that air-dried tubing also works satisfactorily.

CHECKING ANALYTICAL PROCEDURE

The analyst should not try to analyze any refrigerant until he can demonstrate that the absorption train and the dry air train are in good working order. As soon as he can get results like those in Table I, he is ready to check the analytical procedure.

One way to check on the routine handling of the equipment is to use a standard sample known to contain a known amount of water. A useful sample is one that has been distilled through phosphorus pentoxide; if distilled fairly slowly, it will be almost

Table IV. Water in Freon 12

Sample	Source	P.P.M.	Sample	Source	P.P.M.
50	A	5.9	53	A'	8.8
51	A	6.0	54	A'	10.5
52	A	5.4	55	A'	9.0
	Av.	5.8			9.4
56	B	1.8	59	B'	3.9
57	B	1.8	60	B'	3.5
58	B	1.7	61	B'	3.9
	Av.	1.8			3.8
62	C	2.5	64	J	1.1
63	C	2.4	65	J	1.5
	Av.	2.5			1.3
66	D	32.3	71	I	10.7
67	D	31.6	72	I	9.2
68	D	29.9	73	I	9.4
69	D	31.0			
70	D	31.6			
	Av.	31.3			9.8
74	G	26.9	76	H	19.5
75	G	24.4	77	H	18.2
	Av.	25.7			18.9

Table V. Analyses of Dry Samples

Sample No.	H_2O, P.P.M.
78	0.3
79	−0.3
80	0.3
81	0.7
	Av. 0.3

bone dry. A very convenient dryer can be made of stainless steel, so that the distillation may be carried out at room temperature. If the analyst can find consistently less than 1 p.p.m. of water, his procedure may be assumed to be all right.

In this laboratory, a standard sample is often prepared in a refrigeration unit containing a 0.25-hp. compressor and an adsorbent type of drier. In Table V may be found analyses of such standard samples, where about 400 grams of refrigerant were used. These values are considered highly satisfactory and the routine is in order when such results can be obtained.

Standard samples can also be made by filling a sample cylinder with water vapor under controlled conditions, say at 32° F., and then charging a controlled weight of bone-dry refrigerant into the same chamber.

There is a possible second way of checking. The refrigerant from cylinder A (Table III) was examined at a time when the routine was under control; no such control existed when cylinder B was analyzed. If the average for the three samples is not about the same as the original, the routine is probably out of control. This method is rather indirect and there is more work involved than in the other method.

If the absorption train and the air supply can be checked as indicated and if a sample thoroughly dried can be run without getting more than 1 p.p.m., the technique is under control.

ACKNOWLEDGMENT

The writer wishes to express his appreciation of the assistance in this work rendered by associates in the Carrier Corporation. Especially should attention be called to P. F. Klens, who took the brunt of the discouragement in the first work; to Michael Kin, who did such a painstaking job in refrigerant sampling; and to Anna Mathill, who has depicted so forcefully in the drawings the apparatus that was used.

LITERATURE CITED

(1) Benning, A. F., Ebert, A. A., and Irwin, C. F., *Refrig. Eng.*, **55**, 166–70 (1948).
(2) Griest, W. P., *Ibid.*, **42**, 316–18 (1941).
(3) Kinetic Chemicals, Inc., *Tech. Paper* 8 (1931).
(4) Weaver, E. R., and Riley, Ralph, Anal. Chem., **20**, 216–29 (1948).

Received July 23, 1948.

DESIGN OF AN ULTRAVIOLET ANALYZER

GILBERT KIVENSON, J. J. OSMAR, and E. W. JONES[1]
Mellon Institute of Industrial Research, Pittsburgh, Pa.

A design is presented for a double-beam ultraviolet colorimeter employing interrupted radiation and a tuned amplifier. Drift and noise are comparatively low, and over-all stability and sensitivity are good.

IN A study of methods of instrumentation for GR-S polymerization plants, the utilization of an ultraviolet colorimeter for continuous analysis and control of the styrene and butadiene streams seemed an attractive possibility. The ultraviolet spectrophotometer was being successfully used for the analysis of styrene mixtures in the laboratory and some attempts had been made to adapt it to continuous flow operation. In addition, such techniques as light chopping and the use of tuned amplifiers seemed to offer a solution to some of the electronic problems encountered in the ordinary spectrophotometer. An instrument using these features was therefore designed and built. The experimental model was tested with typical plant mixtures and its properties were evaluated. This paper describes the features and performance of the instrument as compared to earlier designs and presents the experimental test results.

[1] Present address, 3114 Iowa St., Pittsburgh, Pa.

PRELIMINARY CONSIDERATIONS

The composition (*6*) of a typical styrene-butadiene feed stream is given in Table I.

It was desired to determine styrene continuously in this stream with as high an accuracy as possible.

A number of nondispersive ultraviolet instruments have been built on single- and double-beam principles (*2, 4, 5*).

Table I. Styrene-Butadiene Feed Stream

Component	% by Weight	Component	% by Weight
Styrene	29.3	Ethylbenzene	0.3
1,3-Butadiene	66.1	Isopropylbenzene	0.2
2-Butene	1.9	Methylacetylene	0.1
Vinylcyclohexene	0.8	Propylene	0.1
1-Butene	0.7	Pentenes	0.1
1,2-Butadiene	0.4		

The circuit by Hanson (2) utilizes a mercury arc source, a 935 phototube, and direct current amplifier. The arrangement of Klotz and Dole employs a mercury germicidal lamp as a source and a one-tube amplifier. Previous experiments made by the authors with steady radiation instruments indicated, however, that an interrupted light–alternating current amplifier system would be more suitable for the long operation periods necessary in plant work. Flicker photometers are described by Dobson (1) and others. In these instruments the radiation is alternately passed through a known material (or adjustable light stop) and through the material to be measured. The present instrument was designed on a similar principle.

THEORY

A problem occurring on consideration of the system was that of absorption cell thickness. The extinction coefficient of styrene (for a 1-cm. light path at a wave length of 300 millimicrons) is approximately 1000; this indicates that a cell thickness of 0.02 mm. is necessary to give a transmittance of only 1%. A much smaller spacing would be needed to bring the transmittance to an easily measured value. Such cells would be not only difficult to construct but troublesome to maintain in plant operation.

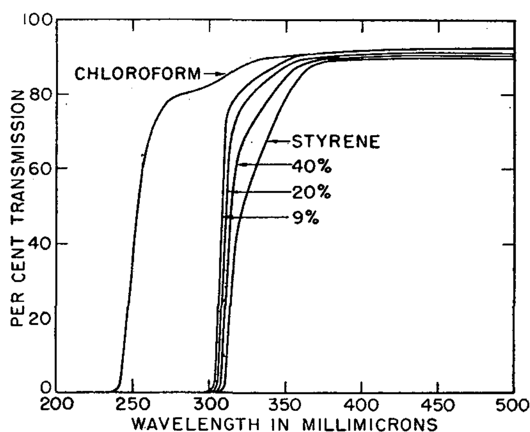


Figure 1. Cutoff Curves of Styrene-Chloroform System

To permit the use of thicker cells, an automatic diluting apparatus was considered for a time, but the concentrations required (of the order of 12 mg. of sample per liter of solvent) made this type of arrangement appear impractical.

A cutoff method was then developed to permit the use of cells with larger spacings. Figure 1 shows the cutoff curves obtained by scanning various styrene-chloroform mixtures (1-cm. cell) with a Beckman spectrophotometer. Chloroform was substituted for butadiene for convenience in handling. There appeared to be sufficient energy differences to determine styrene in its various dilutions in the 28 to 31% range, particularly if the band width were limited by filters.

If a relatively narrow band were to be used for the analysis, there would be some question as to its width and position. The position of the band determines to a large extent the shape of the calibration curve. Figure 2 presents a series of curves made in the Beckman spectrophotometer with the styrene-chloroform system. The band width was approximately 5 millimicrons and the position of the center of the band is the parameter in Figure 4. An almost linear calibration curve was obtained at 320 millimicrons but the sensitivity is approximately one half that at 310 millimicrons. In actual operation with filters a band width as narrow as this is difficult to achieve, so that the "optimum band position" becomes less significant.

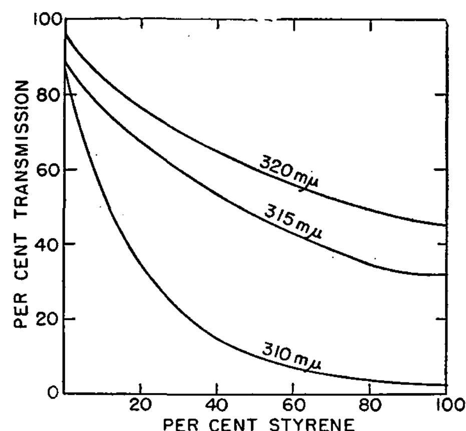


Figure 2. Effect of Band Position

The curves of Figure 1 were combined with the emission curve of a hydrogen source, the transmittance curve of a Corning No. 986 filter, and the spectral response curve of an RCA 935 photocell by determining the product at each wave length. The resultant curves for the styrene-chloroform system are set forth in Figure 3. The areas under each were determined and plotted against the concentration to give the calibration curve, *A* in Figure 4, which has adherence to Beer's law.

If the emitted light is confined to a 5 mμ band centered at 310 mμ the theoretical calibration curve obtained is *B* in Figure 4. The apparent extinction coefficients for the broad and narrow band widths are 0.15 and 0.40, respectively.

DESIGN OF PRESENT INSTRUMENT

Perspective views of the instrument are given in Figures 5 and 6.

Radiation is provided by a Beckman hydrogen discharge tube. The light is divided and focused back on an interrupter disk that chops the radiation 15 times a second. The beams are sent alternately through two cells, one containing a standard and the other the flowing sample. The transmitted light is then alternately refocused by a quartz lens in each beam onto a 935 phototube. A Corning red purple Corex filter (No. 986) is used directly before the phototube. The front surface spherical mirrors (Perkin Elmer 30-cm. focal length) are employed 18 degrees off-axis. In this position the image of the source can be distorted to a thin horizontal line parallel to the knife-edge surfaces of the interrupter disk. This effect permits a very sharp cutting of the light beams and considerably reduces the time of overlap between the two beams. The resulting signal (after phase discrimination) is a square wave.

The simple input circuit of the phototube is illustrated in the block diagram of Figure 7.

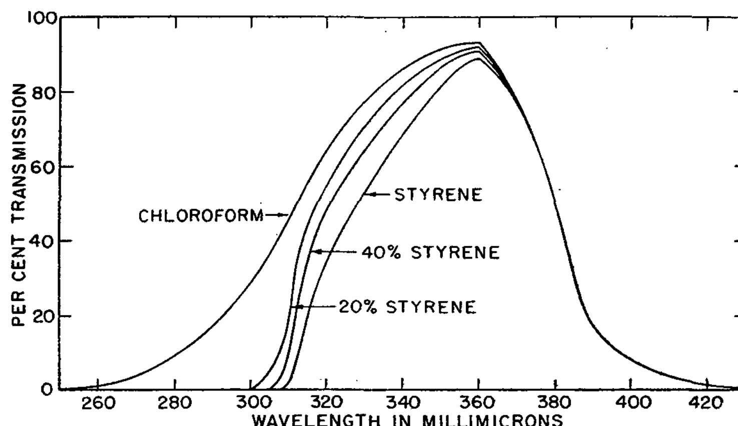


Figure 3. Resultant Curves Obtained from Consideration of Source, Filter, Phototube, and Sample Characteristics

Coupling is accomplished through a 0.1-mfd. condenser. A Western Electric tuned amplifier (Type KS-10,281) having a band pass at 15 cycles filters out harmonics and boosts the signal to recorder voltages. At a gain of approximately 400 the maximal signal obtained (by blocking one light beam) is 4.97 millivolts. This is the total "working" signal available for analysis. The minimal noise level (with both beams balanced) is 0.02 millivolt. The minimal detectable concentration change would therefore be about 0.4%.

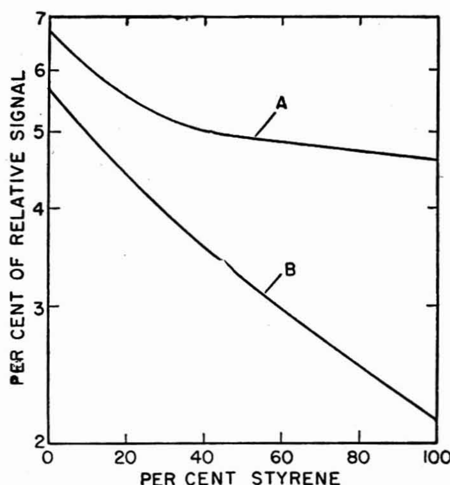


Figure 4. Theoretical Calibration Curve with and without Filter

The chopper is driven by an 1800 r.p.m. Bodine synchronous motor geared down by one half to give the 15-cycle chopping frequency.

With the sample in both beams and the filter in place, the total energy incident on the phototube is of the order of 10^{-4} microwatt. The power consumed by the source is 19 watts. Greater illumination intensity could easily be obtained, but the over-all sensitivity is sufficient for this analysis.

The absorption cells were of a special pressure construction (*3*). The cells are made of quartz plates separated by a spacer 1.5 mm. thick. The cell spacing used is approximately the smallest value that would be practical for plant use. Although thicker cells would permit the analysis to be performed, the minimal dimension governs because of the decreasing effect of impurity concentration changes with thinner cells.

The method of balancing consists of filling both cells with a representative sample of the material, blocking one beam completely, and adjusting the opposing concave mirror for maximal signal as indicated on an output meter or recorder. The light block is then removed and the other mirror is adjusted until the minimal signal is obtained. Fine adjustment of the two beams can be made by the use of two light trimmers mounted in the light paths. The minimal signal consists of the random noise effects (Johnson noise, microphonics, light source variation, etc.) and the beam "change-over" noise. The latter arises from the overlap of the two beams and is produced in the period when both beams are either off or on. This gives a nonrandom signal, which can, however, be eliminated by incorporating certain circuit changes.

Table II. Styrene in Plant Samples

Sample No.	Styrene in Original Sample, %	Styrene after Dilution, %	Styrene Read from Calibration Curve, %	Deviations from Actual Percentage	Deviations from Mean
1	98.86	28.00	30.0	+2.0	+1.7
2	94.21	28.00	30.0	+2.0	+1.7
3	92.11	28.00	27.0	−1.0	−1.3
4	96.30	28.00	27.0	−1.0	−1.3
5	99.66	28.00	26.5	−1.5	−1.9
6	95.80	28.00	30.0	+2.0	+1.7
7	95.08	28.00	26.5	−1.5	+1.9
8	95.53	28.00	30.0	+2.0	+1.7
9	92.74	28.00	28.0	0.0	−0.3
		Av.	28.3		

EXPERIMENTAL RESULTS

With a 27–73 styrene-chloroform mixture in both cells as the zero condition, a calibration curve was made by varying the material composition in the analytical cell. The curve in Figure 8 covering the 25 to 31% styrene range is typical and agrees with that obtained from integration of the cutoff curves. With the average sensitivity over this range established by the calibration curve, several long-period runs were made. In some of these runs styrene was placed across both beams, in others the cells remained empty. In one run styrene was added to one side only and the beams were balanced by partially blocking off the empty cell. The maximal drift per 24 hours as observed did not exceed 14.7% of full scale, corresponding (Figure 9) to a styrene concentration change of 1.6%.

Two general testing methods were used. In the first, samples of styrene drawn from plant streams over a number of months were analyzed by freezing point methods and diluted with chloroform to a common styrene content. With pure styrene in the comparison cell, these samples were analyzed in the instrument and the readings referred to the original calibration curve. The results are given in Table II.

These tests were made under fairly rigorous conditions, as the use of pure styrene in one beam instead of a sample of a composition resembling that being analyzed considerably reduces the signal-to-noise ratio. In addition, the interference effects of the impurities in the blended plant samples are greatest in this case. In actual plant operation one would take a typical sample (containing the impurities) as a standard and the variations in the impurities from batch to batch would have less significance.

In the second testing method liquid butadiene was added to a plant styrene sample (95.53% styrene) to produce mixtures ranging from 27 to 32% styrene and these mixtures were run in the analyzer. The calibration curve obtained was used to determine the

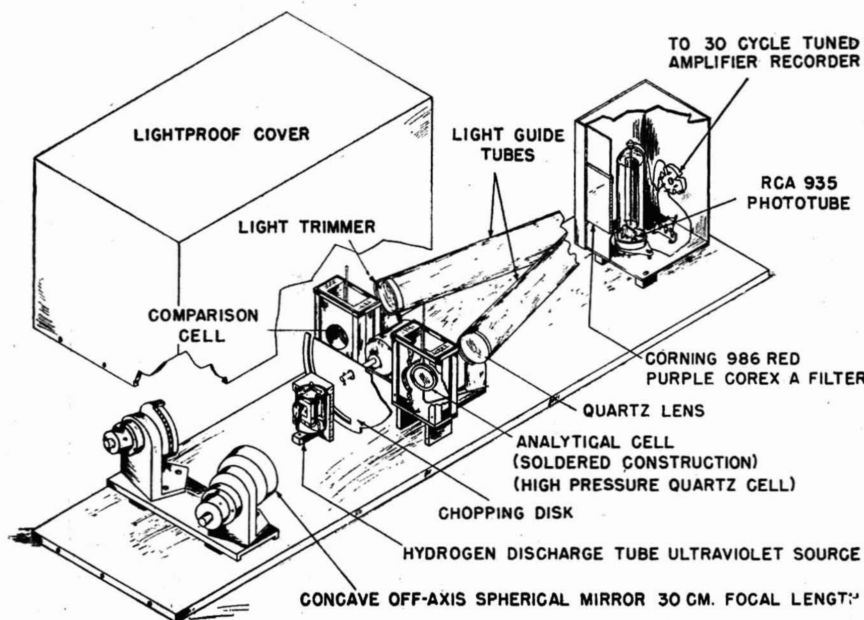


Figure 5. Perspective Drawing of Apparatus

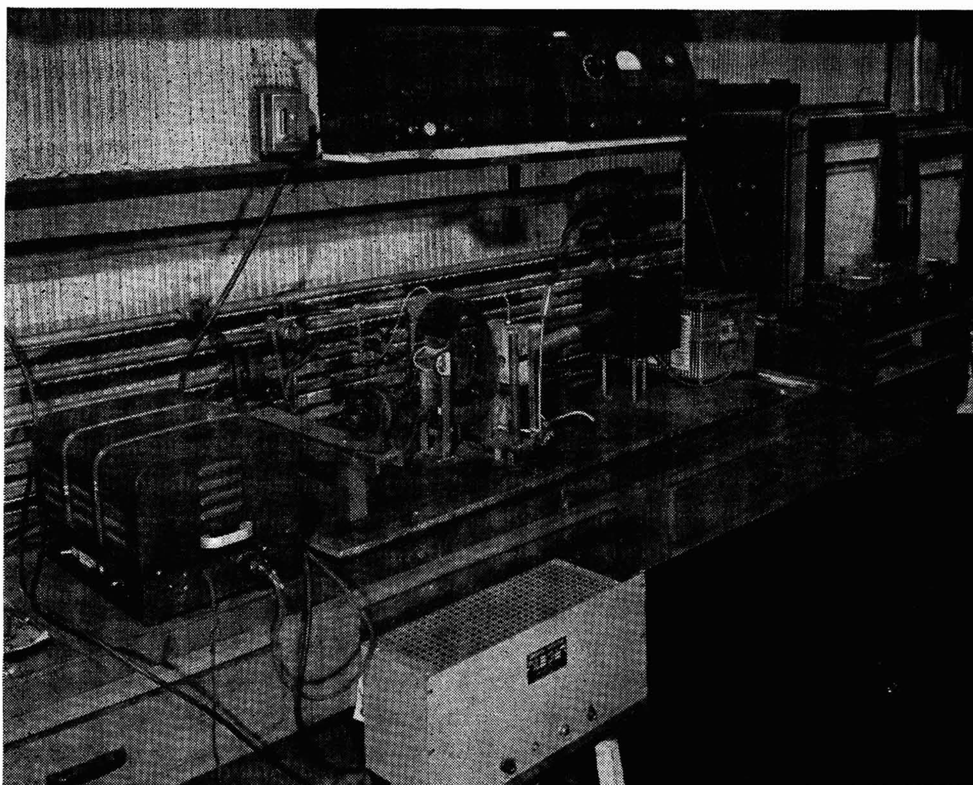


Figure 6. Double-Beam Analyzer with Cover Removed

CONCLUSIONS AND RECOMMENDATIONS

The instrument in its present form should be suitable for analyses of styrene-butadiene streams with an average reproducibility of about ±0.7%. For the analysis of lower concentrations of styrene the accuracy and reproducibility to be expected should be much greater. The use of the cutoff principle instead of the standard absorption band technique makes more convenient some analyses that otherwise would require elaborate automatic dilution equipment or a manually operated spectrophotometer.

It would appear from the experience with this instrument that the following additions would afford higher stability and reproducibility.

A more stable hydrogen tube would help the reproducibility at high sensitivity. Some work can be done on the regulation of these tubes based on the emission rather than on the voltage and current input.

Light scattering and refractive index effects will, of course, add noise to the output of this type instrument. Serrated inner sur-

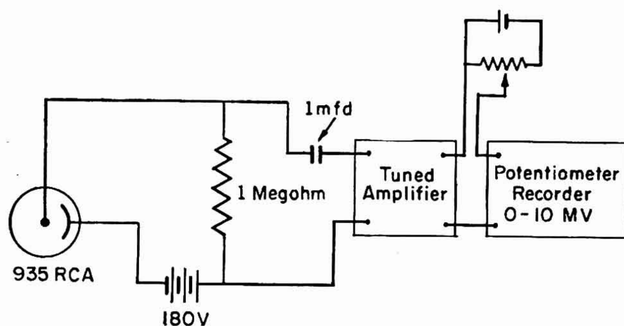


Figure 7. Block Diagram

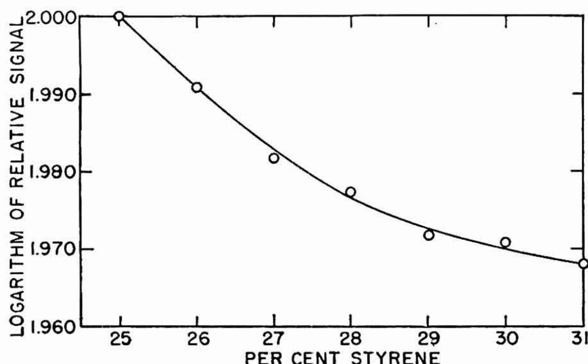


Figure 8. Calibration Curve for 27.0% Styrene in Comparison Cell

styrene content of blended styrene-butadiene samples from the feed stream of a GR-S reactor unit. Pure styrene was again used as the comparison material. Table III presents typical results.

The deviations in this case were somewhat less, and more representative of average instrumental performance as based on the stability studies.

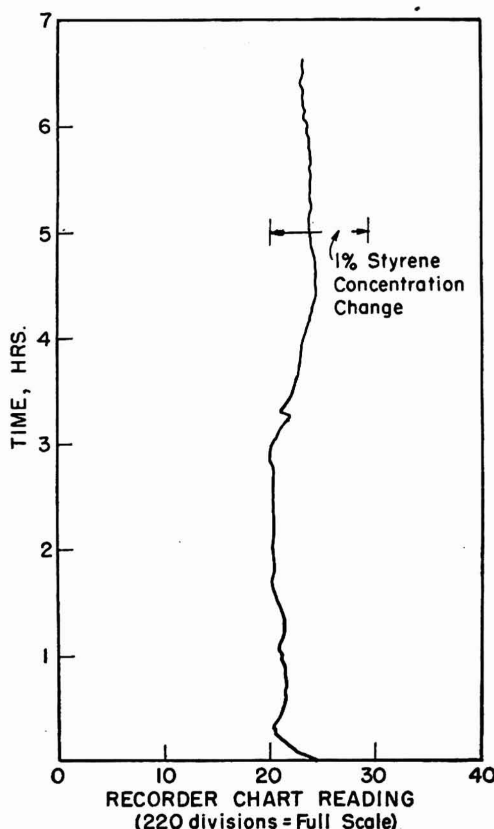


Figure 9. Instrument Stability Run

Table III. Styrene in Styrene-Butadiene Plant Samples

Plant Sample No.	Styrene Determined by Plant Material Balance, %	Styrene Found in Ultraviolet Instrument, %	Percentage Deviation
1	29.2 ± 0.5	29.8	+0.6
2	29.3 ± 0.5	28.0	−1.3
3	29.3 ± 0.5	29.9	+0.6
4	29.5 ± 0.5	29.7	+0.2
		Av.	±0.7

faces and the precise matching of absorption cells would reduce the unwanted signal to a minimum.

A synchronized commutating switch, which might increase the ratio of signal to background is being considered for incorporation into another model of the analyzer. It would be mounted on the chopping motor shaft and control the output so that the change-over signal could be more readily eliminated.

ACKNOWLEDGMENTS

The authors would like to express their appreciation of the help given them by Ralph Steinback, Albert Roth, and Myrtle Rider of this laboratory. They are also indebted to E. E. Stahly and O. W. Burke for administrative guidance and encouragement, and to Howard Cary of the Applied Physics Corporation for helpful suggestions.

LITERATURE CITED

(1) Dobson, G. M. B., *Proc. Roy. Soc.*, (*London*), 104, 248 (1923).
(2) Hanson, V. F., Ind. Eng. Chem., Anal. Ed., 13, 119 (1941).
(3) Kivenson, G., Roth, A., and Rider, M. A., *J. Am. Optical Soc.*, in press.
(4) Klotz, I. M., Ind. Eng. Chem., Anal. Ed., 15, 277 (1943).
(5) Klotz, I. M., and Dole, M., *Ibid.*, 18, 741 (1946).
(6) Natl. Bur. Standards, *Rept.* 46-08-02 (Aug. 7, 1946).

Received September 10, 1948. Part of the program sponsored by the Office of Rubber Reserve, Reconstruction Finance Corporation, and approved by that office for publication.

Pneumatic Autodetector for Infrared Gas Analysis

R. D. MILLER[1] and M. B. RUSSELL
Department of Agronomy, Cornell University, Ithaca, N. Y.

The absorption of bands in the infrared by heteroatomic gas molecules provides a method for continuous analysis of gas streams. High sensitivity to minor components, such as carbon dioxide in the atmosphere, may be obtained with relatively simple apparatus in which the detecting element consists of a cell containing the component for which analysis is desired. A major difficulty in the application of the self-detection principle is the control of drift. A simple analyzer designed to minimize drift is described.

THE increasing exploitation of selective absorption in the infrared by various molecular species is furnishing new and sensitive methods to the analytical chemist. Several infrared gas analyzers (*1–4, 8, 11*) for continuous analysis of gas mixtures avoid the expensive optical components of the infrared spectrometer and are related to ordinary colorimeters in their conception and design. However, the low energy of infrared radiations requires new techniques of measurement, and the complexity of the absorption spectra requires new concepts of filtering.

The most effective filter for isolation of the bands absorbed by one component of a gas mixture is a quantity of the same component. A filter cell containing a component, X, will absorb only certain well defined bands characteristic of X. This absorption is in accord with Beer's law, though interactions with other components and variations in total pressure may cause marked deviations. If a beam of infrared entering such a filter has traversed a sample cell containing a gas mixture which includes X, energy in the region of the absorption bands of X will have been partially removed from the beam and the energy in these bands subsequently absorbed by the filter cell will be correspondingly diminished; the energy absorbed by the filter cell is then an inverse function of the concentration of X in the mixture.

Two methods of measuring the energy absorbed by the filter cell may be applied. The first method, aptly known as the negative filter method, compares the total radiant energy emerging from the filter cell with that which entered it. The second method measures the heating of the filter cell itself resulting from the absorption of the residual energy in the absorption bands. If the absorption bands of some other component present in the sample overlap those of X, a second filter containing the interfering component must be placed in the path to remove the interfering bands.

The usual application of the negative filter method is illustrated in Figure 1, *A*. Twin beams of radiation from a source, S, traverse a sample cell, C, containing a gas mixture which includes X. One of the emerging beams passes through a filter cell, F, filled with X. The other beam passes through a dummy cell, F', containing a nonabsorbing gas such as oxygen. The two beams are absorbed by temperature-sensitive elements, D, D', of a differential thermopile or bolometer. Overlapping bands of other components are removed by additional filter cells, F''. The beams reaching the receiver are identical except in the region of the absorption bands of X. These bands have been partially removed from the beam which traverses the dummy cell, depending on the concentration of X in the sample, whereas absorption of these bands has been virtually completed by the filter in the other beam. Thus, the two beams represent the energy entering and leaving the filter cell, respectively. The presence of other absorbing components in the sample affects both beams equally, so that the two beams cancel at the receiver except for the bands absorbed by X. The resultant thermoelectric signal from the receiver is inversely related to the concentration of X in the sample.

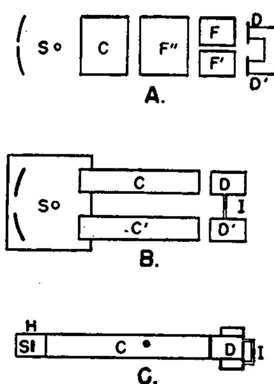


Figure 1. Infrared Gas Analyzers

A. Typical negative filter analyzer
B. Twin-path analyzer
C. Single-path analyzer

[1] Present address, Division of Soils, University of California, Berkeley 4, Calif.

The alternative method has been called the positive filter method. In this method, the radiant energy absorbed by the filter gas provides the basis for measurement of the concentration of the same gas in the sample. It is suggested here that the term "autodetector" is more descriptive of the method, as the "filter" is in reality a selective self-detector. The energy extracted from the beam by absorption reappears as thermal energy which may be measured thermoelectrically, or by the resultant pressure-volume changes in the detector gas. Pfund (*6*, *8*) placed thermocouples in the detector cell in such a way that they would not absorb energy from the beam but would respond to changes in the temperature of the detector gas. Luft (*4*) measured pressure-volume changes with the aid of a flexible diaphragm, and Pfund (*7*), Kidder and Berry (*3*), and Barnes (*1*) all mention the use of a drop of fluid in a capillary for observing pressure-volume changes.

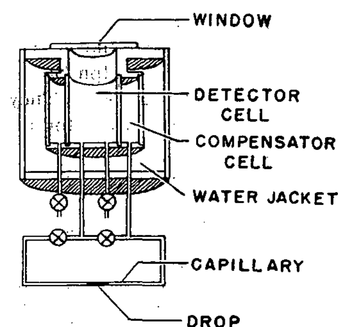


Figure 2. Pneumatic Autodetector for Single-Path Analyzer

Simplified sectional sketch

The negative filter method requires measurement of a small difference of energy between two strong beams, whereas the autodetector measures the same increment directly. Under favorable conditions, it would be possible to make simultaneous analyses for several components with a train of autodetectors (*1*), but this is impossible with the negative filter method. In spite of these considerations, development of the negative filter method has outstripped the development of the autodetector.

The autodetector analyzer described in this paper was developed specifically for measuring small changes in the carbon dioxide content of an air stream resulting from passage through a chamber in which plants were growing. At the beginning of the developmental work, no infrared gas analyzer of adequate sensitivity at the low concentration of carbon dioxide normally found in air (0.03%) was available, though the negative filter analyzer recently described by Fastie and Pfund (*2*) has sufficient sensitivity in this range.

EXPERIMENTAL

Although a successful analyzer was constructed, explorations of the potentialities of the method were by no means complete when circumstances ended the work. The utility of certain features of the design of the analyzer warrants publication of the progress made.

Two analyzers were built. The first, a twin-path differential analyzer shown diagrammatically in Figure 1, *B*, resembled autodetector analyzers previously described in the literature and was essentially identical with the analyzer recently patented by Kidder and Berry (*3*). This analyzer consisted of a source, *S*, two parallel sample cells, *C*, *C'*, and two parallel detector cells, *D*, *D'*. An air-tight box enclosed the external optical path to exclude carbon dioxide and to provide a filter corresponding to *F"* in Figure 1, *A*. The detector cells were connected by a length of glass tubing 2 mm. in inside diameter containing an indicator drop, *I*, of diethyl phthalate. A pair of mirrors reflected twin beams from a Globar source through the sample and detector cells.

This analyzer was abandoned in favor of a single-path analyzer when it became clear that the optical aperture attainable with the available mirrors was too low to give adequate sensitivity in the desired range. This detector was subject to excessive drifts unless special precautions were taken to control ambient temperature, a difficulty mentioned in connection with analyzers of this type by Williams (*10*). It was found that by surrounding the detector cells with a mass of water to provide high thermal inertia, drifts due to temperature fluctuations of the surroundings could be minimized.

A relatively large optical aperture was attained with a single-path analyzer, diagramed in Figure 1, *C*. This was accomplished without the aid of lenses or mirrors by making the source housing, *H*, the sample cell, *C*, and the detector cell, *D*, from sections of brass tubing. These were placed end to end, so that diverging radiations from the source were reflected in a zigzag path through the sample cell into the detector cell.

Fastie and Pfund used this principle in their negative filter analyzer and report an effective optical aperture of *f* 0.7 with polished gold surfaces. The aperture attained with the brass tubing used in these experiments was undoubtedly inferior to this value, as little effort was expended in polishing the internal surface of the sample cell used.

The autodetector for the single-path analyzer consisted of two concentric cells of approximately equal volume, as shown in Figure 2. The inner cell was the detector cell and the outer, connected to the inner by a glass capillary with indicator drop, provided compensation against ambient temperature changes. Only the inner cell was allowed to "see" radiation. A water jacket surrounded the two cells to provide high thermal inertia. The concentric arrangement of the two cells gave a symmetry toward random temperature gradients which was very effective in reducing drift.

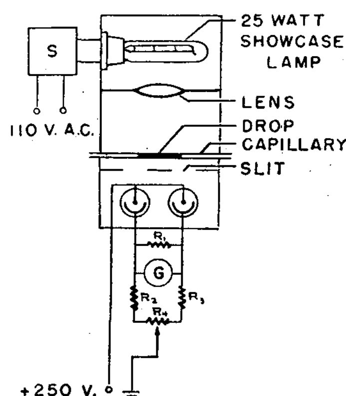


Figure 3. Photoelectric Drop Position Indicator

R_1. Damping resistance
R_2, R_3. 5 megohms
R_4. Galvanometer zero
S. Voltage stabilizer

The detector was essentially a differential gas thermometer in which a difference in temperature of the inner and outer cells was measured by the position of the indicator drop in the capillary. In operation, radiant energy absorbed by the carbon dioxide in the detector cell is converted to thermal energy, raising the temperature of the gas until the losses by conduction and convection balance the gains by absorption from the beam. Thermal expansion is opposed by the compensator cell, so that the drop moves to a position which depends only on the mean temperature difference between the two cells. At room temperature the drop position is essentially independent of ambient temperature changes of the detector as a whole. A decrease in the carbon dioxide in the sample cell increases the energy absorbed by the carbon dioxide in the detector cell; an increase in the internal temperature gradient results, and new steady state is reached. The increased temperature differential between the inner and outer cells causes an adjustment of relative volumes indicated by a displacement of the drop in the capillary.

The displacement of the drop for an increase in the carbon dioxide content of the sample from 0 to about 300 p.p.m., the concentration normally found in air, was very small, of the order of 1 mm.

Figure 3 shows a photoelectric position indicator which effectively amplified this motion about 200 times. The drop was utilized as a cylindrical lens (*3*) to focus light from the filament of a showcase bulb on a slit behind and parallel to the capillary. Two photocells, centered approximately behind the ends of the drop, were illuminated by light focused on the slit by the drop. As the drop moved, illumination of one photocell was

increased while illumination of the other decreased. The two photocells constituted arms of a Wheatstone bridge. Balance or lack of balance of the bridge was indicated with a Leeds & Northrup Type R galvanometer (0.00042 microampere per mm.) whose deflections were recorded photographically at a distance of 1 meter.

For linear response of a position indicator of this type, design should provide for changes in intensity of illumination of the targets without accompanying changes in the areas illuminated. The position indicator used here was apparently linear within limits of error over an appreciable range. The use of a long straight filament as a light source and the relatively small drop displacements involved contributed to this property. Still greater amplification is possible with this system if the slit is shortened, reducing the amount of background light admitted by portions of the capillary which are always filled by the drop. This reduces the range of linearity, however, and once amplification sufficient to show the noise level of the analyzer has been attained, no advantage is obtained by further amplification. Stabilization of the line voltage to the showcase bulb was essential for stability of the indicator.

CONSTRUCTION

The analyzer was constructed from stock materials without the services of a skilled mechanician. Dimensions and design were therefore suited to available materials and simple lathe operations.

A length of brass tubing 2.86 cm. (1.125 inches) in inside diameter was the heart of the analyzer; sections of this tubing formed the source housing, the sample cell, and the detector cell, each constructed so that when the components were placed end to end, a continuous light path was obtained.

The source was improvised from a flat coil of Nichrome wire from an automobile cigar lighter mounted approximately in the center and perpendicular to the axis of a 5.1-cm. (2-inch) length of the 2.86-cm. (1.125-inch) brass tubing. The latter was mounted inside a tube of larger diameter which formed a water jacket through which tap water was circulated for cooling. The coil attained a bright red heat (about 750° C.) drawing 10 amperes from a 6-volt storage battery. The coil consisted of seven turns of flat Nichrome ribbon (about 0.8 by 1.5 mm.) with an over-all diameter of about 14 mm., a very compact and convenient source.

The sample cell used in most of the experimental work was a 1-meter length of the brass tubing mentioned. Flanges were soldered to the ends, and the end nearest the source was bolted to a similar flange on the source housing with a muscovite mica window (about 0.01 mm. thick) sandwiched between. At the detector end of the cell, a similar mica window was held in place by a brass plate bolted to the flange. Initially, two side tubes near opposite ends of the sample cell were used for sample flow, but later, three additional side tubes equally spaced along the cell were added to reduce the velocity of flow in the vicinity of the windows during rapid sample replacement. Samples were introduced through the second and fourth tubes and were swept out through the remaining three.

A satisfactory reflecting surface was obtained by cleaning the inside of the cell with silver polish, after which a pad of steel wool was drawn through the cell several dozen times. The resulting surface was an improvement over the initial state, but lacked the bright appearance of highly polished brass. The interior surfaces of the detector and source housing were polished to a high luster while chucked in a lathe.

The detector was the most complicated component. It was made from three sections of brass tubing and three end plates. The essential features of the construction are discernable in Figure 2. The sections of tubing which enclose the detector and compensator cells were silver-soldered to the end plates, while the outer tube enclosing the water jacket was sealed to the end plates with red Glyptal enamel. A hole in the outer wall permitted introduction of water to the jacket.

Four lengths of eighth-inch copper tubing were soft-soldered into the back plate of the detector and amplifier cells and passed through the outer end plate. These provided means for introducing the detector gas, connections to the capillary containing the indicator drop, and a means of equalizing pressures in the two cells. Four needle valves were required for convenient operation. Two of these merely isolated the system after the detector gas had been introduced, another was used to close off the capillary during filling to prevent the indicator drop from being accidentally blown out of the capillary, and the fourth permitted series connection of the cells during filling, equalization of pressures during warm-up, or adjustment of the drop position.

A capillary of the same outside diameter as the copper tubing was selected and was joined to the latter by slipping a brass ferrule over the junction and painting with red Glyptal enamel. The inside diameter of the capillary was approximately 2 mm., permitting free motion of the indicator drop. Diethyl phthalate was found to work well as an indicator fluid, having relatively low viscosity and low vapor pressure. It did not tend to stick in the capillary as did some other liquids. The capillary was bent slightly to form a shallow V, so that when pressures were equalized in the two cells, the drop centered itself by gravity.

The detector cell was a 2-inch length of the 1.125-inch tubing. This length was chosen for convenience in construction, as it was reasoned that dilution of the detector gas with a nonabsorbing gas would permit distribution of absorption within the cell as desired. Because 2 mm. of carbon dioxide at normal temperature and pressure will absorb 88% of the radiation in the strong 4.2 micron band (*5*), the use of pure carbon dioxide in the detector would cause most of the absorption to be in the vicinity of the window. Experiments seemed to indicate, however, that this made little difference to the response as compared with the deeper penetration in mixtures of carbon dioxide and nitrogen.

Thin mica windows such as were used for the sample cell were unsuitable for the detector window. Although the mica used transmitted approximately 90% of the radiation in the region of the 4.2 micron band, it absorbed strongly in other regions, and might be expected to produce a spurious signal in the detector if other absorbing gases were present in the sample. Equally disconcerting was the tendency of the mica to flex suddenly under the influence of temperature and pressure changes within the cell. Instead, a rock salt window, cemented to the detector with red Glyptal enamel, was used for the detector window.

The drop position indicator was assembled in a rectangular metal box with removable sides. A smaller metal box mounted inside the first contained the photocells and on the front of this inner box was mounted an adjustable slit arrangement which permitted control of the width, tilt, and length of the slit behind each end of the drop. The detector was mounted on top of the larger box. A third metal box housed the showcase lamp. The lens for focusing the light from the filament to a narrow band along the capillary was mounted on a plate clamped between the light housing and the large box.

For usage where a continuous record was not required, the drop position indicator might be replaced by a low-power microscope of the traveling objective or optical micrometer type. Magnification of fifty times would permit measurement of drop position with as great precision as was obtained with the photographic record of the galvanometer trace, as the width of the trace is much greater than the apparent width of the cross hair in the optical micrometer.

OPERATION AND CALIBRATION

Although drift was greatly reduced in the single-path analyzer as compared to the split-path analyzer, it was not entirely eliminated. The improvement in drift control and the increased optical aperture of the single path analyzer more than balanced the loss of compensation for fluctuations of the source, though the latter became the limiting factor in determining the sensitivity of the instrument. After aging at red heat for several hours, the source became relatively steady.

Because differential measurements were desired, it was possible to make these measurements without appreciable error arising from drift by alternating the flow through the sample cell of the two samples to be compared. If the concentrations were identical, the drop remained stationary or drifted slowly. If the concentrations were unequal, the drop oscillated back and forth, giving a zigzag galvanometer trace. The amplitude of this oscillation was independent of the drift and was proportional to the difference in the concentration of the two samples.

The analyzer was calibrated with samples of air compressed into tanks and analyzed gravimetrically for carbon dioxide. Additions of carbon dioxide or dilution with nitrogen before analysis gave samples that differed slightly from the standard sample. These samples were flowed alternately through the

sample cell by manual opening and closing of the valves on the tanks. For maximum reproducibility, provision must be made for automatic switching and constant flow rates.

The behavior of the analyzer could be varied by adjusting the distance between the sample window and the detector window. The greatest response to a small change in concentration was obtained by placing these windows as close together as possible, a distance of about $^1/_{32}$ inch, but when this was done the noise level of the source was emphasized, apparently through heating of the mica window and conduction to the sample cell. The optimum spacing was a compromise between diminished noise level and reduced response. A practical spacing (about 2 mm.) gave an average response of about 8-mm. galvanometer deflection for a 10 p.p.m. change in concentration when the sample concentrations were of the order of 300 p.p.m. and a noise level which was confined to a range equivalent to 3 to 5 p.p.m.

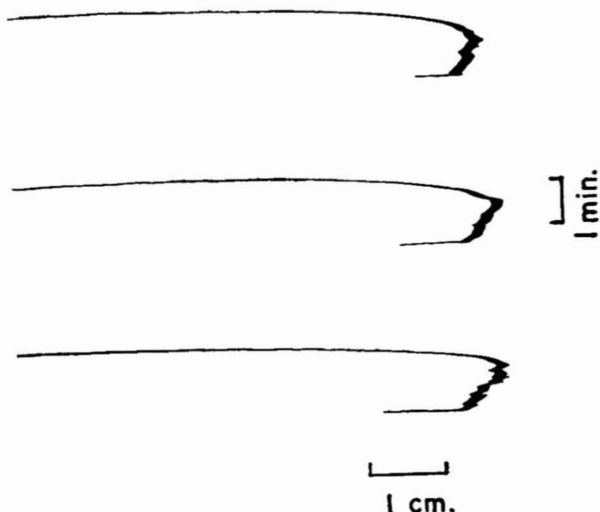


Figure 4. Part of Typical Galvanometer Trace for Intermittent Flow of Alternate Samples of Nitrogen and Air

Warming of the mica windows caused another difficulty. Variations in the velocity of flow of samples produced spurious signals in the receiver, resulting from uneven cooling of the windows. In order to assure uniform sample temperatures, samples were passed through a coil of copper tubing immersed in water before entry into the sample cell. The spurious signals were largely eliminated by increasing the number of inlets and outlets. A more satisfactory solution in the absence of non-absorbing windows might be the addition of a short dead cell at each end of the sample cell.

DISCUSSION

The optimum path length for the measurement of carbon dioxide in air is of the order of 4.4 meters for the strong absorption band between 4.2 and 4.3 microns. The optimum length would be slightly larger than this if all the weaker bands were considered, but it is probable that many of these bands were absorbed by the muscovite windows, for this material is not transparent over a wide range in the infrared (*9*). The sample cell used in most of these experiments was 1 meter in length, but because of the indirect path of some of the radiations, its effective length was greater, depending on the efficiency of reflection. The reflectivity of most metals is high in the infrared; copper, for example, reflects about 97% of the incident radiation in the 4-micron region. Radiations leaving the source at an angle of 45° to the axis of the sample cell would be reflected thirty-five times before

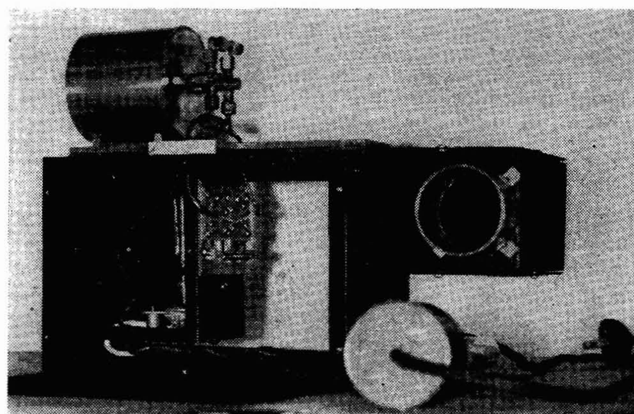


Figure 5. Detector Mounted on Box Containing Drop-Position Indicator Assembly

Capillary containing indicator drop, adjustable slits, and photocell housing (inner box, near side removed) are exposed, but lens for focusing light from showcase bulb (removed from housing) is hidden. Photograph by S. A. Taylor

emerging from a copper tube 2.86 cm. (1.125 inches) in inside diameter and 1 meter long. The intensity of this radiation would thus be reduced by a factor of 0.97^{35} or to about one third of the initial intensity. This suggests that the optimum path length depends on the geometry of the cell and its reflectivity as well as the optimum path estimated from the absorption coefficients of the gas, and will be appreciably less than the latter. An increase in response of about 20% was obtained by substituting a 45-cm. (18-inch) cell for the 1-meter cell, but because the relative reflectivity of the two cells was unknown, no valid conclusions could be drawn. It seems probable that high quality reflecting surfaces would be superior to those used in these experiments, permitting the use of lower source temperatures with no loss in the intensity of the desired spectral range reaching the detector, but with marked reduction in the shorter wave length region of the source spectrum. It is possible that the noise level due to fluctuations of the source might be reduced with lower source temperatures.

No effort was made to determine the time constant of the detector, as the limiting factor in determining the shortest practical sample alternation cycle was the rate of replacement of one sample with another. This in turn was limited by the cooling effect of the samples on the window. However, at flow rates of about 4 liters per minute, 30 seconds of flow produced maximum displacement and essentially complete replacement. If flow were halted, the cooling effect became noticeable, but if both samples were alternated at constant flow rates without interruption, the cooling effect was assumed to cancel out.

A portion of a galvanometer trace obtained during a calibration run is reproduced in Figure 4. This portion was selected for reproduction, because it illustrates the cooling effect as well as the noise level of the source. Similar peaks were recorded some 25 cm. to the left of those shown during the apparent gaps in the record.

As the record strip moved upward, air containing 299 p.p.m. of carbon dioxide was passed through the cell for 1 minute; flow was halted for 1 minute; nitrogen was then swept through the cell for 1 minute; flow was again halted for 1 minute and the cycle was repeated. Portions of three such cycles are shown, the peaks corresponding to the air portion of the trace. Maximum displacement was attained before flow was halted and the trace drifted slowly to the left as the windows warmed up after flow had been stopped. This same drift to the left was observed in the opposing peaks when the cell was filled with nitrogen. The return to the same point with each cycle is indicative of the canceling of the cooling effect if continuous flow of alternate samples were maintained. The irregularity of the peaks themselves, superimposed on the drift to the left, is characteristic of the noise level due to fluctuations of the source. When the

equalizing valve was opened, these fluctuations all but vanished; the remaining noise was attributed to the position indicator.

The utility of the analyzer for continuous measurements over extended periods was impaired by the persistence of drift, which made it necessary to recenter the drop from time to time by momentarily opening the equalizing valve on the detector. The direction and magnitude of the observed drift were variable and may have been caused by slow changes in the source temperature, as compensation of the detector itself was apparently good. Drifts equivalent to 4 p.p.m. per minute were sometimes observed. Inasmuch as the analyzer was not compensated for fluctuations of the source, stabilization of the source deserved more attention than it received.

Considering the simplicity of this analyzer, and its ability to detect changes of less than 3% of a 300 p.p.m. concentration of carbon dioxide, this analyzer was considered successful. However, improved performance might be expected from an analyzer with short dead cells at the ends of the sample cell for insulation purposes, high quality reflecting surfaces, and a more stable source, or perhaps reduction of source noise by an independent feedback circuit.

ACKNOWLEDGMENT

The writers gratefully acknowledge indebtedness to Van Zandt Williams of the American Cyanamid Company for benefits derived from conversations which contributed materially to the progress of the work, and for checking the transmission of the mica used for windows.

LITERATURE CITED

(1) Barnes, R. B., U. S. Patent 2,431,019 (Nov. 18, 1947).
(2) Fastie, W. G., and Pfund, A. H., *J. Optical Soc. Am.*, **37**, 762 (1947).
(3) Kidder, R. E., and Berry, J. W., U. S. Patent 2,443,427 (June 15, 1948).
(4) Luft, K. F., *Z. tech. Physik*, **24**, 97 (1943).
(5) McAlister, E. D., *Phys. Rev.*, **49**, 704 (1936).
(6) Pfund, A. H., *Science*, **90**, 326 (1939).
(7) Pfund, A. H., U. S. Patent 2,212,211 (Aug. 20, 1940).
(8) Pfund, A. H., and Gemmill, C. L., *Bull. Johns Hopkins Hospital*, **67**, 61 (1940).
(9) White, J. U., *J. Optical Soc. Am.*, **37**, 713 (1947).
(10) Williams, V. Z., *Rev. Sci. Instruments*, **19**, 135 (1948).
(11) Wright, N., and Herscher, L. W., *J. Optical Soc. Am.*, **36**, 195 (1946).

RECEIVED July 30, 1948.

Automatic Recording of Polarographic Data

Obtained with Platinum Electrodes

L. B. ROGERS[1], H. H. MILLER, R. B. GOODRICH[2], AND A. F. STEHNEY[3]
Oak Ridge National Laboratory, Oak Ridge, Tenn.

Polarographic analyses appear to be feasible using a platinum microelectrode and the usual automatic recording technique. The effects on the half-wave potential and the diffusion current of using different rates of polarization, larger electrode areas, and stirring have been examined. Under controlled conditions, the precision of the measurements is somewhat lower than for the dropping mercury electrode.

PLATINUM electrodes have been used for obtaining polarographic information by Laitinen and Kolthoff (*4*) who determined the reproducibility of data obtained by a manual procedure, and by Miller (*9*) who suggested a modified procedure in which the deposit was stripped from the solid electrode after each point. Because the method of obtaining a curve point by point is very time-consuming, it appeared desirable to examine the possibility of employing the usual polarographic procedure involving a continuously changing potential.

Zlotowski (*15*) and Walen and Haissinsky (*14*) used automatic recording with solid electrodes to obtain electrochemical information about reactions, but they did not examine the polarographic aspects of the procedure. After the present investigation had been started, Müller (*10*) reported polarographic studies in which solutions of electrolytes flowed past a stationary platinum electrode in a glass capillary. From Matheson (*7*) it was learned that polarographic studies with stationary electrodes had been carried out by H. A. Robinson of the Dow Chemical Company using an oscillographic technique (*8*). Since the completion of the study reported here, other papers (*1, 11, 12*) have appeared on the general subject of polarographic techniques applicable to solid electrodes.

In examining the possibilities of recording polarographic data continuously, it was necessary to study variables such as the effect of changing the size of the electrode, the effect of stirring the solution, and the effect of applying voltage continuously at different rates of change. The criteria used to check the polarographic reliability of the data were the reproducibility of the general shape of the curve, of half-wave potentials, and of diffusion currents. The chief consideration for quantitative analysis was the linearity of the relationship between the concentration of reducible ion and the diffusion current.

Silver was selected for this study because it has a simple redox reaction which is thermodynamically reversible, because knowledge of such a system is necessary if more complex systems are to be understood, and because the reaction illustrates an application of the platinum electrode to the analysis of an ion which is reduced in the region of potential that is positive in relation to the saturated calomel electrode (S.C.E.).

EXPERIMENTAL DETAILS

Reagents and Solutions. All chemicals used in the investigation were reagent grade, and all solutions were prepared with distilled water. The concentrations of standard stock solutions were known to better than 1%.

The standard polarographic solution was 5.00×10^{-4} *M* in sil-

[1] Present address, Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.
[2] Present address, Electronics Division, National Bureau of Standards, Washington, D. C.
[3] Present address, Department of Chemistry, University of Chicago, Chicago, Ill.

ver ion and 0.100 M in potassium nitrate. The pH, adjusted by the addition of about 2 drops of 6 N nitric acid, was 4.00 ± 0.01.

Tank nitrogen, used for removing oxygen from the polarographic cell, was freed from oxygen by passing it successively through three bottles of ammoniacal cuprous chloride followed by a bottle of 6 N sulfuric acid.

Apparatus. The platinum electrodes were made by fusing platinum wire into a soft-glass tube and making electrical contact in the usual way by filling the tube with mercury. The rotating electrode used in this study was similar to the one described by Laitinen and Kolthoff. The electrode was coated with cerésin wax several times, following which the platinum was scrapped to expose about 2.5 mm. of clean wire.

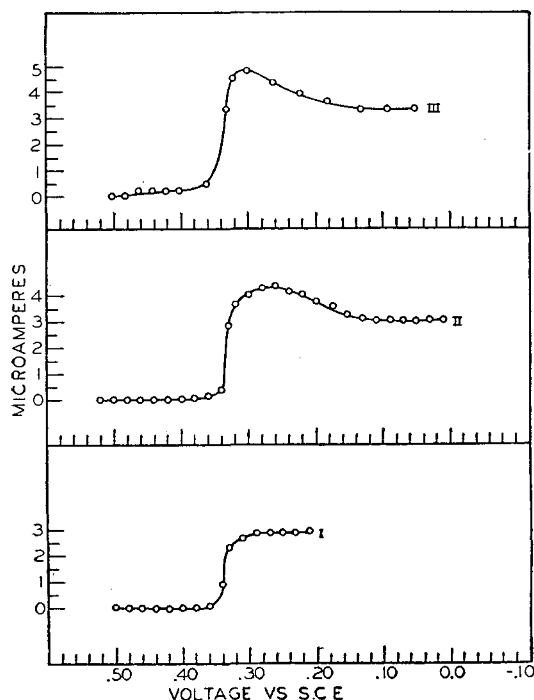


Figure 1. Curves Recorded Continuously

Using a 6-mm. wire electrode (0.10 sq. cm. area) in quiet solution
I. Manual
II. 1.46 mv./sec.
III. 4.38 mv./sec.

An agar bridge saturated with potassium nitrate connected the polarographic solution with a saturated calomel electrode. In order to be able to make a correction for IR drop, the resistance of the cell was measured before each run with a conductivity bridge, Model RC-1B, made by Industrial Instruments, Inc.

Polarograph Models XII and XX, manufactured by E. H. Sargent and Company, were used for continuous recording. Although it was possible to use these instruments to obtain "manual" current-voltage curves, these curves were usually obtained with a setup consisting of a Leeds & Northrup potentiometer, a Rubicon galvanometer, and an Ayrton shunt.

A thermostat was felt to be unnecessary for most of this work. The experiments were carried out at room temperature, which was usually 26° ± 2° C. Each of the series of studies concerning the relationship between diffusion current and concentration of the reducible ion was completed in quick succession, during which time the temperature of the room (and the solution) did not change noticeably—i.e., ±0.1° C. However, a bath maintained at 25.0° ± 0.1° C. was employed in studying the effect of the concentration of reducible ion on the half-wave potential.

For certain portions of this study it was necessary to stir the polarographic solution during a run. Mild stirring was obtained by bubbling nitrogen through the solution. For faster rates of stirring, a motor-driven glass rod with a 60° bend 2.5 cm. (1 inch) above the end was used. Its speed was adjusted to 365 r.p.m. by means of a Variac.

Procedures. CLEANING ELECTRODES. Preliminary tests showed that the electrode could be cleaned by imposing upon it a sufficiently positive potential, or by dipping it into 6 N nitric acid for 2 minutes or more, washing it with distilled water, and then drying with Kleenex before using. Because the acid treatment was faster, it was employed throughout this study.

DEAERATION OF POLAROGRAPHIC SOLUTIONS. Although deaeration was not necessary, in that silver ion was reduced before dissolved oxygen, the step was carried out in order to eliminate a possible variable.

POLAROGRAPHY. The manual technique of Laitinen and Kolthoff was employed to establish standard curves. When curves were recorded automatically, the rate of change of potential was calculated in each case from the length of time required by the slide-wire to change the applied voltage by one or more volts.

RESULTS

General Comparison of Results from Manual and Continuous Runs. As shown in Figure 1, continuously recorded curves usually had round maxima, whereas maxima were rarely observed in manual curves. Although the presence of maxima seemed to be the rule in continuous recording, some runs, which were duplicates of others for which maxima had been found, showed no signs of a maximum.

Maxima were expected from experience with the Laitinen and Kolthoff technique and they indicate that the rate at which the system reaches "diffusion equilibrium" is slower than the rate at which the voltage changes (3). Evidence for such an explanation is found in the observation that these maxima are not of the same type as those encountered with the dropping mercury electrode, in that the presence of gelatin exerts no repressive effect on them. If the maxima do owe their existence to a change with time in the flux of silver ion at the electrode surface, one would expect slower rates of polarization to produce curves with small maxima. However, the irregular occurrence of maxima prevented the authors from reaching a quantitative conclusion concerning the effect of the rate of polarization on the height of the maximum.

In Table I are listed the average values for the half-wave potential and the diffusion current obtained with three sizes of electrodes. Values listed in this table have been corrected for IR drop and residual current and represent the average of six or more runs. The instrumental limits of accuracy were considered to be about ±0.01 volt and ±0.1 microampere. However, the reproducibility limits of the experimental measurements were usually wider. Thus, although most of the values for half-wave potentials (in quiet solutions) fell within ±0.01 volt of the average, some varied by 0.02 volt. Disagreement among the values for the diffusion currents was more marked, and the differences increased with the size of the average diffusion current.

Table I shows that the half-wave potential is independent of the rate of polarization. The slightly positive shift observed for the 6-mm. electrode is within the limits of experimental error. The half-wave potential for a continuously recorded curve obtained by using the opposite direction of polarization also agreed within the limits of error with the values listed in Table I. Although faster rates of polarization did not affect the half-wave potential, they did produce larger diffusion currents in some instances.

Effect of Electrode Size. The size of the electrode does not affect the half-wave potential. As one would expect, an increase in the electrode area appeared to produce no important change in the shape of the polarographic wave after it had been corrected for IR drop.

Table I. Half-Wave Potentials and Diffusion Currents of Silver in Quiet Solutions

	Rate of Applied Voltage							
	Manual		1.46 Mv./Sec.		2.92 Mv./Sec.		4.38 Mv./Sec.	
	$E_{1/2}$, volt	i_d, μa.	$E_{1/2}$, volt	i_d, μa.	$E_{1/2}$, volt	i_d, μa.	$E_{1/2}$, volt	i_d, μa.
1. 1-mm. electrode (0.02 sq. cm.)	0.34	0.8	0.33	0.8	0.34	1.0	...	...
2. 6-mm. electrode (0.10 sq. cm.)	0.33	3.2	0.33	3.0	0.35	3.9	0.35	4.1
3. Foil electrode (2.14 sq. cm.)	0.34	29.4	0.34	32.7	...	...	0.33	32.7

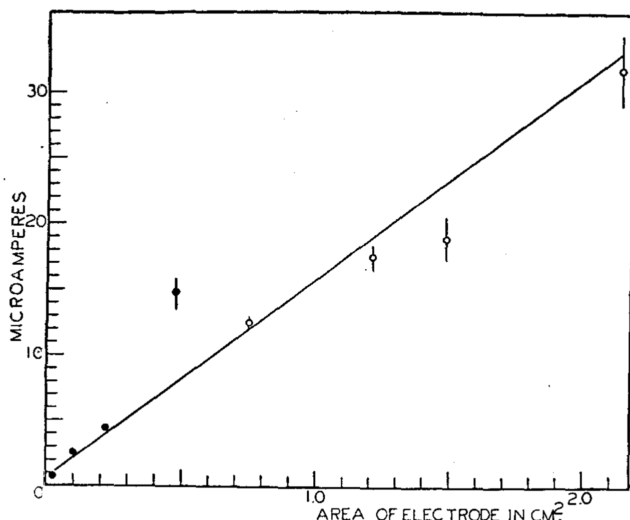


Figure 2. Relation between Electrode Size and Diffusion Current in Quiet Solution

O Foil electrodes
O Wire electrodes
Rate of polarization, 1.46 mv./sec.

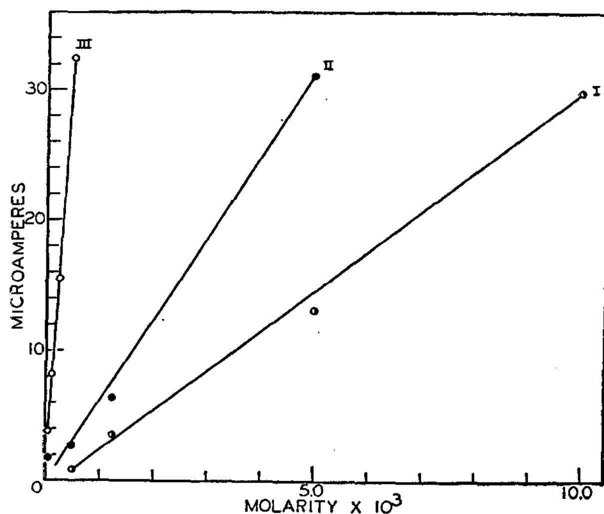


Figure 3. Relation between Concentration of Silver Ion and Diffusion Current

I. 1-mm. wire (0.02 sq. cm.)
II. 6-mm. wire (0.10 sq. cm.)
III. Foil (2.14 sq. cm.)
Rate of polarization, 1.46 mv./sec.

Difficulty was experienced in obtaining a good curve showing the known relationship between diffusion current and electrode area, despite care in measuring and cleaning each electrode. Therefore, Figure 2 served only to substantiate the expected trend. This figure illustrates the error that might be introduced in trying to predict the size of a diffusion current for an electrode by comparing its plane area to the area of a second electrode. It emphasizes the need for calibrating each electrode with a standard solution. Likewise, it is advisable to determine the residual current for each electrode individually.

A comparison of the curves on Figure 3 emphasizes the desirability of selecting an electrode area according to the region of concentration that is being examined—smaller electrodes are more suitable for higher concentrations and larger electrodes for lower concentrations of reducible ions.

Effect of Stirring. One would expect the results from stirred solutions to be similar to those obtained either with a rotating electrode or by flowing a solution past the stationary electrode, because in each case there is a movement of the solution past the surface of the electrode. This expectation was verified by the absence of maxima as well as the general results described below.

Stirring markedly decreased the reproducibility of both the half-wave potential and the diffusion current. In many cases, no half-wave potential could be calculated because of failure to obtain a diffusion current plateau. When half-wave potentials could be determined, the values were often spread over a range of 0.06 volt and the average value appeared to be somewhat lower than that for unstirred solutions. In general, these findings were consistent with those of Müller (*10*) and Laitinen and Kolthoff (*5*).

Faster rates of stirring not only produced larger diffusion currents but also decreased the probability of finding a diffusion current plateau. The probability for a particular electrode and a fixed rate of stirring could, however, be increased by using a faster rate of polarization. These trends are consistent with studies of the rotating electrode (*5*).

Relation between Concentration of Reducible Ion and Diffusion Current. One set of results is shown in Figure 3, where each point represents the minimum diffusion current, which was usually constant for more than 0.2 volt, for a single determination. Attempts to duplicate these curves were very successful. For currents greater than 3 microamperes, differences between two values for a given solution were usually less than 10%, often 5%. For currents less than 3 microamperes, agreement between duplicates nearly always fell within the 0.1 microampere limit mentioned. Thus, the relationship between diffusion current and concentration of silver was linear but the precision was not as high as that obtained with the usual dropping mercury electrode.

Relation between Concentration of Reducible Ion and Half-Wave Potential. Deposition of an element on a solid electrode is analogous to the deposition of an element insoluble in mercury on the usual dropping mercury electrode. Therefore, a shift of the half-wave potential to more negative potentials with dilution of the reducible ion should be found (*2*) in accordance with the equation

$$E_{1/2} = E^\circ + \frac{RT}{nF}\ln\frac{C_s f_s}{2} + \frac{pRT}{nF}\ln C_x F_x \qquad (1)$$

where subscript s refers to the reducible ion, subscript x to the complexing ion, p to the number of coordinating groups, C to the molar concentration, and f to the activity coefficient of the ion. The activity of the deposit is assumed to be unity. The sign of the potential in Equation 1 is reversed from the convention in Latimer (*6*), so that it agrees with the sign of the polarographic electrode.

In polarography, where the concentration of the reducible ion is almost always less than 1% of the total ionic strength, f_s is essentially unaffected by differences in the concentration of the reducible ion in two otherwise identical solutions. The third term need not be considered, providing the concentration of complexing agent is held constant. Similarly one can ignore corrections for liquid junction potentials, overvoltage, etc., by assuming that these factors will remain constant. A test of Equation 1 can, therefore, be made easily.

Table II shows that the change in the half-wave potential agrees very well with the value of −0.59 volt predicted by the equation. Because of this shift, it is essential to specify the concentration of an ion whenever the half-wave potential is reported for a reaction in which one component is deposited. The average half-wave potential listed in Table I (0.33 volt) does not agree with the value (0.29 volt) calculated for a 5.0 × 10⁻⁴ M solution from Table II. It is felt that the latter is a better value because the analyses were obtained under more carefully controlled conditions.

Table II. Effect of Changes in Concentration of Silver Ion on Half-Wave Potential

(In 0.1 M potassium nitrate at pH 4.00)

Concentration, M	$E_{1/2}$ Trial 1	$E_{1/2}$ Trial 2	$E_{1/2}$ Average	$\Delta E_{1/2}$
1.000×10^{-2}	+0.372	+0.375	+0.374	
				−0.055
1.000×10^{-3}	+0.316	+0.322	+0.319	
				−0.057
1.000×10^{-4}	+0.275	+0.259	+0.262	

Table III. Effect of Concentration on Half-Wave Potential

(For ferric to ferrous reduction in 0.1 M hydrochloric acid)

Concentration, M	$E_{1/2}$ Trial 1	$E_{1/2}$ Trial 2	$E_{1/2}$ Average	$\Delta E_{1/2}$
1.00×10^{-2}	+0.514	+0.505	+0.510	
				+0.003
1.00×10^{-3}	+0.520	+0.506	+0.513	
				+0.006
1.00×10^{-4}	+0.527	+0.511	+0.519	

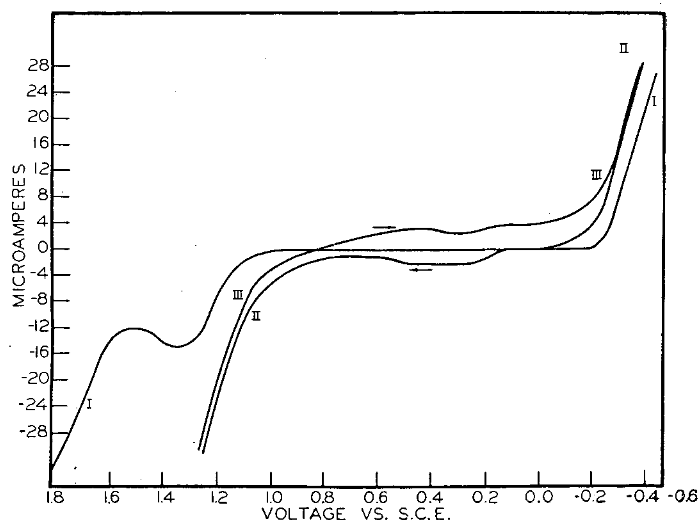


Figure 4. Comparison of Residual Currents

Obtained with stationary platinum electrode and rotated platinum microelectrode in 0.1 M HCl
I. Rotated microelectrode, potentials started at zero; 0.050 sq. cm. area, 600 r.pm.
II. Stationary electrode, 2.1 sq. cm. area, potentials started at zero
III. Stationary electrode potential started at approximately 1.3 volt

A shift in half-wave potential with dilution might not result if a soluble ion were produced. In the general equation

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{C_{ox} f_{ox}}{C_{red} f_{red}} + \frac{RT}{nF} \ln \frac{K_{ox}}{K_{red}} + \frac{RT}{nF} \ln \frac{(Cf)^p}{(Cf)^q} \quad (2)$$

the last two terms can usually be disregarded in the light of considerations discussed in connection with Equation 1, and the remainder of the equation can be simplified by assuming that, at $E_{1/2}$, C_{ox} equals C_{red} and f_{ox} equals f_{red}.

The results given in Table III show a slight drift of the half-wave potential toward more positive values for the more dilute solutions of iron. The drift may be a real one resulting from the simplifying assumptions that were introduced, but poor reproducibility of the measurements limits the validity of such a conclusion. Unfortunately, the attempts to measure a 1.00×10^{-5} M solution were unsuccessful.

Comparison of Curves Obtained with Large Stationary Electrode and Rotated Microelectrode. Electrodes of larger area are more suitable than microelectrodes for analyses of dilute solutions. Because a rotated electrode, compared to a stationary electrode, offers a similar increase in sensitivity, the following study was carried out to determine which approach was better.

First a comparison was made of the residual currents—i.e., blank runs—for the two electrodes in 0.1 M hydrochloric acid by starting at zero potential and proceeding toward negative potentials until hydrogen was evolved. An analogous wave was obtained by starting at zero potential and going toward positive potentials until oxygen was evolved. Compositive curves were constructed for each electrode, and are shown in Figure 4 as curves I and II.

If, instead of starting at zero potential and going negative, the start was made at a potential where the oxygen was being evolved, the curve for the stationary electrode did not coincide with the one described above. Throughout most of the region of positive potentials the residual current in the latter case was of the same order of magnitude but opposite in sign to that found when the potential was applied in the opposite direction. Curve III in Figure 4 is a representative example. The sign of residual current for the rotating electrode also depended upon the direction of polarization, but the differences were less conspicuous because the residual current was much smaller, on the order of 0.1 microampere or less.

Another comparison of the two types of electrodes was made by recording curves for each electrode under conditions of an actual analysis. One set of curves for the reduction of silver ion is illustrated by Figure 5. (The curves have not been corrected for IR drop.) In a similar study of the reduction of ferric ion (to ferrous) in 0.1 M hydrochloric acid, the shapes and sizes of the curves corresponded closely, the only difference being a more nearly symmetrical S-shape for curve III.

The results indicate that although the particular stationary electrode used in this study gave a larger diffusion current than the rotating electrode, the curves from the rotating electrode were easier to interpret because of the smaller residual current, the sharper initial break in the deposition curve, and the usual absence of a maximum. The half-wave potentials were within ±0.01 volt of the theoretical reversible value for 5.0×10^{-6} M silver in a 0.1 M solution of potassium nitrate.

Maxima unexpectedly appeared in some of the curves of the rotating electrode. Many of the maxima were relatively large, and they were often immediately preceded by an inflection in the polarographic wave as shown in Figure 6. Although this maxi-

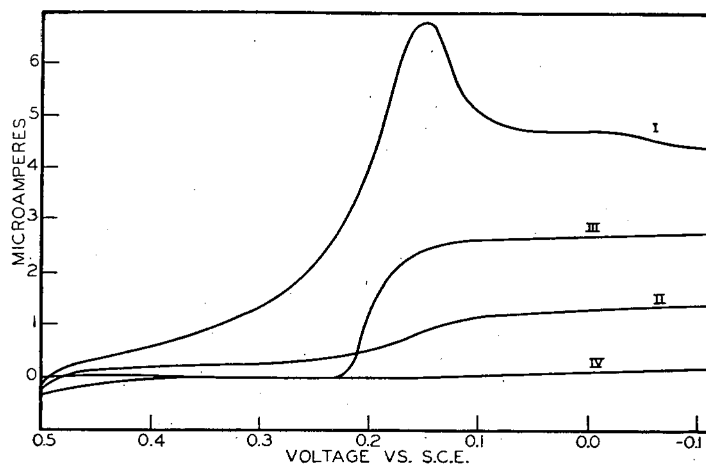


Figure 5. Comparative Curves

Obtained with stationary platinum electrode and rotated microelectrode for solution of 5.0×10^{-5} M $AgNO_3$ in 0.1 M KNO_3 and 0.01% gelatin at pH 4.0
I. Stationary platinum electrode, 2.1 sq. cm. area
II. Blank (residnal current) with stationary electrode
III. Rotated platinum microelectrode, 0.050 sq. cm. area, 600 r.p.m.
IV. Blank (residul current) with rotated microelectrode

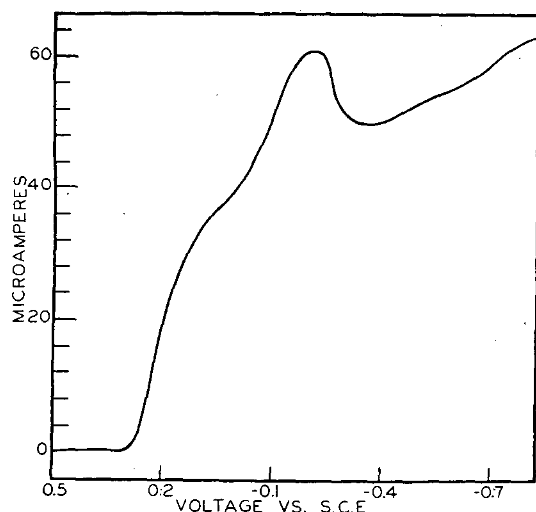


Figure 6. Polarographic Maximum

Obtained with rotated platinum microelectrode in solution containing 5.0 × 10^{-5} M $AgNO_3$ in 0.1 M KNO_3 and 0.01% gelatin at pH 4.0. Rate of polarization, 4.65 mv./sec.

mum was undoubtedly connected with the discharge of silver, it was probably the result of a brief discharge of hydrogen. Curve II in Figure 4 shows a similar but less striking maximum which was probably due to oxygen evolution.

Applications. The fact that polarographic procedures offer a rapid method for the determination of normal and formal (*13*) potentials has been known for some time (*2*). If a solid platinum electrode is used instead of a dropping mercury electrode for studying deposition reactions, calculations can be simplified because there is no longer a need for considering displacement of the wave as a result of amalgam formation.

The recording of curves for ions other than silver has been tested and found to be as satisfactory as for silver. Thus, it is possible to use the usual polarographic recording technique to make qualitative and semiquantitative analyses for ceric, permanganate, and dichromate ions whose analyses have heretofore been complicated by the spontaneity of their reactions with mercury. Similarly, oxidation of hydrazine and chromic ion, which cannot be performed because of the anodic dissolution of the dropping mercury electrode, has been examined with a platinum electrode. These studies will be reported later.

Solid electrodes simplify analyses in solutions containing hydrofluoric acid because it is possible to use a plastic cell to hold the solution and to coat, with wax, the glass in which the platinum electrode is embedded. It appears plausible to expect a solid electrode to be useful for studies in liquid ammonia and similar solvents.

ACKNOWLEDGMENT

The authors are indebted to D. E. Ehrlinger for making some of the measurements reported in this paper and to Kathryn Odom for helping to prepare the manuscript.

Work performed for Atomic Energy Commission under Contract W-35-058 eng. 71 with Monsanto Chemical Company and Contract 7405 eng. 26 with Carbide and Carbon Chemicals Corporation.

LITERATURE CITED

(1) Harris, E.D., and Lindsey, A. J., *Nature*, **162**, 413 (1948).
(2) Kerlinger, H., in Kolthoff, I M., and Lingane, J. J., "Polarography," p. 155, New York, Interscience Publishers, 1941.
(3) Laitinen, H. A., and Kolthoff, I. M., *J. Am. Chem. Soc.*, **61**, 3344 (1939).
(4) Laitinen, H. A., and Kolthoff, I. M., *J. Phys. Chem.*, **45**, 1061 (1941).
(5) *Ibid.*, **45**, 1079 (1941).
(6) Latimer, W. M., "Oxidation Potentials," New York, Prentice-Hall, 1938.
(7) Matheson, L. A., private communication.
(8) Matheson, L. A., and Nichols, N., *Trans. Am. Electrochem. Soc.*, **73**, 193 (1938).
(9) Miller, S. D., *Trudy Vsesoyuz. Konferentsii Anal. Khim.*, **2**, 551 (1943).
(10) Müller, O. H., 110th Meeting, AMERICAN CHEMICAL SOCIETY, Chicago, Ill., Sept. 9 to 13, 1946; *J. Am. Chem. Soc.*, **69**, 2992 (1947).
(11) Randles, J. E. B., *Analyst*, **72**, 310 (1947).
(12) Skobets, E. M., and Kacherova, S. A., *Zavodskaya Lab.*, **13**, 133 (1947).
(13) Swift, E. H., "System of Chemical Analysis," p. 50, New York, Prentice-Hall, 1940.
(14) Walen, R. J., and Haissinsky, M., *J. phys. radium* (7), **10**, 202 (1939).
(15) Zlotowski, I., *Roczniki Chem.*, **14**, 640, 651, 666 (1934).

RECEIVED May 17, 1948. Presented in part before the East Tennessee Section of the AMERICAN CHEMICAL SOCIETY, Knoxville, Tenn., May 24, 1947, and later in more detail before the Division of Analytical and Micro Chemistry at the 113th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.

Chemicotoxicological Examination of Foods

A Systematic Procedure

N. I. GOLDSTONE, *Department of Health, City of New York, N. Y.*

A systematic procedure is presented for the isolation and detection of 26 common toxic substances, comprising the four groups: volatile, metallic, alkaloidal, and nonalkaloidal. Sensitive analytical methods and confirmatory tests fitted into a methodical sequence are described in detail.

THE branch of the science of toxicology that deals with the isolation and detection of poisons is divided into two major classifications: the forensic, involving a crime either premeditated or accidental, to which scientific principles first began to be applied during the eighteenth century; and industrial poisoning, the object of aggressive social and scientific attack only for the past 50 years. A number of adequate texts (*3–5, 8–10, 14–22, 25–27, 30*) have been published in both categories, and these include precise chemical methods for the detection and estimation of a large number of toxic substances. In the forensic field the emphasis is naturally placed on the examination of the cadaver and body organs, with a chapter incidentally devoted to a discussion of the detection and identification of poisons in foods and related products. The latter subject is constantly receiving more attention in connection with the growing interest in the related field of trace elements in food (*7*).

Most textbooks present the subject in a tabular form incorporated within the framework of the particular system of classification preferred by its author, describing the various members of each group with their properties and physiological responses, in addition to analytical methods for detection and estimation. But nowhere in the literature is there to be found a simple, comprehensive, and systematic analytical procedure whereby the chemist without any considerable experience in this particular field is

enabled to proceed in an orderly manner to separate and identify toxic substances.

In large cities cases of suspected food poisoning are daily occurrences, and because community laws often make it obligatory on the part of the attending physician to report such cases to the public health authorities, a laboratory must be efficiently maintained for the analysis of the foods involved, often with the requirement that numerous samples be examined concurrently. The author has worked out a simple and sensitive procedure for chemical analysis which may prove of interest to food and health control laboratories, consultants, and perhaps also the industrial laboratory which will sooner or later be called upon to investigate

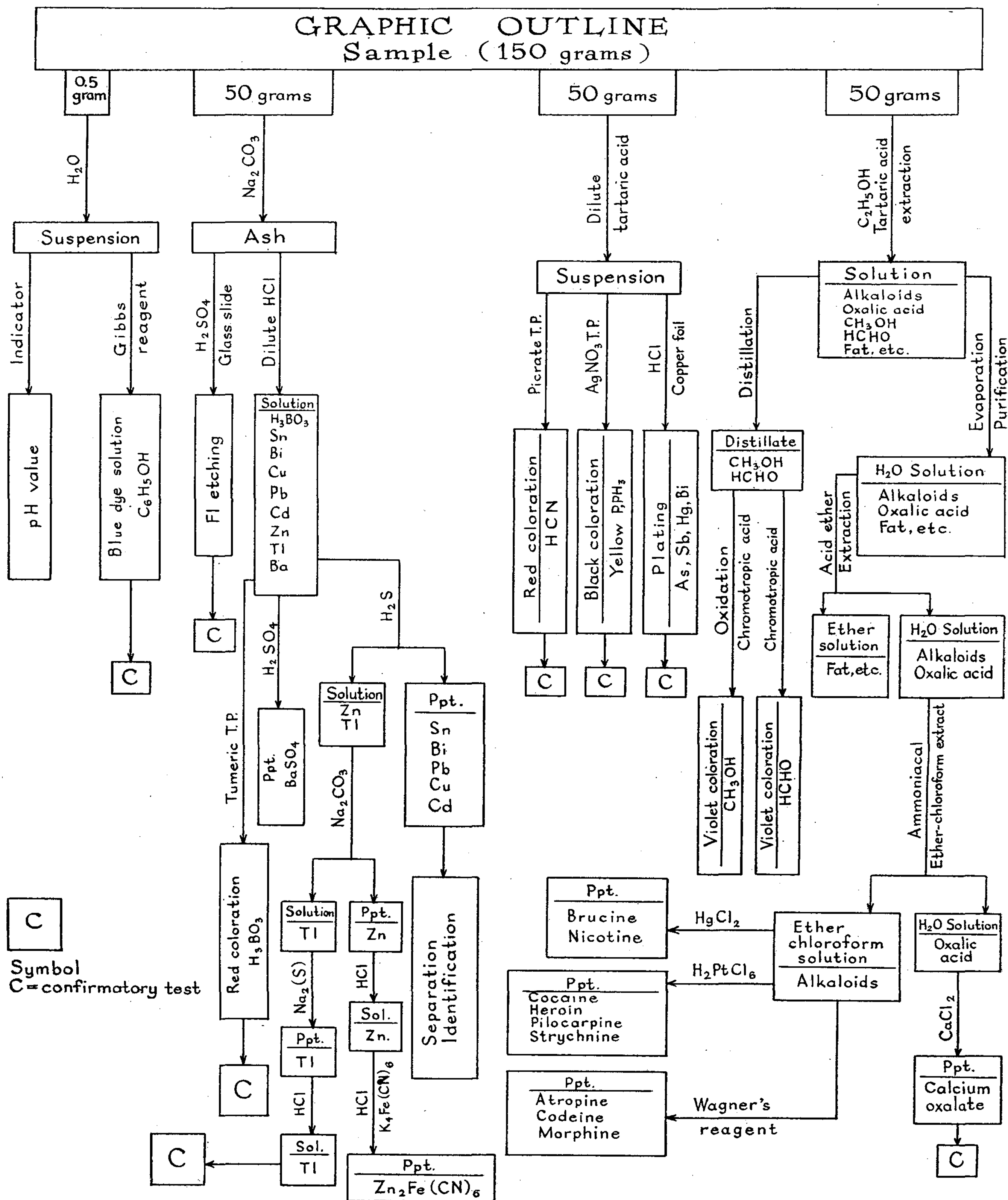


Table I. Substances Detected by Routine Toxicological Examination

Volatile	Metallic	Alkaloidal	Nonalkaloidal
Cyanides	Arsenic	Atropine	Borates
Yellow phosphorus	Antimony	Brucine	Oxalates
Zinc phosphide	Bismuth	Cocaine	Fluorides
Phenol	Mercury	Codeine	
Methanol	Lead	Heroin	
Formaldehyde	Cadmium	Morphine	
	Thallium	Pilocarpine	
	Zinc	Strychnine	
	Barium		

a food complaint originating in the company lunchroom. It might even be included in a course in qualitative analysis for the advanced student, as a practical application of analytical chemistry.

There are several systems used in classifying poisons, one, for example, based on physiological action, and another on chemical properties, overlapping to some extent, but for analytical purposes the system based on the method of isolation adopted by McNally (*22*) is the most logical one: (1) volatile, (2) metallic, and (3) alkaloidal and nonalkaloidal.

A schematic procedure must naturally fall far short of being all-inclusive. It can provide only for the detection of a limited number of all the foreign substances that might possibly find their way into a food product, but experience shows that when contamination does occur, it is confined almost invariably to a relatively small number of toxic substances, generally the active principles of commercial insecticides, rodenticides, or disinfectants which are usually found in a household, retail establishment, or processing plant. Excluded of necessity are complex organic compounds, toxic to man, sometimes occurring naturally in animal or plant tissue, and poisonous substances produced in food by microbic activity. The isolation and detection of these involve special, complicated procedures which so far have defied integration into a simple routine procedure.

Sometimes the preliminary organoleptic examination offers a clue to the presence of an unusual contaminant, whose characteristic odor, appearance or taste is easily recognizable. Analytical procedure is then focused on direct isolation and detection of the suspected substance. The history of the case, which should always be available to the analyst, may also provide a valuable base for analytical attack.

Aside from the obvious saving of time and expense resulting from the use of a systematic analytical procedure, it is of especial value where the size of the sample is limited to only a few small scraps left over from the meal supposedly responsible for the toxic symptoms.

The routine toxicological examination performed in the laboratories of this bureau on foods and allied products provides for the detection of the substances listed in Table I, with the exception of alkaloids, methanol, and formaldehyde, which are looked for only when the history of the case or the nature of the sample indicates a reasonable likelihood of their presence.

REAGENTS

Ammonium Molybdate Solution. Dissolve 10 grams of molybdic acid, MoO_3, in a mixture of 15 ml. of ammonium hydroxide (specific gravity 0.90) and 27 ml. of water. Cool and pour slowly with constant stirring into a cool mixture of 49 ml. of nitric acid (specific gravity 1.42) and 115 ml. of water. Keep in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant solution from any sediment and preserve in a glass-stoppered bottle.

Bromine Water Solution. Transfer about 5 grams of liquid bromine to a glass-stoppered bottle and cover with 100 ml. of water.

Calcium Chloride Solution. Dissolve 10 grams of calcium chloride in water and dilute to 100 ml.

Copper Foil. Cut a sheet of clean copper foil into pieces 1 cm. square and store in a dry glass-stoppered bottle.

Chromotropic Acid Solution. Dissolve 5 mg. of chromotropic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid, in 10 ml. of a mixture of 9 ml. of concentrated sulfuric acid and 4 ml. of water.

Gibbs Reagent. Dissolve 0.1 gram of 2,6-dibromoquinonechloroimide in 25 ml. of 95% ethyl alcohol. Stored in a brown glass-stoppered bottle in refrigerator, it remains stable for a week. Discard when solution turns brown. (Obtainable from Applied Research Institute, New York, N. Y.)

Mercuric Chloride Solution. Dissolve 5 grams of mercuric chloride in water and dilute to 100 ml.

Phenol Solution. Dissolve 100 mg. of phenol in water and dilute to 100 ml.

Picric Acid Test Paper. Wet a sheet of filter paper with a saturated water solution of picric acid and allow excess liquid to drain. Air-dry and cut into strips 1 × 7 cm.

Platinic Chloride Solution. Dissolve 5 grams of platinic chloride, $H_2PtCl_6.6H_2O$, in water and dilute to 100 ml.

Potassium Chromate Solution. Dissolve 5 grams of potassium chromate in water and dilute to 100 ml.

Potassium Ferrocyanide Solution. Dissolve 3.5 grams of potassium ferrocyanide in water and dilute to 100 ml.

Potassium Iodide Solution. Dissolve 10 grams of potassium iodide in water and dilute to 100 ml.

Potassium Permanganate Solution. Dissolve 5 grams of potassium permanganate in water and dilute to 100 ml.

Phosphoric Acid Solution. Dissolve 6 grams of sirupy phosphoric acid (85%) in water and dilute to 100 ml.

Silica. Fluorine-free powdered silica or glass.

Silver Nitrate Solution. Dissolve 10 grams of silver nitrate in in water and dilute to 100 ml.

Sodium Bisulfite Solution. Dissolve 5 grams of sodium bisulfite in water and dilute to 100 ml.

Sodium Borate Buffer Solution, a saturated solution of sodium biborate in water.

Sodium Carbonate Solution, a saturated solution of sodium carbonate in water.

Sodium Chloride Solution. Dissolve 5 grams of sodium chloride in water and dilute to 100 ml.

Sodium Polysulfide Solution. Dissolve 48 grams of sodium sulfide, $Na_2S.9H_2O$, and 4 grams of sodium hydroxide in water, add 1.6 grams of powdered sulfur, shake until sulfur dissolves, filter, and dilute to 100 ml.

Standard Buffer Solutions, pH range from 4.0 to 8.0 at 0.5 intervals. Made as described by Clark and Lubs (*29*) or most conveniently from definite volume solutions of standard tablets supplied by Coleman Electric Company, Maywood, Ill.

Standard Zinc Chloride Solution. Dissolve exactly 100 mg. of chemically pure zinc in hydrochloric acid and dilute to 1000 ml. Each milliliter of solution contains 0.1 mg. of zinc.

Turmeric Test Paper, purchased commercially.

Universal Indicator Solution. Selected indicators combined in one solution (*6*, *24*), purchased commercially.

Wagner's Reagent. Dissolve 1.27 grams of iodine and 2 grams of potassium iodide in water and dilute to 100 ml.

APPARATUS

Fluoride Etching Crucible. A satisfactory crucible for performing the etching test for fluorides is not available commercially, but may easily be fashioned in the laboratory.

Place a 30-ml. tall-form porcelain crucible on a wire gauze over a Bunsen burner and melt sufficient printer's linotype metal almost to fill the crucible. After cooling remove the mold by gently tapping the overturned crucible. Clamp the mold in a turning lathe and bore out to shape and approximate dimensions shown in Figure 1. Place the top edge against a piece of sandpaper set on a flat surface and rub until smooth.

For the cover, hammer a slug of lead on a flat metal surface to a thickness of 1 mm. and cut to size with a pair of shears. Smooth with sandpaper and punch a small hole in center.

Clean after each test by soaking in hot alkali solution and scrubbing with a wad of steel wool.

PROCEDURE

Organoleptic Examination. APPEARANCE. Examine the material with a magnifying glass for the presence of extraneous substances such as glass fragments, wood splinters, mold, or powdery substance not characteristic of the type of food under consideration. Evidence of fermentation or decomposition usually indicates bacterial contamination and may be toxicologically significant. In the case of canned goods note the physical condi-

tion of the container. Defects such as spring or swell, rust marks, pinhole leaks, or corrosion of internal metal surface may be relevant.

Odor. The presence of toxic substances such as yellow phosphorus, cyanides, phenols, and commercial solvents, even in very low concentration is often revealed by their characteristic odors. Rancidity and sour odors commonly result from bacterial contamination.

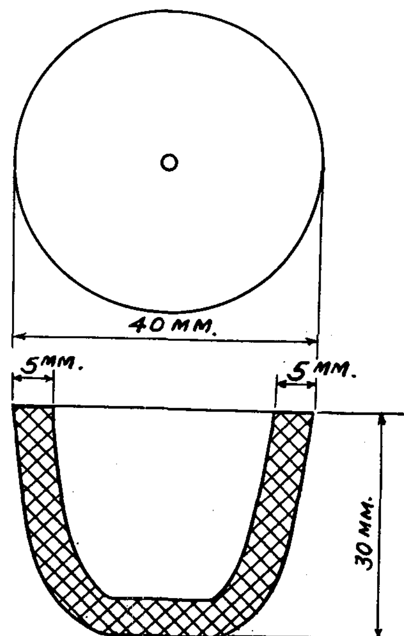


Figure 1. Fluoride Etching Crucible and Cover

Taste. From the standpoint of personal health hazard, and esthetically, the analyst is reluctant to taste specimens, but the history of the case generally includes a statement by the patient giving an abnormal taste reaction, often of doubtful reliability, but occasionally offering a directing clue.

pH Value. In a test tube macerate 0.5 gram of sample in 2 ml. of distilled water. Allow suspended matter to settle, decant a few drops of the supernatant liquid onto a white spot plate and add 1 drop of universal indicator. Compare against standard buffer solutions to which 1 drop of indicator has been added.

Phenol. To the residue remaining in the test tube in the pH value determination add 5 ml. of sodium borate buffer solution, shake, and test with litmus paper to ensure alkalinity. (If the solution is not alkaline, add a drop or two of sodium hydroxide solution, never ammonium hydroxide.) Allow to settle and decant or filter into another test tube. A perfectly clear solution is not essential. Divide the solution between two test tubes, and to one serving as a control add 1 drop of dilute phenol solution. Now add 3 drops of Gibbs (*1, 13*) reagent to each tube and shake. The formation of the deep blue indophenol dye indicates the presence of phenol.

Confirmatory Test. Transfer 10 to 25 grams of sample to a distilling flask, cover with 75 ml. of water, make slightly acid with sulfuric acid, and distill 50 ml. into a separatory funnel. Shake out the distillate with two 25-ml. portions of ethyl ether and evaporate the combined ether extracts slowly on a steam bath. Take up the residue in 5 ml. of sodium borate buffer solution, then add 3 drops of Gibbs reagent. The presence of phenol is confirmed by the formation of the deep blue indophenol dye.

Cyanides, Yellow Phosphorus, and Zinc Phosphide. Macerate 50 grams of sample in 50 ml. of water in a 250-ml. Erlenmeyer flask and add 10 ml. of tartaric acid solution. Suspend over the surface of the liquid a test paper strip moistened with a drop of silver nitrate solution, and a picric acid test paper strip moistened with a drop of sodium carbonate solution. Warm the mixture for 15 minutes at 50° C. on a steam bath. Presence of hydrocyanic acid is indicated by a red rose coloring of the picric acid paper. Blackening of the silver nitrate paper may indicate the presence of yellow phosporus or zinc phosphide. Volatile substances such as formaldehyde, formic acid, and hydrogen sulfide also blacken silver nitrate; hence a positive paper strip test must be confirmed by the distillation test.

Confirmatory Test. Suspend 25 grams of sample in 200 ml. of water, make slightly acid with sulfuric acid, and distill in a dark room, using an ordinary distilling apparatus with an upright condenser, or preferably that described by McNally (*23*). Presence of yellow phosphorus is confirmed by the appearance of a luminous ring in the upper part of the condenser. Minute amounts of hydrocyanic acid and yellow phosphorus will reveal their presence by characteristic odors if the condenser exit is cautiously smelled. If zinc phosphide is present phosphine is generated and this also has a very characteristic odor. Allow the vapors to condense into a flask containing a few milliliters of dilute nitric acid. Phosphorus and phosphine are oxidized to phosphoric acid, which is precipitated as the yellow phosphomolybdate on the addition of ammonium molybdate solution.

Reinsch Test for Arsenic, Antimony, Bismuth, and Mercury. Place 20 ml. of concentrated hydrochloric acid in the Erlenmeyer flask containing the material used in the paper strip test for phosphorus and cyanide. Drop in a strip of copper foil and allow to simmer on a hot plate for 0.5 hour. The presence of arsenic, antimony, or bismuth is indicated by deposition of a bluish-black plating of the reduced metal on the copper foil. Mercury salts deposit a shiny silvery plating of the free metal.

Confirmatory Tests. Carefully wash the plated copper foil with water, dry with alcohol and ether, place in a small dry test tube, and cautiously heat over a small flame. Arsenic, antimony, and mercury are deposited on the cooler area of the inner surface of the tube directly above the copper foil. Examine through a low powered microscope. Arsenic, as the trioxide, is deposited in characteristic octahedral crystalline form, mercury as a mass of minute opaque globules, and antimony as an uncharacteristic amorphous smudge. Bismuth does not volatilize, but its presence can later be confirmed in the ash of the sample.

Ashing. Transfer 50 grams of sample to a porcelain crucible, wet down with 1 ml. of saturated sodium carbonate solution, dry in an oven, carefully burn over a Bunsen flame, and complete to a gray or white ash at 500° C. in a muffle furnace.

Fluorides. Transfer a portion of the ash to a metal etching test crucible, moisten with a drop of water, and cautiously add concentrated sulfuric acid, drop by drop, until effervescence ceases. Wet the top edge of the crucible with sulfuric acid to form a seal, place cover on, and set a glass microscope slide over hole in cover. Heat the crucible on a hot plate for 1 hour, wash and dry the slide, and examine its surface for any etching produced by the generation of hydrofluoric acid. When the etching is very light from a small concentration of fluorine, breathing on it will render it more distinct, or its roughness may be felt by gently scratching with the fingernail.

Hydrofluoric acid in the presence of a borate forms a volatile borofluoride which does not have an etching action on glass. Hence when boron is present its interference must be eliminated by a separation of calcium borate from calcium fluoride based on the insolubility of the latter in dilute acetic acid (*11*).

In a similar manner, hydrofluoric acid reacts with silica to form the volatile fluosilicic acid, and this too lacks the ability to etch a glass surface. Here, however, it is unnecessary to make a separation, for the formation of fluosilicic acid serves as the basis of an even more sensitive test for a soluble fluoride than the etching test, for which it may be substituted or used as a confirmatory test, in the manner adapted by Gettler and Ellerbrook (*12*) for the detection of fluorine in tissues.

Confirmatory Test. Transfer a pinch of the dry ash to a 5-ml. porcelain crucible, mix with an equal amount of powdered glass or silica, cautiously add a few drops of concentrated sulfuric acid, and immediately cover with a microscope slide, from the under surface of which is suspended a small drop of sodium chloride solution. Place the crucible on a hot plate maintained at a temperature of 150° C. and put a drop of cold water on the upper surface of the slide directly over the suspended drop, to retard evaporation. After 5 minutes' heating remove the slide, allow the suspended drop to dry in the air, and examine under a microscope (450 magnifications) for six-pointed stars or hexagonal crystals of sodium fluosilicate. Ten micrograms of fluorine under this treatment should be detected without difficulty.

Borates. Dissolve the remainder of the ash in 20 ml. of water and make slightly acid to litmus paper with hydrochloric acid. Moisten a strip of turmeric test paper with a drop of the solution and allow to dry in air. Presence of a borate is indicated by a cherry red coloring of the test paper, which changes to a dark blue-green on wetting with a drop of ammonium hydroxide and is restored by acid.

Soluble Barium Salts. Add 5 ml. of concentrated hydrochloric acid to the solution of the ash obtained in the test for borates and evaporate to dryness on a steam bath. Redissolve the residue in 25 ml. of hot water, filter, and wash into a 125-ml. Erlenmeyer flask. To 1 ml. of the filtrate in a test tube add a few drops of

dilute sulfuric acid. A white precipitate of barium sulfate indicates the presence of a soluble barium salt.

Lead, Bismuth, Copper, and Cadmium. Pass a current of hydrogen sulfide gas through the filtrate obtained in the test for barium salts for 15 minutes and allow to stand until the precipitate coagulates. Pass through a paper filter, wash, and retain the filtrate for the detection of zinc and thallium. The precipitate, which may contain tin, lead, copper, bismuth, and cadmium, is subjected to the conventional procedure for separating and identifying metals of this group, found in any textbook on qualitative analysis.

Zinc. Boil the filtrate obtained in the separation of the copper group to remove hydrogen sulfide and make alkaline with sodium carbonate solution, precipitating zinc, iron, and the alkaline earth metals. Filter, wash with water, and retain the filtrate for the detection of thallium. Return precipitate and paper to the original flask, add 25 ml. of dilute hydrochloric acid, 5 ml. of bromine water to oxidize any iron present, boil to remove excess bromine, and add an excess of ammonium hydroxide to precipitate iron and alkaline earth phosphates. The zinc remains in solution. Cool, filter into a Nessler tube, add 10 ml. of hydrochloric acid (1 to 1), then 1 ml. of potassium ferrocyanide solution, and dilute to 100 ml. Presence of zinc is indicated by the formation of a white precipitate of zinc ferrocyanide. Because many foodstuffs, particularly the proteins, contain small amounts of zinc, it is advisable for the analyst to run a control along with the sample to accustom himself to make rough estimations of small concentrations of zinc. Pipet 2 ml. of standard zinc chloride solution, add the reagents, and compare the turbidities in both tubes.

Thallium. Add 1 ml. of sodium polysulfide solution to the alkaline filtrate obtained in the detection of zinc. A brown precipitate of thallium sulfide indicates the presence of thallium. Let stand until the precipitate coagulates, filter and wash, dissolve the precipitate in a few milliliters of dilute sulfuric acid, boil to remove hydrogen sulfide, cool, and neutralize exactly with ammonium hydroxide, using litmus paper as indicator.

CONFIRMATORY TEST. Divide the solution into two equal portions in test tubes. Make one portion slightly alkaline with ammonium hydroxide and add 1 ml. of potassium iodide solution. A yellow crystalline precipitate of thallium iodide is formed. To the other test tube add 1 ml. of potassium chromate solution, producing a yellow precipitate of thallium chromate.

Extraction of Alkaloids. Transfer 50 grams of sample to a Florence flask, macerate in 50 ml. of 80% alcohol, add 5 ml. of tartaric acid solution, and reflux on a steam bath for 1 hour. Connect the flask with a suitable condenser and distill over 5 ml. of liquid, retaining this for the detection of methanol and formaldehyde if the nature of the material is such that the presence of either or both of these substances is suspected. Filter the mash, wash well with 80% ethyl alcohol, and evaporate the filtrate on a steam bath to a volume of 5 ml. Slowly add 50 ml. of 95% ethyl alcohol, stirring and breaking up any clumps formed with a glass rod, again filter, and wash with ethyl alcohol. Evaporate on a steam bath to remove the alcohol, dilute to a volume of 25 ml. with water, and transfer to a separatory funnel. Extract with three 25-ml. portions of ethyl ether, wash the combined ether extracts twice with 2 ml. portions of water, and add the washings to the original water solution. This ether extract from acid solution may contain in addition to fat such compounds as salicylic acid, acetyl salicylic acid, barbituric acid, acetanilide, chloral hydrate, DDT, phenols, and organic solvents, which may be tested for if their presence is suspected.

Make the water solution distinctly alkaline to litmus paper with ammonium hydroxide and extract with three 25-ml. portions of ethyl ether, followed by two extractions with 25-ml. portions of chloroform. Retain the water solution for the detection of oxalates. After washing the combined solvent extracts with several 2-ml. portions of water, pass through a dry paper filter, evaporate slowly on a steam bath to remove the solvents, and take up the residue in 4 drops of water.

Of the common alkaloids this residue may contain atropine, brucine, codeine, heroin, morphine, cocaine, nicotine, pilocarpine, and strychnine. With a glass rod transfer 3 separated drops to a glass microscope slide. To the first drop by means of a glass rod add a drop of Wagner's reagent, to the second a drop of mercuric chloride solution, and to the third a drop of platinic chloride solution. The formation of a precipitate in any of the drops indicates the presence of an alkaloid. For identification examine the slide under a microscope without stirring or covering (100 to 150 magnifications) and compare crystal characteristics with known controls prepared in the same manner, and also with comparison chart. Confirmatory tests for specific alkaloids may then be applied.

Oxalates. Make the water solution obtained in the extraction of alkaloids slightly acid with hydrochloric acid and warm on a steam bath to remove residual ether and chloroform. Add 1 ml. of calcium chloride solution, make ammoniacal, filter, and wash the precipitate with water. Redissolve the precipitate in 5 ml. of hot dilute hydrochloric acid, filter, wash with water, evaporate the filtrate almost to dryness on a steam bath, cool, take up in 25 ml. of 95% ethyl alcohol, and then add 25 ml. of ethyl ether. Filter through paper and repeat if necessary until a clear solution is obtained. Evaporate off the ether and alcohol on a steam bath and take up residue in a few milliliters of water. Add 1 ml. of calcium chloride solution and make ammoniacal. The presence of oxalic acid is indicated by the formation of a white silky precipitate of calcium oxalate.

Table II. Characteristics of Microchemical Tests for Alkaloids (2)

	Reagent	Description of Crystals
Atropine	Wagner's	Rods and triangular plates, singly *and in groups*
Brucine	Mercuric chloride	Transparent, rectangular plates and rosettes of thin plates
Cocaine	Platinic chloride	Delicate feathery crystals
Codeine	Wagner's	Red-brown precipitate, crystallizing in yellow blades, extending in branches
Heroin	Platinic chloride	Spherical clusters of golden yellow needles around a nucleus
Morphine	Wagner's	Heavy red-brown precipitate in shining overlapping plates extending in branches
Nicotine	Mercuric chloride	Radiating transparent blades in slight excess of H_2SO_4. Featherlike blades with HCl
Pilocarpine	Platinic chloride	Layers of thin, yellow triangular plates
Strychnine	Platinic chloride	Clusters of wedge-shaped needles moving about in the field

CONFIRMATORY TEST. Filter the precipitate, wash with water, and dissolve in a small amount of hot dilute hydrochloric acid. The decolorization of a drop of potassium permanganate solution added confirms the presence of oxalic acid.

Methanol and Formaldehyde (28). Transfer 1 drop of the distillate obtained in the extraction of alkaloids to each of two test tubes. To the first tube add a drop of water, a drop of phosphoric acid solution, and a drop of potassium permanganate solution, let stand for 1 minute, then add sodium bisulfite solution drop by drop until the permanganate color is discharged. If a brown color remains add another drop of phosphoric acid solution. To both tubes now add 5 ml. of freshly prepared chromotropic acid solution and heat in a water bath at 60° C. for 10 minutes. The appearance of a violet color in both tubes indicates the presence of formaldehyde and possibly methanol. If the color appears only in the tube oxidized with permanganate, methanol alone is present.

DISCUSSION

Wherever variations from accepted analytical methods are found, they are slight and in the interest of easier manipulation and isolation of the particular substance the analyst is seeking to identify. In the detection of oxalates, for example, the intermediate step of precipitating all the insoluble calcium salts is merely a convenient short-cut for separating oxalic acid from most of the extraneous matter absorbed into the alcoholic extract. Similarly, the isolation of zinc is effected more readily through the ammonium hydroxide precipitation of interfering metals than by the hydrogen sulfide separation.

As the contamination of a food product with a small amount of toxic substance generally does not affect the pH value appreciably, the inclusion of this determination in the scheme requires an explanation. Its utility lies in detecting the possible presence of a caustic alkali or acid, besides serving as a clue to some other abnormality. A good illustration occurred in the instance where the author examined a sample of granulated sugar taken from a public lunchroom, which had accidentally been contaminated with trisodium phosphate, causing a "food poisoning." The pH value immediately gave a clue to the presence of an alkali, and its identification followed soon after.

The presence of an alkaloid in a food product is a rare occurrence, but there is nevertheless a logical reason for the inclusion of this group. Sometimes in poisoning cases patent medicines or drug products in addition to specimens of urine, blood, or vomitus are submitted for analysis along with food products. The proce-

dure is also applicable to these, and the examination would be incomplete without a search for alkaloids. The author's record of case histories includes a sample of whisky to which morphine had been added with malicious intent. Caution is necessary in the interpretation of analytical results. Routine toxicological examination of foods produces negative results in a majority of cases, for it is rather unusual for foods to be contaminated with chemical poisons. The incidence of the latter is much lower than that of bacterial contamination. Chemical poisons have a characteristically rapid action on the system, although exceptions have been noted in cases where the amount ingested was just enough to induce a delayed physiological response. The rule generally followed is that a time interval of less than 2 hours between consumption of the suspected food and the onset of toxic symptoms points to a chemical causative agent, without ruling out the possibility of a bacterial toxin as the offender. Frequently both chemical and bacteriological findings are negative even where more than one victim has complained of gastric disturbances. The analyst may then be apt to question his results and fear that perhaps he has overlooked something. Experience will give him greater confidence. A more thorough investigation of the background of the case may elicit the information that the victim has a history of chronic gastric disorder, and his latest attack is unrelated to the food suspected. Even where food poisoning involves a number of individuals partaking of a common meal, in the absence of positive chemical and bacteriological findings the phenomenon of mass hysteria must not be overlooked. In some cases sampling is incomplete, the victim suspecting only a single item of the whole meal consumed and submitting this alone for analysis. The question of the purity of the rest of the meal thus remains unanswered.

Many foodstuffs during processing and canning absorb traces of such metals as copper, tin, and lead. The amounts are usually less than the normal tolerances considered allowable and safe in foodstuffs and yet great enough to produce slight though observable turbidities in the hydrogen sulfide precipitation. Such minute concentrations must be ignored as insufficient to produce acute toxic effects.

Frequently in cases of food poisoning the attending physician may prescribe such medications as bismuth or calomel. The history of the case should include a statement as to the medication administered, to safeguard the analyst against an erroneous interpretation where he finds these metallic substances in specimens of stomach contents or urine submitted for analysis.

Whenever qualitative tests indicate the presence in a food product of a quantity of toxic substance sufficient to produce an observable physiological response, a quantitative determination is essential to a correct diagnosis of the cause of intoxication. It is beyond the scope of this paper to discuss the extensive literature on this subject, and the analyst is referred to standard books on toxicology which include detailed quantitative methods.

The sensitivity of the entire procedure is great enough to permit its designation at the microchemical level, as it provides for the detection of as little as 1 mg. of substance in all instances and well below this quantity in some. As outlined, the procedure assumes sufficient sample to provide 50 grams each for the three major analytical schemes, in addition to a reserve retained as an insurance against a laboratory accident, for a check analysis or quantitative determination. If the entire sample is limited to a few grams, greater care in handling is required. The procedure remains unchanged, except that smaller apparatus is used and the volume of reagents and dilutions are somewhat reduced. Recently published texts on microchemical qualitative analysis may furnish the analyst with ideas on manipulative technique which he can adapt. If the concentration is such that 1 gram or less of foodstuff contains a few milligrams of toxic substance, no analytical problem arises; this quantity is detectable regardless of the size of the sample. A normal helping of a dinner course, say, 100 grams, containing only several milligrams of a toxic metal such as cadmium or antimony, is capable of inducing an acute physiological response, yet if only a small fraction of the helping is available as a sample, the contaminant may escape detection. Such a set of circumstances is rather improbable, but granting its occurrence, the chemist is at a disadvantage until greater sensitivity in analytical method is achieved.

Sometimes very small samples are amenable to successful analysis, if some thought is given to reasonable probabilities. Recently the author examined a slice of bread in the center of which was embedded a small clump of green foreign material weighing not more than 1 or 2 mg. The possibilities were that the material consisted of green mold, Paris green, Bordeaux mixture, or a coal-tar dye. The particle was carefully removed from the bread and divided into two portions. Microscopic examination eliminated mold growth. The substance proved to be water-soluble, and hydrogen sulfide gave no black or brown turbidity, denying the presence of the copper-bearing insecticides. A green coloration was imparted to a small strand of wool immersed in a warm dilute acid solution of the material, proving the presence of an acid coal-tar dye, probably a confectionery food color commonly used in bake shops.

SUMMARY

The means of isolating and detecting in food and allied products 26 specific substances toxic to man, classified in four groups, are described in detail, and the manner of isolating a number of other compounds which may have toxicological significance is indicated. Confirmatory tests are included where they are of value. The entire procedure is systematized into a compact analytical sequence, economical in time and material. Directions for molding a metal crucible especially adapted for the detection of fluorides are given.

LITERATURE CITED

(1) Am. Public Health Assoc. and Am. Water Works Assoc., "Standard Methods of Water Analysis," 8th ed., p. 245, 1936.
(2) Assoc. Offic. Agr. Chemists, "Official and Tentative Methods of Analysis," 6th ed., p. 740, 1945.
(3) Autenrieth, W., "Laboratory Manual for Detection of Poisons and Powerful Drugs," 6th ed., Philadelphia, P. Blakiston's Son & Co., 1928.
(4) Bamford, F., "Poisons, Their Isolation and Detection," Philadelphia, P. Blakiston's Son & Co., 1940.
(5) Brookes, V. J., and Alyea, H. N., "Poisons, Their Properties, Chemical Identification, Symptoms, and Emergency Treatments," New York, D. Van Nostrand Co., 1946.
(6) Burg, J. H. van der, *Chem. Weekblad*, 36, 101–2 (1939).
(7) Calvery, H. O., *Food Research*, 7, 313 (1942).
(8) Davison, F. R., "Synopsis of Materia Medica, Toxicology, and Pharmacology," 3rd ed., St. Louis, C. V. Mosby Co., 1944.
(9) Erb, R. C., "Poisoning the Public," Philadelphia, Dorrance & Co., 1937.
(10) Feigl, F., "Qualitative Analysis by Spot Tests," 2nd English ed., New York, Nordemann Publishing Co., 1939.
(11) Furman, N. H., "Scott's Standard Methods of Chemical Analysis," 5th ed., p. 404, New York, D. Van Nostrand Co., 1943.
(12) Gettler, A. O., and Ellerbrook, L., *Am. J. Med. Sci.*, 197, 625 (1939).
(13) Gibbs, H. D., *J. Biol. Chem.*, 72, 649 (1927).
(14) Gonzales, T. A., Vance, M., and Helpern, M., "Legal Medicine and Toxicology," New York, Appleton-Century Co., 1937.
(15) Hamilton, Alice, "Industrial Toxicology," New York, Harper & Bros., 1934.
(16) Jacobs, M. B., "Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," New York, Interscience Publishers, 1941.
(17) Kobert, R., "Kompendium der praktischen Toxikologie," Stuttgart, F. Enke, 1912.
(18) Lanza, A. J., and Goldberg, J. A., "Industrial Hygiene," New York, Oxford University Press, 1939.
(19) Lehmann, K. B., and Flury, F., "Toxicology and Hygiene of Industrial Solvents," Baltimore, Williams & Wilkins Co., 1943.
(20) Leschke, E., "Clinical Toxicology," tr. by C. P. Stewart and O. Darrer, London, J. & A. Churchill, 1934.

(21) Maas, A. R., "Poisons, Their Detection and Estimation," in N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed., New York, D. Van Nostrand Co., 1943.
(22) McNally, W. D., "Toxicology," p. 3, Chicago, Industrial Medicine, 1937.
(23) *Ibid.*, p. 21.
(24) Merck's Index, 5th ed., p. 601, Rahway, N. J., 1940.
(25) Sollmann, T. H., "Manual of Pharmacology," 4th ed., Philadelphia, W. B. Saunders Co., 1932.
(26) Tanner, F. W., "Food-Borne Infections and Intoxications," Champaign, Ill., Twin City Printing Co., 1933.
(27) Underhill, F. P., "Toxicology or Effects of Poisons," 2nd ed., Philadelphia, P. Blakiston's Son & Co., 1936.
(28) U. S. Pharmacopoeia, XIII, p. 20, 1947.
(29) *Ibid.*, p. 871.
(30) Witthaus, R. A., "Manual of Toxicology," New York, William Wood & Co., 1911.

Received August 19, 1948.

Determination of Relative Color Density of Liquids

A Rapid Photoelectric Method

LOUIS LYKKEN and JOHN RAE, JR.[1]
Shell Development Company, Emeryville, Calif.

A rapid method for the reproducible photoelectric determination of the relative color density of liquid products involves measurement of the optical density of the test material relative to that of an easily prepared liquid color standard selected to approximate the test material in hue and color density. The method is particularly applicable to the determination of colored substances present in the wide variety of liquid products exhibiting spectral characteristics like those of normal lubricating oils and other "naturally colored" liquids having smooth, spectrophotometric absorption curves with maximum absorption in the near ultraviolet. The results obtained are easily visualized in terms of real psychophysical significance and readily correlated with such phenomena as oxygen degradation of lubricating oils, gasolines, motor fuel blends, solvents, polymers, and other materials. This method is especially useful as a specification method for measuring color density which is often taken as a criterion of purity, or as a control method for following manufacturing or refining processes.

As AN indication of the purity or degree of refinement of many products, color is often the only criterion that is readily available to and appreciated or understood by the consumer. The measurement of color is a very useful research tool, particularly for following the course of chemical reactions in purification, aging, and oxidation studies. Moreover, with modern improved photoelectric colorimetric equipment, color considerations are becoming increasingly important and useful to the research chemist. For these reasons, methods for measuring color are of widespread interest to the chemical industries.

The several methods available for the complete description of color (*3*) require the use of unnecessarily expensive equipment or involve somewhat complex visual measurements. Moreover, the results obtained by these comprehensive methods are unnecessarily complicated for many purposes. In many instances, a measure of the total transmittance of a given test material in the visible region of the spectrum is sufficient for the color description required and, indeed, is often more useful than spectrophotometric analysis in the study of certain types of chemical reaction, such as oxidation.

In the American petroleum industry, the most widely used "total transmittance" or color density method is the National Petroleum Association (NPA) or A.S.T.M. union color number method (*1*) for measuring the color density of lubricating oils. This method depends upon visually matching the color density of the light transmitted by the test material with one of a series of colored glasses. However useful this method has been in the past, it is limited by poor reproducibility because different observers seldom strike the same compromise among the three attributes of color sensation—hue, saturation, and lightness (*3*). Furthermore, the glass color standards are difficult to duplicate spectrally from set to set and they provide a discontinuous scale which can be evaluated only at fixed intervals; color values falling between these points can only be roughly estimated. Other visual methods such as the Saybolt (*2*) and Hazen (*7*) methods for measuring color density are subject to errors similar to those mentioned in connection with the National Petroleum Association method.

Among the first to suggest overcoming these difficulties by the use of a photoelectric colorimeter were Story and Kalichevsky (*9*) who, in 1933, described a photoelectric method for measuring the color of liquid petroleum products. However, the photoelectric method was slow to gain acceptance by industry. Perhaps the chief contributing factor was the lack of precise photoelectric colorimeters which have come into common use only during the past decade and even today are not being used to best advantage in many laboratories.

In 1942, Diller, DeGray, Wilson, and co-workers (*4*, *5*) described a photoelectric method based on absolute transmittance and using a tungsten filament light source, a broad band filter, and a barrier-layer type of photocell to measure the amount of the light transmitted through the test material contained in a specified round cell. In this method, no provision was made for inevitable changes in instrument response resulting from variations in spectral characteristics of the light source, in photocell response, and in spectral characteristics of the light filter employed. For these and less obvious reasons, the method has not been generally accepted. A recent contribution to photoelectric methods for color density evaluation has been made by Osborn and Kenyon (*8*). In their thorough treatment of the subject, these authors have rendered an excellent discussion of the theoretical aspects and have described a rather elaborate method for setting up color standards for instrument calibration, preparatory to measuring the color density of a given line of spectrally similar products. Another interesting contribution to the field of photoelectric color measurement has been made by Whyte (*10*), who devised several color grading systems for tallows and greases.

Any specification method should give the same results regardless of the peculiarities of the particular apparatus or instrument

[1] Present address, Shell Oil Company, Inc., Houston, Tex.

used. Because different colorimeters may not give the same response even when they are of the same make, and the response of a given instrument may change significantly from month to month, any specification method for the measurement of color density should be designed to compensate for variations in colorimeter response. Prior to the work of Osborn and Kenyon (8), no established photoelectric color measurement method provided for this necessary requirement. Osborn and Kenyon compensated for instrument response variations by use of a carefully selected set of color comparison standards. The same result was achieved independently in these laboratories by use of an easily prepared single comparison standard for a number of products, having the same general spectral characteristics and covering an approximately twentyfold color concentration range. Auxiliary comparison standards are used for relatively dark and relatively light liquids.

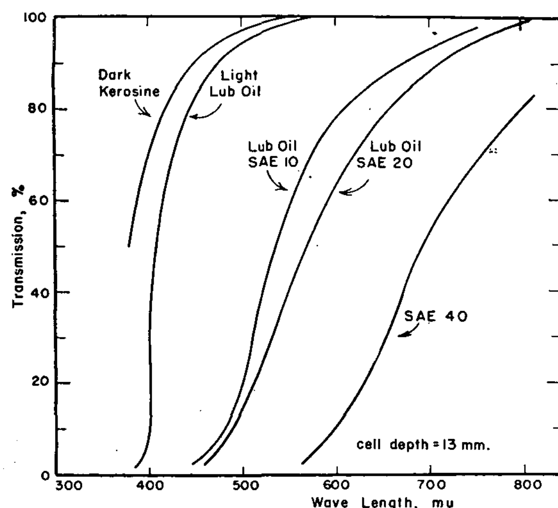


Figure 1. Spectral Characteristics of Typical Petroleum Products

The method given in this paper uses Gardner-type color comparison standards (6) composed of an aqueous solution of iron and cobalt chlorides acidified with hydrochloric acid. These standards are easily prepared, universally reproducible, and stable indefinitely, provided they are kept at a moderate room temperature (20° to 25° C.). They have been generally accepted by industry and tested over a period of years in various commercial visual color methods.

In the method described here, the relative color density of a liquid is obtained by measuring the optical density of the liquid and of a given color comparison standard, using any of several commercially available photoelectric colorimeters equipped with a specified broad band light filter, a suitable light reduction mask, and light absorption cells of specified depth having parallel, planar faces. The relative color density of the test material is calculated by dividing its optical density by that of the color comparison standard. The result obtained is, therefore, a direct comparison of the color density of the test material to that of the standard. It is of direct psychophysical significance, as the light filter is chosen so that the net response of the colorimeter approximates the response of the normal eye. Moreover, as a consequence of Beer's law, relative color density is, to a fair approximation, proportional to the color concentration in the test material. For example, a relative color density of 2.00 simply means that the test material is twice as dark as the comparison standard, a value of 1.00 indicates that the test material has the same color density as the standard, and a value of 0.00 indicates "waterwhiteness."

The relative color density method is empirical, inasmuch as the value obtained is of significance only when expressed with relation to the color comparison standard used and, to a lesser extent, with relation to the length of the light path used. It does not indicate the hue of the sample but merely measures the total light absorption of the sample; thus, it is possible for samples visually differing in hue or saturation to have the same relative color density. The method is particularly useful for measuring color changes in a series of liquids exhibiting similar spectral characteristics. In fact, for such a series of liquids, an approximate correlation of relative color density values with I.C.I. tristimulus values could be made in a manner similar to that described by Diller and coworkers (4). However, in the applications for which the relative color density method has been found useful, the results obtained from such a correlation would appear to be of little practical value. Results of similar magnitude and reproducibility would undoubtedly be found with an I.C.I. tristimulus green (luminosity) filter (3) in place of the chosen broad band filter but, for all practical purposes, the results would still be empirical and subject to the limitations of interpretation or correlation found for the relative color density values.

The relative color density method is designed particularly as a specification or control method for lubricating oils and similar products, but is generally applicable to any nonaqueous or aqueous solution. It is particularly applicable to materials, such as petroleum products, which show predominant absorption in the near-ultraviolet portion of the visible spectrum (see Figure 1). The method is most precise when applied to samples having color densities close to that of the comparison standard (relative color density of unity), especially when the spectral characteristics of the test material are similar to that of the standard. The precision decreases rapidly with increasing color density values greater than 2.

APPARATUS

Any sensitive photoelectric colorimeter may be used, if it is provided with a tungsten-filament, incandescent light source and with one or more barrier-layer type photocells, and constructed to permit use of the parallel, planar-surface glass cells described below.

The glass light "correction" filter must have the relative spectral characteristics shown in Figure 2. It is desirable that the transmittance at any wave length be within 5% of the value shown; greater variations are permissible, provided they are proportional over the entire spectral range. Because the filter has a relatively high transmittance, it is sometimes necessary to reduce the intensity of the incident light in order to obtain proper adjustment of the colorimeter, especially when adjusting the 100%

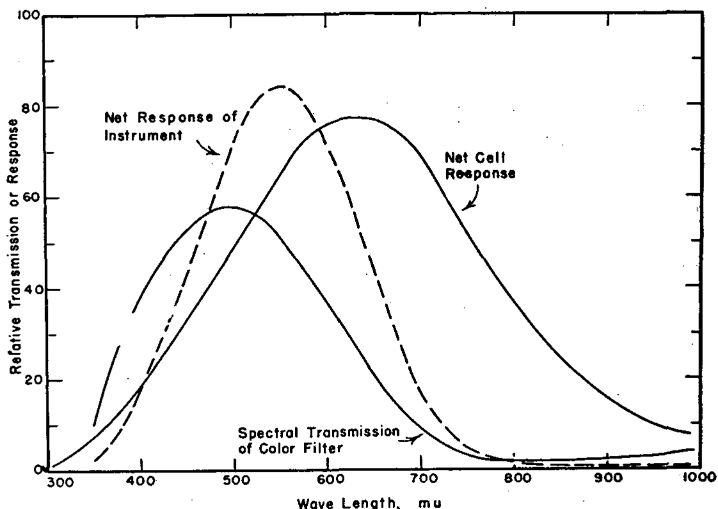


Figure 2. Effect of Color Filter upon Instrument Response

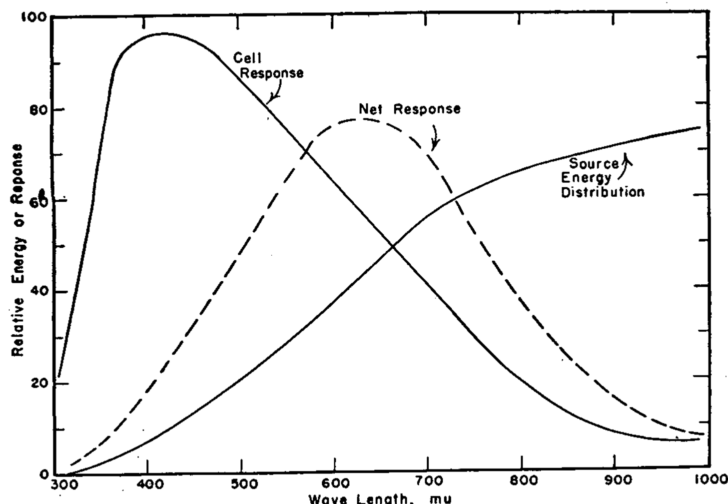


Figure 3. Spectral Distribution of Photocell, Net Instrument Response, and Energy of Light Source

Table I. Composition of Standard Color Solutions

Standard	Iron *G./100 ml.*	Cobalt *G./100 ml.*
A	9.70	1.61
B	2.77	0.537
C	0.0333	0.0134

transmittance setting. Satisfactory reduction of the amount of light entering the sample cell can be accomplished by use of a screen, or a mask, prepared from black photographic paper having small, uniformly distributed holes or slits of appropriate dimensions.

Note. This filter is usually referred to as the North Sky filter; it is made of Aklo glass obtainable from the Corning Glass Works. It has been chosen to transmit a somewhat wider band than a filter accurately duplicating the luminosity response of the average eye to daylight because such a filter spreads the density scale at the upper and lower ends in a useful manner without materially affecting the correlation with other colorimetric measures such as A.S.T.M. union color numbers.

Matched pairs of glass cells are necessary to permit measurement of the light transmittance of 50 ± 10, 10 ± 2, and 2 ± 0.5 mm. layers of test material. These cells should have parallel, planar faces and be of proper dimensions to permit use in the colorimeter employed. A 2-mm. cell depth may conveniently be obtained by inserting an 8-mm. glass block (of clear optical glass) in a 10-mm. cell.

STANDARD COLOR SOLUTIONS

Iron Stock Solution. Dissolve 500 grams of C.P. ferric chloride hexahydrate in 120 ml. of 0.6 *N* hydrochloric acid and filter through glass wool. Determine the iron content of the solution as follows:

Accurately weigh 0.8 to 1.2 grams of the test solution into a glass-stoppered weighing bottle and transfer to a 250-ml. Erlenmeyer flask containing 30 to 40 ml. of 0.6 *N* hydrochloric acid. Heat the solution to boiling and add 10% stannous chloride solution dropwise until the solution is colorless, being careful not to add more than 2 drops in excess. Cool to room temperature, dilute to about 80 ml., add 10 ml. of 5% mercuric chloride solution, and allow to stand for 4 to 6 minutes. Add 3 ml. of 85% phosphoric acid and 6 drops of 0.2% barium diphenylamine sulfonate indicator solution, and titrate with standard 0.1 *N* potassium dichromate solution until 1 drop produces a deep purple color which does not fade within 5 seconds. Calculate the iron concentration in the stock solution.

Cobalt Stock Solution. Dissolve 100 grams of C.P. cobalt chloride hexahydrate in 300 ml. of 0.6 *N* hydrochloric acid. Determine the cobalt content of the solution as follows:

Pipet exactly 1 ml. of the test solution into a weighed platinum dish, add 5 ml. of 18 *N* sulfuric acid, and cautiously evaporate to dryness. Ignite in a muffle furnace at 500° ± 25° C. for 5-minute periods until a constant weight is obtained. From the weight of cobalt sulfate, calculate the cobalt concentration in the stock solution.

Standards A, B, and C. Weigh a quantity of the iron stock solution calculated to contain exactly the quantity of iron given in Table I; transfer to a 100-ml. volumetric flask, using a minimum amount of 0.6 *N* hydrochloric acid to aid in the transfer. Introduce into the same volumetric flask, either from a buret or from a graduated pipet, a volume of the cobalt stock solution calculated to contain exactly the amount of cobalt given in Table I. Cool to room temperature, dilute to 100 ml. with 0.6 *N* hydrochloric acid, and mix thoroughly.

SAMPLE PREPARATION

The sample must be essentially free from turbidity or suspended solids. If it appears turbid when viewed through a thin layer—e.g., the 2-mm. absorption cell—filter through a fine filter paper or clarify in a centrifuge before measuring the color.

PROCEDURE

Select a pair of matched 10-mm. colorimeter cells. Fill one cell with distilled water and the second with the sample to be tested. Polish the cell surfaces with a clean, lint-free cloth or tissue and place the water cell in position in the colorimeter. Adjust the colorimeter to a scale reading of zero optical density (100% transmittance). Replace the water cell with that containing the sample and record the resulting scale reading. Reinsert the water cell and check the instrument adjustment. If any readjustment is made, obtain a new reading for the sample. Discard the sample.

Clean and dry the cell and fill with color standard B. Proceeding as directed for the sample, obtain a colorimeter reading for the standard. (This measurement of the standard need be made only sufficiently often to ensure constancy. In most cases, one reading per week will suffice.)

Calculate the relative color density as directed below. If the value obtained is greater than 2.0, repeat the color density measurement using standard A and matched 2-mm. colorimeter cells. If the value obtained is less than 0.1, repeat the measurement using standard C and matched 50-mm. cells. In borderline cases, make and report measurements with both combinations of standard and cell depth.

CALCULATION

If the colorimeter reads directly in optical density, or in units proportional to optical density, calculate the relative color density by means of the following equation:

$$\text{Relative color density} = \frac{R}{S}$$

where R = colorimeter reading for the sample, and S = colorimeter reading for the standard.

If the colorimeter scale is graduated in terms of transmittance, calculate the relative color density by means of the following equation:

$$\text{Relative color density} = \frac{2 - \log R}{2 - \log S}$$

where R and S are expressed in per cent transmittance.

In reporting the relative color density, specify the standard used and the depth of the absorption cell. If the sample has been clarified in any way, report this fact.

DISCUSSION

In any photoelectric color measurement, there are four fundamental factors involved: (1) the spectral energy distribution of the light source, (2) the spectral response of the photocell, (3) the spectral characteristics of the light filter used, and (4) the depth of test material through which the light passes. The effects of the first three upon instrument response are illustrated in Figures 2 and 3. Common photoelectric colorimeters are generally equipped with a tungsten filament light source and a barrier-layer, photovoltaic type of photocell. For these colorimeters, consideration of the response relationships involved (Figures 2 and 3) makes it clear that only a broad band filter such as the North Sky filter will lead to a net response approximating that of the normal eye.

For reasons previously stated, the authors have chosen Gardner-type iron-cobalt color comparison standards to compensate for variations in response from colorimeter to colorimeter. Comparison of Figure 4 and Figure 1 shows that the spectral characteristics of these standards closely approximate those of typical petroleum products except for the spectral region above 700 millimicrons. However, this difference can be neglected, as the net response of the colorimeter is comparatively small in this region (Figure 2).

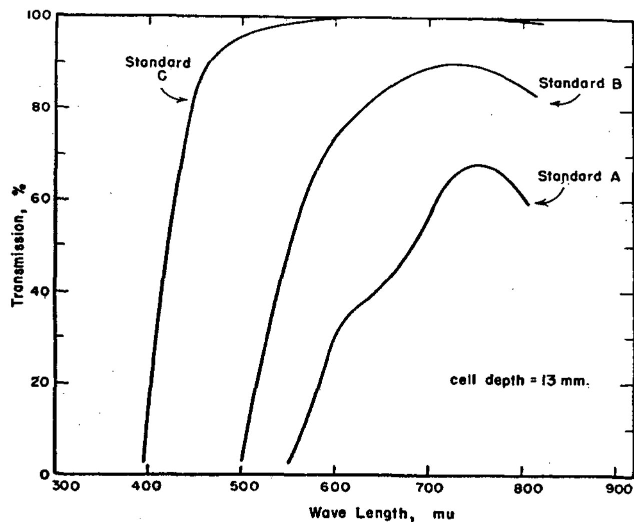


Figure 4. Spectral Characteristics of Standard Color Solutions

With regard to the stability of the chosen standards A, B, and C described above, repeated optical density measurements over a period of 4 months indicated that they are stable when kept at a moderate room temperature (20° to 25° C.). However, when not in use, they should be kept in tight glass-stoppered bottles, as standards A and B, particularly, have a tendency to absorb water from the air.

Although the authors have chosen the particular color standards described for use in their work, it is intended that other suitable standards should be used for specific applications, particularly those involving specification testing. The standard selected for a particular application should approximate as closely as possible the color density and spectral characteristics of a sample of the test material which just passes the test or has a color density in the most critical range.

In order to check the reproducibility and general usefulness of the proposed method, sixteen samples of petroleum products and colored aqueous solutions, designated as S-50 to S-65, inclusive, were prepared (Table II). Their relative color density values were determined on five commercially available photoelectric colorimeters: the Klett-Summerson photoelectric colorimeter (Model 900-3), the AC Model Fisher electrophotometer, the Hellige-Diller photoelectric colorimeter (Model 405-A), the Cenco-Sheard-Sanford photoelectric colorimeter (Catalog No. 12,340), and the Lumetron colorimeter (Model 402-E). Table III gives the results of the measurements made in 10-mm. cells relative to standard B. Table IV gives those made in 40- and 50-mm. cells relative to standard C.

The results in Table III indicate that for those samples in which the relative color density values are between 0.1 and 2.0, good agreement is obtained by the five different instruments; in this range, the average deviation from the mean of the relative

Table II. Description of Color Test Samples

Sample No.	Description of Sample
S-50	Lubricating oil, SAE 10
S-51	Lubricating oil, SAE 20
S-52	Lubricating oil, SAE 50
S-53	Lubricating oil (union color less than 1)
S-54	Lubricating oil, SAE 50
S-55	Lubricating oil, SAE 40
S-56	Lubricating oil, SAE 30 (abnormal color)
S-57	Lubricating oil, highly fluorescent
S-58	Light kerosene (ordinary water-white kerosene)
S-59	Dark kerosene (sample S-58 containing 2% by volume of SAE 10 oil)
S-60	Aqueous inorganic standard A (contains 9.70 grams of iron and 1.61 grams of cobalt diluted to exactly 100 ml. with 0.6 *N* hydrochloric acid)
S-61	Aqueous inorganic standard B (contains 2.77 grams of iron and 0.537 gram of cobalt diluted to exactly 100 ml. with 0.6 *N* hydrochloric acid)
S-62	Aqueous inorganic standard C (contains 0.0333 gram of iron and 0.0134 gram of cobalt diluted to exactly 100 ml. with 0.6 *N* hydrochloric acid)
S-63	Aqueous inorganic solution X (contains 120 grams of nickelous chloride hexahydrate in 14 liters of 0.2 *N* hydrochloric acid solution)
S-64	Aqueous inorganic solution Y (contains 0.0514 gram of iron and 0.0214 gram of cobalt diluted to 2000 ml. with 0.6 *N* hydrochloric acid)
S-65	Aqueous inorganic solution Z (contains 700 grams of copper sulfate pentahydrate in 14 liters of approximately 0.1 *N* sulfuric acid solution)

Table III. Relative Color Density Values

(Obtained with five makes of photoelectric colorimeters)

	Relative Color Density, Standard B, 10-Mm. Cell				
Sample No.	Fisher electrophotometer	Klett-Summerson	Lumetron Model 402E	Cenco-Sheard-Sanford	Hellige-Diller
S-50	0.76	0.73	0.71	0.79	0.77
S-51	1.03	1.02	1.04	1.06	1.05
S-52	1.79	1.90	1.94	1.86	1.83
S-53	0.05	0.04	0.01	0.05	0.03
S-54	Too dark	5.31	5.04	4.47	5.14
S-55	Too dark	3.77	3.87	3.52	3.86
S-56	2.85	3.07	3.09	2.93	2.91
S-57	1.66	1.78	1.74	1.72	1.69
S-60	2.47	2.64	2.70	2.48	2.44
S-61	1.00	1.00	1.00	1.00	1.00
S-62	0.06	0.04	0.03	0.02	0.02
S-63	0.07	0.05	0.05	0.04	0.03
S-65	0.27	0.29	0.43	0.31	0.31

Table IV. Relative Color Density Values of Light Samples

(Obtained with four makes of photoelectric colorimeters)

	Relative Color Density, Standard C, 50-Mm. Cell			
Sample No.	Fisher electrophotometer	Lumetron Model 402E	Cenco-Sheard-Sanford	40-Mm. Cell, Klett-Summerson
S-53	1.12	0.98	1.00	1.18
S-58	Too light	Too light	Too light	Too light
S-59	0.63	0.49	0.58	0.64
S-62	1.00	1.00	1.00	1.00
S-63	1.67	2.17	1.74	1.36
S-64	0.14	0.11	Too light	0.09

Table V. Precision of Relative Color Density Results Obtained in Different Laboratories

	Relative Color Density for Indicated Standard and Cell Depth[a]								
	Standard A, 2-Mm. Cell Depth			Standard B, 10-Mm. Cell Depth			Standard C, 50-Mm. Cell Depth		
		Deviation from Average			Deviation from Average			Deviation from Average	
Sample No.	Av. value	Mean	Maximum	Av. value	Mean	Maximum	Av. value	Mean	Maximum
S-50	...	...	...	0.74	0.03	0.06	...	...	...
S-51	...	...	...	1.03	0.03	0.11	...	...	...
S-52	0.56	0.03	0.09	1.90	0.05	0.15	...	...	...
S-53	...	...	...	...	...	...	1.23	0.30	0.87
S-54	1.64	0.07	0.18	...	...	...	...	...	...
S-55	1.25	0.05	0.12	...	...	...	...	...	...
S-56	0.82	0.05	0.17	...	...	...	...	...	...
S-57	0.60	0.02	0.04	1.73	0.05	0.16	...	...	...
S-58	...	...	...	...	...	...	0.05	0.13	0.45
S-59	...	...	...	...	...	...	0.66	0.25	0.80
S-60	1.00	0.004	0.04	...	...	...	...	...	...
S-61	...	...	...	1.00	0.005	0.05	...	...	...
S-62	...	...	...	...	...	...	1.00	0.004	0.04
S-63	...	...	...	...	...	...	1.80	0.30	1.47
S-64	...	...	...	...	...	...	0.21	0.13	0.50
S-65	...	...	...	0.31	0.06	0.17	...	...	...

[a] Based on unpublished results collected by Subcommittee VI of A.S.T.M. Committee D-2 from 12 cooperating laboratories utilizing seven different makes of commercial photoelectric colorimeters.

Table VI. Relative Color Density Values of Color Test Samples, Showing Their Stability over a Period of Four Weeks

(Instrument: Fisher electrophotometer)

Sample No.	First Week			Second Week			Third Week			Fourth Week		
	Standard A 2.4-mm. cell	Standard B 10-mm. cell	Standard C 50-mm. cell	Standard A 2.4-mm. cell	Standard B 10-mm. cell	Standard C 50-mm. cell	Standard A 2.4-mm. cell	Standard B 10-mm. cell	Standard C 50-mm. cell	Standard A 2.4-mm. cell	Standard B 10-mm. cell	Standard C 50-mm. cell
S-50	0.21	0.76	...	0.21	0.75	...	0.21	0.79	...	0.21	0.77	...
S-51	0.26	1.03	...	0.27	1.03	...	0.28	1.03	...	0.27	1.05	...
S-52	0.60	1.79	...	0.59	1.78	...	0.60	1.83	...	0.59	1.83	...
S-53	...	...	1.12	...	...	1.14	...	...	1.02	...	...	1.08
S-54	1.58	...	...	1.60	...	...	1.62	...	...	1.61	...	...
S-55	1.38	...	...	1.26	...	...	1.27	...	...	1.25	...	...
S-56	0.85	2.85	...	0.86	2.81	...	0.86	2.88	...	0.86	2.91	...
S-57	0.63	1.66	...	0.65	1.65	...	0.64	1.68	...	0.63	1.69	...
S-58	...	...	...	...	...	...	...	...	...	...	...	...
S-59	...	...	0.63	...	...	0.61	...	...	0.52	...	...	0.63
S-60	1.00	2.47	...	1.00	2.43	...	1.01	2.55	...	1.00	2.44	...
S-61	0.37	1.00	...	0.37	1.00	...	0.36	1.00	...	0.35	1.00	...
S-62	...	...	1.00	...	...	1.00	...	...	1.00	...	...	1.00
S-63	...	...	1.67	...	...	1.67	...	...	1.54	...	...	1.62
S-64	...	...	0.14	...	...	0.14	...	...	0.08	...	...	0.15
S-65	...	0.27	5.70	...	...	5.70	...	...	5.42	...	0.31	5.44

color density value for a single sample ranges from 0.01 to 0.04. For all the samples in Table III the average deviation from the mean of the relative color densities for a single sample ranges from 1.0 to 12.5%, with an average relative error of 4.4%. The relative color density data obtained with standard C (Table IV) show an average relative error of 11.6%.

These sixteen samples were also cooperatively tested in a program sponsored by Subcommittee VI of A.S.T.M. Committee D-2. Relative color density measurements were made in accordance with the described method in twelve different laboratories using a total of seven different makes of photoelectric colorimeters. The data obtained, given in Table V, show that the reproducibility of the method in different laboratories using common photoelectric colorimeters is approximately the same as the precision found by the authors (Tables III and IV).

Inasmuch as the color samples were being tested over a long period of time, their relative color densities were measured on the Fisher electrophotometer once a week over a period of 4 weeks in order to determine whether the color density of any of the samples changed with time. The results, given in Table VI, indicate that little or no change took place. The data also indicate the high degree of repeatability obtainable when the same colorimeter is used for a series of color measurements.

Color densities relative to standards A and B were obtained for sixty samples of lubricating oils representing twelve commercial brands (Table VII). These color measurements were made on the Fisher electrophotometer and the Klett-Summerson photoelectric colorimeter. In addition, the A.S.T.M. union color numbers (*1*) of these samples were determined. In most cases, the final A.S.T.M. union color numbers reported were obtained by averaging the readings obtained by three different operators. The results in Table VII demonstrate the good instrument-to-instrument reproducibility obtained by the proposed method and its applicability to lubricating oils and materials of similar color characteristics. Table VIII shows the reproducibility of the relative color density and A.S.T.M. union color (*1*) methods and shows that the precision of the relative color density values is considerably better than that of the visual method when the de-

Table VII. Relative Color Densities and Union Colors of Sixty Commercial Lubricating Oils Representing Twelve Brands

(Obtained with two colorimeters)

Description of Oil Sample	Standard A, 2.4-Mm. Cell		Standard B, 10-Mm. Cell		Union Color
	Fisher electrophotometer	Klett-Summerson	Fisher electrophotometer	Klett Summerson	
Brand A					
SAE 10	0.26	0.27	1.08	0.99	3 1/2
SAE 20	0.39	0.40	1.43	1.47	4
SAE 30	0.56	0.53	1.88	1.94	5−
SAE 40	0.52	0.46	1.70	1.80	5−
SAE 50	0.61	0.58	1.97	2.08	5
SAE 60	0.93	0.88	2.98	3.20	7+
Brand B					
SAE 10	0.34	0.31	1.20	1.21	4
SAE 20	0.36	0.39	1.37	1.40	4 1/2
SAE 30	0.51	0.49	1.72	1.76	5−
SAE 40	0.42	0.43	1.47	1.53	4 1/2
SAE 50	0.45	0.41	1.47	1.51	4 1/2
SAE 60	0.57	0.53	1.90	2.01	5+
Brand C					
SAE 10	0.28	0.26	1.02	1.01	4−
SAE 20	0.34	0.33	1.16	1.17	4+
SAE 30	0.56	0.54	1.73	1.88	5
SAE 40	0.62	0.61	1.89	2.00	5
SAE 50	0.61	0.59	1.84	1.98	5
SAE 60	0.70	0.69	2.07	2.21	6−
SAE 70	0.99	0.99	3.12	3.39	7+
Brand D					
SAE 10	0.31	0.32	1.07	1.06	4−
SAE 20	0.29	0.31	0.99	1.00	3 1/2+
SAE 30	0.44	0.45	1.38	1.43	4+
SAE 40	0.35	0.33	1.11	1.13	4−
Brand E (green)					
SAE 10	0.67	0.65	2.18	2.31	5+
SAE 20	0.73	0.73	2.28	2.46	6
SAE 30	0.67	0.65	2.18	2.32	5+
SAE 40	0.65	0.62	2.13	2.27	5+
SAE 50	0.73	0.70	2.23	2.38	6
SAE 60	0.89	0.86	2.75	2.98	7
SAE 70	0.97	0.97	3.08	3.35	7+
Brand F (pale)					
SAE 10	0.15	0.14	0.67	0.66	2 1/2
SAE 20	0.16	0.15	0.75	0.74	2 1/2
SAE 30	0.24	0.22	0.98	0.96	3
SAE 40	0.26	0.25	1.02	1.02	3
SAE 50	0.44	0.42	1.46	1.51	4
Brand G					
SAE 10	0.28	0.27	0.91	0.92	3 1/2
SAE 20	0.47	0.46	1.50	1.59	4 1/2
SAE 30	0.60	0.57	1.87	2.01	5
SAE 40	0.77	0.75	2.39	2.59	6
SAE 50	1.03	1.03	2.95	3.25	7
SAE 60	1.36	1.34	Too dark	4.52	8+
SAE 70	1.24	1.23	Too dark	4.08	7+
Brand H					
SAE 10	0.19	0.19	0.68	0.69	3
SAE 20	0.22	0.21	0.75	0.74	3 1/2
SAE 30	0.26	0.24	0.85	0.82	3 1/2
SAE 40	0.28	0.26	0.94	0.93	3 1/2 +
SAE 50	0.65	0.59	2.03	2.15	5
SAE 60	1.02	0.95	3.21	3.50	7
SAE 70	1.68	1.66	Too dark	Too dark	Too dark
Brand I (Penn.)					
SAE 10	0.21	0.17	0.61	0.61	3
SAE 20	0.78	0.78	2.12	2.31	5+
SAE 30	0.98	0.94	2.72	2.99	6+
SAE 40	1.25	1.23	Too dark	3.88	8
SAE 50	1.57	1.57	Too dark	5.31	8+
Brand J					
SAE 10	0.28	0.25	0.93	0.91	3 1/2
SAE 20	0.44	0.41	1.39	1.43	4+
SAE 30	0.67	0.61	2.03	2.15	5+
Brand K					
SAE 30	0.43	0.42	1.37	1.42	4+
SAE 40	0.59	0.56	1.89	1.99	4 1/2
Brand L (Hi-Duty)					
SAE 70	1.69	1.71	Too dark	5.58	Too dark

viations are considered on a relative percentage basis. This is true even for samples S-55, S-56, and S-60, which are really too dark for accurate measurement relative to standard B.

Color data gathered in the past have often been expressed in A.S.T.M. union color numbers and, therefore, it is useful to know the relationship between any new color system and union color. Using data similar to those given in Table VIII, the relative color density values relative to standards A and B (measured in 2.4- and 10-mm. cells, respectively), were plotted against the corresponding A.S.T.M. union color numbers. The resulting curves (Figure 5) give an approximate correlation of relative color density and the A.S.T.M. union color scales.

Table VIII. Reproducibility of Relative Color Density and A.S.T.M. Union Color Number Results

Sample No.	Relative Color Density Standard B, 10-Mm. Cell[a]		A.S.T.M. Union Color Number[b]	
	Av.	Maximum deviation	Av.	Maximum deviation
S-50	0.75	0.04	3	0.5
S-51	1.04	0.02	3.5+	0.5+
S-52	1.86	0.08	5−	0.5−
S-55	3.75	0.23	7.5	0.5
S-56	2.97	0.12	7	1
S-57	1.72	0.06	5+	0.5
S-60	2.55	0.15	5.5	0.5

[a] Measurements made using colorimeters of five different makes.
[b] Based on unpublished results collected by Subcommittee VI of A.S.T.M. Committee D-2 from 12 cooperating laboratories.

In the practical application of the method, a discontinuity of calculated values occurs in progressively darker oils when it becomes necessary to change from one specified combination of cell depth and standard to another. From a reproducibility standpoint, this discontinuity is serious only in borderline cases. Table IX demonstrates the degree of constancy of the ratio of relative color densities obtained with standard B (10-mm. cell) to those obtained with standard A (2-mm. cell) for various oils and for three different makes of colorimeters. Apparently, a definite relationship exists between the two sets of relative color density values but it is not sufficiently constant from one material to another to permit accurate conversion from one scale to another.

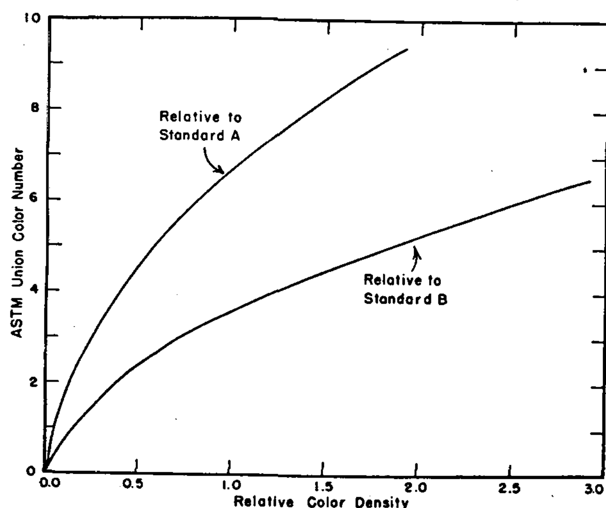


Figure 5. Correlation of Relative Color Density with A.S.T.M. Union Color Numbers

This variation is probably attributable to differences in spectral transmission properties of some of the samples. However, neither reflectance nor fluorescence appears to bear any relationship to this variation. The most logical use of the average ratios would be for approximate conversion of a series of values from one system to another when a transition of systems is necessary because of color changes during the progress of a series of experiments.

Table IX. Reproducibility of Relative Color Density Values

[Ratio of relative color density with standard B (10-mm. cell) to relative color density with standard A (2-mm. cell)]

Description of Oil Sample	Fisher Electrophotometer		Klett-Summerson		Hellige-Diller	
	Ratio	Deviation	Ratio	Deviation	Ratio	Deviation
Brand A						
SAE 10	5.25	1.43	5.41	1.51	5.38	1.58
SAE 20	4.54	0.72	4.56	0.66	4.73	0.93
SAE 30	3.86	0.04	4.08	0.18	4.10	0.30
SAE 40	4.08	0.26	4.04	0.14	4.19	0.39
SAE 50	3.72	−0.10	3.89	−0.01	3.87	0.07
Brand B						
SAE 10	4.35	0.53	4.60	0.70	4.44	0.64
SAE 20	4.26	0.44	4.45	0.55	4.53	0.73
SAE 30	4.04	0.22	4.32	0.42	4.20	0.40
SAE 40	4.32	0.50	4.45	0.55	4.40	0.60
SAE 50	3.90	0.08	4.10	0.20	4.16	0.36
SAE 60	3.96	0.14	4.19	0.29	4.14	0.34
Brand C						
SAE 10	4.71	0.89	4.82	0.92	4.32	0.52
SAE 20	4.23	0.41	4.03	0.13	3.97	0.17
SAE 40	3.53	−0.29	3.94	0.04	3.65	−0.15
SAE 50	3.50	−0.32	3.68	−0.22	3.43	−0.37
SAE 60	3.36	−0.46	3.55	−0.35	3.33	−0.47
SAE 70	3.37	−0.45	3.67	−0.23	3.49	−0.31
Brand D						
SAE 10	4.27	0.45	4.30	0.40	4.23	0.43
SAE 20	4.35	0.53	4.49	0.59	3.96	0.16
SAE 30	3.84	0.02	3.97	0.07	3.72	−0.08
SAE 40	3.89	0.07	4.17	0.27	3.84	0.04
Brand E (green)						
SAE 10	3.49	−0.33	3.77	−0.13	3.66	−0.14
SAE 20	3.29	−0.53	3.48	−0.42	3.51	−0.29
SAE 30	3.45	−0.37	3.53	−0.37	3.68	−0.12
SAE 40	3.46	−0.36	3.74	−0.16	3.62	−0.18
SAE 50	3.38	−0.44	3.50	−0.40	3.57	−0.23
SAE 60	3.48	−0.34	3.75	−0.15	3.44	−0.36
SAE 70	3.47	−0.35	3.87	−0.03	3.60	−0.20
Brand F (pale)						
SAE 10	4.94	1.12	4.39	0.49	4.65	0.85
SAE 20	4.40	0.68	4.19	0.29	4.05	0.25
SAE 30	4.22	0.40	3.97	0.07	4.18	0.38
SAE 40	4.03	0.21	3.86	−0.04	3.68	−0.12
SAE 50	3.47	−0.35	3.77	−0.13	3.71	−0.09
Brand G						
SAE 10	3.80	−0.02	3.52	−0.38	3.33	−0.47
SAE 20	3.44	−0.38	3.49	−0.41	3.44	−0.36
SAE 30	3.27	−0.55	3.47	−0.43	3.12	−0.68
SAE 40	3.27	−0.55	3.55	−0.33	3.38	−0.42
SAE 50	3.00	−0.82	3.35	−0.55	3.19	−0.61
SAE 60	...	...	3.64	−0.36	3.08	−0.72
SAE 70	...	...	3.50	−0.40	3.02	−0.78
Brand H						
SAE 10	4.43	0.61	4.32	0.42	4.61	0.81
SAE 20	4.16	0.34	3.80	−0.10	3.21	−0.59
SAE 30	3.91	0.09	3.95	0.05	4.00	0.20
SAE 40	4.35	0.53	4.17	0.27	4.32	0.52
SAE 50	3.56	−0.26	3.75	−0.15	3.69	−0.11
SAE 60	3.48	−0.34	3.90	0.00	3.72	−0.08
SAE 70	...	...	...	...	2.62	−0.17
Brand I (Penn.)						
SAE 10	3.56	−0.26	4.00	0.10	4.15	0.35
SAE 20	2.99	−0.83	3.17	−0.73	3.23	−0.57
SAE 30	2.81	−1.01	3.15	−0.75	3.11	−0.69
SAE 40	...	...	3.15	−0.75	2.94	−0.86
SAE 50	...	...	3.29	−0.61	2.96	−0.84
Brand J						
SAE 10	4.08	0.26	4.08	0.18	4.79	0.99
SAE 20	3.68	−0.14	3.92	0.02	4.03	0.23
SAE 30	3.43	−0.39	3.75	−0.15	3.70	−0.10
Brand K						
SAE 30	3.65	−0.17	3.84	−0.06	3.82	0.02
SAE 40	3.54	−0.28	4.00	0.10	3.98	0.18
Brand L (Hi-Duty)						
SAE 70	...	...	3.20	−0.70	2.73	−1.07
Average	3.82	...	3.90	...	3.80	...
Mean deviation	...	0.42	...	0.34	...	0.43
Maximum deviation	...	1.43	...	...	1.51	1.58

APPLICATIONS

During the past two years, the relative color density method has given satisfactory results for a variety of materials, especially those in the color density range of standards A and B. It has been particularly useful in following the color changes occurring in experiments involving oxygen degradation of materials such as lubricating oils, gasolines, motor fuel blends, solvents, and polymers. It has also given considerable aid in determining the degree of refinement or purity of many chemical preparations.

ACKNOWLEDGMENT

The authors wish to thank F. D. Tuemmler for his interest and suggestions during the course of this work, and D. R. McCormick and S. M. Woogerd for their assistance in the experimental work.

LITERATURE CITED

(1) Am. Soc. Testing Materials, "A.S.T.M. Standards on Petroleum Products and Lubricants," Method D155-45T, November 1948.
(2) *Ibid.*, Method D156-38.
(3) Am. Soc. Testing Materials, "Symposium on Color," March 1941.
(4) Diller, I. M., Dean, J. C., DeGray, R. J., and Wilson, J. W., Ind. Eng. Chem., Anal. Ed., 15, 367-73 (1943).
(5) Diller, I. M., DeGray, R. J., and Wilson, J. W., *Ibid.*, 14, 607-14 (1942).
(6) Gardner, H. A., and Sward, G. G., "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," 10th ed., Washington, D. C., Institute of Paint and Varnish Research, 1946.
(7) Hazen, Allen, *Am. Chem. J.*, 14, 300-10 (1892).
(8) Osborn, R. H., and Kenyon, W. C., Ind. Eng. Chem., Anal. Ed., 18, 523-30 (1946),
(9) Story, B. W., and Kalichevsky, V. A., *Ibid.*, 5, 214-17 (1933).
(10) Whyte, L. K., *J. Am. Oil Chem. Soc.*, 24, 137-40 (1947).

Received August 23, 1948.

Determination of Oil in Oil-Field Waste Waters

H. DARWIN KIRSCHMAN, *University of California, Los Angeles, Calif.*, AND RICHARD POMEROY, *Montgomery and Pomeroy, Pasadena 1, Calif.*

In analyses of oil-field waste waters "oil" is considered as the relatively nonvolatile liquid component that contributes to the formation of oil films and deposits. The nonsaponifiable hexane-soluble fraction most closely represents "oil content" in this sense. In any analytical procedure that uses a solvent, removal of this solvent prior to weighing or volumetric measurement must be accomplished in a manner to minimize evaporation of the oil. Drying the oil at room temperature after boiling off the solvent has been found satisfactory. In the wet-extraction method, samples of low oil content (below 25 p.p.m.) yield about 95% of the oil in two extractions and 99% in three; higher percentage recovery is attained at higher oil contents. Naphthenic acids are extracted with the oil and must be separated by saponification. A new procedure gives results differing by an average of less than 1 p.p.m. on duplicate samples. Ferric chloride is unsuitable as a flocculating agent, because it produces sulfur in the extract if the waste water contains sulfide. Zinc salts are satisfactory. Results by the flocculation method are reproducible with an average difference below 1 p.p.m. on duplicates, but the results are about 2 p.p.m. lower than those of the wet-extraction method, because of incomplete trapping of the oil by the floc and incomplete removal of the oil from the floc. Because the wet-extraction method gives results of superior accuracy in less elapsed time, the authors consider it generally preferable.

THE determination of oil in oil-field waste waters is of considerable importance where pollution control agencies have set up standards of quality for wastes discharged into bodies of natural water, or where the efficiency of facilities for waste water treatment must be evaluated. In general, procedures previously recommended have not been investigated with enough thoroughness to provide an adequate basis for judging their accuracy and suitability; the results of such investigations, if any have been made, are not available in published form.

This paper reports the results of an investigation undertaken to develop procedures that will yield valid results in terms of a reasonable understanding of the objectives of the "oil" determination. Two basic plans, the "wet extraction" procedure and the "flocculation" procedure, have been elaborated and compared.

CONSTITUENTS CONSIDERED AS OIL

Before evaluating analytical procedures for determination of the oil content of waste water, a decision should be made as to what materials are to be included in the category of oil. Oil-field waste waters contain all the hydrocarbons of natural gas and oil from methane up, plus asphaltic and resinous materials, fatty acids, and other organic matter. The hydrocarbons having boiling points above normal atmospheric temperature—i.e., isopentane (2-methylbutane) and heavier—could be considered as constituting the oil component of the sample. When the oil is separated by solvent extraction, either with or without the aid of flocculation, there is no practical way of separating the solvent from the extracted oil without the loss of highly volatile fractions.

In one published procedure for determination of oil in waste waters an attempt is made to overcome this difficulty by partially distilling the sample and separating the distilled oil from the water by gravity, with a subsequent volumetric measurement (*1*). But even in this procedure, a small amount of ethyl ether is used to collect all the oil in a capillary tube. Because of the necessity of evaporating this ether, all the pentanes and at least part of the hexanes are lost. Some type of distillation procedure may be the only way to get accurate results as far as highly volatile components are concerned, but any such procedure, if exact, is certain to be complicated and too lengthy to be of value for routine testing. The best way out of this difficulty is to ignore hydrocarbons that evaporate rapidly at room temperature, and to consider that "oil content," for practical purposes, means the oil that remains as such after moderate exposure to the air. This is a logical view, in so far as the pollutional character of the water is concerned, for the highly volatile oils do not contribute to oily films on the surface of polluted streams. The volatile hydrocarbons may contribute to explosive atmospheres in sewers, but this condition may result from the presence of hydrocarbon gases as well as vaporizable oils. From an analytical standpoint this is a problem entirely separate from oil content.

The final delimitation of the category designated as "oil" will depend in part upon the practicability of laboratory procedures. The objective chosen in this research was the separation of the components that are relatively nonvolatile liquids at room temperature and contribute to the formation of oil films and deposits.

With this in mind a solvent should be chosen which will dissolve the oils effectively, but will have a minimum solvent action on nonliquid materials. In drying the separated oil prior to weighing, a procedure should be followed in which it will be possible to evaporate the solvent used in the analysis, together with fractions of the oil similar to the solvent in volatility, but without too great evaporation of heavier fractions. Solvent and drying technique must be chosen before comparisons of extraction procedures can be made.

Table I. Solubility of Montebello Crude Oil in Solvents

(100 ml. of solvent plus 600 mg. of crude oil)

Solvent	Insoluble Residue, % of Sample
Neohexane	10.3
Cyclopentane	4.8
Carbon tetrachloride	1.4
Benzene	1.0
Chloroform	0.95

CHOICE OF SOLVENT

Among the solvents that may be considered in the analysis of oil-field waste waters, some—for example, benzene, the ethers, chloroform, and carbon tetrachloride—dissolve not only the liquid hydrocarbons but also materials of the asphaltene class. Alkane solvents, on the other hand, have very little solvent action on the asphaltenes. Naphthenic hydrocarbons, such as cyclopentane, are intermediate in action. The relative strengths of various solvents toward petroleum components are revealed by treating small samples of crude oil with the solvents and weighing the insoluble residue. A series of tests of this sort with Montebello crude is shown in Table I.

When strong solvents are used in extractions of oil-field waste waters, and the dried extract is treated with hexane, an insoluble residue remains, which generally amounts to about 10% of the total extract. These hexane-insoluble residues from crude oil or from extractions of oil-field waste waters are black, amorphous solids, typically asphaltenes. Samples of these residues from various sources have been examined many times, and have not shown an oily or tarry consistency, with the exception of a single anomalous case (*3*).

The decision as to the inclusion of asphaltenes as a part of "oil content" depends on the purpose of the analysis. Crude oils hold asphaltenes in solution to some extent; hence these components might be included as possibly contributing to the total quantity of an oily phase separating from waste waters. It does not necessarily follow, however, that such materials would always be a part of the oily phase. Because they are not themselves oils, and the objective is to determine, as nearly as possible the "relatively nonvolatile liquids," the decision in this research was to consider only the alkane-soluble material as oil. The solvent selected for this purpose is essentially a mixture of isomeric hexanes, sold as "mixed hexanes" and hereinafter referred to as "hexane." In certain steps of the procedures stronger solvents are used, but the final separation is made with hexane. The standard procedure of the American Public Health Association for determining "grease" in sewage (*2*) also uses an alkane solvent (petroleum ether).

DRYING OIL PREPARATORY TO WEIGHING

In any practical analytical procedure, the oil will be separated in the form of a dilute solution in an organic solvent. The solvent must then be removed by distillation or evaporation and the containing vessel brought to equilibrium with the laboratory air. To secure information about the losses of oil due to evaporation and to develop a suitable technique for drying the extracted oil prior to weighing, a study was made of the evaporation losses of small samples of crude oil when exposed to the air.

The oils used were Montebello crude having an A.P.I. gravity of 25 (specific gravity 0.902) and Santa Maria crude with an A.P.I. gravity of 10 (specific gravity 1.00).

Small samples of the crudes were weighed into 300-ml. conical flasks, spread adequately over the bottoms of the flasks, and allowed to stand at room temperature, with subsequent weighings at appropriate intervals. In one case, 10 ml. of chloroform were added to the oil with subsequent evaporation of the chloroform by a stream of air until it was apparently all gone. Results are shown in Table II.

Table II. Loss of Oil Due to Evaporation

Type of Crude Oil	Original Weight of Crude Oil, Mg.	Time, Hours 0.25	0.5	1	2	3	4	6	24
		Per Cent Change of Weight							
Montebello	530.1	−1.2	−1.9	−2.4	−2.9	−3.5	...	...	...
Montebello	48.4	−1.2	−1.6	−3.1	−3.5	−4.5	...	...	...
Santa Maria	544.3	−1.2	−2.2	−3.1	−3.6	−4.1	−4.3	−4.5	...
Santa Maria + chloroform	593.7	+28	+8	−1.8	−3.5	−4.1	−4.3	−4.5	−5.0

A comparison of the two samples of Montebello crude shows that the percentage loss of weight is greater for the smaller sample, as would be expected, yet the difference is relatively slight. The experiment also shows relatively little difference in behavior of the two crudes. Rather surprisingly, the heavy Santa Maria crude shows a slightly greater loss in weight than the less dense Montebello crude. A greater range of behavior would no doubt be found if a greater variety of crudes were tested.

The fourth test shows that some of the added solvent remained with the oil for an hour or more, but after 2 hours the figures for percentage of loss are the same as for the sample to which no chloroform had been added.

VOLATILITY LOSSES DURING DISTILLATION OF SOLVENT

The losses attending the process of distillation of the solvent were studied.

In each test a sample of Montebello crude was weighed into a 300-ml. conical flask, and a 200-ml. portion of solvent was added, and then distilled off. In the distillation process, a water bath was used for heating and the flask was connected to the condenser by corks and a glass angle tube 10 mm. in diameter. The solvent was distilled down to a volume of 3 to 5 ml. The flask was then disconnected and the last of the solvent removed by tilting to pour out the vapor, reheating, if necessary, by a momentary immersion in the water bath and tilting again, until removal of the solvent appeared to be complete. The flask was then placed upright near the balance and weighed at intervals. The results are shown in Table III.

The losses are substantially greater than when the samples were merely exposed to the air, and generally increase with increasing boiling point of the solvent used. Exceptions are noted in the case of benzene at 1 and 2 hours, but this was probably due to incomplete removal of the benzene.

The last line of Table III shows the results of re-use of a solvent previously used in a similar experiment. The accumulation in the solvent of volatile fractions of the crude oil evidently diminishes subsequent losses. This was observed also with other solvents in preliminary experiments. After this behavior became apparent, all solvents were redistilled before re-use, and roughly 20% discarded at the end of the distillation. When seeking the most accurate results on small quantities of oil, it is desirable to purify the solvents by two successive distillations.

The object of the analysis is to separate relatively nonvolatile oils. Hence it is desirable to hold the losses of volatile fractions down to the minimum consistent with complete removal of the solvent. The loss of these fractions, however, does not diminish the usefulness of the results if the procedure gives reasonably reproducible values.

The foregoing experiments led to the adoption of a procedure substantially as outlined above—distillation on a water bath, with removal of the last of the solvent by gentle warming and tipping of the flask. Subsequently the flask is supported in the balance room for 1 to 2 hours in an inverted position. When the quantity of oil is too great to permit this, the flask is left on its side for approximately one day. The tare weight of the flask is determined after weighing flask plus oil, by rinsing out the oil

Table III. Loss of Oil During Distillation of Solvent

Solvent	Boiling Point of Solvent, ° C.	Original Weight of Oil, Mg.	Time, Hours: 1	2	3	24
			% Change from Original Weight of Oil			
Ethyl ether	35	497.1	−7.0	−8.5	− 8.[illegible]	− 9.5
Methylene chloride	40	498.4	−7.5	−8.6	− 8.[illegible]	− 9.7
Chloroform	61	505.7	−7.8	−9.6	−10.0	−10.7
Benzene	80	504.	−3.4	−9.0	....	−11.00
Methylene chloride[a]	40	528.8	−4.4	−4.7	....	....

[a] Sample re-used as recovered by distillation from previous analysis.

Table IV. Effect of Acidification upon Quantity of Hexane Extract

	Acidified Sample	Not Acidified	Difference
	Parts per million of extract		
First extraction	264	141	123
Second extraction	42	15	27
Third extraction	19	6	13
Total	325	162	163

with the solvent and allowing the flask to stand in the balance room for 2 hours or more.

WET-EXTRACTION PROCEDURE

The wet-extraction method has been shown to be suitable for the determination of grease in sewage and certain industrial wastes (*3*). Detailed examination of its performance as applied to oil-field waste waters revealed two problems requiring special investigation: possible extraction of organic acids from the water and attaining complete extraction of the oil.

The magnitude of the first effect became apparent when successive extractions were made of two identical samples of Santa Fe Springs waste water, one of which had been acidified, while the other was left at its normal pH value of 7.6. Results are shown in Table IV.

The increase of extracted material in the acidified sample amounted to 163 p.p.m. in three extractions, which indicates that organic acids are potentially a source of large errors when the pH is low enough to permit their extraction.

In another test, a sample of Wilmington oil-field waste water was extracted with hexane, using high speed stirring. The total extract recovered was dissolved in an ether-alcohol solution and titrated with sodium hydroxide. Subsequently hexane and water were added and the mixture was shaken, thus transferring the oil to the hexane layer and leaving the saponified acids in the aqueous phase. Two additional extractions were also made of the original waste water sample using chloroform, with subsequent titration with base. For comparison purposes, the weights of extract obtained by a hexane extraction at pH 11, by the flocculation method, and by a hexane extraction of the saponified chloroform extract are included in the quantitative results summarized in Table V.

The result obtained by hexane extraction at pH 11 led to the hope that this might afford a simple way to prevent extraction of the acids. An attempt was made to analyze Santa Fe Springs waste water by this means, but it was impossible to prevent the extraction of fatty acids until the pH was raised to such a value that the voluminous precipitate of calcium carbonate and magnesium hydroxide prevented complete recovery of the oil.

Corrections for extracted acids might be made on the basis of a titration of the extract, using an assumed equivalent weight for the acids. This equivalent weight is variable, however, and if the acid content is high and the oil content is low, as in the case of the Wilmington water (Table V), uncertainty of the correction will be large relative to the true oil content.

The most practical way to overcome this difficulty appears to be extraction under conditions suitable for complete recovery of the oil, regardless of the amount of organic acids extracted, and a subsequent separation of these acids by saponification. The details are given in the elaboration of the procedure below.

COMPLETENESS OF EXTRACTION OF OIL BY DIFFERENT TECHNIQUES

Attempts to extract oil from oil-field waste water by manually shaking with hexane gave unsatisfactory results (Table VI). Complete extraction could not be attained with a reasonable expenditure of time and energy.

If the oil were present in the waste waters entirely in the form of colloidal droplets, complete extraction should be readily attained. Much of the difficulty is no doubt due to the fact that a considerable amount of the oil is bound up with particles of asphalt and other solid material, so that effective contact between solvent and oil is not easily attained. With a solvent, such as benzene or chloroform, which will dissolve asphaltic materials, the extraction end point should be more rapidly approached. To determine the correctness of this concept, samples of oil-field waste water were subjected to successive extractions with chloroform, employing manual shaking (Table VII).

Comparison of Tables VI and VII shows, as expected, that the extraction by manual shaking approaches an end point more rapidly when using chloroform than when using hexane.

Although the oil can be quantitatively recovered by manual shaking with chloroform, this requires considerable expenditure of time and effort. Mechanical agitation was then tried as an easier method.

A sewing-machine motor was equipped with a Monel stirrer 35 mm. in diameter which could be lowered into a wide-mouthed 1-gallon bottle. Use of a rheostat controlled the speed of rotation to about 2000 to 4000 r.p.m. Both hexane and chloroform were tried; 200 to 300-ml. portions of solvent were used in each extraction with similar but not identical water samples of 2 to 3 liters.

It is evident that mechanical agitation gives much better recovery in each extraction than manual shaking, and that there is little difference in this case between the two solvents. (However, longer periods of agitation employed with hexane may have compensated for some difference in solvent action.) Each extraction yielded 75 to 80% of the oil remaining in the sample; thus substantially complete removal can be effected in four extractions and for approximate purposes two or three extractions would be satisfactory.

Table V. Quantity and Acidity of Extracts

	Weight of Extract, Mg.	Me. of Acids
First extraction, hexane at pH 7.2	16.8[a]	0.028
Two additional extractions with chloroform	30.3	0.13
Hexane extraction of identical sample at pH 11	12.4	0.005
Flocculation method, hexane extraction	13.0	...
Chloroform extraction with saponification and hexane extraction of unsaponified oil	12.5	...

[a] Saponification left 11.8 mg. of oil.

Table VI. Hexane Extraction Using Manual Shaking

Extraction No.	Shaking Time	Oil Recovered	
	Min.	*P.p.m.*	*%*
1	2	15	28
2	2	13	25
3	2	9	17
4	30	15	28

Table VII. Removal of Oil by Successive Extractions, Using Chloroform

Method of Agitation	Sample 1		Sample 2	
	P.p.m.	*%*	*P.p.m.*	*%*
Manual shaking, 5 min.	28.8	70.5	26.8	53.5
Second manual shaking, 5 min.	6.7	16.3	13.7	27.3
Third manual shaking, 5 min.	3.2	7.8	7.8	15.5
Additional motor stirrer extraction, 5 min.	2.2	5.4	1.9	3.7
Total extract	40.9	100.00	50.2	100.00

Table VIII. Hexane and Chloroform Extractions Using Mechanical Stirring

Extraction No.	Sample 1, Hexane, 15-Min. Stirring in Each Extraction		Sample 2, Chloroform, 5-Min. Stirring in Each Extraction	
	P.p.m.	% of total recovered	P.p.m.	% of total recovered
1	95.4	81	102.2	82
2	16.8	14	15.7	13
3	4.3	4	5.8	4
4	1.1	1	(1.3)[a]	1[a]
Total	117.6	100	125.0	100

[a] Assuming that an additional 1% would be recovered in fourth extraction.

Table IX. Extraction of Oil by High-Speed Mixing with Hexane

Time, Minutes	Oil in First Extraction, % of Total	Oil in Emulsion Layer, % of Total	Total Extracted, %	% Remaining in Water
1	70	2.7	73	27
5	83	7.3	90	10
15	81	12.7	94	6
30	90	2.0	92	8

Table X. Duplication of Results by Wet-Extraction Method

Water No.	Oil Content, Parts per Million			
	First analysis	Second analysis	Av.	Difference
1	3.0	3.4	3.2	0.4
2	7.5	6.3	6.9	1.2
3	8.7	8.0	8.3	0.7
4	12.4	12.5	12.4	0.1
5	34.4	36.0	35.2	1.6
6	70.0	69.5	69.7	0.5
7	74.0	76.0	75.0	2.0
8	125.2	124.8	125.0	0.4

Av. difference between 1st and 2nd analyses 0.85

In contrast to sewage, in which the sample yields its grease content readily on moderate shaking with the solvent for short periods of time, the oil-field waters require vigorous agitation. During this agitation, a certain amount of viscous emulsion is produced which accumulates between the water and solvent layers when the mixture is allowed to settle. In the experiments shown in Table VIII, this emulsion layer was left with the water to be subjected to subsequent extractions. It appeared likely that a substantial portion of the oil unrecovered after each successive extraction by high speed motor stirring might be present in this emulsion layer. Accordingly, a series of tests was run with four identical samples, in which the emulsion layers were in each case separately extracted. The time of stirring was also varied. Table IX presents the results.

After agitation for 5 minutes or more the amount of the oil remaining in the water is 10% or less of the total oil content. Agitation for 1 minute gives poorer removal, but there is relatively little advantage in times longer than 5 minutes.

When chloroform is used as the first extracting solvent, the problems of sludge or emulsion layers become somewhat different than when hexane is used. When chloroform and waste water are vigorously agitated, and allowed to settle for a few minutes, three principal layers separate: an aqueous phase on the top; a bottom layer which generally consists of droplets of chloroform separated by aqueous films; and, between the two, a "sludge" layer of water, solvent, air, and solid matter. In the recommended procedure set forth below the water is poured from the top of the bottle used for agitation and the lower layers are transferred to a separatory funnel. Subsequently, the bottom layer in the funnel, consisting principally of chloroform, is run into a second separatory funnel. This operation usually causes the separation of clear chloroform, apparently by disrupting the films that separate the chloroform droplets. The sludge layer is returned to the water for a second extraction, whereby any oil that it contains is largely removed by dilution in successive extractions.

With the usual oil-field waste waters of moderate oil content this sludge layer appears very light in color after the second extraction. The small fraction of the original oil content of the sample remaining in this layer may be neglected in most cases, but when more voluminous than usual and when maximum accuracy is desired, a third extraction may be indicated or this sludge layer may be separately extracted with a small portion of solvent.

At the conclusion of an analysis, a small amount of emulsified chloroform remains in the water and settles to the bottom of the vessel after a few hours' standing. The amount is generally so small that additional operations to recover its oil content are not worth while.

LABORATORY DIRECTIONS FOR WET-EXTRACTION PROCEDURE

Transfer the sample of water (about 2.5 liters) to a 1-gallon bottle with a sufficiently wide mouth to admit a motor-driven stirrer but not wider than necessary, so that loss by spray during agitation may be kept down. Add a 30 to 50-ml. portion of chloroform to the original sample bottle, taking care to rinse off the stopper, and shake. Add this solvent to the water sample and repeat the process with fresh portions of chloroform until the bottle is sufficiently cleaned for the accuracy desired in the analysis. Add to the water enough more chloroform to make a total of about 200 ml. and then subject it to 5 minutes' stirring with a motor-driven agitator at sufficient velocity of rotation to keep the solvent and water well mixed.

Decant most of the supernatant water back into the original sample bottle and pour the chloroform with the remaining water into a 500-ml. separatory funnel. Run the unclear solvent layer off into a second separatory funnel. It will usually become clear with a small amount of viscous sludge at the solvent-water interface. If the solvent layer is not cleared by this procedure, allow the second funnel to stand for a few minutes and give it a single, sharp shake which will usually break the "emulsion" and give a clear solvent layer. With care to keep the stem of the separatory funnel free from water, run the clear chloroform through a filter paper into a 300-ml. conical flask.

Add the water remaining in the first separatory funnel to the original sample bottle. Wash the sludge in the second funnel out of the funnel top into the water and repeat the extraction process as previously outlined.

While the second extraction is being made, connect a condenser to the flask containing the filtered chloroform solution and distill the chloroform by partially surrounding the flask with hot water. When the volume is reduced to 10 to 20 ml., add the second extract to the same flask and distill in a similar fashion down to a volume of about 1 ml. Remove the last portion of solvent by pouring the vapor out of the flask. To the cooled flask, add 5 ml. of ethyl ether, followed by 10 ml. of ethanol or 2-propanol, about 1 ml. of 1 *N* sodium hydroxide, and 2 drops of phenolphthalein indicator solution. Now wash the contents of the flask with 200 ml. of hexane into a separatory funnel containing about 200 ml. of distilled water. Gently shake the mixture, then draw off the water layer. Repeat this washing with water until the water shows no color of the phenolphthalein.

Draw off the last portion of wash water and filter the hexane layer into a 300-ml. conical flask. A 50-ml. pipet equipped with a rubber suction bulb is convenient for the transfer of hexane to the filter. Wash the filter paper well with small portions of hexane. Distill off the hexane down to a volume of about 1 ml. Remove the flask from the water bath, and remove the vapor by tipping. Wipe off the outside of the flask with lintless cloth or paper and place it neck down through an iron ring on a stand near the balance; weigh after 1 to 2 hours. (If the quantity of oil is so large that it may run out of the flask, lay the flask on its side and weigh the next day.) To obtain the tare weight of the flask, wash it out with several portions of hexane and again bring to equilibrium with the atmosphere. Inasmuch as the flask is now cool, a longer time is needed; 2 hours are adequate.

Reproducibility of results attainable by this procedure is indicated by the series of analyses of duplicate samples shown in Table X.

FLOCCULATION METHOD

The flocculation procedure as developed by the Committee on Waste Disposal of the American Petroleum Industry (*1*) recommends that the final measurement of the separated oil be made volumetrically in a special apparatus. This volumetric

Table XI. Wet Extraction Versus Flocculation with Zinc Carbonate

(Comparison of wet-extraction and flocculation methods. All figures in parts per million)

Line	Oil Recovered from	Samples 1	2	3	4	5	6	7	8	9
1	First extraction, first floc	3.21	4.15	1.89	5.70	3.41	2.98	4.26	19.68	29.7
2	Second extraction, first floc	0.88	0.69	0.85	0.06	0.00	1.00	0.65	1.38	...
3	Extraction of second floc	0.05	0.75	0.06	0.70	0.06	0.29	1.19	0.52	1.5
4	Total by floc	4.14	5.59	2.80	6.46	3.47	4.27	6.10	21.58	31.2
5	Wet extraction of filtered water	2.10	1.54	0.61	2.00	2.16	0.23	0.43	1.04	3.6
6	Total recovered	6.24	7.13	3.41	8.46	5.63	4.50	6.53	22.62	34.8
7	By standard wet extraction	4.60	7.10	4.05	6.22	5.48	3.92	6.62	22.20	35.1
8	Difference, line 7 − line 1	−1.39	−2.95	−2.16	−0.52	−2.07	−0.94	−2.36	−2.52	−5.4
9	Difference, line 6 − line 7	+1.64	+0.03	−0.64	+2.24	+0.15	+0.58	−0.09	+0.42	+0.30

measurement is only slightly faster than weighing and is decidedly less accurate. In the present research it was desired to secure results of maximum accuracy, often using samples from which the yield of oil was only a few milligrams, and to obtain results suitable for comparison with gravimetric results secured by the wet-extraction method. Hence the extraction of the floc was followed by the removal of solvent, drying, and weighing of oil in the manner previously described for the wet-extraction procedure.

Tests of the flocculation method were first made with ferric chloride as the flocculating agent. It was found that if the waste water sample contained sulfide, the material extracted from the dried ferric hydroxide floc included sulfur. Other flocculating agents were then tried. Aluminum hydroxide and zinc carbonate appeared most suitable. Both trapped the oil just as well as iron hydroxide and neither yielded sulfur when used with sulfide-containing waters. Zinc carbonate is more compact and filters much more easily than aluminum hydroxide and therefore was used in most of the flocculation experiments. A number of tests for acidity in the material extracted from the floc by hexane showed no evidence of the presence of organic acids.

The procedure finally adopted for the flocculation method is as follows:

To a sample of 2 to 3 liters, add 5 millimoles each of zinc acetate and sodium carbonate in solution. After thorough mixing, allow the floc of zinc carbonate to settle and filter the supernatant liquid through a qualitative paper. Toward the end of the filtration, transfer the floc to the filter paper and allow the paper to stand in the air until thoroughly dry. Wash out the original sample bottle with 50 to 100 ml. of hexane to remove any oil on the walls and stopper. Separate the water with a separatory funnel and transfer the hexane to a Soxhlet apparatus, taking care that no drops of water are included. Place the dried filter paper and floc in a Soxhlet thimble and extract for 2 to 3 hours with hexane. At the end of the extraction period, reduce the volume of solvent in the receiving vessel to 2 to 3 ml. Disconnect the flask and remove this last portion of solvent as directed in the wet-extraction procedure. After removal of the solvent, place the flask in an inverted position near the balance for 1 to 2 hours; then weigh. Wash the oil out of the flask with several small portions of solvent and dry the flask as before to secure its tare weight.

Early tests on duplicate samples by the two methods showed that results were generally somewhat lower by the flocculation method. This discrepancy was found to be due to incomplete removal of the oil by the floc and incomplete extraction of the oil from the floc by hexane. This is well demonstrated by the series of comparative experiments shown in Table XI, in which repeated flocculations of the water, repeated extractions of the floc, and a wet extraction of the water after flocculation give a basis for comparison with the results secured by the wet-extraction method as previously described.

The first group of seven waters had oil contents below 10 p.p.m. For these, on the average, a single flocculation and extraction yielded 61% of the total oil recovered. A re-extraction of the first floc yielded another 10%, and second flocculation gave 7% additional. From the remaining water, another 22% was recovered by a single wet extraction. The total recovery averaged 110% of the amount found by the proposed wet procedure, using two extractions. A third extraction presumably would have yielded an additional 5%, leaving a discrepancy of 5%. This difference probably is not significant, as it would average only 0.5 ± 1.5 mg. of oil in the samples taken. This may be considered satisfactory agreement, in view of the fact that the two groups of analyses involve five operations and ten flask weighings on each sample.

With samples of higher oil content, the discrepancy between the two methods is relatively less, but nevertheless substantial. Thus sample 8, containing 22.2 p.p.m. as determined by two wet extractions, yielded 89% of this amount by a single flocculation and extraction, and 106% by two flocculations, re-extraction, and wet extraction of the water. Sample 9, showing 35.1 p.p.m. by two wet extractions, yielded 85% of this amount by the simple flocculation procedure, and 99% by double flocculation and wet extraction of filtrate.

RELATIVE MERITS OF FLOCCULATION AND WET-EXTRACTION METHODS

The wet-extraction method, as previously shown, gives results (Table X) which, on samples with 3 to 125 p.p.m. of oil, are duplicable within an average difference less than 1 p.p.m. On samples of oil content up to 35 p.p.m. a comparison of the results of the wet-extraction procedure with those obtained by two successive flocculations followed by a wet extraction showed differences averaging less than 1 p.p.m. (Table XI). These facts indicate that the wet extraction method gives a reliable measure of the oil content of the sample; "oil" is understood to mean the hexane-soluble, nonsaponifiable, relatively nonvolatile liquid component of the waste water.

The flocculation method gives results that are similarly reproducible and consistent among themsevles, but in waters of low oil content are about 2 p.p.m. lower than the wet-extraction method. As it has been demonstrated that this amount of additional oil actually can be recovered from the water by an additional wet-extraction operation, it may be concluded that the discrepancy is due to incomplete recovery by the flocculation method.

With adequate equipment, the working time per analysis is about the same for the two methods. However, results can be obtained in considerably less elapsed time by the wet-extraction method. Six hours of elapsed time are adequate for a wet-extraction analysis, but in the flocculation method the precipitated floc must be dried at least overnight, so that results cannot be secured in less than 24 hours.

ACKNOWLEDGMENT

The authors acknowledge the sponsorship of the Los Angeles County Sanitation Districts and the Santa Fe Springs Waste Water Disposal Company for research on this subject.

LITERATURE CITED

(1) Am. Petroleum Inst., "Report on Disposal of Refining Wastes," 3rd ed., Sec. I, Appendix 5, Sheets 1–5, April 1941.

(2) Am. Public Health Assoc., "Standard Methods for Examination of Water and Sewage," 9th ed., p. 155, 1946.

(3) Pomeroy, Richard, and Wakeman, C. M., Ind. Eng. Chem., Anal. Ed., 13, 795 (1941).

Received October 29, 1948.

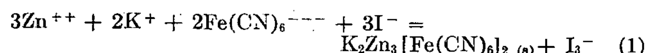
Iodometric Determination of Zinc

EUGENE K. MAUN AND ERNEST H. SWIFT

California Institute of Technology, Pasadena, Calif.

The iodometric determination of zinc has been studied. Under the conditions of the procedure recommended the necessity for stepwise addition of ferricyanide and successive titrations of iodine has been eliminated and a stable end point obtained. Under these conditions it is necessary to increase by an empirical factor of 1.019 the stoichiometrically calculated amount of zinc. The titration is rapid, and the end point is sensitive and stable. A precision of 1 to 2 parts per thousand can be expected.

IN THE course of an investigation of the zinc ferricyanides, a method, preferably volumetric, was needed for the determination of zinc. As a result of considerable experience with various modifications of the conventional titration with ferrocyanide, the method first proposed by Lang and subsequently investigated by various others (*1, 2, 4, 6, 12, 13*) was tried. This method involves the addition of an excess of ferricyanide and iodide to the zinc solution, whereupon iodine is produced as a result of a combination of precipitation and oxidation-reduction reactions which can be expressed by the following over-all equation:



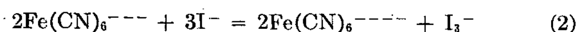
$$3Zn^{++} + 2K^{+} + 2Fe(CN)_6^{---} + 3I^{-} = K_2Zn_3[Fe(CN)_6]_{2\,(s)} + I_3^{-} \quad (1)$$

The iodine is titrated with thiosulfate to the conventional starch-iodine end point. The advantages of this end point over the various end-point methods used in the direct titration of zinc with ferrocyanide were obvious; however, certain features of the iodometric method were inconvenient or troublesome. Thus, the necessity for adding the ferricyanide in small portions, followed by titration with thiosulfate after each addition, made the titration tedious and time-consuming. Unless the excess of ferricyanide was carefully controlled there was a return of the end point because of oxidation of iodide by the excess of ferricyanide. Finally, previous workers had found necessary an empirical factor of considerable magnitude, as the reaction represented by Equation 1 is not stoichiometric.

Because of these facts there seemed justification for an experimental investigation of the various factors and conditions involved in the method. The results of this study and a modified procedure are given below.

DISCUSSION OF METHOD AND OF PREVIOUS WORK

The over-all equation given above (Equation 1) represents a combination of the two following reactions:



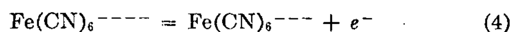
$$2Fe(CN)_6^{---} + 3I^{-} = 2Fe(CN)_6^{----} + I_3^{-} \quad (2)$$

and

$$2Fe(CN)_6^{----} + 3Zn^{++} + 2K^{+} = K_2Zn_3[Fe(CN)_6]_{2(s)} \quad (3)$$

An obvious requirement of the method is that Reaction 2 shall proceed from left to right only when the ferrocyanide concentration is kept at an exceedingly small value by precipitation of the potassium zinc ferrocyanide. That this requirement has not been met satisfactorily in previous methods is shown by a pronounced tendency for a return of the starch-iodine color after completion of the titration in spite of the expedient of adding the ferricyanide in successive small amounts in order to keep its concentration at a low value.

The value of the formal potential for the half-cell reaction



$$Fe(CN)_6^{----} = Fe(CN)_6^{---} + e^{-} \quad (4)$$

has been found to be approximately −0.71 volt in 1 *F* sulfuric, perchloric, or hydrochloric acid; −0.56 in 0.1 *F* and −0.48 in 0.01 *F* hydrochloric acid; and −0.46 in 0.01 *F* sodium hydroxide (*5, 15*). [Because Equation 1 represents a combination of precipitation and oxidation reactions, volume formal concentrations (formula weights per liter of solution) are used in order to avoid uncertainty as to equivalent weights.] These values indicate that pH control would play an important part in the equilibrium established in solutions containing ferricyanide and iodide. In addition, a rate effect is known to be involved, as it has been established that the rate of Reaction 2 is first order with respect to ferricyanide concentration and second order with respect to iodide concentration (*3, 8, 9, 16*). As a result of these considerations studies have been made of the effect upon the method of dilution, of the iodide and ferricyanide concentrations, of the pH of the solution, and of the time elapsing during and after the titration.

As a result of his first investigation, in which the titrations were made in essentially neutral solutions, Lang (*12*) reported reproducible values which were 1.65% low. This deviation was attributed to the formation of a 6.6% solid solution of zinc ferrocyanide in potassium zinc ferrocyanide. That zinc ferrocyanide is formed during the precipitation has been confirmed by de Koninck and Prost (*11, 12*) and by Saito (*10, 14*). As a result of subsequent titrations, made in sulfuric acid solutions, Lang (*13*) found values 1.60% low. Aster (*1*), Hibbard (*6*), and Casto and Boyle (*2*) used this value as the basis for an empirical correction factor. In this study no conditions have been found under which the necessity for such a correction factor is eliminated, although its value is somewhat dependent upon the conditions of the titration.

EXPERIMENTAL

Reagents and Solutions. Where not otherwise specified, reagent grade chemicals were used. Approximately 0.1 *F* solutions of sodium thiosulfate containing 0.01% sodium carbonate were prepared in boiled distilled water, and were standardized against Bureau of Standards potassium dichromate.

Approximately 0.1 *F* solutions of potassium ferricyanide were prepared by dissolving the solid in distilled water at room temperature. These solutions were stored in dark bottles and kept out of the light when not in use.

Potassium iodide free from iodate was used. Saturated solutions of potassium hydrogen phthalate, approximately 0.45 *F* and with a pH of 3.9, were prepared either by heating an excess of the solid in distilled water, then cooling and filtering, or by stirring an excess of the reagent with distilled water and allowing the mixture to stand several hours. This reagent gave results identical with those obtained with material prepared by heating phthalic anhydride with potassium hydroxide and bringing this mixture to the same pH and formality.

Most of the standard solutions of zinc were prepared by dissolving weighed amounts of shavings of Bureau of Standards "freezing point" zinc in excess hydrochloric or nitric acid, and boiling to eliminate nitrous oxides in case nitric acid was used. One solution was prepared by dissolving reagent grade zinc sul-

fate heptahydrate in distilled water, then analyzing for zinc by precipitation as zinc sulfide and ignition to zinc sulfate according to the procedure of Jeffreys and Swift (7). Another solution was made from zinc oxide which had been previously heated to dull redness for several hours in the electric oven, weighed, and dissolved in an excess of 6 F hydrochloric acid. Additional solutions of approximately known zinc concentration were used only to determine the relative effects caused by various changes of conditions.

Recommended Procedure. As a result of the numerous experiments which are summarized in the tables, the following procedure was finally developed, applicable to 100- to 250-mg. quantities of zinc, in which an option is provided whereby the pH may be controlled by means of either a phthalic acid–monohydrogen phthalate buffer or a hydrogen sulfate–sulfate system.

Pipet 25.00 ml. of the zinc solution into a 500-ml. conical flask, and neutralize to incipient precipitation of zinc hydroxide (or to a pH between 4 and 6) by alternate addition of ammonium hydroxide or sulfuric acid as required. Wash down the walls of the flask with 100 to 125 ml. of distilled water, and add a freshly prepared solution of 3 grams of potassium iodide in 50 ml. of distilled water. Add 25 ml. of saturated (0.45 F) potassium hydrogen phthalate solution, followed by 6 ml. of 0.5 F sulfuric acid. (Or, if use of the sulfate buffer is preferred, add 5 grams of sodium sulfate, followed by 2 ml. of 0.5 F sulfuric acid.) Add 30 to 35 ml. of 0.1 F potassium ferricyanide, swirl the solution, cover the flask with a watch glass, and place it in the dark for 5 minutes. Titrate with 0.1 F thiosulfate, swirling the contents of the flask, until the iodine color is indistinct and the yellow ferricyanide color predominates (this is approximately 2 ml. before the end point). Add 5 ml. of 0.4% starch solution and titrate slowly until the solution changes from a brownish to a clear bright yellow. (One unfamiliar with the end point should prepare a comparison solution by dissolving 0.5 to 1 gram of zinc sulfate heptahydrate in 25 ml. of distilled water and treating this solution by the above procedure, except that finally an excess of 0.1 to 0.5 ml. of thiosulfate should be added.)

Multiply the amount of zinc calculated on the basis of Equation 1 by the factor 1.019—that is, 1 liter of 0.1 F thiosulfate solution corresponds to 9.99$_3$ grams of zinc.

EXPLANATION OF TABLES AND DATA

Where not otherwise stated, the recommended procedure was used in obtaining the data shown below. The pH measurements were made with a Beckman pH meter after completion of the titration; pH values in brackets, as (3.0), were estimated from previous measurements on the same buffer system. Where the concentration of ferricyanide is reported this refers to the ferricyanide after Reaction 1 has occurred but before titration of the iodine; hence in most cases the volume is 250 ml.

In the tables the following abbreviations or symbols are used:

Because under no conditions has it been found possible to eliminate the necessity for an empirical correction factor, per cent error designates percentage deviation from the calculated zinc value based on the assumption that Reaction 1 is stoichiometric. Thus an error of -1.6% represents results in agreement with the correction factor of Lang which was mentioned above. V_n $Na_2S_2O_3$ indicates the volume of 0.1 N thiosulfate required to titrate the iodine present n minutes after reaching the end point. KI, formal concentration, before titration, represents the concentration of iodide calculated on the assumption that Reaction 1 has proceeded quantitatively with formation of triiodide; this concentration remains roughly constant during the titration, as the dilution factor is roughly equivalent to that caused by increase in iodide by reduction of the triiodide.

Effect of Dilution. The effect of the volume of the solution during the time the reactions represented by Equation 1 are taking place was investigated in a series of preliminary experiments which showed that when the volume is less than 100 ml. and the conditions otherwise are those of the standard procedure, iodine tends to be formed after the end point because of Reaction 2. With small volumes, an error of less than -1.6% is obtained which is attributed to the compensating effect of Reaction 2. With small volumes, and especially at lower pH values (1.5 to 2.5), high results are obtained if the amount of zinc is small and leaves a large excess of ferricyanide. Furthermore, the results are very dependent upon the time required for titration. It was found that dilution tended to minimize these effects and in most later experiments such quantities of solutions and water were used that the volume before beginning the titration of the liberated iodine was at least 200 ml. If the initial volume was 500 ml. the end points were indistinct and the errors averaged -2.0% or greater. The experiments tabulated in Table I show the effect of certain deviations from the standard procedure. In the first series of determinations the effect of volume changes is seen.

Effect of Iodide Concentration. The effect of variations in the iodide concentration are shown by the second series of determinations in Table I. Preliminary experiments had demonstrated that high concentrations of iodide cause instability of the end point, especially at lower pH values. As a result of these experiments, the amount of iodide to be used has been fixed at 3 grams in a volume of 200 to 250 ml. This amount results in iodide concentrations before the titration ranging from 0.05 to 0.06 F. Although this is lower than the concentration usually recommended, no evidence of loss of iodine has been observed.

Effect of Concentration of Excess Ferricyanide. In the third series of determinations shown in Table I the effect of variations in the concentration of ferricyanide can be seen. The volume of ferricyanide required by Equation 1 is approximately 27 ml. Other experiments have shown that concentrations of excess ferricyanide greater than 0.005 F cause high values for zinc and instability of the end point. It has also been found that

Table I. Effect of Deviations from General Procedure

In these experiments 25.00 ml. of a 0.1638 F zinc nitrate solution were taken and treated by the standard procedure with the deviations shown. The per cent error values are the results of at least three titrations which agreed to within 0.1% in most cases, never more than 0.2%. Except where noted, the end points were stable for at least 10 minutes. The phthalate buffer system was used in all experiments except series 5

Expt. No.	Volume before Titration, Ml.	KI Added, Grams	0.5 F H_2SO_4 Added, Ml.	pH of Titrated Solution	0.1 F $K_3Fe(CN)_6$ Added, Ml.	Error (−), %	Remarks
1 a	100	3	6	2.2–2.4	30	1.80	Ppt. voluminous and gelatinous
b	150	3	6	2.2–2.4	30	1.72	
c	200	3	6	2.2–2.4	30	1.75	
d	250	3	6	2.2–2.4	30	1.77	
e	500	3	6	2.2–2.4	30	2.05	End points indistinct
2 a	250	1	6	2.2–2.4	30	...	Premature and returning end points
b		2	6	2.2–2.4	30	1.73	
c		3	6	2.2–2.4	30	1.73	
d		5	6	2.2–2.4	30	1.77	
e		10	6	2.2–2.4	30	1.70	V_{10} $Na_2S_2O_3$ 0.01 ml. V_{15} $Na_2S_2O_3$ 0.05 ml.
3 a	250	3	6	2.2–2.4	30	1.77	V_{10} $Na_2S_2O_3$ 0.01 ml.
b		3	6	2.2–2.4	35	1.77	V_{15} $Na_2S_2O_3$ 0.07 ml.
c		3	6	2.2–2.4	45	1.60	V_{15} $Na_2S_2O_3$ 0.12 ml.
d		3	6	2.2–2.4	65	1.30	V_{15} $Na_2S_2O_3$ 0.19 ml.
4 a	250	3	0	3.6	30	1.77	
b		3	3	2.8	30	1.70	
c		3	6	2.3	30	1.75	
d		3	12	1.65	30	1.60	V_{15} $Na_2S_2O_3$ 0.07 ml.
				Sulfate Buffer			
5 a	250	3	0	3.9	30	1.80	
b		3	1	3.4	30	1.73	
c		3	2	3.0	30	1.73	
d		3	3	2.6	30	1.70	
e		3	4	1.5	30	1.60	

the excess of ferricyanide is less critical if the solution is buffered nearer to a pH of 3, and that under these conditions the average error is nearer −1.85% than the value of −1.65 found by Lang. It seems probable that under the conditions used by Lang and others Reaction 2 may operate as a compensating factor, possibly because of the effect of the lower pH.

Effect of pH of Solution. An inspection of Table I shows that with pH values less than 2, the error is −1.6 and the end point becomes unstable; other experiments have shown that with pH values from 2.2 to 3.5 the error is much more constant and in general ranges from −1.8 to −1.9%. In addition, recurrence of the end point is more pronounced at the lower pH values. Higher pH values than 3 do not appear to give substantial improvement in the stability of the end point and tend to result in local precipitates of zinc hydroxide. The results obtained by the sulfate buffer indicate that there is no specific action of the buffer systems so long as the same pH is attained. The phthalate system is recommended for accurate work, as it is more efficient for maintaining a value of approximately 3.

Table III. Confirmatory Analyses

Expt. No.	Potassium Hydrogen Phthalate, Added	$K_3Fe(CN)_6$ Added	pH at End Point	Zinc Taken	Zinc Found	Error	V_5 $Na_2S_2O_3$	Remarks
	Millimoles	*Millimoles*		*Millimoles*		%	*Ml.*	
1 a	11.0	3.0	(3.0)	3.822	3.756	−1.75	...	Recurs in 5 min.
b	11.0	3.0	(3.0)	3.822	3.756	−1.75	...	
2 a	11.0	3.0	(2.9)	3.767	3.697	−1.9	...	
b	11.0	3.0	(2.9)	3.767	3.700	−1.8	...	
c	11.0	3.0	(2.9)	3.767	3.695	−1.9	...	
3 a	11.0	3.0	(2.9)	4.128	4.049	−1.9	...	
b	11.0	3.0	(2.9)	4.128	4.049	−1.9	0.05	
4 a	11.0	4.0	3.01	3.475	3.414	−1.8	0.01	
b	11.0	4.0	2.99	3.475	3.414	−1.8	0.01	Recurs in 3 min.
5 a	11.0	5.0	(3.0)	7.653	7.510	−1.87	...	
b	11.0	5.0	(3.0)	7.653	7.510	−1.87	...	
6 a	10.3	5.0	2.10	4.992	4.896	−1.9	0.03	
b	10.5	5.0	2.50	4.992	4.898	−1.9	0.025	
c	20.8	5.0	2.98	4.992	4.888	−2.1	0.02	
7 a	11.0	5.0	3.72	4.992	4.902	−1.8	...	
b	11.0	5.0	3.78	4.992	4.896	−1.9	0.008	Recurs in 1 min.

Effect of Time of Standing before Titration. The experiments recorded in Table II were made for the purpose of determining the effect of allowing solutions containing the reactants to stand before beginning the titration. The work of Saito (*10, 14*) indicates that a precipitate of more uniform composition should result; because Reaction 1 is somewhat slow, there should be less tendency toward low titration values and recurrent end points. On the other hand there would be more tendency toward high values because of Reaction 2 or because of oxidation of iodide by oxygen. Photochemical catalysis of these reactions was minimized by storage in the dark during the time of standing. The effect of pH upon Reaction 2 is shown by a comparison of experiments 8 and 10 with experiments 3b, c, and d, Table I.

Table II. Effect of Time of Standing before Titration

In these tests 24.96 ml. of a 0.1426 *F* zinc sulfate solution were taken and treated by the standard procedure. The volume before titration was 250 ml. and 11 millimoles of potassium hydrogen phthalate were present in all experiments. The pH at the end point was approximately 3

Expt. No.	Time in Dark before Titration	$K_3Fe(CN)_6$ Added	Error	Stability of End Points
	Min.	*Millimoles*	%	
1	0	2.5	−1.9	Recurs
2	0	3.0	−1.85	Recurs, V_2 $Na_2S_2O_3$ 0.01 ml.
3	0	3.0	−2.0	Recurs
4	0	3.0	−1.8	
5	5	3.0	−1.8	
6	5	3.0	−1.8	
7	0	3.5	−2.1	Recurs in 2 minutes
8	10	3.5	−1.85	
9	0	5.0	−2.0	Recurs
10	10	5.0	−1.8	

Effect of Quantity of Zinc Taken. The amount of zinc taken may affect the composition of the precipitate and hence the value of the empirical factor; the time required for completion of Reaction 1; and the visibility of the end point. In addition, the smaller the quantity of zinc the greater the excess of ferricyanide. An extensive series of experiments has shown that with quantities of zinc varying from approximately 1 to 7.5 millimoles no such effects were observed.

In other experiments solutions containing a known amount of zinc were titrated to the end point according to the recommended procedure, then known quantities of iodine were added and the solutions were again titrated. In all cases the recovery of the iodine was quantitative within the experimental methods involved. In another experiment a potassium zinc ferrocyanide precipitate was prepared by titrating a sample of zinc according to the recommended procedure, adding excess zinc solution (to remove all ferricyanide), and again titrating. The precipitate obtained was washed by decantation until it was free of zinc ion. A portion of this precipitate was then introduced into a reaction mixture prepared according to the recommended procedure, except that only 10 to 15 ml. of 0.1 *F* ferricyanide solution were added. A known quantity of iodine was then added and titrated by thiosulfate; again the iodine was completely recovered.

Experiments have shown that as much as 30 millimoles of chloride is without apparent effect; that two- to three-fold variations in the potassium ion concentration are without significant effect; and that acetate is without effect when the pH is maintained at 3 or less. The effects of other ions upon this procedure should be essentially the same as those found by Lang (*12, 13*) and by Casto and Boyle (*2*).

Confirmatory Analyses. The data obtained from a series of confirmatory analyses, especially selected in order to evaluate the empirical factor under various conditions, have been collected in Table III. On the basis of these analyses (and of numerous other experiments) the recommendation is made that the empirical factor 1.019 be used in calculating the quantity of zinc found by titrations by the recommended procedure. Considering the magnitude of this factor, the reproducibility of the values is surprisingly good, the average deviation being less than 0.1%.

The recommended procedure was used in these analyses except for the variations stated or shown in Table III. In series 4, 17 millimoles of chloride were present. In series 6, 40 millimoles of chloride were present, 10 of which were added as hydrochloric acid; no sulfuric acid was added. Series 7 was the same as Series 6 but with 8.7 millimoles of ammonium hydroxide added.

As a further test of the method the recommended procedure was given to a class of sophomore students, who were asked to make titrations of a zinc solution which was prepared from the Bureau of Standards zinc mentioned above, and calculated to be 0.1654 *F*. They used thiosulfate solutions which they had prepared and standardized as part of their class work, and reported their values without the use of a correction factor. When the correction factor 1.019 was applied to the values from 22 students on 66 titrations an average formality of 0.1656 was obtained, the average deviation being 0.08%.

In many cases the titrated solution showed no significant return of the iodine color even after standing up to 20 minutes.

ACKNOWLEDGMENT

The authors are indebted to Roland N. Smoot for carrying out the series of experiments from which the data collected in Table I were obtained.

LITERATURE CITED

(1) Aster, E., *Verfkroniek*, 6, 236 (1933); *Chem. Zentr.*, 105, I, 88 (1934).
(2) Casto, C. C., and Boyle, A. J., IND. ENG. CHEM., ANAL. ED., 15, 623 (1943).
(3) Donnan, F. G., and LeRossignol, K., *J. Chem. Soc.*, 83, 703 (1903).
(4) Gamzulov, Ya. I., *Zavodskaya Lab.*, 3, 984 (1934).
(5) "Gmelins Handbuch der anorganischen Chemie," 8th ed., Vol. 59A, pp. 281, 287, 290, 292; Vol. 59B, pp. 629–30, 1932.
(6) Hibbard, P. L., IND. ENG. CHEM., ANAL. ED., 6, 423 (1934).
(7) Jeffreys, C. E. P., and Swift, E. H., *J. Am. Chem. Soc.*, 54, 3219 (1932).
(8) Just, G., *Z. phys. Chem.*, 63, 513 (1908).
(9) Kiss, A. V., *Rec. trav. chim.*, 52, 289 (1933).
(10) Kolthoff, I. M., and Furman, N. H., "Potentiometric Titrations," 2nd ed., p. 324, New York, John Wiley & Sons, 1931.
(11) Koninck, L. L. de, and Prost, E., *Z angew. Chem.*, 9, 460, 564 (1896); *J. Chem. Soc.*, 1896, Abstracts, II, p. 675.
(12) Lang, R., *Z. anal. Chem.*, 79, 161 (1929).
(13) *Ibid.*, 93, 21 (1933).
(14) Saito, S., *Bull. Inst. Phys. Chem. Research (Tokyo)*, 8, 921, Abstracts 2, 107.
(15) Swift, E. H., "System of Chemical Analysis," p. 542, New York, Prentice-Hall, 1939.
(16) Wagner, C., *Z. phys. Chem.*, 113, 261 (1924).

RECEIVED October 11, 1948.

Determination of Water in Nitrogen Tetroxide

GERALD C. WHITNACK AND CLIFFORD J. HOLFORD
U. S. Naval Ordnance Test Station, Inyokern, Calif.

A reliable and convenient method has been developed for the determination of small amounts of water that contaminate nitrogen tetroxide. It is believed that water reacts with nitrogen tetroxide to form nitric acid and hence nitric acid is the contaminant. The gas, in the presence of a stream of dry nitrogen, is passed over anhydrous sodium carbonate at 280° C. and then over metallic copper at 600° C. Most of the acidic substances are removed by anhydrous sodium carbonate, and remaining traces of oxides of nitrogen are completely removed by passage over metallic copper. The water released by these reactions is absorbed by anhydrous calcium sulfate and weighed. For samples containing about 0.5% water the precision of the determination corresponds to a standard deviation of 0.006% absolute.

THE determination of water in nitrogen tetroxide in the past has not been accomplished in a satisfactory manner. Water will react with nitrogen tetroxide, forming nitric acid or nitric and nitrous acids (*4, 9*). The acid or acids must be neutralized in such a manner as to release the water, which can then be collected and weighed.

The present report describes in detail the construction and operation of equipment applicable for the precise and convenient analysis of water in nitrogen tetroxide.

MATERIALS AND APPARATUS

The anhydrous calcium sulfate was 8-mesh indicating Drierite (W. A. Hammond Drierite Company). The indicator for oxides of nitrogen was a solution of diphenylamine (Eastman Kodak Company) in concentrated sulfuric acid. Nitrogen tetroxide used in developing the method was Matheson Company commercial grade. Purified nitrogen tetroxide was obtained by the method of Giauque and Kemp (*3*).

The assembled apparatus is shown in Figure 1. The Pyrex combustion tubes were approximately 300 mm. long, 13 mm. in inside diameter, and 17 mm. in outside diameter, and fitted with ₮ 10/30 joints at both ends. Combustion tube *E* was packed with anhydrous sodium carbonate (J. T. Baker Chemical Company analytical grade), which was dried for 12 hours at 120° C. Combustion tube *F* was packed with copper oxide (wire form, J. T. Baker Chemical Company), and then was reduced with hydrogen at 200° to 300° C. U-tube *A* contained Drierite and was used to ensure dryness of the nitrogen entering the system.

The reaction vessel, *B*, consisted of a 15 × 2.5 cm. (6 × 1 inch) Pyrex tube fitted with a 5 × 1 inch hollow ₮ 29/42 glass stopper. Attached to the inside of this glass stopper was a glass hook from which plunger *C* was suspended. The plunger, filled with iron filings and weighing approximately 20 grams, was small enough to fall freely the length of the reaction vessel. The combustion tubes were heated in hinged combustion tube furnaces, *G* and *H*. The furnace temperatures were controlled by rheostats. A glass coil, *J*, with ₮ 10/30 joints, was placed between combustion tube *F* and weighing tube *K* for flexibility. Weighing tubes *K* and *L* were standard Schwartz calcium chloride drying tubes 100 mm. long with two hollow ₮ 14/20 ground joint stoppers and were filled with Drierite. The absorption bulb, *M*, contained an indicator solution of diphenylamine for detecting the presence of oxides of nitrogen in the escaping gas stream. Connections marked *X* (Figure 1) were sealed with de Khotinsky cement. A good flexible grade of rubber tubing served as connections marked *Y* (Figure 1).

For convenience in preparing ampoules of samples to be analyzed, a stock ampoule cooled to −20° C. was filled with about 50 grams of liquid nitrogen tetroxide directly from the cylinder. Small sampling ampoules of nitrogen tetroxide, of such size that they would freely enter the reaction vessel, were then prepared for analysis. The cooled stock ampoule was placed in an upright position with its stem protruding upward to a small opening in a stainless steel plate (placed for safety over the stock ampoule). The tared sample ampoule was then warmed and inverted, and its stem was placed in the stock ampoule below the surface of the liquid with its bulb resting on the rim of the hole in the stainless steel plate. The bulb of the sampling ampoule was then cooled with a cloth dipped in a mixture of dry ice and acetone. When filled, the sampling ampoule was quickly sealed, using a hand torch, and placed in a desiccator over Drierite for later analysis.

Analyses of several samples of pure nitrogen tetroxide, in which the samples were obtained in an evacuated system, indicated that the former technique of sampling was entirely adequate and offered a slight advantage, because the problem of recovering small broken particles of glass was eliminated when the ampoule was broken in the reaction vessel. It was not possible to obtain a preweight of an empty ampoule by the latter method.

PROCEDURE

A small ampoule containing 0.5 to 1.0 gram of nitrogen tetroxide is weighed and carefully placed in reaction vessel *B*. The ground-glass stopper containing plunger *C* is then put in place and sealed with de Khotinsky cement. A beaker, *N*, containing a dry ice–acetone mixture, is placed around the lower part of the reaction vessel (Figure 1). This lowers the vapor pressure of the liquid, and, when the ampoule is broken, prevents too rapid passage of the gas over the anhydrous sodium carbonate. The furnace temperatures are adjusted to 280° C. for *E* and 600° C. for *F*. The air and water are removed from the apparatus in a stream of dry nitrogen. Complete removal is assumed when U-tubes *K* and *L* give constant weight within ±0.2 mg. on successive weighings at 1-hour intervals.

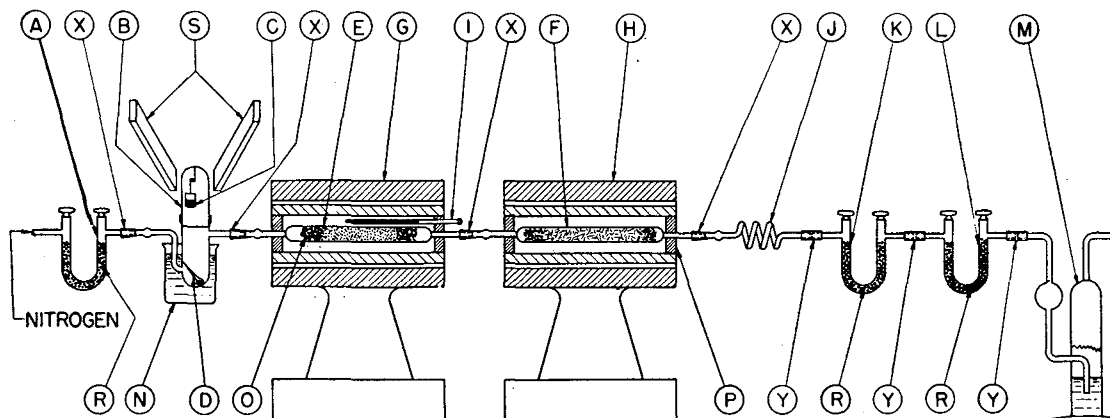


Figure 1. Assembled Apparatus

A. U-tube (drying)
B. Reaction vessel
C. Plunger
D. Ampoule of nitrogen tetroxide
E. Combustion tube
F. Combustion tube
G, H. Electric furnaces
I. Thermometer
J. Glass coil
K, L. U-tubes (weighing)
M. Absorption vessel (diphenylamine)
N. Ice bath
O. Glass wool
P. Asbestos (wrapping)
R. Drierite
S. Bar magnets
X. Connections (cup and cone)
Y. Connections (rubber)

The plunger is then removed from the glass hook in the glass stopper with the aid of two bar magnets, *S*, and allowed to drop, breaking the ampoule of nitrogen tetroxide. The dry ice–acetone bath is now removed from the reaction vessel and the liberated gases are allowed to pass over the heated anhydrous sodium carbonate and metallic copper in the stream of dry nitrogen. At the end of the run the reaction vessel and exposed portions of the apparatus preceding the weighing tubes are heated with an alcohol lamp to expel the last traces of the sample through the reaction tubes and the water into the weighing tubes. The weighing tubes are then removed from the apparatus, wiped with lens paper, and weighed. The percentage of water in the liquid nitrogen tetroxide is computed from the increase in weight of the weighing tubes.

Data. A sample from a cylinder of Matheson commercial nitrogen tetroxide was analyzed for water by the method described. Six aliquots from this sample showed an average of 0.445% water with a standard deviation of about 0.006% absolute (Table I).

Table I. Determination of Water in Commercial Nitrogen Tetroxide

Nitrogen Tetroxide	Water	Water
Grams	*Mg.*	%
1.2153	5.4	0.44
1.1653	5.3	0.45
0.8079	3.6	0.45
0.8952	3.9	0.44
0.9022	4.0	0.44
0.7543	3.4	0.45
1.2895[a]	13.9	1.08
0.7295[a]	7.5	1.03

[a] Sample of Solvay Products nitrogen tetroxide containing 12 to 15% nitric oxide. Index of precision is based on first 6 samples (Matheson Co. product).
Average (of first 6), $\bar{x}$ = 0.445%
Standard deviation, s = 0.0055% abs.
Standard deviation of mean (of 6) s_m = 0.0022%
Confidence range, 0.445 ± 0.0057%

Six samples of purified nitrogen tetroxide were analyzed for water. Data presented in Table II show an average of 0.02% water with standard deviation of 0.01% absolute. On the basis of these results a confidence range of 0.02 ± 0.01% may be expected on samples of purified nitrogen tetroxide containing traces of water.

To ascertain the precision and reliability of the method, a few experiments were made in which a known amount of distilled water was added to a known amount of pure nitrogen tetroxide by breaking ampoules of water and nitrogen tetroxide simultaneously in the reaction vessel. The results (Table III) indicate that the method has a precision, shown by a standard deviation obtained from six values, of about 7 parts per thousand.

The indexes of precision used in the statistical analysis of data presented in Tables I, II, and III are as follows:

Standard deviation (estimate)

$$s = \sqrt{\Sigma(x - \bar{x})^2/(n - 1)} \quad (1)$$

Standard deviation of mean of n

$$s_m = s/\sqrt{n} \quad (2)$$

Confidence range (fiducial limits)

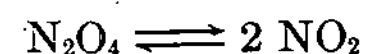
$$= \bar{x} \pm t s_m \quad (3)$$

In the above

$\bar{x}$ = mean of n observations of x
t = Student's t for the significance level desired and $n-1$ degrees of freedom (*2*). For the 1 in 20 significance level and means of 6 (5 degrees of freedom) t is 2.571.

DISCUSSION

The molecule of nitrogen tetroxide is considered to have the formula N_2O_4 at temperatures below −11.0° C. and to dissociate into NO_2 as the temperature rises (*1*).



$$N_2O_4 \rightleftharpoons 2\,NO_2$$

At the temperature of the average laboratory the gas phase equilibrium is shifted to the right and the gas will contain both the simple molecule NO_2 and the dimer N_2O_4. As the liquid nitrogen tetroxide in the reaction vessel warms up, the gas passes

Table II. Determination of Water in Purified Nitrogen Tetroxide

Nitrogen Tetroxide	Water Found	
Grams	*Mg.*	*%*
2.0134	0.2	0.01
1.6750	0.4	0.02
2.4298	0.6	0.02
1.3237	0.6	0.04
2.1023	0.2	0.01
1.9934	0.6	0.03

Average, $\bar{x}$ = 0.02%.
Standard deviation, s = 0.012% abs.
Standard deviation of mean (of 6), s_m = 0.0048%
Confidence range, 0.02 ± 0.012%.

Table III. Recovery of Water Added to Purified Nitrogen Tetroxide

Nitrogen Tetroxide Present	Water Added	Water Found	Water Recovered
Mg.	*Mg.*	*Mg.*	*%*
465.0	33.7	33.7	100.00
339.1	25.6	25.6	100.00
637.3	26.9	26.9	100.00
222.9	12.5	12.7	101.60
211.2	16.4	16.5	100.61
139.8	26.2	26.2	100.00

Average, $\bar{x}$ = 100.37%
Standard deviation, s = 0.65% abs.
Standard deviation of mean (of 6), s_m = 0.27%
Confidence range, 100.37 ± 0.68%
Accuracy, $\bar{x}$ − true value = 0.37%

over the heated anhydrous sodium carbonate. Sodium nitrate and sodium nitrite are formed and carbon dioxide is released as a gas.

$$2NO_2 + Na_2CO_3 \longrightarrow NaNO_3 + NaNO_2 + CO_2$$

The reaction of nitrogen tetroxide and water is generally written to indicate the formation of nitrous and nitric acids (*1*, *4*).

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$

Water in nitrogen tetroxide then would be present as acids. In obtaining the data for Table III, it was observed that samples of purified nitrogen tetroxide and limited amounts of distilled water gave a green color when broken simultaneously in the reaction vessel. It is known that pure nitrogen trioxide is a blue liquid and that pure nitrogen tetroxide is an amber colored liquid, and the presence of the two liquids would result in a green color. The samples of nitrogen tetroxide which were used in the experiments (Table III) had been shown to be free of water (Table II), and free of nitric oxide by the method of Milligan (*6*). Thus, the green color resulting from the reaction of pure nitrogen tetroxide and distilled water is probably due to the formation of nitrogen trioxide. The nitrogen trioxide would be present if nitric oxide were one of the products of the reaction of the pure nitrogen tetroxide and water (*9*).

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \quad (4)$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \quad (5)$$

Melvin and Wulf (*5*) studied the reaction of nitrogen tetroxide and water by ultraviolet absorption. They found that nitrous acid bands were plain only when nitric oxide was added in excess, the nitric oxide effecting an increase in the concentration of nitrous acid. They favored the formation of nitric acid and nitric oxide, because the bands due to nitric oxide appeared in ultraviolet. The authors of this paper believe that the water present in nitrogen tetroxide under the conditions described is in the form of nitric acid. A further investigation of the products from the reaction of pure nitrogen tetroxide and limited amounts of water should solve this problem.

Assuming that the water in liquid nitrogen tetroxide is present as nitric acid or as nitric and nitrous acids, we may write the following reactions which take place at 280° C. in the anhydrous sodium carbonate tube.

$$2HNO_3 + Na_2CO_3 \longrightarrow 2NaNO_3 + CO_2 + H_2O \quad (6)$$

$$2HNO_2 + Na_2CO_3 \longrightarrow 2NaNO_2 + CO_2 + H_2O \quad (7)$$

When nitric or nitrous acid comes in contact with anhydrous sodium carbonate at a temperature of 280° C. sodium nitrate and sodium nitrite, respectively, are formed, and carbon dioxide and water are released as gases. The water is absorbed by the Drierite in the weighing tubes. The carbon dioxide is not absorbed by the Drierite and passes through the apparatus unchanged.

To test the effect of carbon dioxide on Drierite, under the conditions of the analysis, a sample of carbon dioxide snow was used as a pure source and the gas was passed over the Drierite in the weighing tubes. Constant weight of the tubes indicated no interference from the gaseous carbon dioxide.

The furnace temperature of 280° C. in the anhydrous sodium carbonate tube is high enough to ensure the release of all the water formed in the reaction and low enough to prevent any decomposition of sodium nitrate, sodium nitrite, or sodium carbonate. At the temperature of the anhydrous sodium carbonate tube some of the nitrogen dioxide is dissociated into nitric oxide and oxygen ($NO_2 \rightleftarrows NO + {}^1/_2O_2$) (*8*). In early experiments traces of oxides of nitrogen were found in the Drierite of the weighing tubes. A solution of diphenylamine in concentrated sulfuric acid indicated the presence of traces of oxides of nitrogen in the exit gas stream. A channeling of the gases through the anhydrous sodium carbonate was first thought to be the source of trouble. This possibility was discarded when traces of the oxides of nitrogen were still found in the exit gas stream, after the gases were allowed to pass through two tubes filled with anhydrous sodium carbonate and heated to 280° C. It is known that at a temperature of 150° C. nitrogen dioxide begins to be measurably dissociated into nitric oxide and oxygen (*7*). As nitric oxide and oxygen come out of the heated anhydrous sodium carbonate tube and come in contact with the cooler part of the apparatus, they will re-form nitrogen dioxide. Consequently, oxides of nitrogen will appear in the exit gases. When the escaping oxides of nitrogen come in contact with the water absorbed on the Drierite, a reaction giving nitric acid or nitric and nitrous acids occurs. This gives rise to increased weight in the weighing tubes and the data calculated as water are in error. To overcome this source of error, a tube containing metallic copper heated to 600° C. was placed in the apparatus in tandem with the tube of anhydrous sodium carbonate. A negative test was then obtained for oxides of nitrogen in the exit gases and on the Drierite. The final data were obtained with the apparatus including a tube filled with metallic copper and heated to 600° C. for complete removal of oxides of nitrogen.

Commercial nitrogen tetroxide may contain some nitric oxide as an impurity. If present the nitric oxide is probably in the liquid nitrogen tetroxide as the compound nitrogen trioxide

$$NO + NO_2 \rightleftharpoons N_2O_3$$

Nitrogen trioxide in the gaseous state is almost completely dissociated into nitric oxide and nitrogen dioxide (*4*), and hence under the conditions of the analysis the equilibrium would be shifted to the left.

ACKNOWLEDGMENT

The authors gratefully acknowledge the many helpful suggestions and constructive criticism of the contents of this report given them by Ross W. Moshier, G. B. L. Smith, and Sol Skolnik.

The authors wish also to express their thanks to Charles M. Drew for help in construction of the apparatus, to D. S. Villars, Jersey City Junior College, for advice on statistical treatment of data, and to A. G. Whittaker and Lynwood Barker for samples of purified nitrogen tetroxide.

This paper is published with the permission of L. T. E. Thompson, technical director of the Naval Ordnance Test Station.

LITERATURE CITED

(1) Dennis, L. M., and Nichols, M. L., "Gas Analysis," rev. ed., p. 228, New York, Macmillan Co., 1929.
(2) Fisher, R. A., "Statistical Methods for Research Workers," 10th ed., London, Oliver & Boyd, 1948.
(3) Giauque, W. F., and Kemp, J. D., *J. Chem. Phys.*, 6, 40 (1938).
(4) Jacobs, M. B., "Analytical Chemistry of Industrial Poisons, Hazards and Solvents," 1st ed., p. 281, New York, Interscience Publishers, 1941.
(5) Melvin, E. H., and Wulf, O. R., *J. Chem. Phys.*, 3, 755–9 (1935).
(6) Milligan, L. H., *J. Phys. Chem.*, 28, 545 (1924).
(7) Stack, S. S., *Gen. Elec. Rev.*, 41, 106 (1938).
(8) Taylor, H. S., "Treatise on Physical Chemistry," Vol. 1, p. 328, New York, D. Van Nostrand Co., 1924.
(9) Yost, D. M., and Russell, H., "Systematic Inorganic Chemistry," p. 78, New York, Prentice-Hall, 1944.

RECEIVED October 4, 1948.

Determination of Fungicides in Varnishes and Wood Sealers

Salicylanilide, Pentachlorophenol, and Mercurial Fungicides

MELVIN H. SWANN
Paint & Chemical Laboratory, Aberdeen Proving Ground, Md.

Methods of analysis to ensure the presence of specified quantities of fungicides in wood preservative sealers are needed. In separating salicylanilide and pentachlorophenol from varnishes, use is made of their solubility in alkalies, insolubility in acids, and slight solubility in water. They are then determined colorimetrically. Mercurial fungicides can be reduced to the metallic state, separated and determined quickly and accurately without hazards or difficulties encountered in standard procedures for determining mercury in organic substances.

SALICYLANILIDE has been determined in mildew-proofing materials for cotton duck webbing (*6*) by extraction with a suitable solvent and digestion with sulfuric acid by the usual micro-Kjeldahl method. This determination is based on the nitrogen content of the fungicide and is unsuitable for resinous materials, because the determination of salicylanilide by its nitrogen content would involve the tedious and difficult decomposition of organic matter. In addition, the determination would be questionable where such resins as urea-formaldehyde or melamine-formaldehyde resins are present, because of their high nitrogen content.

Pentachlorophenol, in isolated form, has been estimated by its hydroxyl or halogen content but must be extracted from resinous materials before such determinations can be made with accuracy. When pentachlorophenol is present there is no way of proving the absence of other halogen-bearing compounds, except in production control where the resin and solvents can be tested qualitatively for halogens before the fungicides are added. In addition, pentachlorophenol must be extracted from the sealer for positive qualitative identification.

The solubility properties of the two fungicides permit their separation from oil and resin bases. They are extracted with strong alkali from an ether or benzene solution, then acidified and re-extracted with ether, from which they are re-extracted with a weaker alkaline solution. The final purification is made by diluting an aliquot portion to sufficient volume to hold the fungicide in aqueous solution while the remaining impurities are precipitated and separated by filtration.

The violet color of ferric salicylate that results when salicylic acid or its salts react with ferric chloride, is used to determine the salicylanilide colorimetrically following its extraction. Pentachlorophenol is determined colorimetrically in the extract by the yellow color of tetrachloroquinone, formed when pentachlorophenol reacts with nitric acid (*2*). The colorimetric determination of either fungicide is not affected by the presence of the other. Simple qualitative tests will show the presence or absence of either fungicide in the extract.

There are several mercury compounds used as fungicides in wood sealers—phenyl mercuric oleate, phenyl mercuric naphthenate, phenyl mercuric *o*-benzoic sulfamide, etc. When mercurial fungicides are used, they compose approximately 1% of the nonvolatile portion of the sealer. The ratio of organic matter to mercury is so great that relatively large samples must be used. The excess of organic matter present necessitates prolonged digestion when the usual methods of decomposing organomercury compounds are employed.

A method has been described by Rauscher (*3*), in which amines are used for the reduction of mercury to the metallic state in such compounds as oxides, salts, and isolated organomercury compounds. This method has been modified slightly to give excellent results with wood sealers. The method is relatively brief and may be used with standard laboratory equipment. High temperatures and the complete decomposition of organic matter are avoided. Relatively large samples may be used if desired. The metallic mercury that may separate in finely divided form is washed by decantation. Possible losses from volatility of mercury are avoided by never exposing the metal to air. The method is equally effective with all types of mercurial fungicides and results are accurate and reproducible to less than 0.1%.

ANALYTICAL PROCEDURE

Extraction and Purification of Salicylanilide and Pentachlorophenol. A sample of the varnish, not exceeding 3.0 grams, is weighed by difference from a test tube into a 250-ml. pear-shaped separatory funnel containing 40 ml. of absolute ethyl ether (if the resin precipitates in ether, benzene is substituted in the first and second funnels). The sample and solvent are mixed by swirling and 20 ml. of 2.5% aqueous sodium hydroxide solution are added. The funnel is vigorously shaken and the layers are allowed to sepa-

rate completely. The aqueous layer is drawn off into a second separatory funnel and again shaken with 40 ml. of ether. After separation, the lower layer is drawn off and shaken a third time with ether. The aqueous layer is then filtered through paper (medium porosity) previously dampened with water, into a 400-ml. beaker. Four more extractions are made, using additional 20-ml. portions of 2.5% aqueous sodium hydroxide. The same funnels and solvent are used for the washing. All aqueous layers are filtered through the same funnel and paper.

All portions of the aqueous layers are collected in the same beaker, along with the water used to wash the paper. A raised cover is placed on the beaker, a glass rod is inserted to prevent bumping, and the ether is driven off by immersing in a water bath. Volume is reduced to approximately 80 ml. on a steam bath and the sample is cooled. It is then transferred to a 100-ml. volumetric flask and brought to volume with water.

One half of the sample, or 50 ml., are transferred to a 250-ml. separatory funnel with a pipet, and acidified (pH 1.0) with 6 *N* hydrochloric acid, added dropwise. Accutint indicator paper No. 20 is helpful in obtaining the desired pH. Acidification of the aqueous solution precipitates the fungicides, which can then be taken up with ether. The fungicide is extracted with three 20-ml. portions of C.P. ethyl ether, the combined ether extracts are washed with 5 ml. of water, and the water is discarded.

The fungicide is next extracted from the ether with 100 ml. of 0.1 *N* sodium hydroxide, used in 20-ml. portions. Each alkaline layer is filtered through paper (medium porosity) previously dampened with water, into a 400-ml. beaker. The paper is finally washed with water. A raised cover is placed on the beaker, a glass rod is inserted, and the ether is driven off in a water bath. The beaker is transferred to a steam bath, the cover is removed, and the sample is evaporated to dryness. It is then transferred to an oven and heated for 1 hour at 110° C. Upon removal from the oven, 25 ml. of water are added and the sample is warmed on a steam bath until completely dissolved. It is then cooled and transferred with water to a 50-ml. volumetric flask. The sample is brought to volume and held for final purification and qualitative or quantitative analysis.

Qualitative Identification. To show the presence or absence of salicylanilide or pentachlorophenol, a 10- or 20-ml. portion of the sample is withdrawn and acidified (pH 1.0) by adding 6 *N* hydrochloric acid slowly and with constant stirring. It is then warmed for a few minutes in a water bath at 50° C. and cooled in ice or cold running water. If as little as 3 or 4 mg. of either fungicide are present, it will precipitate from solution. It is separated by filtration and identified qualitatively.

Salicylanilide can be detected by the violet color of ferric salicylate formed when ferric chloride is added, or by the Tafel reaction for anilides (*5*). The former is conducted by dissolving several milligrams of the salt in a few milliliters of ethyl alcohol, adding 80 to 100 ml. of water, and removing the alcohol by evaporating to a volume of 40 or 50 ml. When 1 ml. of ferric chloride solution (1.0 gram of ferric chloride hexahydrate in 100 ml. of 1.0 *N* acetic acid) is added dropwise, a stable violet color forms immediately if salicylanilide is present. To apply the Tafel reaction for anilides, several milligrams of the fungicide are dried in an oven at 50° C. and dissolved in 3 ml. of concentrated sulfuric acid in a small test tube and 1 drop of a saturated aqueous solution of potassium dichromate is added without agitation. An intense violet color appears for several seconds, finally changing to green when shaken.

The presence of pentachlorophenol is readily detected by a strong positive reaction for halogens by Beilstein's copper wire test (*4*).

Colorimetric Procedure for Salicylanilide. (Because the maximum amount that can be determined by the following procedure is 5 mg. of salicylanilide, it is necessary to withdraw several aliquots of different volumes from the extracted sample.)

Aliquots of 2, 5, and 10 ml. are transferred to 250-ml. beakers and diluted to approximately 75 ml. with water. Each sample is then slowly and carefully acidified with hydrochloric acid to exactly pH 5.0. A pH meter is used for the adjustment and 6 *N* hydrochloric acid is used first, followed by 0.1 *N* acid for the final adjustment, to avoid overdilution of the sample. The samples are allowed to stand 1 hour, then filtered through double thicknesses of paper of fine porosity into 100-ml. volumetric flasks. The paper and beaker are rinsed with water. Exactly 2 ml. of ferric chloride solution (1.000 gram of ferric chloride hexahydrate in 100 ml. of 1.0 *N* acetic acid) are added, and samples are diluted to volume. The violet color is compared at once, preferably in a Fisher electrophotometer, against a tube of water, using a green light filter (approximate wave length 525 millimicrons).

The weight of salicylanilide in each aliquot taken is determined from a graph previously prepared as directed below. If the amount of salicylanilide in two of the three aliquots fails to agree proportionally, they are probably too large and smaller aliquots should be withdrawn.

Preparation of Graph. If salicylanilide of known purity is not available, a quantity of the commercial product is dissolved in aqueous sodium hydroxide, diluted to 100 to 200 ml., acidified (pH 1.0) with hydrochloric acid, filtered, and washed with water. The fungicide is dried overnight in an oven at 50° C. A quantity is weighed with fourth decimal accuracy, dissolved in absolute ethyl alcohol, C.P. grade, and diluted to definite volume with alcohol. Aliquots of 1 to 5 mg. are withdrawn into 250-ml. beakers, diluted with water to 150 ml., and evaporated on a steam bath to approximately 75 ml. Each is transferred to a 100-ml. volumetric flask and color is developed as above.

Colorimetric Procedure for Pentachlorophenol. (Because the maximum amount that can be held in solution during the final purification process is 5 mg. of pentachlorophenol, it is necessary to withdraw several aliquots of different volumes from the extracted sample.)

Aliquots of 2, 5, and 10 ml. are transferred to 600-ml. beakers and 400 ml. of distilled water are added. Each sample is acidified (pH 1.0) with concentrated hydrochloric acid and allowed to stand 1 hour. Accutint indicator paper No. 20 is helpful in obtaining the desired acidity. The samples are filtered through double thicknesses of paper of fine porosity into 600-ml. beakers and the filter papers are washed with water. Each is then neutralized with sodium hydroxide and an excess of 5 ml. of 10% sodium hydroxide is added. The samples are then placed in a boiling water bath and the volume is reduced to 20 to 30 ml. The samples are cooled, transferred with water to separatory funnels, and acidified (pH 1.0) with 6 *N* hydrochloric acid and the pentachlorophenol is extracted with three 20-ml. portions of C.P. benzene.

The benzene extractions are combined and washed with 5 ml. of water. The combined benzene layers of each aliquot sample are filtered through paper (coarse porosity), previously dampened with benzene, into glass-stoppered 250-ml. Erlenmeyer flasks. Ten milliliters of 10 *N* nitric acid and 1 ml. of 10% hydrochloric acid are added. A small strip of paper is inserted at the side of each glass stopper and the flasks are placed in a water bath at 70° C. for 20 minutes. Each sample is then cooled, transferred to a 250-ml. separatory funnel, and washed twice with 150 ml. of distilled water. The water washings are discarded and the benzene layers are filtered twice through paper of medium porosity, previously dampened with benzene. The second filtration is made directly into 100-ml. volumetric flasks. The papers are washed with benzene and the yellow benzene solution is diluted to volume. The flasks are shaken thoroughly and allowed to stand from 10 to 30 minutes. The color is then compared in an electrophotometer against a tube of water, using a blue light filter (approximate wave length, 425 millimicrons).

The weight of pentachlorophenol in each aliquot taken is determined from a graph previously prepared as directed below. If the amount of fungicide in two of the three aliquots fails to agree proportionally, they are probably too large and an indefinite amount of pentachlorophenol has precipitated out during the final purification.

Preparation of Graph. If pentachlorophenol of known purity is not available, a quantity of the commercial product is dissolved in aqueous sodium hydroxide, diluted to 100 to 200 ml., acidified (pH 1.0) with hydrochloric acid, filtered, and washed with water. It is then dried overnight in an oven at 50° C. A quantity is weighed with fourth decimal accuracy, dampened with absolute ethyl alcohol, dissolved in C.P. benzene, and diluted to a definite volume. Aliquots of 1 to 5 mg. are withdrawn into 250-ml. glass-stoppered, Erlenmeyer flasks. Volume is made up to approximately 60 ml. with benzene and the color is developed as in the colorimetric procedure.

Calculations. If a = milligrams of fungicide in aliquot taken, b = size of aliquot in milliliters, c = size of original sample of sealer, in grams, and d = per cent of solids in sealer, expressed decimally, then $\frac{10 \times a}{b \times c \times d}$ = % of fungicide in sealer, calculated on the solids basis.

If it is likely that phenolic fungicides other than pentachlorophenol are present it will be necessary to separate the latter by precipitation. Fifty milliliters of the sample in 2.5% alkaline solution are acidified, to pH 1.0, with hydrochloric acid and diluted to 100-ml. volume. After standing at least 12 hours, the temperature is adjusted to 25° ± 1° C. and the sample is filtered through porous glass crucibles of medium porosity, containing a layer of asbestos. The filtrate is used to make the transfer; no water is used. Three milligrams of pentachlorophenol will be lost because of its slight solubility, and correction must be made in calculating. Other phenolic fungicides, if present, will remain in the filtrate.

The precipitated residue is dissolved while still wet, by passing 100 ml. of 0.1 N sodium hydroxide through the crucible several times, washing finally with water. The sample is then transferred to a 400-ml. beaker, evaporated to dryness on a steam bath, transferred to an oven, and heated for 1 hour at 110° C. The original procedure is followed from this point.

Extraction of Metallic Mercury from Mercurial Fungicide Sealers. A sample of the sealer, not exceeding 5.0 grams, is carefully weighed by difference into a 100-ml. round-bottomed flask having a standard-taper, ground-glass joint. Five milliliters of mineral spirits are added to prevent coagulation of the varnish while the more volatile solvents are driven off by heating the open flask on a steam bath for 30 minutes. Five milliliters of diethanolamine and approximately 0.15 gram of sodium metal, cut into small pieces and wiped dry with absorbent paper, are added. Finally, several glass beads are added and a water-cooled condenser is attached. The sample is boiled gently for 45 minutes. The fungicide is reduced and metallic mercury collects in the bottom of the flask. After cooling, the condenser is washed down with either C.P. acetone, or absolute methyl alcohol, whichever appears to be the better solvent for the products remaining after refluxing.

Table I. Accuracy of Determination

Fungicide Solution	Varnish	Type of Resin	Sample Size	Fungicide Present	Fungicide Determined
Grams	*Grams*		*Grams*	*Gram*	*Gram*
3.0428	48.5016	Alkyd	4.8105	0.01188	0.01145
3.4629	68.7330	Linseed oil	3.0322	0.01706	0.01683
1.1803	36.6071	Phenolic	5.2622	0.01928	0.01870

The condenser is removed and the sample is diluted with acetone or methyl alcohol to approximately 50 ml. It is mixed by swirling and the metallic mercury is allowed to settle into the bottom of the flask. A trap is connected to a source of vacuum and a curved glass jet is connected to the trap with vacuum tubing. With gentle suction, the solvent and resinous portions of the sample are drawn off by holding the point of the jet against the side of the flask, near the bottom. All but a few milliliters are drawn off and the mercury is washed by adding 50-ml. portions of solvent, swirling, allowing the mercury to settle, and drawing off the washings. When the washings appear free of resinous matter, the mercury is washed with distilled water by the same process. At all times, the mercury is covered with the washing liquid. It is then dissolved in a minimum amount of concentrated nitric acid, diluted to approximately 75 ml. with water, and filtered through paper into a 100-ml. volumetric flask. The sample is then diluted to volume with water.

Quantitative Determination of Extracted Mercury. The gravimetric determination of mercury in solution with Reinecke's salt (*1*) is the method best suited to complete the analysis.

An aliquot estimated to contain from 2 to 20 mg. of mercury is drawn off into a 250-ml. beaker or flask. It is diluted to 40 to 50 ml. with water and 0.1 N potassium permanganate solution is added to the first appearance of pink color. The sample is then made approximately 0.5 N with hydrochloric acid (4 or 5 ml. of 6 N hydrochloric acid). It is heated on a steam bath and Reinecke's reagent is added dropwise—1 ml. of reagent per milligram of mercury estimated to be present. Reinecke's reagent (ammonium tetrathiocyanatediamine chromate) is made by dissolving 1.0 gram in 100 ml. of 0.05 N hydrochloric acid and filtering. A fresh solution is used.

The sample is allowed to stand at least 5 minutes and filtered through a fritted-glass crucible containing an additional mat of fine-fibered asbestos, previously dried for 1 hour at 110° C. and weighed. The precipitate is washed with hot water and the crucible is dried for 1 hour at 110° C. and weighed. Additional reagent is added to the filtrate and allowed to stand several hours. If precipitate appears, it is added to the crucible.

Calculation. Weight of precipitate × 0.2396 = weight of mercury in aliquot.

ACCURACY OF METHOD

To determine the accuracy of the method, weighed quantities of fungicide solutions of known composition were added to various types of varnishes so as to approximate the composition of wood sealers. Table I shows some of the results obtained from sealers made from 11.73% solution of phenyl mercuric oleate.

DISCUSSION

The recommended volumes of solutions and solvents specified in the purification process for salicylanilide and pentachlorophenol are based on the partition of a compound soluble in two immiscible liquid media and must not be varied because it would reduce maximum separation and accuracy. Large ether volumes are used in the ether extractions, so that the large particles of precipitated fungicides are dissolved in the first extract to prevent clogging of the separatory funnel. Three such extractions are sufficient.

To develop the procedures for extraction and purification of salicylanilide and pentachlorophenol and to measure accuracy, known quantities (40 to 50 mg.) of the fungicides were dissolved in 40 ml. of benzene in separatory funnels. Weighed quantities of various types of resins were added in such proportions as to approximate the composition of wood sealers. The resins used were glyceryl phthalate alkyds, linseed oil, and modified phenolics as specified in U. S. Army Specification 3-186. The extraction and purification processes were then followed as outlined and the colorimetric procedure was conducted to determine the degree of recovery. Accuracy to 0.1% is obtained.

The graphs for colorimetric determination of both fungicides are straight lines. Under certain conditions, the graph for salicylanilide may curve slightly in the upper portions owing to the difficulty of obtaining a ferric chloride solution of exact composition. Ferric chloride hexahydrate is so hygroscopic that it is advisable to weigh a lump of the salt in a closed weighing dish and calculate the amount of 1.0 N acetic acid that must be added to produce a solution of the concentration recommended. For the same reason, a large quantity should be made, sufficient to complete all samples under test. When a new quantity of ferric chloride solution is made, it is necessary to check it with known amounts of salicylanilide against the existing graph and to regraph the known quantities. This variation is due partially to the fact that the iron salt is always present in excess and imparts some of its own color to solution. If 0.05 molar ferric chloride solution is used in place of the recommended 1% solution, equivalent amounts of salicylic acid could be used in place of salicylanilide for preparing the graph. However, at this concentration of ferric chloride the range of the graph is reduced to such an extent that not more than 2 mg. of salicylanilide in a 100-ml. volume can be determined with accuracy.

These methods of analysis were developed for use only on fungistatic varnishes and are not suitable, for example, for determining pentachlorophenol in treated wood.

LITERATURE CITED

(1) Mellan, Ibert, "Organic Reagents in Inorganic Analysis," p. 454, Philadelphia, Blakiston Co., 1941.
(2) Monsanto Chemical Co., private communication on modification of quantitative colorimetric determination of pentachlorophenol in permasan wood treating formulations.
(3) Rauscher, W. H., Ind. Eng. Chem., Anal. Ed., 10, 331 (1938).
(4) Ruigh, W. L., *Ibid.*, **11**, 250 (1939).
(5) Tafel, J., *Ber.*, **1892**, 412.
(6) U. S. Army Specification **AXS-1247**, "Mildew-Proofing of Cotton Duck Webbing, Belting, and Thread" (July 24, 1945).

Received March 5, 1948.

Method for Identifying Isobutylene

EDWIN D. PARKER AND L. A. GOLDBLATT
Bureau of Agricultural and Industrial Chemistry, United States Department of Agriculture, New Orleans, La.

A method for the identification of isobutylene (2-methylpropene) is based on the catalyzed absorption of isobutylene in phenol and the formation of 4-*tert*-butylphenol. This reaction may also be applied to the identification of 2-methyl-1-butene and 2-methyl-2-butene by formation of 4-*tert*-pentylphenol.

IN WORK on the thermal decomposition products of Diels-Alder adducts of certain terpenes, it became necessary to establish the presence of small amounts of isobutylene (2-methylpropene). Isobutylene has been identified chemically by formation of the nitroso chloride (*3*), the nitrosate (*3*), the nitrosite (*6*), and the dibromide (*2*), but none of these methods is entirely satisfactory.

Isobutylene reacts with phenol in the presence of a catalyst to form the butyl ether which readily rearranges to form 4-*tert*-butylphenol, melting at 99° C. However, this reaction apparently has not been used for identifying isobutylene, although the high melting point and good yields reported (*4*) would seem to make the reaction a promising one. In the present work, this reaction was investigated as a means of identifying isobutylene and was found suitable. The reaction conditions are not critical and the apparatus required is simple. The method was also found suitable for the identification of the pentenes, 2-methyl-1-butene and 2-methyl-2-butene. All three olefins were successfully identified among the decomposition products of various terpene Diels-Alder adducts. Deliberate admixture of isobutylene with equal volumes of ethylene, propylene, or acetylene did not interfere with the formation and isolation of 4-*tert*-butylphenol. Admixture of isobutylene with an equal volume of butadiene decreased the yield somewhat but pure 4-*tert*-butylphenol was isolated without difficulty.

APPARATUS AND EXPERIMENTAL PROCEDURE

The reaction is carried out in a test tube (20 ml.) fitted with a side arm and one-hole rubber stopper carrying a glass tube drawn to a point and extending to within 1 or 2 mm. of the bottom (Figure 1). The tube is heated by a suitable bath. The isobutylene is displaced from the storage container by water added from a separatory funnel and may be dried by passage through a calcium chloride drying tube, if desired, before being passed into the reaction tube. Unabsorbed gas is collected over water in a graduate.

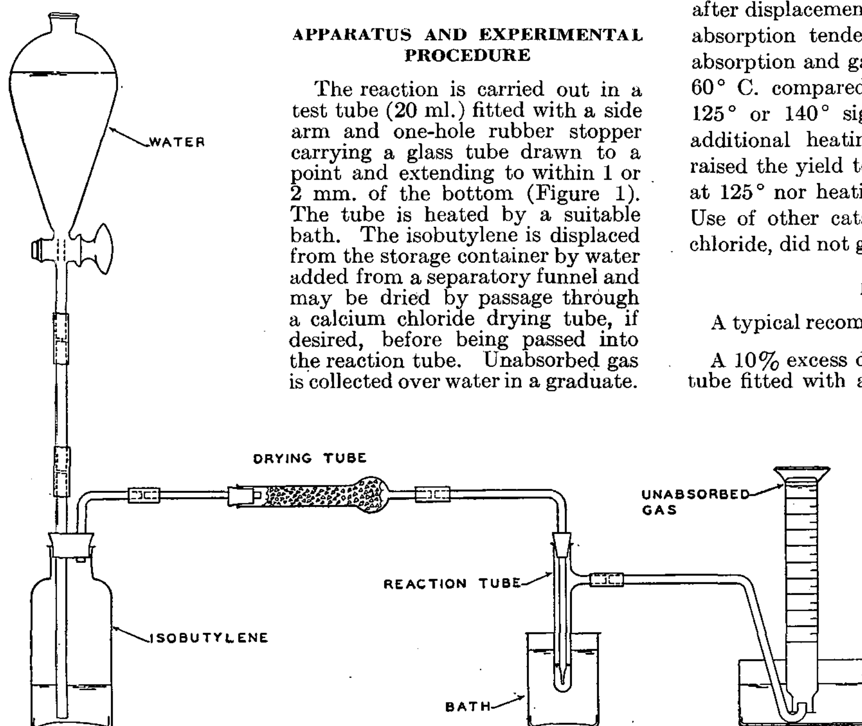


Figure 1. Apparatus for Absorption of Isobutylene

The isobutylene was prepared by refluxing 25 ml. of *tert*-butyl alcohol with 8 grams of hydrated oxalic acid (*1*). The gas was collected in 500-ml. storage bottles by displacement of water and stored until use. Three procedures were found to be satisfactory for absorbing the olefin in the phenol-catalyst mixture. In the first method, the gas is bubbled through the mixture by displacement of the gas in the storage bottle; water is added from a separatory funnel at such a rate as to result in substantially complete absorption, and unabsorbed gas is collected and measured. In the second, which can be used only if the isobutylene is fairly pure, the gas is passed into the closed reaction tube under a head of about 75 cm. (30 inches) of water after most of the air has first been removed by evacuation. In the third method, the side arm of the reaction tube is kept open until about 20 ml. of gas have passed through, the side arm is then closed off by means of a pinch clamp, and the isobutylene is absorbed as in method 2. If the absorption slows down, owing to an accumulation of unreacted gas, the side arm can again be opened to purge the tube of such gas.

A number of trials were made to observe the effect of variation in the quantity of phenol and the quantity and concentration of the catalyst; drying of the isobutylene; temperature of the reaction mixture during absorption; and additional heating. Additional excess phenol tended to increase the rate of absorption but did not increase the yield significantly. The presence of small amounts of moisture did not significantly affect the yield, and use of 96% sulfuric acid and isobutylene dried by passage over calcium chloride gave substantially the same yield as 75% sulfuric acid used with isobutylene which was not dried with calcium chloride after displacement by water. An increase in temperature during absorption tended to decrease the time required to complete absorption and gave somewhat higher yields (10% total yield at 60° C. compared to 15% at 80°); but additional heating at 125° or 140° significantly increased yield. Thus, 1 hour of additional heating at 125° after absorption was completed raised the yield to 75%. Neither heating for more than 1 hour at 125° nor heating for 1 hour at 140° further increased yield. Use of other catalysts, such as oxalic-boric acid or aluminum chloride, did not give as good results as did sulfuric acid.

RECOMMENDED PROCEDURE

A typical recommended procedure is given below:

A 10% excess of phenol (2.17 grams) is placed in a 20-ml. test tube fitted with a side arm and 0.1 ml. of concentrated sulfuric acid is added. The test tube is then shaken by hand and placed in an oil bath maintained at 90° C. The side arm is connected by a short length of glass tubing to an inverted graduate filled with water to measure the volume of any unabsorbed gas. The mouth of the test tube is fitted with a one-hole rubber stopper carrying a glass gas inlet tube drawn to a point and extended to within 1 or 2 mm. of the bottom. A bottle containing 500 ml. of isobutylene is fitted with a two-hole rubber stopper carrying a 500-ml. separatory funnel and an outlet tube, and the outlet tube is connected to the gas inlet tube of the reactor. The isobutylene is displaced by adding water

from the separatory funnel at a rate sufficient to cause bubbling in the absorption tube but substantially no escape of unabsorbed isobutylene into the inverted graduate. This requires 20 to 30 minutes and about 20 ml. of unabsorbed gas (chiefly air displaced from the system) are collected in the graduate. The reaction tube is then disconnected, the temperature of the bath is raised to 125°, and heating is continued for an additional hour. The hot reaction mixture is then poured into 40 ml. of water and shaken vigorously by hand to remove the acid and any unreacted phenol. Crystallization occurs soon after shaking is begun. The colorless needles so obtained are filtered off by suction, washed with 5 to 10 ml. of water, and dried to constant weight in a vacuum desiccator.

Using this procedure, 2.45 grams (76% yield) of product melting at 89.6° to 97.2° were obtained. An additional 0.1 gram of product was obtained by rinsing the reaction tube and extracting the aqueous filtrate with petroleum ether. Recrystallization by solution in aqueous alkali and acidification with hydrochloric acid raised the melting point to 98–100° and this recrystallized product did not depress the melting point of an authentic sample of 4-*tert*-butylphenol.

EXTENSION TO PENTENES

The reaction may be extended to the pentenes, 2-methyl-1-butene and 2-methyl-2-butene.

Thus, 1.56 grams of 2-methyl-1-butene were distilled into an absorption tube containing 2.0 grams of phenol and 0.2 gram of 75% sulfuric acid. The mixture was heated for 1 hour at 125° C. and poured into 20 ml. of water. There were thus obtained 2.60 grams of nearly colorless needles of 4-*tert*-pentylphenol, melting point 82° to 90° C., which after two crystallizations from petroleum ether melted at 94° to 96° C. and did not depress the melting point of an authentic sample of 4-*tert*-pentylphenol. Correspondingly, 1.7 grams of 2-methyl-2-butene reacted with 2.3 grams of phenol containing 0.2 gram of 75% sulfuric acid and gave 2.74 grams of crude 4-*tert*-pentylphenol, melting at 83° to 91°. After two crystallizations from petroleum ether, the purified product melted at 94° to 96° C.

Although these two pentenes give the same *tert*-pentylphenol, they may be readily differentiated from one another by their physical constants. Thus, 2-methyl-1-butene boils at 31.0° C. and has n_D^{20} 1.3777 (*5*), whereas 2-methyl-2-butene boils at 38.4° C. and has n_D^{20} 1.3878 (*5*).

ACKNOWLEDGMENT

The authors are indebted to Clora B. Heath for checking the method and for testing its applicability to the synthetic mixtures.

LITERATURE CITED

(1) Davis, H. S., *J. Am. Chem. Soc.*, **50**, 2778 (1928).
(2) Hurd, C. D., and Spence, L. U., *Ibid.*, **51**, 3568 (1929).
(3) Ipatieff, W. N., and Solonina, A. A., *J. Russ. Phys. Chem. Soc.*, 33, 496 (1901); *Brit. Abstracts*, **82**, I, 1 (1902).
(4) Natelson, S., *J. Am. Chem. Soc.*, **56**, 1585 (1934).
(5) Sherrill, M. L., and Walter, G. F., *Ibid.*, **58**, 744 (1936).
(6) Sidorenko, K. W., *J. Russ. Phys. Chem. Soc.*, **38**, 955 (1906); *Brit. Abstracts*, **92**, I, 270 (1907).

Received September 10, 1948.

Chemical Estimation of Tetraethyl Pyrophosphate

A. R. WREATH and E. J. ZICKEFOOSE[1], *Victor Chemical Works, Chicago Heights, Ill.*

The biologically active tetraethyl pyrophosphate content of the technical grade product and of the so-called "hexaethyl tetraphosphate" can be determined by a method which involves the preferential hydrolysis of the accompanying polyphosphoric acid esters in a 25% aqueous acetone solution at room temperature and the absorption of these products on an Amberlite IR-4B resin, followed by the alkaline hydrolysis of the column effluent containing the tetraethyl pyrophosphate by excess standard base and back-titration with standard acid.

THE chemical estimation of tetraethyl pyrophosphate presented here was developed during an investigation of so-called "hexaethyl tetraphosphate" made by either the Schrader (*4*) or Woodstock (*6*) process. Hall and Jacobsen (*3*) have reviewed the properties and preparation of hexaethyl tetraphosphate and of tetraethyl pyrophosphate and have concluded that the latter is the biologically active constituent. Toy has recently presented a new method for the preparation of several tetraalkyl pyrophosphates including tetraethyl pyrophosphate (*5*).

The only method published to date (*2*) for the chemical estimation of tetraethyl pyrophosphate involves initial extraction of the active ingredient from an aqueous solution by chloroform. The tetraethyl pyrophosphate in the extract is subsequently hydrolyzed by heating to 50° C. overnight to form diethyl orthophosphate, which is then determined by titration with standard alkali.

[After this manuscript was submitted for publication a paper on determination of tetraethyl pyrophosphate in mixtures of ethyl phosphate esters was published (*1*). Tetraethyl pyrophosphate is removed from mixtures of ethyl phosphate esters by a benzene extraction after selective hydrolysis of the higher polyphosphate esters. It is subsequently determined by hydrolysis with alkali.]

[1] Present address, A. S. Aloe Company, St. Louis, Mo.

In the new and improved procedure for estimation of tetraethyl pyrophosphate in the technical grade product or in the hexaethyl tetraphosphate the sample is first dissolved in 25% aqueous acetone. The ethyl polyphosphates are hydrolyzed rapidly to acidic products which are removed by an acid-absorbing resin, Amberlite IR-4B. Under the same conditions tetraethyl pyrophosphate is not appreciably hydrolyzed and remains in solution. Alkaline hydrolysis of the latter to the diethyl orthophosphate is effected subsequently by an excess of standard base and this excess is determined by titration with standard acid.

MATERIALS AND APPARATUS

Acetone, 25% solution in water. Five hundred milliliters of acetone, commercial grade, are mixed with 1500 ml. of water and cooled to 25° C.

Sodium hydroxide, 0.1 *N*.

Hydrochloric acid, 0.1 *N*.

Amberlite IR-4B resin, analytical grade, Resinous Products and Chemical Company, Philadelphia, Pa., obtained from Fisher Scientific Co., St. Louis, Mo.

Beckman pH meter, Model G, or any other good glass electrode apparatus.

Methyl red indicator, 0.1% aqueous solution.

Preparation and Use of Resin Column. Thirty grams of Amberlite resin, screened to remove all particles under 30-mesh, are slurried with water and poured into a 100-ml. buret contain-

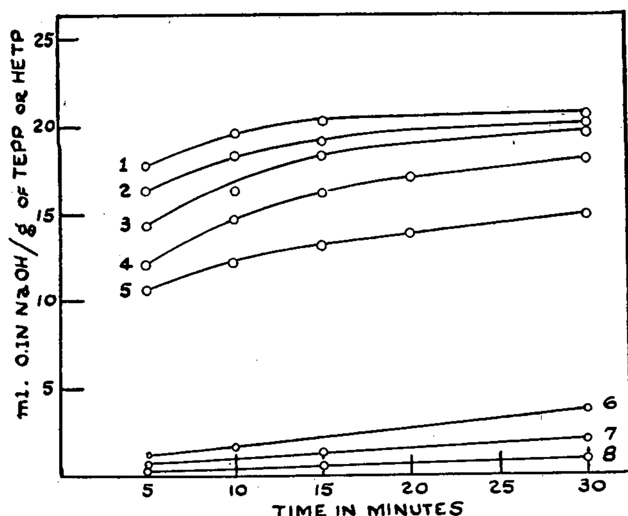


Figure 1. Hydrolysis of Tetraethyl Pyrophosphate and Hexaethyl Tetraphosphate in Acetone-Water Solutions at 25° C.

Hexaethyl tetraphosphate in water (1), 20% acetone (2), 25% acetone (3), 33% acetone (4), and 50% acetone (5), tetraethyl pyrophosphate in water (6), 20% acetone (7), and 25% acetone (8).

ing a glass wool plug at the bottom. The resin column is washed with 150 ml. of 3% aqueous sodium hydroxide solution at a flow rate of approximately 5 ml. per minute and rinsed with water at a flow rate of approximately 25 ml. per minute until the effluent is colorless to phenolphthalein. The water is displaced with 25% aqueous acetone solution and the column is ready for use. The column should not be allowed to run dry or channeling may result. The liquid level is maintained at all times approximately 2.5 cm. (1 inch) above the resin bed.

It is advisable to expand the resin bed after each determination before the introduction of a new sample, because the resin tends to pack in the column as it absorbs acidic material. This renovation is accomplished simply by back-washing with 25% aqueous acetone which is introduced at the base of the column until the liquid level reaches the top of the buret. After the absorbent settles the solution is drained off to the customary height of 2.5 cm. above the resin bed. The column is now ready to receive the next sample.

After eight to ten samples have been passed through the column it is necessary to remove the absorbed acidic material. Regeneration of the resin is accomplished by repeating the initial treatment with sodium hydroxide, water, and acetone as described above.

PROCEDURE

Place the material to be analyzed in a glass-stoppered weighing bottle or weight buret and transfer a 2.5-gram sample (1.0 gram if the tetraethyl pyrophosphate content is over 50%), weighed to the nearest milligram by difference, to 50 ml. of 25% aqueous acetone contained in a 125-ml. separatory funnel. Mix the sample with the acetone solution by swirling and allow it to stand 15 minutes at 25° ± 2° C. The use of a glass weighing bottle having a ground-in dropper is recommended for the weighing operation in order to exclude atmospheric moisture.

Permit the solution of the sample to run through the column by gravity at a rate of approximately 25 ml. per minute. Wash the column and funnel with three 50-ml. portions of 25% aqueous acetone, added successively, and maintain the 2.5-cm. liquid level above the resin at all times.

Catch the combined effluent in a 250-ml. volumetric flask, dilute to volume with water, mix, and transfer a 100-ml. aliquot to a 250-ml. beaker. Add 50 ml. of 0.1 N sodium hydroxide, stir well, and allow to stand at room temperature for 30 minutes; then back-titrate with 0.1 N hydrochloric acid to a pH of 6.0 using the glass electrode assembly. Methyl red may be used as a suitable indicator if a pH meter is not available. Calculate the percentage of tetraethyl pyrophosphate by use of the following formula:

$$\frac{\text{Net ml. of 0.1 } N \text{ NaOH} \times 0.0145 \times 1.016 \times 2.5 \times 100}{\text{weight of sample}} = \% \text{ tetraethyl pyrophosphate}$$

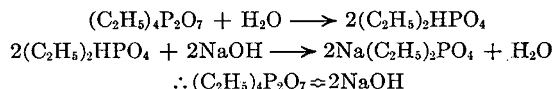
or

$$\frac{\text{Net ml. of 0.1 } N \text{ NaOH} \times 3.67}{\text{weight of sample}} = \% \text{ tetraethyl pyrophosphate}$$

A single determination may be completed in 60 to 65 minutes. Samples can be so staggered that a series of ten determinations may be completed in 3.25 hours.

DISCUSSION

The method presented here makes use of the fact that ethyl acid phosphates and ethyl acid polyphosphates are absorbed by a basic resin. Ethyl polyphosphates are first allowed to hydrolyze to acidic esters in a 25% aqueous acetone solution and the acidic compounds so formed are then removed by the acid-absorbing resin, Amberlite IR-4B. Tetraethyl pyrophosphate is not appreciably hydrolyzed under the recommended conditions. It is, however, subsequently hydrolyzed in the presence of an excess of standard alkali to the diethyl orthophosphate; the excess alkali is determined with standard acid to a pH of 6.0.



$$(C_2H_5)_4P_2O_7 + H_2O \longrightarrow 2(C_2H_5)_2HPO_4$$

$$2(C_2H_5)_2HPO_4 + 2NaOH \longrightarrow 2Na(C_2H_5)_2PO_4 + H_2O$$

$$\therefore (C_2H_5)_4P_2O_7 \approx 2NaOH$$

A previous investigation in this laboratory had demonstrated that acetone is one of a number of solvents with which tetraethyl pyrophosphate may be conveniently diluted—i.e., only slight reaction will occur over a considerable period of time as evidenced by the development of an acid reaction. It is furthermore not necessary to remove the solvent later in the procedure.

Solutions of so-called hexaethyl tetraphosphate were prepared using water and aqueous solutions of acetone containing 20, 25, 33, and 50% of the latter. The acidity of each was determined after various time intervals. Data depicted graphically in Figure 1 indicate that hydrolysis in water solution increases markedly up to 15 minutes, after which the change is much slower. Consequently, the 15-minute time period was chosen as the required time for hydrolysis of the polyphosphate esters. Solutions of tetraethyl pyrophosphate were also prepared using water and aqueous solutions of acetone containing 20 and 25% of acetone. The increase in acidity of each of these as a function of time was likewise determined. On the basis of these data the 25% acetone in water solution was chosen for the analytical determination of tetraethyl pyrophosphate as permitting hydrolysis of the polyphosphates present, while minimizing that of the tetraethyl pyrophosphate. Curve 8 shows that pure tetraethyl pyrophosphate hydrolyzes to the extent of only 0.7% in 15 minutes.

If a sample of pure tetraethyl pyrophosphate is treated according to the above method, a loss of approximately 1.6% is noted, presumably due to adsorption by the resin or hydrolysis, or both (Table I). This error is, however, fairly constant and is the basis for the factor 1.016 used in the calculation.

Up to as many as eight determinations may be made using the same resin column before regeneration as indicated by successive

Table I. Determination of Tetraethyl Pyrophosphate Using Amberlite IR-4B Resin Column

	% Tetraethyl Pyrophosphate		
	Pure TEPP	Commercial TEPP	
Determination	(100%)	Series I	Series II
1	98.5	40.5	35.2
2	98.6	40.6	35.3
3	98.5	40.3	35.6
4	98.5	40.9	35.5
5	98.5	40.9	35.4
6	98.4	40.6	35.5
7	98.0	40.9	35.3
8	98.2	40.5	35.4
9	...	...	36.1[a]
10	...	...	36.8[a]
Average	98.4	40.7	35.4
Average deviation	± 0.2	± 0.2	± 0.1
Precision	± 0.6	± 0.6	± 0.3

[a] Not included in average.

Table II. Determination of Tetraethyl Pyrophosphate

Sample	Bioassay %	Chemical Assay %
1	40.0	39.0
2	40.0	37.0
3	9.0	11.0
4	35.0	35.0
5	40.0	41.0
6	38.0	37.0

runs, the results for which are given in Table I. A second series of successive determinations, using a product of lower pyrophosphate content, revealed the presence of unabsorbed acid in the column effluent after it had been used for eight samples. The precision as calculated from three times the average deviation is ±0.5%.

A bioassay method and the above chemical method was compared on six samples of hexaethyl tetraphosphate and the technical grade product of tetraethyl pyrophosphate. The data presented in Table II show good agreement between the two methods. Using the bioassay the MLD/50 for pure tetraethyl pyrophosphate was found to be 0.80 mg. per kg., when male white mice were used.

ACKNOWLEDGMENT

The authors wish to thank L. F. Audrieth and W. H. Woodstock for their helpful suggestions, W. B. Coleman for conducting the bioassays of the samples employed in this study, and A. D. F. Toy, who prepared and furnished samples of pure tetraethyl pyrophosphate.

LITERATURE CITED

(1) Dvornikoff, M. N., and Morrill, H. L., ANAL. CHEM., 20, 935 (1948).
(2) Hall, S. A., and Jacobsen, M., *Agr. Chem.*, 3, 30 (1948).
(3) Hall, S. A., and Jacobsen, M., *Ind. Eng. Chem.*, 40, 694 (1948).
(4) Schrader, G. (to I. G. Farbenindustrie), Ger. Patent 720,577 (1942) vested in Alien Property Custodian; U. S. Patent 2,336,302 (1943).
(5) Toy, A. D. F., *J. Am. Chem. Soc.*, 70, 3882 (1948).
(6) Woodstock, W. H., U. S. Patent 7,402,703 (1946).

RECEIVED October 18, 1948.

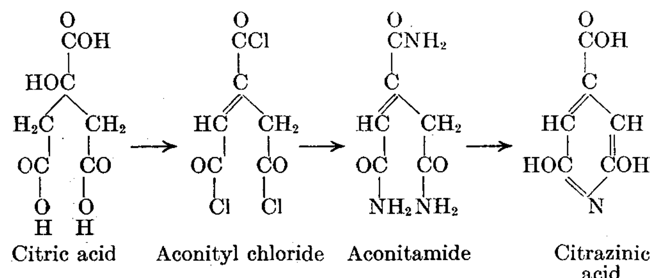
Fluorometric Method for Determination of Citric Acid

ELMER LEININGER AND SIDNEY KATZ, *Michigan State College, East Lansing, Mich.*

A quantitative fluorometric method is described for the determination of citric acid based upon its transformation into the highly fluorescent compound, ammonium citrazinate. The effect of changes in various operating conditions at each step in the procedure is discussed. The method is applicable to determinations of 10 to 75 micrograms of anhydrous citric acid. One hundred micrograms of tartaric and malic acids per sample do not interfere. Sulfate ion and hydroscopic compounds interfere. Application to determinations of citric acid in citrus juices is described.

A FLUOROMETRIC method for the determination of citric acid and citrate ion is based upon the reactions employed by Feigl (*2*) in a qualitative test for citric acid.

When anhydrous citric acid and anhydrous sodium carbonate are refluxed with thionyl chloride, aconityl chloride is formed. After the excess thionyl chloride is volatilized, aconitamide is formed by exposure of the aconityl chloride to ammonia gas at room temperature. Citrazinic acid is formed by treatment of the aconitamide residue with 76% sulfuric acid at 165° C. Upon neutralization with ammonium hydroxide the solution of ammonium citrazinate exhibits an intense blue fluorescence in ultraviolet light. The solution is diluted to a definite volume and the fluorescence intensity is determined.



REAGENTS

Thionyl Chloride, Eastman No. 246. It must be protected from the moisture of the air at all times. The practical grade causes lower fluorescence intensity and is not satisfactory.

Sodium Carbonate, anhydrous, C.P.

Ammonia, from a compressed gas cylinder.

Sulfuric Acid, 76 to 77%. Concentrated sulfuric acid (73 ml.) is added to 35 ml. of water with cooling. The specific gravity (20°/4° C.) of the solution must be within the range of 1.681 to 1.692.

Sodium Salicylate Solution. A standard solution is prepared by dissolving 2.000 grams of reagent grade sodium salicylate in water and diluting to 1000 ml. It may be preserved from mold growth with a few drops of toluene.

Citric Acid Solution. A standard stock solution is prepared by dissolving 7.000 grams of C.P. citric acid monohydrate in water and diluting to 1000 ml. The concentration is checked by titration with standard base. The standard stock solution may be preserved with a few drops of toluene. Two tenfold dilutions of this standard stock solution give a working standard containing 64 micrograms of anhydrous citric acid per ml. The working standard may be conveniently preserved by making it 0.3 N with respect to hydrochloric acid during the dilution.

Lead Acetate Solution. Normal lead acetate (75 grams) is dissolved in water and 0.5 ml. of glacial acetic acid is added. The solution is diluted to 250 ml.

APPARATUS

Fluorescence intensities are measured with a Lumetron fluorescence meter Model 402EF with 25-ml. cells. The primary filter permits maximum transmittance in the spectral region of 365 millimicrons. The secondary filters consist of a combination of a yellow filter, furnished by the Photovolt Corporation for use in vitamin B_1 determinations, which does not transmit emission below 400 millimicrons and a Corning lantern blue filter No. 5543. This combination of secondary filters permits maximum transmittance corresponding to the region of greatest fluorescence

intensity of the ammonium citrazinate solution—that is, in the spectral region of 430 to 450 millimicrons.

The specially constructed apparatus is illustrated in Figure 1. For the thionyl chloride reaction a 25-ml. Pyrex Erlenmeyer flask, *A*, is fitted to a Pyrex tube, *B*, 15 mm. in diameter and 260 mm. in length, by means of a ground joint. The Pyrex tube serves as a reflux condenser and a drying tube. A constriction in the tube 160 mm. from the ground joint retains a plug of fine glass wool, 130 mm. of Dehydrite, and a covering plug of glass wool. When not in use the tube is plugged with clean cork stoppers. The ground joint is not sufficiently smooth as purchased and is polished with fine grinding compound, so that the joint will not leak under vacuum. For the volatilization and removal of the excess thionyl chloride a three-way stopcock, *C*, is connected to the upper end of the drying tube by *C*-1, to the vacuum pump by *C*-2, and to a capillary tube by *C*-3.

The transformation of aconityl chloride to aconitamide is carried out in an ammonia chamber, *D*, which is an L-shaped box of the following dimensions: horizontal section 5 cm. wide, 8 cm. high, and 30 cm. long; vertical section 5 cm. in both horizontal directions and 15 cm. high. The horizontal section accommodates six flasks at a time. Ammonia gas from the compressed gas cylinder enters through a tube on the right-hand end of *D*.

After the flask with the reflux tube attached has been placed in the chamber the tube is loosened with the aid of a wooden block, *E*, and removed. The block is 150 mm. in length, fits loosely within the vertical section of the ammonia chamber, and has a hole 20 mm. in diameter bored through it lengthwise. It fits over the reflux tube and rests on the lip of the flask. The reflux tube, being considerably longer than the block, is held by the top and the assembly is raised a few mm. from the floor of *D* while the block is tapped gently against the lip of the flask to make it drop free of the tube. A cover, *F*, is placed over the opening on top of the ammonia chamber in order to retain a high ammonia concentration.

FLUORESCENCE METER SETTING AND CALIBRATION

The fluorometer is set to give a reading of 100 with standard sodium salicylate solution (2.000 grams per 1000 ml.) and a reading of 0 with distilled water. The fluorescence intensity of sodium salicylate at this concentration varies only slightly over the range of 20° to 30° C. and therefore temperature control is unnecessary.

A calibration curve, which is very nearly linear, is prepared from instrument readings obtained from at least six well distributed points by carrying amounts of anhydrous citric acid ranging from 10 to 75 micrograms through the procedure described below. Proper volumes of the working standard (containing 64 micrograms of anhydrous citric acid per ml.) are measured out with accurately calibrated pipets. If more convenient, a series of dilutions of the citric acid may be prepared so that 1-ml. samples are used in all cases.

DETERMINATION OF CITRIC ACID IN SOLUTIONS FREE FROM INTERFERENCES

Analytical Procedure. A sample solution containing 10 to 75 micrograms of citric acid, preferably 1 ml. or less, is accurately measured into the 25-ml. reaction flask *A*. The flask is heated for 2 hours in a vacuum oven at 65° to 70° C. in order to obtain an anhydrous residue.

Approximately 15 mg. of anhydrous sodium carbonate and 2 ml. of thionyl chloride are added to the sample. The combination reflux condenser and drying tube, *B*, is connected to the reaction flask and the flask is heated in an oil bath maintained at 95° to 100° C.

After refluxing for 20 minutes, the reaction flask with the tube attached is removed from the oil bath and the excess thionyl chloride is volatilized and evacuated through tube *B* and the three-way stopcock, *C*. During this operation the reaction flask is given a swirling motion to prevent spattering of the contents. Gentle heat may be applied with the palm of the hand to hasten the volatilization. The reaction flask is evacuated for 4 minutes after the residue appears dry and then air is allowed to flow into the flask by means of capillary *C*-3. The evacuation and flooding with dry air are repeated three times, using 1-minute periods of evacuation.

The flask with the condenser attached is introduced into the ammonia chamber (under a hood). A slow current of ammonia is passed into ammonia chamber *D*. The tube is disengaged from the reaction flask by means of wooden block *E*, and lifted from the chamber. The cover is then replaced over the chamber opening. After 10 minutes the flask is removed from the ammonia chamber, approximately 2 ml. of 76% sulfuric acid are added, and the flask is tipped and rotated to bring the sulfuric acid in contact with the entire residue.

The flask is then heated for 6 ± 0.5 minutes at 162° to 168° C. in an oil bath. At this point the solution should be colorless to straw colored. After removal from the oil bath, the solution is diluted with 5 ml. of water and transferred quantitatively to a 100-ml. glass-stoppered volumetric flask, using 25 ml. of wash water. The solution is made alkaline to litmus with dilute ammonium hydroxide (6 *N*), made up to 100 ml., mixed thoroughly, and brought to 24° ± 0.5° C., and the fluorescence intensity is determined with the fluorometer.

Discussion. The reaction between citric acid and thionyl chloride must take place in the complete absence of water in ordre to obtain reproducible results. The sample is dried effectively in a minimum of time without decomposition by use of a vacuum oven at 70° C.

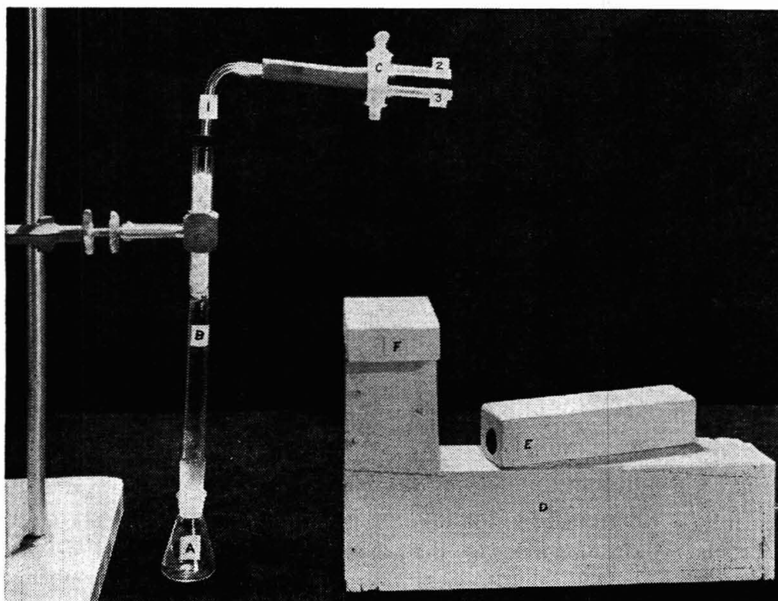


Figure 1. Apparatus for Determining Citric Acid

The direct action of thionyl chloride on citric acid produces much tarry material and the final citrazinate solution is only weakly fluorescent. In the presence of anhydrous sodium carbonate darkening does not occur during this reaction and the final fluorescence intensity is increased approximately tenfold. From 10 to 50 mg. of sodium carbonate give maximum fluorescence. The thionyl chloride reaction reaches a maximum after 15 minutes' refluxing.

Exposure to water during or after refluxing lowers the fluorescence intensity and therefore the reaction vessel is protected with a drying tube until it is placed in the atmosphere of gaseous ammonia. The only satisfactory drying agent found was Dehydrite. A water pump is satisfactory for the removal of excess thionyl chloride by evacuation.

Ammonia gas rather than ammonium hydroxide is used to change the aconityl chloride to aconitamide because it facilitates the control of conditions in the reaction that follows. The time of exposure to ammonia is not critical. The reaction is apparently complete in less than 1 minute in some cases; long exposure does no harm.

Table I. Variation of Fluorescence Intensity with Sulfuric Acid Concentration for Constant Amounts of Citric Acid

Concentration of Sulfuric Acid, %	Fluorometer Reading
68.9	67.9
72.7	83.4
74.8	85.5
76.9	85.3
78.5	85.7
80.0	76.5
81.5	68.2

Table II. Variation of Fluorescence Intensity with Temperature of Oil Bath for Constant Amounts of Citric Acid

Temperature of Oil Bath, ° C.	Fluorometer Reading	Temperature of Oil Bath, ° C.	Fluorometer Reading
100	12.8	160	82.1
130	52.5	165	83.9
145	72.5	170	83.8
150	79.4	175	80.8
155	83.8	180	80.0

Table III. Reproducibility of Fluorometric Method

Number of samples, N	29
Citric acid present in each sample	60.0 micrograms
Average fluorometric reading, $\bar{x}$	77.0 units
Average deviation of fluorometric readings	1.2 units
Standard deviation of fluorometric readings	1.6 units

Standard deviation $= \left[\Sigma\frac{(x - \bar{x})^2}{N - 1}\right]^{1/2}$

In the transformation of aconitamide to citrazinic acid the concentration of sulfuric acid and the temperature of the oil bath should be controlled rather closely. Table I illustrates the variations of fluorescence intensity as the concentration of sulfuric acid is varied and Table II illustrates the variations of fluorescence intensity as the temperature of the oil bath is varied. When 76 to 77% sulfuric acid and a temperature of 162° to 168° C. were used for 4 to 8 minutes, consistently good results were obtained.

The final solution should be alkaline to litmus, but an excess of ammonium hydroxide does not change the fluorescence intensity. The temperature of the solution has a marked effect on the fluorescence intensity; an increase of 5° C. decreases the intensity approximately 10%.

Table III demonstrates the reproducibility of fluorescence intensity readings for 29 of 31 samples taken. Each sample consisted of 60.0 micrograms of anhydrous citric acid.

Compounds that decompose to discolor the solutions resulting from this series of reactions interfere. Tartaric and malic acids fall into this classification. However, if tartaric and malic acids are present in amounts less than 100 micrograms per sample taken, the interference is slight; 500 micrograms per sample cause approximately 5% decrease in measured fluorescence intensity. Sulfate ion in very small amounts interferes, causing a darkening in the thionyl chloride reaction and a loss of fluorescence. Hygroscopic compounds interfere, owing to the presence of water of hydration after the drying period.

The procedure requires 3 hours, of which 2 hours is the drying period.

CITRUS JUICES

The method of the Association of Official Agricultural Chemists (*1*) for the separation of citric acid from citrus fruit juices has been modified in that hydrochloric acid is substituted for sulfuric acid and smaller volumes are used. In general, the protein matter is coagulated and separated by filtration along with solids from the juices. The citrate is precipitated as the lead salt, washed, and put back into solution as citric acid by precipitating the lead as its sulfide. The elapsed time required for a complete determination by the fluorometric method is 4 hours compared to nearly 24 hours for the standard A.O.A.C. pentabromoacetone gravimetric procedure.

Table IV. Errors Incurred in Separation of Pure Citric Acid

Separation	Citric Acid Present Mg.	Citric Acid Found Mg.	Error %
A	63.3	61.9	
		60.9	
		62.9	
		61.0	
		Av. 61.7	2.4
B	63.3	61.7	
		60.7	
		62.0	
		59.7	
		Av 61.0	3.5
C	63.3	62.5	
		62.9	
		62.0	
		63.4	
		Av. 62.7	0.9
D	63.3	62.7	
		62.5	
		62.3	
		59.9	
		Av. 61.9	2.1

Procedure for Separation of Citric Acid from Citrus Juices. A weight of sample containing 40 to 75 mg. of citric acid is selected. The volume is brought to 15 ml. with water or by evaporation. After 1.5 ml. of 1 N hydrochloric acid are added, the solution is heated to 50° C., and transferred quantitatively into a 100-ml. volumetric flask. The flask is cooled and brought to volume with 95% ethyl alcohol and the solution is well mixed. The solution is filtered through a folded filter paper covered with a watch glass. Fifty milliliters of filtrate are pipetted into a 100-ml. centrifuge tube, 2.5 to 3.0 ml. of lead acetate solution are added and the solution is thoroughly mixed, and centrifuged at 1000 r.p.m. for 15 minutes.

The supernatant liquid is tested with lead acetate solution for complete precipitation. If additional precipitate appears, more lead acetate solution is added and the centrifuging is repeated. The liquid is carefully decanted and discarded, leaving the precipitate in the centrifuge tube. The precipitate is washed by adding 50 ml. of 80% ethyl alcohol in small portions, using a stirring rod to ensure a homogeneous mixture. The stirring rod is rinsed with the last portion of the 80% alcohol. The solution is again centrifuged and decanted as before. The precipitate is suspended by adding 50 ml. of water in small portions while using the stirring rod for thorough mixing. The solution is saturated with hydrogen sulfide and transferred quantitatively to a 100-ml. volumetric flask. It is brought to volume with water; the contents are well mixed and filtered through a folded filter paper. The filtrate is diluted 1 part to 4 parts of water. One-milliliter portions are taken for fluorometric analysis. The citric acid in the original sample is found by multiplying the amount found in the 1-ml. portion by 1000.

Table V. Citric Acid Determinations by Fluorometric and A.O.A.C. Methods for Citrus Juices

	Citric Acid by A.O.A.C. Method, %	Citric Acid by Fluorometric Method, %
Canned grapefruit juice	1.48	1.54
	1.48	1.42
	1.47	1.49
	1.43	1.43
Canned orange juice	0.845	0.858
	0.841	0.820
	0.835	0.863
		0.827

Discussion. The error incurred by passing known amounts of citric acid through this separation and the fluorometric determination is illustrated in Table IV. Four samples, each containing 63.3 mg. of anhydrous citric acid, were used. In each of the four separations four 1-ml. aliquot portions were analyzed. The er-

rors incurred in these separations and determinations are within the same range as those found in the determination alone.

Values obtained by this method for some citrus juices are compared with values obtained by the use of the pentabromoacetone method of the Association of Official Agricultural Chemists (1) in Table V. Each fluorometric result given is an average of four aliquots.

LITERATURE CITED

(1) Assoc. Offic. Agr. Chemists, "Official and Tentative Methods of Analysis," 6th ed., pp. 391–4, 1945.
(2) Feigl, F., Anger, V., and Frehden, O., *Mikrochemie*, 17, 35 (1935).

RECEIVED September 20, 1948. Abstracted from a portion of a thesis submitted by Sidney Katz in partial fulfillment of the requirements for the Ph.D. degree.

Diphenylamine Test for Nitrates in Mixtures of Cellulose Esters

A. G. ROBERTS, *National Bureau of Standards, Washington, D. C.*

Diphenylamine in sulfuric acid is a sensitive reagent for indicating nitrates by producing a blue coloration. Earlier investigations were limited to nitrates in very dilute aqueous solution. Uncertainty exists concerning its use in the higher nitrate range and upon solid materials. An investigation was made of the speed and strength of color development when solutions containing diphenylamine and water were brought into contact with films cast from mixtures of cellulose esters covering a wide range of nitrate compositions. The color development time is a minimum in the region of 2 to 6% nitrogen and increases at higher and lower concentrations. Water content is important; diphenylamine concentration exerts a minor influence. A suitable reagent for general use over a wide nitrate range contains 0.1 gram of diphenylamine, 100 ml. of concentrated sulfuric acid, and 30 ml. of water. Quantitative estimates are possible when films of known nitrate composition are used for comparison.

DIPHENYLAMINE in sulfuric acid has long been known (*6*) as a sensitive reagent for indicating the presence of nitrates by the production of a blue coloration. Because the blue color results from the oxidation of the diphenylamine, strong oxidizing agents such as nitrite, chromate, ferric salts, etc., interfere (*5*).

The work of earlier investigators (*3, 7, 10, 11*) indicated that the sensitivity of the test depends upon the concentrations of diphenylamine and sulfuric acid. They employed reagents containing from 0.008 to 0.67 gram of diphenylamine and from 0 to 150 ml. of water per 100 ml. of concentrated sulfuric acid. These investigations were limited to the detection of very small amounts of nitrate in highly dilute aqueous solution, of the order of 1 mg. of nitrate nitrogen per liter (0.0001%). No investigation appears to have been made of the broad higher nitrate range (from 0.001 to 12.0% nitrogen) or of solid materials such as mixtures of cellulose esters, nor has the time for production of color been emphasized as an effective quantitative criterion. Standard reference works such as the "Modern Plastics Encyclopedia" (*8*), the "Handbook of Chemistry and Physics" (*4*), and others (*2, 13*) are at variance with regard to the indicator reagent compositions recommended.

It was the purpose of this investigation to determine the optimum concentrations of diphenylamine and sulfuric acid in the diphenylamine indicator solution for general use in the detection and estimation of nitrates in cellulosic films having a wide range of nitrate nitrogen compositions.

EXPERIMENTAL

A series of diphenylamine indicator solutions was prepared covering the range of 0.01 to 1.0 gram of diphenylamine per 100 ml. of concentrated (96%) sulfuric acid, and a range of 0 to 150 ml. of water per 100 ml. of concentrated sulfuric acid. These were evaluated with films of various nitrate contents, ranging from 12% nitrogen (as determined by a Kjeldahl titration) in a film composed wholly of cellulose nitrate, to 0.001% nitrogen in a film consisting of a 1 to 12,000 mixture of cellulose nitrate and cellulose acetate butyrate. The cellulose nitrate employed was a dope grade complying with Army-Navy specifications (*1*).

The mixed nitrate-butyrate compositions were obtained by casting films from homogeneous acetone solutions of cellulose nitrate and cellulose acetate butyrate in the desired ratios. The latter was selected as the diluent because it is the standard material for doping fabric surfaces of naval aircraft (*9*) and is widely used in the aircraft industry. The diphenylamine solutions were prepared by suspending the diphenylamine in the water to be added, then adding the concentrated acid. The heat of mixing was thus utilized to effect rapid solution of the diphenylamine. (Maximum sensitivity is achieved only with freshly prepared reagents. The solution gradually deteriorates and should be discarded when it no longer produces an adequate color with a standard nitrate sample.)

The compositions investigated are indicated in Table I.

The time required for a particular color to develop after a single drop of the indicator solution was placed on a test film was found to depend in a consistent manner upon the nitrate content of the film. In order to standardize the time measurement, so as to permit visual resolution of nitrate composition differences among the samples, it was found convenient to use two arbitrarily selected reference colors—viz., a light blue (about 2.5PB 5/8 Munsell) and a deep blue (about 5.0PB 3/8 Munsell). In the extremes of the nitrate compositions tested, where relatively little color is produced, the time required for the appearance of the first observable blue coloration was a useful criterion.

Figure 1 shows the relation between nitrate nitrogen content and the color development time, using the several reference colors, with indicator reagents containing 30 and 50 ml., respectively, of water per 100 ml. of concentrated sulfuric acid. A semilogarithmic plot has been employed solely for convenience in treating the data. Although the data presented are not in-

Table I. Compositions Investigated to Determine Sensitivity of Diphenylamine Test for Nitrate Radical

Water added to sulfuric acid, ml. per 100 ml. of H_2SO_4 (96%)	0, 10, 30, 50, 80, 150
Sulfuric acid in reagent, % by weight	96, 91, 82.5, 75.5, 67, 53
Diphenylamine in reagent, grams per 100 ml. of H_2SO_4 (96%)	0.01, 0.05, 0.10, 0.50, 1.00
Nitrate nitrogen in film, %	0.000, 0.001, 0.005, 0.015, 0.025, 0.050, 0.100, 0.185, 0.36, 0.71, 1.3, 2.4, 4.8, 7.2, 9.6, 10.6, 12.0

tended to be an absolute basis for analysis, they are typical and serve to demonstrate how markedly the time required for color development depends upon the amount of nitrate present. Through use of a suitable reference color—i.e., one for which there is a relatively large change in the time required to develop the reference color for small changes in the nitrate content, as exemplified by the curves in Figure 1 with the steepest slopes—it is possible to resolve differences in nitrate content over a wide range of compositions with a single general-purpose indicator solution; estimation of the amount of nitrate present then becomes practical by comparing the unknown sample with films of known nitrate content.

The usefulness of a particular reference color is determined by the range in which it may be applied. Thus it is evident from Figure 1 that although the time to develop a deep blue color is the most satisfactory criterion for resolution of differences in nitrate composition in the broad middle nitrate range, its use is limited by the insufficiency of color developed in the extremes of nitrate content, where the time for the first observable color to develop becomes practical as a criterion.

DISCUSSION OF RESULTS

Effect of Water Content. Indicator solutions of several diphenylamine concentrations and covering the range of water contents indicated in Table I were tested over the nitrate range from 2 to 11% nitrogen. The concentrated sulfuric acid solution produced charring of the film rather than a blue coloration. The "10-ml." solution—i.e., containing 10 ml. of water per 100 ml. of concentrated sulfuric acid—gave a dirty violet color and erratic results. A pure blue color and consistent results were obtained with the "30-ml." solution. Good results were also obtained with the "50-ml." solution, but strength of color and sensitivity were lower than with the "30-ml." reagent (Figure 1), and the useful range was not so great. No color whatever was obtained with either the "80-ml." or "150-ml." reagents.

On the basis of the above data, 30 ml. of water per 100 ml. of concentrated sulfuric acid were selected as a suitable amount of water to use in the diphenylamine indicator reagent. Such a reagent contains approximately 82.5% sulfuric acid by weight.

Effect of Diphenylamine Content. Indicator solutions having the concentrations of diphenylamine given in Table I and containing the amount of water as determined above were investigated with films in the 2 to 11% nitrogen range. Saturation of color and the rate at which it developed increased with increasing diphenylamine content within this range. A similar series of tests conducted in the low nitrogen range revealed a somewhat greater sensitivity and a lessening of the color development time with decreasing diphenylamine content for compositions below 0.02% nitrogen.

With the higher diphenylamine concentrations investigated the reference color was attained so rapidly as to make difficult the resolution of differences in nitrate composition. On the other hand, the solution containing 0.01 gram of diphenylamine per 100 ml. of concentrated sulfuric acid was low in sensitivity. The intermediate reagent containing 0.1 gram of diphenylamine per 100 ml. of concentrated sulfuric acid plus 30 ml. of water was selected as a general-purpose indicator which would be suitable for use over a wide range of nitrate content.

Effect of Nitrate Content. The general-purpose indicator was evaluated with films covering the entire nitrogen range listed in Table I. The results are shown graphically in Figure 1. Color was found to develop faster with increasing nitrate content up to about 2% nitrogen. There was no appreciable change of color development time with nitrate content in the 2 to 6% nitrogen range. Above approximately 6% nitrogen, color developed more slowly with increasing nitrate content.

Because for any given color development time there are two possible values of the nitrate content, some idea of the approximate range in which the unknown composition lies is needed in order

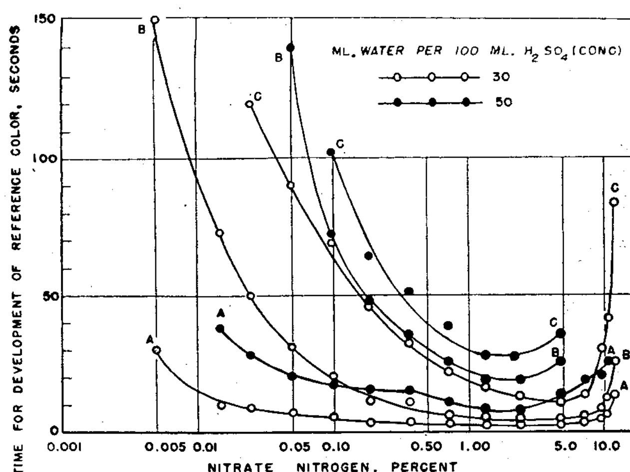


Figure 1. Relation between Nitrate Nitrogen Content and Time Required for Development of a Reference Color with Diphenylamine Indicator Solutions Differing in Water Content

Curves shown are for a reagent containing 0.1 gram of diphenylamine per 100 ml. of concentrated sulfuric acid

Reference color. A. First observable blue
B. Light blue
C. Deep blue

to select the applicable value. Such information, if not already known, can be ascertained by noting whether the time for color development increases or decreases when the specimen is diluted by the casting technique previously described. If, for example, the time for color development increases upon dilution, obviously the sample must be in the lower nitrate range. Resolution of composition differences in the 2 to 6% nitrogen range can be accomplished by quantitatively diluting the specimen to the lower nitrate region before comparison with known standards.

The test is not so sensitive with the solid materials herein described as in the nitrate solutions studied by earlier investigators. The practical lower limit of sensitivity with films of mixed cellulose esters is about 0.003% nitrate nitrogen. Values below 0.005% nitrogen have not been plotted in Figure 1 because of the poor reproducibility of results in this region.

Estimation of Nitrate Content. The principles which have been described make practicable a simple and rapid procedure for the estimation of nitrate nitrogen in a cellulosic film.

Prepare a series of film standards of known nitrate content covering the nitrate range likely to be encountered. Such standards can be prepared by the diluting and casting technique already described. Once prepared, the films may be cut into small test pieces and stored indefinitely for use as needed.

Place a single drop of the diphenylamine indicator solution on the unknown and on the standard samples and note to the nearest second the time required for each sample to develop the reference color. The nitrate content of the unknown sample may then be taken as approximately that of the standard sample whose color development time it most nearly matches. Or, if the diphenylamine reagent is applied practically simultaneously to the unknown and to the standard samples, the nitrate content may be estimated merely by comparing the colors among them at a given time and noting which standard is most closely matched in color by the unknown. If the latter method is employed, the time interval allowed before comparison must be long enough to develop an intensity of color sufficient to enhance differences among the samples, and yet not so long as to obliterate such differences by the production of colors of too high a degree of saturation for visual resolution.

Where two values are obtained (as the color development time has been shown to be a double-valued function of the nitrate content), the correct value can be recognized from such factors as knowledge of the manufacturing process which produced the sample, its texture or appearance, its flammability, or its solubility in certain solvents. In the absence of any such information, the applicable value can be ascertained by noting whether the time for color development increases or decreases when the

specimen is diluted by the techniques mentioned. When the composition lies in the less distinguishable 2 to 6% nitrate nitrogen range, the composition may be more closely approximated by quantitatively diluting the unknown specimen to the lower nitrate region before comparing it with the known standards.

SUMMARY

Speed and strength of color development were used as criteria to evaluate the utility of a variety of diphenylamine indicator solutions with a wide range of nitrate compositions in the form of films cast from mixtures of cellulose esters. The plot of time for color development versus nitrogen content has a minimum value in the 2 to 6% nitrogen region. Water content is shown to be a critical factor, and diphenylamine concentration is found to exert a minor influence. Although no single indicator solution is best for all nitrate contents, a suitable reagent for general applicability in qualitative tests over a wide nitrate range consists of 0.1 gram of diphenylamine, 100 ml. of concentrated sulfuric acid, and 30 ml. of water. The method can be used for estimating nitrate nitrogen content by comparing samples with a series of film standards of known nitrate composition.

ACKNOWLEDGMENT

The author wishes to express appreciation for valuable suggestions to S. G. Weissberg, under whose general supervision this work was performed, and to acknowledge the assistance of Honora A. Mattare in the experimental work.

LITERATURE CITED

(1) Army-Navy Aeronautical Specification **AN-L-C-181**.
(2) Assoc. Offic. Agr. Chemists, "Official and Tentative Methods of Analysis," 6th ed., p. 136, 1945.
(3) Harvey, E. M., *J. Am. Chem. Soc.*, 42, 1245 (1920).
(4) Hodgman, C. D., ed., "Handbook of Chemistry and Physics," p. 1343, Cleveland, Ohio, Chemical Rubber Publishing Co., 1947.
(5) Kolthoff, I. M., and Noponen, G. E., *J. Am. Chem. Soc.*, **55**, 1448 (1933).
(6) Kopp, E., *Ber.*, **5**, 284 (1872).
(7) Letts, E. A., and Rea, F. W., *J. Chem. Soc.*, **105**, 1157 (1914).
(8) "Modern Plastics Encyclopedia," Vol. 3, Chart 1, Table III, New York, Plastics Catalog Corp., 1947.
(9) Reinhart, F. W., and Kline, G. M., *Ind. Eng. Chem.*, **32**, 185 (1940).
(10) Riehm, H., *Z. anal. Chem.*, **81**, 353 (1930).
(11) Smith, L., *Ibid.*, **56**, 28 (1917).
(12) Snell, G. D., and Snell, C. T., "Colorimetric Methods of Analysis," Vol. I, pp. 637–40, New York, D. Van Nostrand Co., 1936.
(13) Treadwell, F. P., and Hall, W. T., "Analytical Chemistry, Vol. I, Qualitative," 4th ed., p. 395, New York, John Wiley & Sons, 1916.

RECEIVED May 28, 1948. Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 114th Meeting of the AMERICAN CHEMICAL SOCIETY, Washington, D. C.

Determination of Glycosidic Methoxyl

CARROLL L. HOFFPAUIR AND RICHARD E. REEVES
Southern Regional Research Laboratory, New Orleans, La.

A method is described for the determination of glycosidic methoxyl based on the hydrolysis of methyl glycosides by strong sulfuric acid to yield methanol. The methanol is separated by disillation and oxidized to formaldehyde, after which it is determined colorimetrically, using a sensitive fuchsin–sulfurous acid reagent. The method is applicable to the determination of small amounts of glycosidic methoxyl. If ether-linked methoxyl is present, as in highly methylated glycosides and cellulose derivatives, it is necessary to plot yield of methoxyl against time and extrapolate to zero time to obtain glycosidic methoxyl values. The method is not applicable in the presence of ester-linked methoxyl or if the sample steam-distills.

WHEN the glucose-glucose bonds in cellulose are ruptured by methyl alcohol in the presence of hydrochloric acid, methoxyl groups are introduced into the cellulose (*7*). In applying the conventional microadaptation of the Zeisel methoxyl method (*2*) to the analysis of such modified celluloses it was noted that glucose or purified cotton cellulose gave blanks that amount to approximately 0.3%. Similar results have been observed with polyhydric alcohols (*1*). These blanks would account for more than half of the methoxyl found by the Zeisel procedure in fully methanolyzed native cotton cellulose and over a third of that on methanolyzed mercerized cellulose; hence the Zeisel method is not suited to the accurate determination of small amounts of methoxyl in these materials.

Freudenberg and Soff (*4*) have suggested a modification of the Zeisel apparatus for measuring acid-labile, glycosidic methoxyl, but their method is not easily adapted to the determination of the very small amounts encountered in methanolyzed cellulose. Inasmuch as the methoxyl in methanolyzed cellulose is hydrolyzed by aqueous acid, consideration was given to the possibility of determining the methyl alcohol so produced. The technique of von Fellenberg (*8*) for the determination of methoxyl in pectin appeared more promising. By substituting acid for alkaline hydrolysis and refining the Schiff colorimetric procedure it was successfully adapted to the present purpose.

The methanol is separated by distillation, and oxidized to formaldehyde by means of an acid solution of potassium permanganate (*3*), and the formaldehyde is determined by a modified colorimetric method (*5*, *6*).

After drastic methanolysis native cotton celluloses yielded 0.20 to 0.25% and mercerized celluloses about 0.5% methoxyl by the present method. Closely agreeing values are also obtained by the Zeisel procedure, if they are corrected for the large blank. With simple methyl glycosides the two methods give values which are in agreement. But with methylated methyl glycosides, such as methyl 2,3,4,6-tetramethyl-β-D-glucoside and methylheptamethyl-β-cellobioside, the Zeisel method measured all the methoxyl groups whereas the new procedure gave erratic results which in some cases were slightly greater than one methoxyl per molecule. In the latter cases it was found that, in addition to the acid-labile glycosidic methoxyl, a trace of ether-linked methoxyl was reacting. Because the two types of linkages are cleaved at vastly different rates, a modified method was developed for glycosidic methoxyl in the presence of ether methoxyl groups. The methods described here are not intended to replace the Zeisel method for the determination of total methoxyl in materials containing appreciable methoxyl, but have proved useful in measuring small amounts of acid-labile methoxyl in materials such as methanolyzed cellulose.

REAGENTS

Potassium permanganate solution, 3.0 grams of potassium permanganate and 15 ml. of phosphoric acid (85%) dissolved in 85 ml. of water.

Oxalic acid solution, 5.0 grams of oxalic acid dissolved in 100 ml. of 18 *N* sulfuric acid.

Standard Methanol Solution. Approximately 2 ml. of absolute methanol are accurately weighed and diluted to 1 liter in a volumetric flask. A 20-ml. aliquot of this solution is diluted to 250 ml. in a volumetric flask. The exact weight of methoxyl in each milliliter of this solution is calculated from the weight of methanol used.

Schiff's Reagent (*5*). Basic fuchsin (rosaniline hydrochloride, 0.5 gram) is dissolved in 500 ml. of water, 5.15 grams of sodium acid sulfite are added, and allowed to stand 15 minutes. Then 17 ml. of 6 *N* hydrochloric acid are added and allowed to stand for at least 3 hours before using. The reagent should be practically decolorized. Some batches of rosaniline hydrochloride give a reagent with appreciable red color. If this is the case, a satisfactory reagent may be obtained by adding 1 gram of decolorizing carbon and filtering before use.

Sulfuric Acid, 72%. Three volumes of concentrated analytical reagent grade sulfuric acid are chilled and diluted with 2 volumes of water.

Acetone, C.P. grade.

SAMPLE MATERIALS

The D-glucose (National Bureau of Standards dextrose), α-D-methylglycopyranoside, α-D-methylmannopyranoside, β-methylcellobioside, 2,3,6-trimethyl-D-glucose, methyl 2,3,4,6-tetramethyl-β-D-glucoside, and methyl heptamethyl-β-cellobioside used in this investigation were crystalline preparations having physical constants in agreement with those recorded in the literature. The methyl 2,3,6-trimethyl-α,β-D-glucoside was a sirup prepared from the crystalline 2,3,6-trimethylglucose by refluxing with methanolic hydrochloric acid. Its total methoxyl content (Zeisel) agreed with that calculated from the formula.

A commercially purified low viscosity sample of cotton linters was used. The purified linters were methanolyzed by heating for 1 hour at 120° C. in an autoclave with 50 parts of methanolic hydrochloric acid. Initial concentrations of both 1 and 3.7% hydrochloric acid were employed, but both concentrations appeared to yield identical products. The methanolyzed linters were methylated with methyl sulfate and sodium hydroxide in an inert atmosphere. Where mercerized linters are indicated, the mercerization was accomplished by treating purified linters at room temperature with 30 parts of 18% sodium hydroxide solution for 0.5 hour, followed by rinsing, souring, rinsing, and drying.

PROCEDURE

In Absence of Ether-Linked Methoxyl. A sample containing 0.3 to 2.0 mg. of methoxyl is weighed into a 100-ml. Kjeldahl flask, 5 ml. of 72% sulfuric acid and 3 glass beads, are added and the sample is allowed to stand with occasional shaking until dissolved. It is then allowed to stand overnight at approximately 27° C., 55 ml. of distilled water are added and distilled slowly into a 50-ml. volumetric flask until at least 36 ml. of distillate have collected. The condenser is rinsed with water into the flask and the solution made to volume. A 10-ml. aliquot is transferred to a 25-ml. volumetric flask, 1 ml. of potassium permanganate solution is added and allowed to stand for exactly 10 minutes. Excess permanganate is destroyed by adding 1.5 ml. of oxalic acid and shaking well. Then 2 ml. of acetone (*6*) and 10 ml. of Schiff's reagent are added and the solution is made to volume and mixed well. After 3 to 3.5 hours it is read in a photoelectric colorimeter equipped with a filter with maximum transmission at approximately 580 mμ, and compared with standard methanol solutions developed in the same way. In the present work an Evelyn colorimeter equipped with a 565 mμ filter was used.

In Presence of Ether-Linked Methoxyl. Eight or more samples are weighed out and treated with 72% sulfuric acid exactly as in the first step in method 1. The solutions are kept at a temperature of 27° C. and at various intervals from 24 to 240 hours samples are diluted and distilled to isolate the methanol. Alternatively a large sample may be treated with 50 ml. of sulfuric acid and 5-ml. aliquots removed at the various time intervals. When all the distillations have been completed, methanol is determined exactly as in the first procedure and the results are plotted on coordinate paper. The point at which the curve of methoxyl *vs.* time in 72% sulfuric acid becomes a straight line is noted (usually 24 to 48 hours at 27°) and all subsequent points are employed for determination of the best straight line, which is extrapolated through these points back to the ordinate, as illustrated by Figure 1. The point of the intercept with the ordinate is regarded as a measure of the glycosidic methoxyl present in the original sample.

DISCUSSION OF RESULTS

That purified cellulose and glucose give essentially a zero blank by the procedure described is shown in Table I, which also illustrates satisfactory recovery of small known amounts of methoxyl added in the form of methanol or α-methylglucoside. In Table II are shown the blank values obtained on various purified celluloses by the Zeisel method. It is doubtful that these values represent true methoxyl, in view of similar values obtained with pure dextrose (0.08, 0.09, 0.10, and 0.12%) and the polyhydric alcohols. Furthermore, the values slowly increase when the time of distillation with hydriodic acid is prolonged.

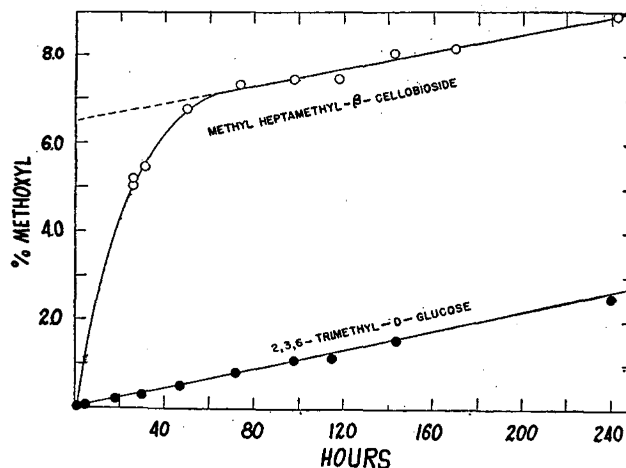


Figure 1. Yield of Methoxyl *vs.* Time

Table I. Recovery of Added Methoxyl

Sample	Added Substance	Methoxyl Found	Methoxyl Theory	Methoxyl Recovery
	Mg.	*Mg.*	*Mg.*	*%*
D-Glucose blank, 0.5 gram	None	0	0	...
		0		...
Purified cellulose blank, 0.1-gram samples	None	0	0	...
		0		...
	0.66, methanol	0.63	0.64	98
		0.65		102
	1.25, α-methylglucoside	0.21	0.20	105
		0.21		105
Purified cellulose blank, 0.5-gram samples	None	0	0	...
		0		...
	0.66, methanol	0.62	0.64	97
		0.60		94
	1.25, α-methylglucoside	0.20	0.20	100
		0.20		100
Methanolyzed, mercerized linters, 0.2-gram samples	None	0.51%	....	...
		0.52%	....	...
	0.66, methanol	1.39	1.65	85
		1.40	1.65	85
	3.12, α-methylglucoside	0.96	1.03	92
		1.08	1.12	97

Table II. Zeisel Blank Values on Purified Celluloses

Substance	Methoxyl Content[a]
	%
1. Purified cotton linters	0 3 0.34, 0.33, 0.34, 0.32, 0.32, 0.31
2. Purified cotton linters refluxed with methanol, then exhaustively extracted with water	0.34, 0.29, 0.28, 0.32
3. Mercerized purified cotton linters	0.23, 0.28
4. Mercerized purified cotton linters after treatment as No. 2	0.41, 0.43
5. α-Cellulose from purified wood pulp mercerized	0.29, 0.33
Average Zeisel value for purified cellulose	0.32

[a] Analyses calculated to anhydrous basis.

It is probable that these Zeisel blanks reflect the low volatility of some higher alkyl iodide produced during the distillation process.

The agreement between glycosidic methoxyl values obtained by the present method and Zeisel methoxyl values after the latter are corrected by subtraction of the blank of 0.32%, shown in Table III, indicates that all the methoxyl entering cellulose on methanolysis becomes the acid-labile glycosidic (or acetal) type. In Table IV is shown the agreement between analytical values and theory for several simple methyl glycosides. The methoxyl contents of these compounds are, however, considerably higher than the optimum range for the method.

In order to explore the limits of the method, several types of organic compounds containing methoxyl groups in glycosidic and other configurations were analyzed by method 1. Results obtained are summarized in Table V. Two of the compounds distilled to some extent, and when saturated aqueous solutions of these compounds were oxidized with permanganate and treated with Schiff's reagent, considerable color was developed. Consequently, the results found in these cases were probably due to interference by the oxidation products of the original compound rather than the release of methanol in the method Thus guiacol, which distills, gave an apparent yield of methoxyl, whereas guiacol acetate, which does not distill, gave no methoxyl. Similarly, anisaldehyde, which distills, gave an apparent yield of methoxyl, whereas *p*-anisidine gave no methoxyl. The value obtained for methyl galacturonide methyl ester is considerably higher than that corresponding to one glycosidic methoxyl, though less than the total methoxyl in the compound; this indicates that ester methoxyl reacts somewhat, but not completely, under the conditions of the determination. This is also shown by the value obtained for citrus pectin, the methoxyl of which is ester-linked.

Table III. Comparison between Glycosidic and Zeisel Methoxyl Analyses on Methanolyzed Celluloses

Treatment Given Purified Cotton Linters	Methoxyl Content[a] Zeisel[b]	Glycosidic method 1
	%	%
1 hour at 120° with methanol—HCl	0.21	0.21
	0.22	0.21
Mercerized, then 1 hour at 120° with methanol—HCl	0.53	0.52
	0.55	0.54
		0.56
		0.57

[a] Calculated on basis of anhydrous fiber.
[b] Zeisel values after subtracting 0.32% blank.

Table IV. Methoxyl Analysis on Methyl Glycosides

Substance	Methoxyl Content Method 1	Theory
	%	%
α-D-Methylglucopyranoside	16.2	16.0
α-D-Methylmannopyranoside	16.0	16.0
β-Methylcellobioside	8.2	8.7

Table V. Results Obtained by Glycosidic Methoxyl Method on Organic Compounds

Compound		Methoxyl Theory	Found
		%	%
Methyl salicylate	2-HOC_6H_4-1-$COOCH_3$	20.40	None
Guiacol	2-CH_3O-C_6H_4-1-OH	25.00	4.8[a]
Guiacol acetate	1-$CH_3COOC_6H_4$-2-OCH_3	18.67	None
p-Anisidine	$CH_3OC_6H_4NH_2$	25.19	None
Anisaldehyde	4-$CH_3OC_6H_4CHO$	22.79	13.0[a]
p-Nitroanisole	$NO_2C_6H_4OCH_3$	20.26	None
p-Methoxybenzyl alcohol	$CH_3OC_6H_4CH_2OH$	22.45	None
Methyl galacturonide methyl esters	$CH_3OCHO(CHOH)_3CHCOOCH_3$	27.93	17.9
Citrus pectin (9.57% methoxyl)		9.57	6.2

[a] Aqueous solution of compound gives color.

Table VI. Analysis of Some Methylated Carbohydrates for Glycosidic Methoxyl

Substance	Glycosidic Methoxyl Content By Method 2	Theory
	%	%
2,3,6-Trimethyl-D-glucose	0.00	0.00
Methyl 2,3,6-trimethyl-α,β-D-glucoside	13.2	13.1
Methyl 2,3,4,6-tetramethyl-β-D-glucoside	11.0	12.4
Methylheptamethyl-β-cellobioside	6.5	6.8
Partially methylated, methanolyzed linters (total methoxyl 27.5%)	0.15	0.16[a]
Partially methylated, methanolyzed linters (total methoxyl 40.9%)	0.16	0.15[a]

[a] Glycosidic methoxyl prior to methylation was 0.20%, from which it follows that theoretical values are calculated to be those indicated. As essentially complete sample recovery was achieved on methylation it is assumed that no fractionation with change of glycosidic methoxyl occurred during methylation process.

The method of treatment applied to substances containing both ether and glycosidic methoxyl is illustrated in Figure 1. It was observed that for compounds containing ether-linked methoxyl the yield of methoxyl varied with the length of time the compound was allowed to react with the 72% sulfuric acid. This suggested that ether-linked methoxyl reacts slowly under the conditions of the determination. The reactivity of ether-linked methoxyl was therefore investigated by analyzing 2,3,6-trimethylglucose by method 2, which involved varying the time of standing with 72% sulfuric acid. When yield of methoxyl was plotted against time a straight line was obtained with a slope of 0.011% methoxyl per hour and an intercept of zero methoxyl. In a similar manner, points were obtained for methyl 2,3,6-trimethylglucoside, methylheptamethylcellobioside, and methyl 2,3,4,6-tetramethylglucoside. For each of these samples a linear relationship between yield of methoxyl and time was obtained in the region between 48 and 240 hours. The best straight lines through the points corresponding to times greater than 48 hours were calculated by the method of least squares, and extrapolated back to zero time. The intercepts which these lines make with the *Y*-axis correct for the small amount of hydrolysis of ether-linked methoxyl and show the content of glycosidic methoxyl. The satisfactory agreement of these extrapolated values with the theoretical values is shown in Table VI.

When the method was applied to fully methylated Empire cotton fiber, previously purified by extractions with alcohol and 1% aqueous sodium hydroxide, the intercept on extrapolation was −0.04%. This small negative value is probably a reflection of the uncertainty of the analytical determinations and the data are interpreted as indicating the absence of acid-labile methoxyl in the sample.

ACKNOWLEDGMENT

The authors are indebted to L. W. Mazzeno for the preparation of some of the materials used in this investigation.

LITERATURE CITED

(1) Araki, T., and Hasi, Y., *J. Chem. Soc. Japan*, 61, 99 (1940).
(2) Assoc. Offic. Agr. Chemists, "Official and Tentative Methods of Analysis," 6th ed., p. 762, 1945.
(3) Dodge, B. F., Ind. Eng. Chem., Anal. Ed., 4, 23 (1932).
(4) Freudenberg, K., and Soff, K., *Ann.*, 493, 68 (1932).
(5) Hoffpauir, C. L., Buckaloo, G. W., and Guthrie, J. D., Ind. Eng. Chem., Anal. Ed., 15, 605 (1943).
(6) Hoffpauir, C. L., and O'Connor, R. T., Anal. Chem., 21, 420 (1949).
(7) Reeves, R. E., Schwartz, W. M., and Giddens, J. E., *J. Am. Chem. Soc.*, 68, 1383 (1946).
(8) Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis," Vol. 2, p. 18, New York, D. Van Nostrand Co., 1936.

Received July 23, 1948. Presented before the Division of Sugar Chemistry and Technology, Symposium on Woods and Wood Sugars, at the 114th Meeting of the American Chemical Society, Portland, Ore.

Analysis of Mixtures of Organic Acids by Extraction

K. R. TSAI, *National Amoy University, Amoy, China*
AND
YING FU, *University of Michigan, Ann Arbor, Mich.*

The extraction method for the analysis of fatty acid mixtures has been critically studied. The effects of dissociation and association of the acids and of the ratios of the volume of extractant to that of the aqueous solution on the accuracy of analysis have been expressed in the form of Equations 10 and 13. In the case of ternary mixtures better results are obtained by the back-extraction of the organic layer with water or dilute aqueous solution than by the extraction of the aqueous solution repeatedly with organic solvent. The method has been successfully applied to the analysis of binary mixtures of acetic, propionic, and butyric acids, and to the ternary mixtures of the above acids either in the absence or in the presence of formic acid.

IN MANY industrial processes, such as wood distillation and fermentation, one often encounters mixtures of substances, especially of organic acids, whose properties are similar. A simple and rapid method for the routine analysis of such systems is highly desirable.

Most of the available methods are based chiefly on differences in solubilities, boiling points, steam volatilities, and capacities to form azeotropic mixtures. In view of the fact that the distribution coefficients of organic compounds between immiscible solvents often differ widely even with homologous substances, and their determination, in the case of acids, involves no manipulation more complicated than ordinary titration, a method based on the distribution principle would seem to have advantages over those mentioned, at least in so far as simplicity and rapidity are concerned. Such a method was proposed by Behrens (*1*) in 1926 and later improved by Werkman and associates (*4*, *5*, *8*).

A mixture of qualitatively known acids, such as an aqueous solution of acetic and propionic acids, whose initial total but not the individual concentrations are known, is extracted with an immiscible organic solvent and the final total concentration after extraction is determined. With the two known total concentrations two equations can be written involving two unknowns, the initial individual concentrations, and, therefore, the unknowns can be evaluated. With three-acid systems, the original mixture is extracted twice with different amounts of organic solvent. In principle, $n - 1$ extractions are required to determine the n initial concentrations. The precision and applicability of this procedure have been studied by Malm, Nadeau, and Genung (*3*) in a comprehensive paper with extensive bibliography.

Even though capable of yielding satisfactory results, this procedure has one serious drawback, in that any experimental error in the analysis may be greatly magnified in the final results. This can be remedied by submitting the procedure to a critical analysis. Once the basic principles are clear, other extraction methods of analytical importance may be developed to suit the purpose at hand.

DERIVATION OF EQUATIONS

When an aqueous solution of an organic acid is shaken with an immiscible organic solvent at constant temperature, the relationship between the equilibrium concentrations, C' of the organic phase and C of the aqueous phase, is given by the familiar distribution law of Nernst:

$$\frac{C'(1 - \beta)}{C(1 - \alpha)} = k \qquad (1)$$

where β and α are, respectively, the degrees of association and dissociation of the acid and k is the distribution constant. Let C^0 and V^0 be the original concentration and volume of the aqueous solution, and V and V' the volumes of the aqueous and organic phases after equilibrium has been reached; then

$$V^0C^0 = VC + V'C' \qquad (2)$$

as the total amount of the acid must remain constant. Combining these two equations one has

$$C = \frac{C^0}{(V/V^0) + k(V'/V^0)(1 - \alpha)/(1 - \beta)} \qquad (3)$$

If the solution is sufficiently dilute, V/V^0 and k are practically constant. By assuming α and β to be small compared with unity, Equation 3 can be written in the following simpler form:

$$C = eC^0 \qquad (4)$$

where the extraction constant, e, represents the fraction of the original acid remaining in the aqueous phase after the extraction, and has a constant value for a fixed V'/V^0.

If the original aqueous solution contains more than one acid, say acetic, propionic, butyric, ..., Nernst's law of independent distribution, which states that Equation 4 is separately applicable to the individual acids, leads to the following expression:

$$C = C_a + C_p + C_b + \ldots\ldots = aC_a^0 + pC_p^0 + bC_b^0 + \ldots\ldots \qquad (5)$$

where C is the total acid concentration of the aqueous phase after extraction, a, p, b, ... are the extraction constants for acetic, propionic, butyric, and other acids, and the subscripts indicate the respective individual acids. The initial condition

$$C^0 = C_a^0 + C_p^0 + C_b^0 \ldots\ldots \qquad (6)$$

together with Equation 5 enables us to calculate the original concentrations of the individual acids in the mixture. Thus for a mixture of acetic and propionic acids, one has

$$C^0 = C_a^0 + C_p^0$$
$$C = aC_a^0 + pC_p^0 \qquad (7)$$

a system of two equations with two unknowns, C_a^0 and C_p^0. Having determined the two total concentrations, C^0 and C, and the two extraction constants, a and p, C_a^0 and C_p^0 can be easily calculated. If the original solution contains acetic, propionic, and butyric acids, the required equations are furnished by submitting the mixture to two separate extractions with different volumes of organic liquid. The available equations are:

$$C^0 = C_a^0 + C_p^0 + C_b^0$$
$$C_1 = a_1C_a^0 + p_1C_p^0 + b_1C_b^0 \qquad (8)$$
$$C_2 = a_2C_a^0 + p_2C_p^0 + b_2C_b^0$$

where subscripts 1 and 2 refer to the first and second extractions. Following Osburn, Wood, and Werkman, these equations are converted into more convenient forms by multiplying with $100/C^0$. For instance, in place of Equation 8 one has

$$100 = 100C_a^0/C^0 + 100C_p^0/C^0 + 100C_b^0/C^0 = A + P + B$$
$$E_1 = 100C_1/C^0 = a_1A + p_1P + b_1B \qquad (9)$$
$$E_2 = 100C_2/C^0 = a_2A + p_2P + b_2B$$

where A, P, and B are the mole percentages of these acids in the original mixture, and the first and second extraction coefficients, E_1 and E_2, represent the mole percentage of the total acids remaining in the aqueous phase after the first and second extractions.

ANALYSIS OF THE METHOD

The applicability of this method depends on the constancy of the extraction constants, a, p, b, etc. As shown in Equation 3, these constants are functions of k, V/V^0, V'/V^0, α, and β, all of which vary with concentration. (The distribution constant is usually identified with C'/C. As long as activity and concentration are identical, k is independent of concentration. Because activity and concentration are no longer identical at higher concentrations, k will not remain constant over a wide range of concentrations.) Therefore, it is relevant to examine the situation more closely. Experience shows that when the solutions are sufficiently dilute, k is practically a constant, $V/V^0 \approx 1$, and $V'/V^0 \approx V'^0/V^0$ (V'^0 is the volume of the organic extracting liquid) if the organic liquid has been first saturated with water. With such weak acids as we are dealing with here, the α of any particular acid is small compared with unity even when the concentration of that acid is very low. The degree of association of any organic acid depends on the concentration of the acid in, and the nature of, the organic solvent. By proper choice of the extracting agent, it is possible either to eliminate the association entirely or to reduce it to a very low value. Therefore, by using sufficiently dilute solutions and proper extracting agent, we may assume, at least as a first approximation, the extraction constants to remain practically unchanged.

In the determination of the extraction constants, standard solutions of a single acid, whose concentration has been adjusted to the same value as that of the unknown mixture, were extracted with definite volumes of an organic solvent. Because the final concentrations of the standard and the unknown are not the same, the α's and β's in the mixture will not be the same as the α^0's and β^0's of the standard. It is interesting to investigate how these deviations would affect the accuracy of the analysis.

The relationship between the extraction coefficient (E_1 or E_2) and the variations of α's and β's is given by the following equation:

$$\Delta E = (V'/V^0)[a^2k_a(\alpha_a - \alpha_a^0)A + p^2k_p(\alpha_p - \alpha_p^0)P + b^2k_b(\alpha_b - \alpha_b^0)B] - (V'/V^0)[a^2k_a(\beta_a - \beta_a^0)A + p^2k_p(\beta_p - \beta_p^0)P + b^2k_b(\beta_b - \beta_b^0)B] \qquad (10)$$

In a mixture of several weak monobasic acids the degree of dissociation, α_i, of acid i is given by

$$\alpha_i = \left[\frac{K_i}{C_i + \sum_j (K_j/K_i)C_j}\right]^{1/2} \qquad (11)$$

where the K's are the dissociation constants of the acids, i, j, etc. From this equation it is evident that α_i will be greater or smaller than α_i^0 as K_j/K_i is smaller or greater than unity. In the present case, the K's stand in the following order:

$$K_a > K \quad > K$$

Therefore, the signs of $(\alpha_a - \alpha_a^0)$ and $(\alpha_p - \alpha_p^0)$ will always be opposite each other. Thus the errors due to the variations in α's tend to neutralize each other to some extent. By using the experimental values of extraction and distribution constants, the corrections for E due to the variation of α's have been calculated for several volume ratios. It was found that they are always small negative quantities. The degrees of association, β and β^0, of acetic acid, say, can be expressed as follows:

$$\beta_a = K_AC_a'(1 - \beta_a)^2 \approx K_Aak_aC^0(A/100)(1 - \beta_a)^2$$
$$\beta_a^0 = K_Aak_a(100/100)(1 - \beta_a^0)^2 \qquad (12)$$

where K_A is the association constant of acetic acid in the organic phase. It follows, therefore, that β's are always smaller than β^0's, and the errors due to these variations are always small positive quantities, if the association is not too large. Thus the errors due to the variations of α's and β's partially compensate each other. Even though these errors are not serious under proper conditions, it is gratifying to know that there is some compensation. However, the above conclusion applies only to small values of α and β. With highly associated and dissociated substances, further analysis is required.

This method has the danger of magnifying the experimental errors. The reason for this will become clear from the following equations relating A, P, and B with the extraction coefficients, E_1 and E_2:

$$\frac{\partial A}{\partial E_1} = \frac{p_2 - b_2}{\Delta}, \quad \frac{\partial P}{\partial E_1} = \frac{a_2 - b_2}{\Delta}, \quad \frac{\partial B}{\partial E_1} = \frac{p_2 - a_2}{\Delta}$$
$$\frac{\partial A}{\partial E_2} = \frac{b_1 - p_1}{\Delta}, \quad \frac{\partial P}{\partial E_2} = \frac{b_1 - a_1}{\Delta}, \quad \frac{\partial B}{\partial E_2} = \frac{a_1 - p_1}{\Delta} \qquad (13)$$

where Δ represents the following determinant:

$$\Delta \equiv \begin{vmatrix} 1 & 1 & 1 \\ a_1 & p_1 & b_1 \\ a_2 & p_2 & b_2 \end{vmatrix} = \begin{vmatrix} (a_1 - b_1) & (p_1 - b_1) \\ (a_2 - b_2) & (p_2 - b_2) \end{vmatrix}$$

Evidently, in order to obtain the maximum accuracy, the two sets of extraction constants should be of such values that the absolute values for the above partial differential coefficients are as small as possible. Insufficient attention to this point will lead to large errors, especially when the percentage of the acid is low. As an illustration, the following case may be cited.

Using isopropyl ether as the extracting agent and adopting $(V'/V^0)_1 = 20/100$ and $(V'/V^0)_2 = 100/60$, the following extraction constants have been obtained:

$$a_1 = 0.89, \qquad p_1 = 0.78, \qquad b_1 = 0.57$$
$$a_2 = 0.58, \qquad p_2 = 0.27, \qquad b_2 = 0.10$$

With these values, Equation 13 gives

$$\partial A/\partial E_1 = -3.7, \quad \partial P/\partial E_1 = -10, \quad \partial B/\partial E_1 = 6.7$$

For a mixture containing 90% A, 5% P, and 5% B, the calculated E_1 should be 86.7. If the experimental value happens to be 86.4, an error of 3 parts per 1000 which is within the ordinary limit of accuracy of volumetric analysis, the calculated value of P from the analysis would be 8% instead of the correct 5%.

From the above example, it is evident that the success of this method of analysis depends chiefly on the proper choice of the extraction constants. Ordinarily, the variations of the extraction constants are achieved by changing the volume ratios, V'^0/V^0. From the authors' experience this procedure does not furnish enough variation, as the two sets of extraction constants are more or less similar. However, there are other ways to establish the variations of these two sets of constants.

1. The aqueous solution is submitted to two separate extractions with different organic solvents. The disadvantage of this procedure is that two different sets of distribution constants will be required.
2. After the first extraction, the aqueous layer is again extracted with the organic solvent. Here the second extraction constant, say a_2, is related to the first by the following equation:

$$a_2 = \frac{a_1}{(V/V^0)_2 + (V'/V^0)_2\{(1 - \alpha_a)/(1 - \beta_a)\}_2k_a} \qquad (14)$$

Simple calculation will show that this procedure will not be able to furnish the desired range of variation.

3. The organic layer from the first extraction is extracted back with water and the resulting aqueous layer is titrated. In this case, the second constant is related with the first by

$$a_2 = \frac{a_1\{(1 - \alpha_a)/(1 - \beta_a)\}_1 k_a}{(V/V')_2 + \{(1 - \alpha_a)/(1 - \beta_a)\}_2 k_a} \quad (15)$$

Apparently this procedure is able to furnish the widest range of variation of the constants. In practice, the following procedure has been found satisfactory. After the first set of extraction constants has been obtained, a few sets of provisional second extraction constants were roughly calculated by means of Equation 15, omitting α and β, for different volume ratios $(V'/V^0)_2$. From these values the particular volume ratio corresponding to the most favorable set of constants—i.e., the set that yields the smallest values for the partial differential coefficients of Equation 13—was adopted for the actual determination of the second extraction constants. By this procedure the following data were obtained at 15° C.:

$$(V'/V^0)_1 = 0.6, \quad a_1 = 0.90, \quad p_1 = 0.67, \quad b_1 = 0.37$$

$$(V'/V^0)_2 = 3.0, \quad a_2 = 0.30, \quad p_2 = 0.48, \quad b_2 = 0.33$$

With these values Equation 13 gives

$$\partial A/\partial E_1 = 1.7, \quad \partial P/\partial E_1 = -0.3, \quad \partial B/\partial E_1 = 2.0$$

which evidently are more satisfactory than those cited previously.

Another point may be noted here. Because the second extraction has to start with an organic layer of different initial total acid concentration, there is no compensation for the errors arising from the variations of α's and β's. In order to minimize this source of error the procedure may be slightly modified by using dilute sulfuric acid instead of water as the extracting agent. The amount of sulfuric acid remaining in the aqueous layer may be determined by running a blank. Using solutions of low initial concentrations is also advantageous.

With the same organic extracting agent and the same volume ratios, the extraction constants of formic acids have been found to be $f_1 = 0.91$, $f_2 = 0.30$. The distribution constant is 0.16. These values are very close to those of acetic acid; hence formic acid cannot be determined by this method in the presence of acetic acid, and vice versa. However, formic acid can be easily determined by other methods without affecting the other acids in the series. In that case, the formic acid can be treated as a known quantity and the other acids determined by this method with the following modified equations:

$$\begin{aligned} 100 &= (F + A) + P + B \\ E_1 - (f_1 - a_1)F \equiv E_1' &= a_1(A + F) + p_1P + b_1B \\ E_2 - (f_2 - a_2)F \equiv E_2' &= a_2(A + F) + p_2P + b_2B \end{aligned} \quad (16)$$

where E_1' and E_2' may be called the corrected extraction coefficients.

EXPERIMENTAL PROCEDURE

I. Analysis of Acetic, Propionic, and Butyric Acids in Absence of Formic Acid. (*a*). DETERMINATION OF EXTRACTION CONSTANTS. Titrate 25 ml. of the standard solution of each acid with carbon dioxide–free standard sodium hydroxide solution (approximately 0.025 N) to the phenolphthalein end point. Denote the volume of the alkali used by V^0. Shake 200 ml. of the standard solution and 120 ml. of water-saturated isopropyl ether in a 500-ml. separatory funnel vigorously for 2 or 3 minutes, and allow to stand in a thermostat for 5 minutes. By this time the mixture will separate into two layers. Titrate 25 ml. of the aqueous layer with the same alkali and designate the titer by V_1:

$$V_1 \times 100/V_0 = a_1(p_1 \text{ or } b_1)$$

Shake 100 ml. of the ethereal layer with 30 ml. of dilute sulfuric acid (0.002 to 0.005 N) vigorously in a dry separatory funnel for 2 to 3 minutes and let it stand for 5 minutes. Titrate 25 ml. of the aqueous layer with standard alkali and denote the titer by V_2. To determine the blank correction due to the sulfuric acid, extract 30 ml. of the dilute acid with 100 ml. of the water-saturated isopropyl ether and titrate 25 ml. of the aqueous layer with standard alkali. Denote the volume used as V_B.

$$(V_2 - V_B) \times 100/V_0 = a_2(p_2 \text{ or } b_2)$$

(*b*). DETERMINATION OF EXTRACTION COEFFICIENTS. Using the "unknown" mixture instead of the standard single acids, the first and second extraction coefficients, E_1 and E_2, are determined by the procedure given in (*a*) [The V's are, of course, different from those in (*a*).]:

$$E_1 = V_1 \times 100/V_0$$

$$E_2 = (V_2 - V_B) \times 100/V_0$$

the total concentration of the unknown being about 0.05 M. After the extraction constants and coefficients have been determined, the individual initial concentrations may be calculated either by Equation 9 or by the nomogram method of Osburn, Wood, and Werkman (*4, 5, 8*).

II. Determination of Acetic, Propionic, and Butyric Acids in Presence of Formic Acid. The extraction constants of the different acids and the extraction coefficients are determined by the same procedure as in I. Determine the mole percentage of formic acid by any known method and calculate the corrected extraction coefficients, E_1' and E_2', by

$$E_1' = E_1 - (f_1 - a_1)F$$

$$E_2' = E_2 - (f_2 - a_2)F$$

III. Analysis of Binary Mixtures of Acetic, Propionic, and Butyric Acids, Using Isoamyl Alcohol as Extracting Agent. Titrate 10 ml. of the acid solution (standard single acid or unknown mixture) with carbon dioxide–free sodium hydroxide and designate the titer as V_0. Pipet 50 ml. of the acid solution and 50 ml. of water-saturated isoamyl alcohol into a dry separatory funnel, shake vigorously for 2 to 3 minutes, and allow to stand in a thermostat until the two layers become clear (about half an hour). Titrate 10-ml. portions of the aqueous layer with standard alkali and designate the titer as V_1.

$$V_1 \times 100/V_0 = a(p, b, \text{ or } E)$$

The composition of the unknown mixture can be obtained either algebraically from the following equations:

Table I. First and Second Extraction Constants of Acetic, Propionic, Butyric, and Formic Acids, at 15° ± 0.5° C.

$$\frac{\text{Ml. of isopropyl ether}}{\text{Ml. of acid solution}^a}\left(\frac{V_0'}{V_0}\right)_1 = \frac{120}{200} \quad \frac{\text{Ml. of ether layer}}{\text{Ml. of 0.005 } N \; H_2SO_4{}^b}\left(\frac{V_0'}{V_0}\right)_2 = \frac{100}{30}$$

First extraction constants	a_1	88.7	Second extraction constants	a_2	32.7
	p_1	67.2		p_2	48.9
	b_1	37.4		b_2	33.3
	f_1	90.0		f_2	30.5

[a] Initial concentration = 0.0500 M.
[b] Initial concentration = 0.00500 N.

Equilibrium concentration of H_2SO_4 in aqueous layer = 0.00472 N.

Table II. Analyses of Mixtures of Three (without Formic) or Four (Including Formic, Known Amount) Fatty Acids

(Extractant, isopropyl ether)

Mixture	Composition Taken				First Extraction Coefficient			Second Extraction Coefficient			Composition Found			
	F	A	P	B	E_1 calcd.	E_1 obsd.	E_1'	E_2 calcd.	E_2 obsd.	E_2'	F^a	A	P	B
1	10	80	5	5	85.2	85.4	85.3	33.3	33.5	33.7	10	80	6	4
2	20	60	10	10	81.7	82.1	81.8	33.9	33.7	34.1	20	61	9	10
3	30	50	10	10	81.8	82.4	82.0	33.7	33.8	34.5	30	50	11	9
4	40	40	5	15	80.5	80.8	80.3	32.7	32.8	33.7	40	40	6	14
5	50	30	15	5	83.6	83.5	82.9	34.1	34.3	35.4	50	29	16	5
6	..	50	10	40	66.0	66.2	...	34.6	34.5	...	..	51	10	39
7	..	25	25	50	57.7	57.8	...	37.1	37.3	...	..	24	26	50
8	..	30	30	40	61.7	61.9	...	37.7	37.8	...	..	30	30	40

[a] F treated as known.

$(V/V')_1 = 200/120$, $(V'/V)_2 = 100/30$.

Table III. Binary Mixture of Acetic, Propionic, and Butyric Acids

(Representative analyses, using isoamyl alcohol as extracting solvent in proportion of 50 ml. of alcohol to 50 ml. of acid. $a = 51.6$, $p = 25.1$, $b = 9.77$ at 24 ± 0.2° C, $C^{\circ} = 0.2000$ N)

Mixture	No.	Mole % of First Acid	
		Taken	Found
Acetic-propionic	1	10.0	10.4
	2	20.0	19.6
	3	80.0	80.4
	4	90.0	90.3
Propionic-butyric	1	10.0	10.3
	2	20.0	20.5
	3	80.0	80.4
	4	90.0	90.4
Acetic-butyric	1	10.0	10.3
	2	20.0	20.3
	3	80.0	80.0
	4	90.0	90.1

$$100 = A + P$$

$$E = aA + pP$$

or graphically by plotting E *vs.* A or P. From such curves the composition of a binary mixture can be read off directly once the E-composition relationship has been ascertained.

Results of representative analyses using the above procedure are given in Tables I to III.

DISCUSSION

The above results were obtained during the early stages of this investigation. Later experience showed that with more careful temperature control it was possible to increase the precision of analysis appreciably.

This method can be applied to other systems than homologous acids. The main requirement is that the distribution and extraction constants of the various components should not be too close to each other. This is true also for any other method, such as partition chromatography (*6*) or countercurrent extraction (*7*), in which distribution plays a role.

In common with many physicochemical methods of analysis, this procedure presupposes the mixture to be known qualitatively. If some unsuspected acid is present in the mixture, this method will obviously lead to erroneous results. This problem has been partially solved by Osburn, Wood, and Werkman by comparing the experimental extraction coefficient with the calculated value obtained from a separate extraction with varying amounts of extracting agent. If the qualitative nature of the mixture differs from that assumed, the two values would not agree. As these investigators pointed out, this is a safeguard but not a remedy, as it does not give the identity of the foreign acid. Therefore, in applying this method to industrial or natural products, it is necessary to submit the mixture to a preliminary qualitative examination by either physical or chemical methods.

The discussion on the effect of association makes it evident that one should use only those organic liquids in which the association is either totally absent or only very small. From this standpoint such polar solvents as the higher alcohols naturally suggest themselves. But other requirements may impose a limitation on the choice of extractants. For example, amyl alcohol would be a good solvent were it not for the fact that with this liquid it takes a long time for the two layers to separate clearly. [Recently it was found that if the volume ratio of alcohol to water is about 1 to 1, the two layers will separate sharply in a short time. But in view of the recent work of Bush and Densen (*2*) this may not be the desired ratio.] In ethyl ether, used by both Behrens and Werkman, the association of fatty acids is not serious, but the solvent is too volatile to be conveniently handled as, according to the procedure recommended, definite volumes of the organic phase have to be transferred from one separatory funnel to another. Isoamyl ether has been tried and rejected because fatty acids are highly associated in this solvent.

In the authors' experience, isopropyl ether, first used by Werkman, is a good extractant, as the association of fatty acids in this liquid is slight and the separation into two phases is rapid. Before use, it should be saturated with water in order to minimize the volume change during extraction. The used solvent may be recovered by washing with dilute alkali and water, drying, and distilling. It may be kept in a colored bottle for a long time without deteriorating or developing acidity. Esters have been used by Malm and associates (*3*), who obtained good results with *n*-butyl and *n*-propyl acetates. Using two parts of butyl acetate to one of water, the spread in values for the extraction constants, a, p, and b is greater than those obtained with amyl alcohol as recorded in Table III.

If the degree of dissociation of an acid is high, the extraction constant varies with concentration and the present method cannot be used without modification.

In principle, this method should be applicable to mixtures containing any number of acids; but in practice, the accuracy of analysis decreases as the number of extractions is increased because the concentration of the aqueous layer is too dilute for accurate titration. With systems containing four or more acids it is advisable to extract two portions of the aqueous mixtures separately with different organic solvents instead of extracting one aqueous solution repeatedly.

NOMENCLATURE

A, P, B, F = mole percentage of acetic, propionic, butyric, and formic acids in original mixture
a, p, b, f = extraction constants for above acids
C = equilibrium total concentration of aqueous phase
C_a, C_p, C_b = equilibrium concentration of acetic, propionic, and butyric acids in aqueous phase
C' = equilibrium total concentration of organic phase
C^0 = initial total concentration of aqueous phase
C_a^0, C_p^0, C_b^0 = initial concentration of acetic, propionic, and butyric acids in aqueous phase
E_1, E_2 = first and second extraction coefficients
E_1', E_2' = extraction coefficients corrected for formic acid
e = extraction constant in general
K_A = association constant of an organic acid
K_i, K_j = dissociation constants of acids i and j
k = distribution constants
V = volume of aqueous phase after extraction
V' = volume of organic phase
V^0 = initial volume of aqueous phase
α = degree of dissociation
α^0 = degree of dissociation in standard solution
β = degree of association
β^0 = degree of association in standard solution

Subscripts a, p, b, f signify acetic, propionic, butyric, and formic acids.

Subscripts 1 and 2 signify the first and second extractions.

ACKNOWLEDGMENT

A grant from the Horace H. Rackham School of Graduate Studies of the University of Michigan is gratefully acknowledged by the senior author. He also wishes to thank Mrs. F. E. Bartell for many suggestions in the preparation of the manuscript.

LITERATURE CITED

(1) Behrens, W. U., *Z. anal. Chem.*, 69, 17 (1926).
(2) Bush and Densen, ANAL. CHEM., 20, 121 (1948).
(3) Malm, C. J., Nadeau, G. F., and Genung, L. B., IND. ENG. CHEM., ANAL. ED., 14, 292 (1942).
(4) Osburn, C. L., and Werkman, C. H., *Ibid.*, 3, 264 (1931).
(5) Osburn, C. L., Wood, H. G., and Werkman, C. H., *Ibid.*, 8, 270 (1936).
(6) Ramsey, L. L., and Patterson, W. I., *J. Assoc. Offic. Agr. Chemists*, 28, 664 (1945).
(7) Sato, Y., Barry, G. T., and Craig, L. C., *J. Biol. Chem.*, 170, 501 (1947).
(8) Werkman, C. H., IND. ENG. CHEM., ANAL. ED., 2, 302 (1930).

RECEIVED June 2, 1947.

Spectrophotometric Determination of Androsterone and Testosterone

P. E. HILMER AND W. C. HESS

Georgetown University School of Medicine, Washington, D. C.

The 2,4-dinitrophenylhydrazones of androsterone and testosterone have been prepared according to the method of Veitch and Milone. The absorption spectra of these compounds after treatment with 0.1 *N* alcoholic potassium hydroxide have been determined. Androsterone hydrazone exhibited maximum absorption at 430 millimicrons, and the maximum for testosterone hydrazone was at 460 millimicrons. A chromatographic method for the separation of the two androgens from the estrogens and a sensitive spectrophotometric method for quantitative estimation of androsterone and testosterone are described.

THE use of 2,4-dinitrophenylhydrazine derivatives by Veitch and Milone (*4*) in this laboratory for the quantitative estimation of the estrogens suggested the possibility of a similar method for the determination of the male hormones. Following their procedure, the dinitrophenylhydrazones of the androgens were prepared by Johnston (*1*), but no attempt was made to separate them from the estrogens. The present paper gives details of a method for the separation of estrone and progesterone from androsterone and testosterone, and a method for the quantitative estimation of these androgens.

EXPERIMENTAL

Preparation of 2,4-Dinitrophenylhydrazones of Androgens. Thirty milligrams of the androgen were dissolved in 50 ml. of redistilled, aldehyde-free ethyl alcohol and refluxed for 2 hours with 10 ml. of a saturated alcoholic solution of 2,4-dinitrophenylhydrazine. After 2 hours, 1 ml. of concentrated hydrochloric acid was added, and refluxing was continued for 2 minutes more. Distilled water was added to the point of cloudiness, and the solution was allowed to cool to room temperature, then placed in the icebox until precipitation was complete. The crude hydrazone was filtered off and washed with 95% ethyl alcohol and water.

Further purification of the compound was effected by the method of Johnston (*1*). The hydrazone was dissolved in a minimum amount of benzene and adsorbed on a column (100 × 15 mm.) of Fisher alumina. Treatment of the column with approximately 100 ml. of a 12% solution of chloroform in benzene resulted in the formation of two bands, one of which (unreacted hydrazine) was eluted by this solvent. The other band (hydrazone) was eluted with approximately 150 ml. of chloroform. The elution of the two separate bands can be easily followed visually. After removal of the solvent by distillation in vacuo, the hydrazone was recrystallized from alcohol and water, and dried in a vacuum desiccator. The hydrazones of the androgens melted in the same range as those reported by Johnston (*1*).

Spectroscopic Analysis. Solutions of androsterone and testosterone hydrazones in chloroform, 2.5 ml. containing 120 and 104 micrograms of hydrazone or 74 and 64 micrograms of hormone per ml., respectively, were treated with 5 ml. of 0.1 *N* alcoholic potassium hydroxide, diluted to a volume of 50 ml. with 95% alcohol, and submitted to spectroscopic analysis in the Beckman spectrophotometer. Readings were made at intervals of 10 millimicrons. The hydrazone of androsterone showed maximum absorption at 430 millimicrons; the maximum for testosterone hydrazone was at 460 millimicrons (Figure 1).

Separation of Androgens from Estrogens. A benzene solution containing not more than 20 micrograms of each of the hydrazones of androsterone, testosterone, estrone, and progesterone was adsorbed on a 100-mm. column of Merck alumina (according to Brockmann) in the apparatus described by Veitch and Milone (*4*). The column was washed with 10 ml. of benzene, 50 ml. of 1% acetone in petroleum ether, and finally chloroform until the washings were colorless. This procedure eluted all the hydrazones except estrone.

After evaporation of the solvent from the eluate, the residue was dissolved in benzene and adsorbed on a 300-mm. column of Florisil. This was washed with 5 ml. of benzene, then eluted with approximately 150 ml. of 20% acetone in petroleum ether. The two bands separated, and the androgens were eluted in the first portion of the acetone–petroleum ether washing. The solvent was evaporated, and the residue was dissolved in 1.25 ml. of chloroform and made to a volume of 25 ml. with 95% alcohol. This solution was used for the spectrophotometric determination.

A 2-ml. aliquot was treated with 8 ml. of 0.1 *N* alcoholic potassium hydroxide, and its absorption was read at 430 and 460 millimicrons. Then 2 ml. of standard solutions of androsterone and testosterone hydrazones, containing 7.75 micrograms of hydrazone per ml. (equivalent to 4.8 micrograms of hormone), were similarly treated with alcoholic potassium hydroxide and read at the two wave lengths. The concentrations of the individual androgens were calculated by means of the formulas of Knudson *et al.* (*2*):

$$C_1 = \frac{k_2^A D^B - k_2^B D^A}{k_2^A k_1^B - k_2^B k_1^A}$$

$$C_2 = \frac{D^A - k_1^A C_1}{k_2^A}$$

where C_1 = concentration of androsterone
C_2 = concentration of testosterone
k_1^A = slope of androsterone hydrazone at 430 millimicrons
k_2^A = slope of testosterone hydrazone at 430 millimicrons
k_1^B = slope of androsterone hydrazone at 460 millimicrons
k_2^B = slope of testosterone hydrazone at 460 millimicrons
D^A = reading of density of mixture at 430 millimicrons
D^B = reading of density of mixture at 460 millimicrons

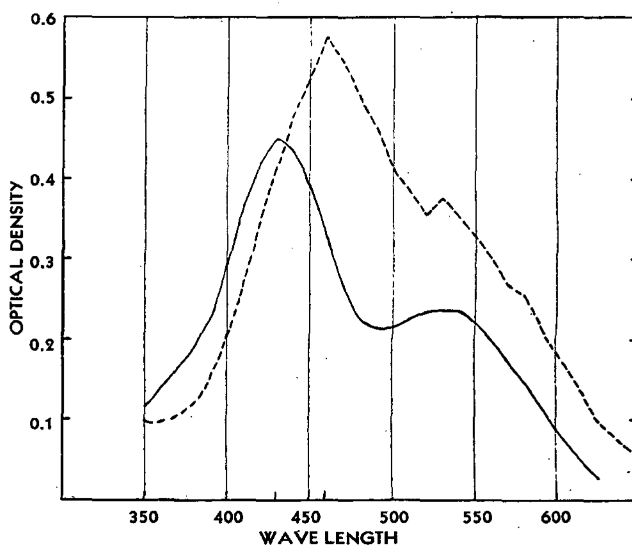


Figure 1. Absorption Curves for Androsterone and Testosterone

Solid line. **Androsterone hydrazone**
Broken line. **Testosterone hydrazone**

Table I. Recovery of Androsterone and Testosterone from Solutions

Hydrazones[a]		Found, γ	% Recovery
1.	Androsterone	15.9 (9.8)[b]	102
	Testosterone	17.3 (10.6)	110
2.	Androsterone	17.1 (10.5)	109
	Testosterone	14.8 (9.1)	95
3.	Androsterone	17.1 (10.5)	109
	Testosterone	14.8 (9.1)	95
4.	Androsterone	16.1 (9.9)	103
	Testosterone	15.8 (9.7)	101
5.	Androsterone	16.1 (9.9)	103
	Testosterone	15.8 (9.7)	101
Average androsterone		16.4 (10.1)	105
Average testosterone		15.5 (9.6)	100

[a] 15.5 γ (9.6 γ) of each used in all tests.
[b] Values in parentheses are androgen equivalents of hydrazones.

The slopes were calculated by dividing the optical densities of the standards at the two wave lengths by the number of micrograms of hydrazone in the volume of standard tested.

In a series of five determinations on solutions containing 15.5 micrograms of the hydrazone of each androgen, the average concentration of androsterone hydrazone was found to be 16.4 micrograms, and the average concentration of testosterone hydrazone was 15.5 micrograms. In terms of free hormone, the average concentration of androsterone was 10.1 micrograms, and of testosterone 9.6 micrograms. These results are summarized in Table I.

This procedure has been used for the determination of the androgens in blood in several preliminary studies.

Five milliliters of blood were deproteinized by the method of Somogyi (*3*). The protein-free filtrate was extracted for 2 hours in a continuous extractor with carbon tetrachloride. After removal of the solvent by distillation, the residue was dissolved in alcohol, and the hydrazone was prepared as described in this paper. The hydrazones were submitted to the chromatographic procedure, and the androgens were estimated in the Coleman spectrophotometer. Initial investigations indicated that 100 ml. of blood contain approximately 2 mg. of testosterone and somewhat more androsterone. This work is still in progress, and these values are only tentative.

ACKNOWLEDGMENT

The authors are indebted to Arthur St. André of Ciba Pharmaceutical Products, Inc., who supplied the androsterone and testosterone used in this investigation.

LITERATURE CITED

(1) Johnston, C. D., *Science*, 106, 91 (1947).
(2) Knudson, H. W., Meloche, V. W., and Juday, C., IND. ENG. CHEM., ANAL ED., **12**, 715 (1940).
(3) Somogyi, M., *J. Biol. Chem.*, 86, 655 (1930).
(4) Veitch, F. P., Jr., and Milone, H. S., *Ibid.*, **158**, 61 (1945).

RECEIVED September 25, 1948. Presented before the Division of Biological Chemistry at the 114th Meeting of the AMERICAN CHEMICAL SOCIETY, Washington, D. C. Investigation supported by a grant from the United States Public Health Service.

MICROBIOLOGICAL ASSAY OF PANTHENOL

ELMER DE RITTER AND SAUL H. RUBIN, *Hoffmann-La Roche, Inc., Nutley, N. J.*

The method of Walter for the microbiological assay of panthenol (the biologically active hydroxy analog of pantothenic acid) has been modified to permit assays in the presence of pantoyl lactone as well as pantoic acid. The lactone is removed quantitatively from water solution by continuous extraction (1 to 2 hours) with ethyl ether. Panthenol in the aqueous residue is then hydrolyzed to pantoic acid for microbiological assay with *Acetobacter suboxydans*. Assay before hydrolysis provides a correction for preformed pantoic acid. By modifying the medium used by Sarett and Cheldelin and using Evelyn colorimeter tubes with continuous shaking, the 60- to 70-hour growth period has been reduced to 20 to 24 hours. In stationary Erlenmeyer flasks suitable growth curves are obtained after 40 hours.

PANTHENOL, α,γ-dihydroxy-*N*-(3-hydroxypropyl)-β,β-dimethylbutyramide, the hydroxy analog of pantothenic acid, was first shown by Pfaltz (*7*) to have the full vitamin activity of the latter in animals. Later work by Burlet (*1*) and in this laboratory (*10*) demonstrated that the physiological availability of panthenol to humans exceeds that of pantothenic acid under stated conditions. This circumstance suggested superior stability, a premise that has been borne out in studies in vitro (*9*), in which panthenol displayed better stability at pH 3 to 5, and especially at pH 4, to which considerable practical interest attaches.

Because panthenol is oxidized to pantothenic acid in the mammal, it has been possible to elaborate a rapid (2-day) bioassay in rats (*3*) wherein the urinary excretion of pantothenic acid is measured after a test dose of panthenol and related to a standard curve of excretion. In the present report, suitable microbiological assay procedures are described.

A direct microbiological assay of panthenol has been described by Walter (*17*), utilizing *Acetobacter suboxydans* as the test organism, but the presence of even a small percentage of pantothenic acid or pantoic acid (α,γ-dihydroxy-β,β-dimethylbutyric acid) invalidates such assays because of the far greater activity of pantothenic and pantoic acids as growth promoters as compared to panthenol. Subsequently Walter (*18*) reported a method using the same organisms for determining panthenol as pantoic acid after complete alkaline saponification. This procedure, a modification of the turbidimetric assay of Sarett and Cheldelin (*12*), employs a fully synthetic medium and is based upon the oxidation of sorbitol to sorbose and determination of the reduction value as a measure of bacterial growth. Preformed pantoic acid, if present, is determined by assay before hydrolysis. This method, however, is not applicable if significant amounts of pantoic acid have undergone lactonization, for pantoyl lactone is also measured as pantoic acid after alkaline hydrolysis but is not corrected for by the assay before hydrolysis because of its slight activity per se as compared to pantoic acid.

In a study of the stability of pantothenic acid, Frost (*5*) presented data obtained by optical rotation measurements regarding the relation between pH and the lactonization of pantoic acid. At pH above 6.0, no lactonization was observed. At pH below 6.0, the rate of lactonization increases as the pH decreases, and at equilibrium, below pH 4.7, lactonization is essentially complete. Because panthenol is considerably more stable in vitro than pantothenic acid between pH 3 and 5 (*9*),

a range commonly encountered in multivitamin preparations, its use in that range is of obvious advantage. Partial hydrolysis at such pH levels during prolonged storage or during rapid aging tests of products containing panthenol will result in the formation of pantoyl lactone.

The present method has been developed to permit rapid microbiological assays of panthenol in the presence of pantoyl lactone as well as pantoic acid. The lactone is removed quantitatively from the aqueous test solution by continuous extraction for 1.5 hours with ethyl ether. The remaining aqueous solution is assayed for pantoic acid before and after alkaline hydrolysis to measure, respectively, preformed and total pantoic acid. The difference represents pantoic acid formed by hydrolysis of panthenol. The standard solution of panthenol is also carried through ether extraction and hydrolysis in order to correct for slight losses in the ether. Pantothenic acid, if present in relatively small amounts (up to 10% of the panthenol) will not interfere seriously with the panthenol assay, as a partial correction for the pantothenate is provided by assay before hydrolysis.

The medium recommended by Sarett and Cheldelin (*12*) for pantoic acid assay with *Acetobacter suboxydans* has been modified in order to obtain suitable growth curves and a shorter incubation period. With the modified medium turbidimetric readings may be taken after 40 hours in stationary, 50-ml. Erlenmeyer flasks or after 20 to 24 hours in Evelyn colorimeter tubes if the latter are shaken continuously. Some practical details on assays by shaking have been given in a previous paper from this laboratory on vitamin B_6 assays (*11*).

STANDARD SOLUTIONS

Panthenol. Dissolve 69.2 mg. of pure panthenol in distilled water, adjust to pH 6.0, and dilute to 1 liter (1 ml. contains the equivalent of 50 micrograms of pantoic acid).

Pantoic Acid. Autoclave 4 ml. of the above standard panthenol solution with 4 ml. of 2 *N* sodium hydroxide for 30 minutes at 6.8 kg. (15 pounds). Cool, add distilled water, adjust pH to 6.0 with 2 *N* and 0.1 *N* hydrochloric acid, and dilute to 1 liter (1 ml. contains 0.2 microgram of pantoic acid).

SPECIAL APPARATUS

Continuous Ether-Extraction Apparatus. A convenient extractor consists of a round-bottomed tube (outside diameter 2.5 cm., over-all length 32 cm.) with a side arm 17 cm. from the bottom for connection by a ball joint to a 250-ml., flat-bottomed distillation flask and with a glass joint at the top for connection to a Corning No. 2600, Friedrichs type, reflux condenser. An inner tube 7.5 mm. in diameter with a perforated ball at the lower end and a funnel at the top rests on the bottom of the extractor and extends almost to the tip of the condenser.

Constant Temperature Room at 30°, needed for 1-day assay. If assays are set up in 50-ml. Erlenmeyer flasks for a 2-day assay, a 30° incubator can be used.

TREATMENT BEFORE MICROBIOLOGICAL ASSAY

Preparation of Test Solution. Dilute liquid preparations in distilled water to a panthenol concentration of about 70 micrograms per ml. Extract solid products, such as tablets, capsules, etc., by blending for 5 minutes, or until thoroughly disintegrated, in distilled water in a Waring Blendor. Take a measured volume of water for the extraction or dilute to volume after blending. Filter or centrifuge and dilute to about 70 micrograms of panthenol per ml.

Ether Extraction. Pipet 20 ml. of the above test solution into the extractor tube, pour about 75 ml. of ethyl ether into the extraction flask, and assemble the extractor on the hot plate.

Extract for 1.5 hours at such a rate that the ether refluxes at least halfway up the condenser. In the setup used in this laboratory, a reflux rate of about 20 ml. per minute allowed quantitative extraction of pantoyl lactone within 1.5 hours. If the presence of solubilizers in the test product leads to the formation of emulsions during the ether extraction, add 3 drops of laboratory aerosol to the extractor tube as required, possibly several times during the course of the extraction.

After 1.5 hours, remove the inner tube, decant as much as possible of the supernatant ether into the extraction flask, and pour the water solution into a 50-ml. Erlenmeyer flask. Warm gently on a steam or water bath to drive off the remaining ether, preferably under a stream of nitrogen to prevent bumping. Avoid prolonged heating or overheating to prevent evaporation of water and changes in concentration.

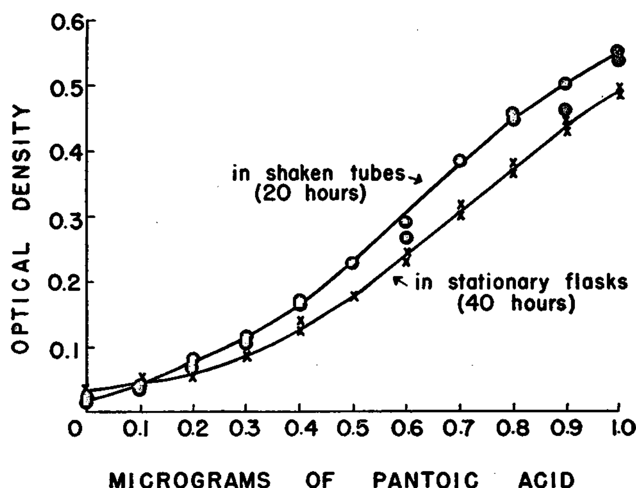


Figure 1. Standard Curves

Extract 20 ml. of standard panthenol solution in exactly the same fashion. As a check on the percentage extraction of the standard panthenol, it is desirable to determine panthenol in the ether extract as described below, after boiling off the ether from the extraction flask. If desired, most of the ether may be recovered by refluxing into a clean, empty extractor tube and taking off only the last 10 ml. on the steam bath.

Alkaline Hydrolysis. Hydrolyze the panthenol in both standard and unknown solutions as follows. Pipet 4 ml. of the ether-free solution into a 125-ml. Erlenmeyer flask, add 4 ml. of 2 *N* sodium hydroxide, cover with a small beaker, and autoclave for 30 minutes at 6.8 kg. (15 pounds). Cool, add distilled water, adjust the pH to 6.0 with 2 *N* and 0.1 *N* hydrochloric acid, and dilute to 1 liter. Avoid excess acid during the pH adjustment to prevent lactonization of pantoic acid.

To the residue in the standard extraction flask, add 2.5 ml. of water and 2.5 ml. of 2 *N* sodium hydroxide, autoclave as above, and dilute to 500 ml. at pH 6.0.

If pantoic acid is expected to be present—i.e., in stability tests of products at pH above 4.7—dilute an aliquot of the aqueous solution after extraction to an estimated free pantoic acid concentration of about 0.2 microgram per ml. at a pH of 6.0.

Determine pantoic acid by the following microbiological procedure in the hydrolyzed standard (both aqueous and ether phases) and in the hydrolyzed and unhydrolyzed unknown solutions after ether extraction.

MICROBIOLOGICAL ASSAY PROCEDURE

Acetobacter suboxydans. Maintain the organism (No. 621 H in the American type culture collection) on slants containing 5% mannitol, 0.5% yeast extract, 0.3% peptone, and 1.5% agar. Incubate the slants at 30° for 60 to 70 hours, then keep in the refrigerator. Prepare new stock slants monthly. If the sensitivity of the organism decreases on repeated transfers from slant to slant, make new slants from a culture that has been transferred through the inoculum broth at least four times.

Test Inoculum. The test inoculum is obtained from a 24-hour culture grown at 30° in an Evelyn tube with continuous shaking in 10 ml. of 1 to 1 diluted basal medium with the Casitone omitted and the acid-hydrolyzed casein increased tenfold. Add 0.1 microgram of pantoic acid and 5 mg. of 1 to 20 liver concentrate (Wilson's paste or powder) per 10 ml. of inoculum broth. Transfer cultures from two tubes to a sterile test tube, centrifuge at least 30 minutes, and resuspend in 10 ml. of sterile saline. This suspension should have an Evelyn reading of about 20 (water = 100) with a 660 mμ filter. For use on successive days make transfers from broth to broth. At least sixty such successive transfers have been used successfully. Broth cultures may be stored at least one day in the refrigerator before use.

Basal Medium. The ingredients of the double-strength basal medium are given in Table I. This is a modification of Sarett and Cheldelin's (*12*) medium as shown.

The Norit A–treated Casitone is prepared as follows: Dissolve 100 grams of Bacto-Casitone (Difco Laboratories, Inc., Detroit, Mich.) in water by stirring, dilute to 1 liter, steam for 10 minutes, and cool. Adjust the pH to 1.5 with concentrated hydrochloric acids, shake for 20 minutes with 70 grams of Norit A, and filter. Readjust the pH to 1.5 and repeat the charcoal treatment. Adjust the pH of the second filtrate to 6.0, steam, cool, and filter. Store in refrigerator under toluene.

Assay Conditions. Into duplicate Evelyn tubes pipet aliquots of standard pantoic acid solution ranging from 0 (4 tubes) to 5 ml. at 0.5-ml. intervals—i.e., at pantoic acid levels of 0 to 1.0 microgram. Set up a similar, single series of tubes for each unknown, omitting the blanks. Add sufficient water to each tube to bring the volume to 5 ml. and add 5 ml. of basal medium (Table I) to each tube. Plug all tubes and autoclave for 15 minutes at 6.8 kg. (15 pounds). Cool at once and inoculate all but two blank tubes with exactly one drop of the inoculum suspension of *Acetobacter suboxydans* from a syringe. Shake all tubes for 20 to 24 hours at 30° and measure growth turbidimetrically in the Evelyn colorimeter with a 660 mμ filter, using the uninoculated blanks to set the instrument at 100.

As an alternative procedure, the assay may be set up in 50-ml. Erlenmeyer flasks without shaking. Incubate a stationary inoculum for 30 to 40 hours. For turbidity readings of the assay after at least 40 hours, swirl each flask vigorously, pour contents into an Evelyn tube, and measure the turbidity as above, but with the 6-ml. aperture of the colorimeter. Do not stopper and shake the flasks before reading, as some clumping of the organisms will occur.

CALCULATIONS

Plot the standard curve on semilog paper with galvanometer readings on the logarithmic scale and micrograms of pantoic acid on the linear scale. This is equivalent to plotting optical density $(2 - \log G)$ against micrograms of pantoic acid on linear coordinate paper. Typical standard curves for both an assay shaken in tubes and a stationary assay in flasks are shown in Figure 1. Read the individual unknown points from the standard curve and calculate average potency in the usual manner.

Table I. Basal Media for Pantoic Acid Assay

	Medium of Sarett and Cheldelin (*12*)	Present Medium
	Grams	*Grams*
Glycerol	100	100
Glucose	5	5
Acid-hydrolyzed casein	10	2
Norit A-treated peptone	5	0
Norit A-treated liver concentrate (Wilson's 1:20)	2	0
Norit A-treated Casitone (Difco)	0	10
Sodium citrate	0	2
	Mg.	*Mg.*
Untreated liver concentrate (Wilson's 1:20)	...	40
Tryptophan	200	200
Cystine	150	150
Adenine	10	10
Guanine	10	10
Uracil	10	10
β-Alanine	2	2
Nicotinic acid	0.2	2
p-Aminobenzoic acid	0.2	2
Thiamine	...	2
Riboflavin	...	2
Pyridoxine	...	2
	γ	γ
Folic acid	...	20
Biotin	...	16
	Ml.	*Ml.*
Salt solution A (*13*)	10	10
Salt solution B (*13*)	10	...
Salt solution C (*8*)	...	20
Lactic acid	...	0.6
Tween 80	...	2
Distilled water to 1 liter at pH 6.0		

Table II. Relative Activity for Growth of *Acetobacter suboxydans*

	Weight Basis	Molar Basis
	%	%
Pantoic acid	100	100
Pantothenic acid	50–85	70–120
Pantoyl lactone		
Autoclaved 15 min.	18	16
Autoclaved 60 min.	63	55
Filtered aseptically[a]	0.5–0.6	0.4–0.5
Panthenol	1–2	1.4–2.8

[a] Filtered through ultrafine sintered-glass bacterial filters.

A = micrograms of pantoic acid per ml. after hydrolysis
B = micrograms of pantoic acid per ml. before hydrolysis
D_A = dilution factor for solution after hydrolysis
D_B = dilution factor for solution before hydrolysis
(D_A and D_B = ml. of final dilution per unit of test product)
1.385 = molecular weight ratio (panthenol/pantoic acid)
0.017 = ratio of activity in pantoic acid assay (panthenol/pantoic acid)

$$\frac{(A \times D_A) - (B \times D_B)}{1 - 0.017} \times \frac{1.385}{1000} = \text{mg. of panthenol per unit of test product}$$

EXPERIMENTAL

Because the relative activity of panthenol in promoting the growth of *Acetobacter suboxydans* under the usual assay conditions is small compared to that of pantoic acid and pantoyl lactone (cf. Table II), it is obvious that even low concentrations of the latter two will interfere with a direct assay of panthenol. Hence, it is necessary to measure panthenol as pantoic acid after complete alkaline hydrolysis. If preformed pantoic acid is the only interfering substance, it may be determined by assay before hydrolysis. The presence of pantoyl lactone, however, invalidates such a correction and necessitates a separation of panthenol from the lactone.

The possibility of a quantitative separation of panthenol and pantoyl lactone by means of solvent extraction was first investigated by distribution studies involving optical rotation measurements. Methyl isobutyl ketone and ethyl ether gave distributions which were favorable for a separation, but the ethyl ether was selected because of its much lower boiling point, which permits greater ease of handling in continuous extraction apparatus. In a single extraction of a 2% aqueous solution of pantoyl lactone with an equal volume of ethyl ether (both solvents previously saturated), 22.7% of the lactone passed into the ether phase. In a similar extraction of panthenol, the amount found in the ether phase was of the order of 0.5%, although the exact value was not determined because of the small differences in rotations involved. These data indicated the possibility of a separation by repeated extraction, but, because multiple extractions in separatory funnels are laborious and time-consuming and may lead to mechanical losses of solvents, continuous extraction was adopted.

Extraction of 20-ml. aliquots of aqueous solutions of pantoyl lactone at graded levels containing the equivalent of 0.2 to 5 mg. of pantoic acid was found to be essentially complete (99.5%) after 1.5 hours in all cases, as determined by assay of the aqueous phase. Parallel assays of the ether phase, however, did not show the expected levels of lactone but indicated losses in some cases up to 25%. On the theory that such losses might be the result of an oxidative reaction, similar extractions were carried out with 25 mg. of ascorbic acid added to both the aqueous and ether phases before extraction. With this addition, it was found possible to achieve recoveries of 96 to 100% of the lactone in the ether extracts.

To determine the percentage extraction of panthenol under the same conditions, a similar series of experiments was carried out with solutions containing panthenol equivalent to 0.8 to 5 mg. of pantoic acid. Assays of the ether extracts of 15 such solutions after alkaline hydrolysis showed an average extraction of 8.6 ± 1.7% (S.D.) with no trend toward differences among the various levels of panthenol. Parallel assays of the aqueous solutions after extraction showed an average retention of 92 ± 2.8% (S.D.) of the panthenol. These data indicate a quantitative over-all recovery of panthenol. Similar tests with aqueous solutions of several freshly prepared, multivitamin preparations containing panthenol showed the other constituents, including solubilizers such as Tween 80, to have little or no effect on the percentage extraction of panthenol. The addition of potassium chloride at levels as high as 16% did not affect the recovery in the aqueous phase by more than 2%.

To test the efficiency of the ether extraction as a means of

separation of panthenol and pantoyl lactone, known mixtures with varying proportions of these two compounds were prepared in aqueous solution and assayed for panthenol (after ether extraction of the lactone and alkaline hydrolysis of the panthenol remaining in the aqueous solution). The results, given in Table III, show clearly the reliability of the procedure for determining panthenol in the presence of pantoyl lactone, even at concentrations of the latter much higher than would normally be encountered.

To determine whether the method would be equally satisfactory when applied to multivitamin solutions, particularly those in which panthenol has undergone partial hydrolysis, experiments such as those shown in Table IV were carried out. Because the stability of panthenol is such that the rate of hydrolytic cleavage under normal storage conditions and even during accelerated aging tests is slow, this solution was acidified to pH 2 with concentrated hydrochloric acid and heated at 45° C. in order to accelerate the breakdown of panthenol. Under these acid conditions the product of hydrolysis is pantoyl lactone. Assays by the present microbiological procedure were compared with rapid bioassays in rats by the excretion method (*3*). As shown in Table IV, satisfactory agreement was achieved regardless of the degree of hydrolysis of the panthenol.

The specificity of the present method for measuring panthenol in the presence of both pantoic acid and pantoyl lactone was further tested by experiments such as those shown in Table V. Pantoic acid and pantoyl lactone were added in various known proportions to two multivitamin solutions containing panthenol, and the latter was determined by the present procedure. Quantitative recoveries of panthenol were obtained in all samples within the normal limits of a microbiological assay method. The acid-hydrolyzed samples are included as examples of solutions that have undergone appreciable decomposition.

DISCUSSION

Attempts to extract pantoyl lactone from pantothenic acid in aqueous solution with ethyl ether have been reported by Sarett and Cheldelin (*12*), but these authors experienced incomplete recoveries in the ether extracts. In the present study similarly, incomplete and variable recoveries of the lactone were obtained in the ether phase after extraction, but this was found to result from partial destruction of the lactone rather than from incomplete extraction from the aqueous solution. Such losses are similar to those observed in ether extraction of 3,3-diethyl-2,4-diketotetrahydropyridine (*2*). In both cases, the addition of ascorbic acid prior to heating the ether prevents or minimizes the losses, indicating that the reactions involved are probably oxidative. To determine the completeness of extraction of the lactone, therefore, it has been necessary to assay the water phase after extraction and alkaline hydrolysis.

The time and rate of ether extraction in the present method have been found sufficient for complete extraction of pantoyl lactone. Because the rate of extraction of panthenol is low, and a valid and reproducible correction for the extracted panthenol can be had by extraction of a standard solution, it has not been deemed advisable to shorten the extraction period further. The possibly incomplete extraction of pantoyl lactone in a shorter time is a much greater potential source of error than a slight variation in panthenol recovery. With standardized extraction conditions, it has been found feasible to determine an average panthenol recovery in the ether extracts. This value can be determined with greater precision by assay of the ether extracts than the aqueous, standard panthenol solution. An unextracted standard may then be hydrolyzed directly for the microbiological assay, and the average recovery value introduced as a correction factor in the calculation of results. As an alternative to the use of standard panthenol for direct hydrolysis, an equivalent amount of either calcium pantothenate or pantoyl lactone can be used.

Attempts in this laboratory to apply the medium of Sarett and Cheldelin (*12*) in the pantoic acid assay did not yield suitable growth curves with *Acetobacter suboxydans*. Introduction of the modifications shown in Table I, however, gave better growth curves routinely (Figure 1) with good agreement between duplicates. Although the reasons for the poor response with the original medium are not entirely apparent, they may be related to possible differences in natural constituents such as the Norit A-treated liver and peptone, or to variations among the bacterial strains. The fact that several cultures obtained from various sources behaved similarly in this laboratory on the two media argues against the latter possibility. Although Sarett and Cheldelin's medium (*12*) supplies all the growth requirements reported by Underkofler *et al.* (*16*) for *Acetobacter suboxydans*, it did not give graded growth in this laboratory with graded amounts of pantoic acid. The addition of untreated liver concentrate caused a marked improvement in the shape of the growth curves, evidently providing an additional factor or factors which make the pantoic acid concentration the limiting growth factor and, hence, provide the desired graded response thereto. The inclusion of enzyme-digested casein (Casitone) shortens materially the time required to reach suitable growth levels. This stimulation by an enzyme digest of casein may be a strepo-

Table III. Assay of Known Mixtures of Panthenol and Pantoyl Lactone in Aqueous Solution

(All values in terms of equivalent amounts of pantoic acid in 20-ml. aliquot taken for extraction)

Panthenol Added *Mg.*	Pantoyl Lactone Added *Mg.*	Panthenol Found *Mg.*	Recovery %
1.0	0.20	1.05	105
	0.40	1.00	100
	0.60	1.02	102
	0.80	1.03	103
	1.00	0.97	97
5.0	1.0	4.9	98
	2.0	4.8	96
	3.0	5.3	106
	4.0	5.1	102
	5.0	5.0	100

Table IV. Comparison of Microbiological Assays and Excretion Bioassays

(Panthenol in multivitamin solution at pH 2.0 and 45° C.)

Days at 45° and pH 2.0	Microbiological Assay *Mg./ml.*	Excretion Bioassay *Mg./Ml.*	Microbiological/Bioassay × 100 %
0	3.8	4.0	95
1	3.5	3.6	97
2	3.3	3.4	97
3	3.0	3.0	100
5	2.7	2.8	97
8	2.5	2.5	100
12	2.2	2.2	100
16	2.0	2.0	100
20	1.8	1.9	95
		Mean	98

Table V. Microbiological Assay of Panthenol in Presence of Pantoic Acid and Pantoyl Lactone

(All content values expressed as milligrams of panthenol per ml.)

Multivitamin Solution	Known Content: Panthenol	Pantoic acid	Pantoyl lactone	Panthenol Found	Recovery, %
A. Initial	4.5	0.6	0.3	4.6	102
	4.5	1.2	0.3	4.4	98
	4.5	1.0	3.0	4.3	96
	4.5	2.0	2.0	4.3	96
Acid hydrolyzed	1.84	1.54	2.66	1.78	97
B. Initial	4.8	0.3	0.6	5.1	106
	4.8	0.4	1.4	4.6	96
	4.8	0.9	2.6	4.8	100
	4.8	1.0	4.0	4.7	98
Acid hydrolyzed	2.5	2.3	2.3	2.5	100

genin effect similar to that described by Sprince and Woolley (*14*) and Wright and Skeggs (*19*) for a variety of other bacteria.

Differences in the sensitivity of response to pantoic acid have been observed, however, with different cultures. These variations appear to be associated with the time of incubation required for attainment of suitable levels of growth. As previously noted, a decrease in the growth rate has been observed after repeated serial transfers of the culture from slant to slant. The concomitant increase observed in the relative activity of pantothenic acid as compared to pantoic acid appears to indicate that this effect is due to a decrease in the efficiency of the organism in synthesizing pantothenic acid from the latter.

With the present culture carried as directed, the use of a heavy inoculum (G = 15 to 20), plus the modified medium, has permitted shortening the time of incubation in stationary flasks from 60 to 40 hours. The use of continuous shaking in Evelyn tubes during incubation permits assays in 20 to 24 hours. Inclusion of Tween 80 in bacterial media was reported by Dubos and Davis (*4*) to enhance the rate and abundance of growth of tubercle bacilli and has been applied extensively with other organisms (*6*). The stimulatory effect of the lactate is similar to that observed by Tosic (*15*), who attributed it to the buffering effect of the bicarbonate formed from the lactate during growth of *Acetobacter turbidans*.

SUMMARY

A microbiological procedure is described which permits assay of panthenol, the biologically active hydroxy analog of pantothenic acid, in the presence of pantoyl lactone as well as pantoic acid. The lactone is removed quantitatively from water solution by continuous extraction with ethyl ether for 1 to 2 hours. Panthenol in the aqueous residue is then hydrolyzed to pantoic acid for microbiological assay with *Acetobacter suboxydans*. Assay before hydrolysis provides a correction for preformed pantoic acid and a partial correction for pantothenic acid. Hence, small percentages of pantothenic acid (up to 10%) will not seriously affect the specificity of the panthenol assay. By modification of the assay medium of Sarett and Cheldelin and by setting up the assay in Evelyn tubes with continuous shaking, the incubation time has been shortened to 20 to 24 hours. Good agreement with bioassays in rats has been demonstrated.

ACKNOWLEDGMENT

Many of the early exploratory trials were carried out by J. M. Cooperman and J. M. Scheiner. M. Weiss and Miss I. Kellermann performed many of the later microbiological experiments. The rat bioassays were done by Miss R. Pankopf and I. Korman.

LITERATURE CITED

(1) Burlet, E., *Z. Vitaminforsch.*, **14**, 318 (1944).
(2) De Ritter, E., Jahns, F. W., and Rubin, S. H., *J. Am. Pharm. Assoc.*, in press.
(3) Drekter, L., Drucker, R., Pankopf, R., Scheiner, J., and Rubin, S. H., *Ibid.*, **37**, 498 (1948).
(4) Dubos, R. J., and Davis, B. D., *J. Exptl. Med.*, **83**, 409 (1946).
(5) Frost, D. V., Ind. Eng. Chem., Anal. Ed., **15**, 306 (1943).
(6) Glassman, H. N., *Bact. Rev.*, **12**, 105 (1948).
(7) Pfaltz, H., *Z. Vitaminforsch.*, **13**, 236 (1943).
(8) Roberts, E. C., and Snell, E. E., *J. Biol. Chem.*, **163**, 499 (1946).
(9) Rubin, S. H., *J. Am. Pharm. Assoc.*, **37**, 502 (1948).
(10) Rubin, S. H., Cooperman, J. M., Moore, M. E., and Scheiner, J., *J. Nutrition*, **35**, 499 (1948).
(11) Rubin, S. H., Scheiner, J., and Hirschberg, E., *J. Biol. Chem.*, **167**, 599 (1947).
(12) Sarett, H. P., and Cheldelin, V. H., *Ibid.*, **159**, 311 (1945).
(13) Snell, E. E., and Strong, F. M., Ind. Eng. Chem., Anal. Ed., **11**, 346 (1939).
(14) Sprince, H., and Woolley, D. W., *J. Am. Chem. Soc.*, **67**, 1734 (1945).
(15) Tosic, J., *Biochem. J.*, **40**, 209 (1946).
(16) Underkofler, L. A., Bantz, A. C., and Peterson, W. H., *J. Bact.*, **45**, 183 (1943).
(17) Walter, M., *Jubilee Vol., Emil Barell* (Hoffmann-LaRoche, Inc., Basle) **1946**, 98.
(18) Walter, M., *Z. Vitaminforsch.*, **18**, 228 (1947).
(19) Wright, L. D., and Skeggs, H. R., *J. Bact.*, **48**, 117 (1944).

Received November 17, 1948. Presented before the Division of Biologica Chemistry at the 114th Meeting of the American Chemical Society, Washington, D. C. Publication 158.

Microdetermination of Carbon and Hydrogen

FRIEDRICH O. FISCHER[1]
Chemical Institute, University of Heidelberg, Heidelberg, Germany

A modification of the proved Pregl micromethod for carbon and hydrogen employs a fully automatic combustion procedure applicable to micro-sized samples of materials of widely varying combustion characteristics. The values obtained are more accurate than the usually accepted ± 0.3% absolute. With 10- to 20-mg. samples and semiautomatic operation, an accuracy of ±0.02% absolute can be attained; this furnishes a method of high accuracy requiring relatively small amounts of sample for such difficult problems as the determination of the constitution of high molecular weight compounds.

PREGL'S micromethod (*10*) has undergone development in three directions: The sample size has been decreased (*2, 9*), the combustion has been made automatic (*4, 5, 11, 13, 16*), and the precision and accuracy have been increased (*3, 6–8*). In the absence of a practicable ultramicrobalance the first and third are mutually exclusive; higher accuracy requires larger amounts of sample. A completely automatic combustion procedure can be recommended fully for routine microdeterminations. It considerably relieves the analyst and gives more uniform results. But where higher accuracy is required and a larger quantity of sample is to be burned, a completely automatic procedure is applicable only when the combustion characteristics of the substance in question have been determined. A semiautomatic procedure is useful in other cases. It is less tedious and leads to more accurate results than can be obtained by manual operation. By using a modification of the Pregl microprocedure, an automatic or semiautomatic combustion, and 10- to 20-mg. samples, it has been found possible to obtain values within ±0.02%. This increase in sample size is small compared to requirements for macroprocedures (*1, 12, 14, 15*) or to amounts needed to carry out a number of microdeterminations for the purpose of obtaining a more accurate average value.

[1] Present address, Schröderstrasse 6, Heidelberg, Germany.

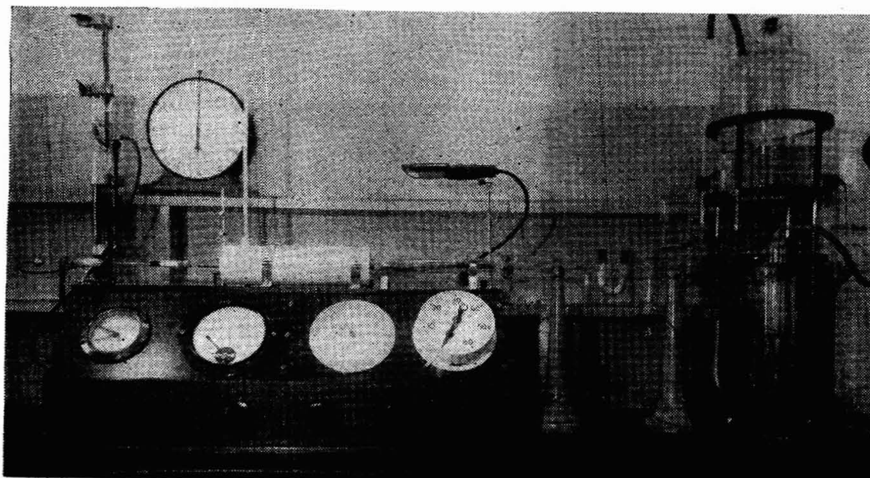


Figure 1. Apparatus

The connection of the combustion tube with the water tube, the most delicate point of the whole apparatus, must be formed in a way to permit the larger amounts of water vapor and carbon dioxide to pass without loss. Replacing the usual rubber connection with a good ground joint accomplishes this and eliminates those errors introduced by improper lubrication of the rubber and the wiping of the absorption tubes before each weighing. The absorption tubes are wiped only before the beginning of a combustion series and after that are handled with chamois gloves and cork plate pincers. When stoppered, the tubes are constant in weight.

To ensure the complete combustion of larger samples, a more active filling of the combustion and absorption tubes can be attained by increasing the surface and activity of the reagents. Appreciable increase in the quantity of reagents, the dimensions of Pregl's apparatus, or the quantity or velocity of gas flow results in an increase in the magnitude of the inherent errors.

Even in the presence of copper oxide an excess of oxygen is essential. The new automatic apparatus causes the slow vaporization of the sample far below its boiling point, and thus ensures excess oxygen.

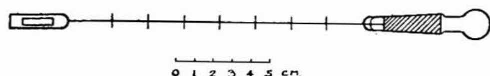


Figure 2. Platinum Tube

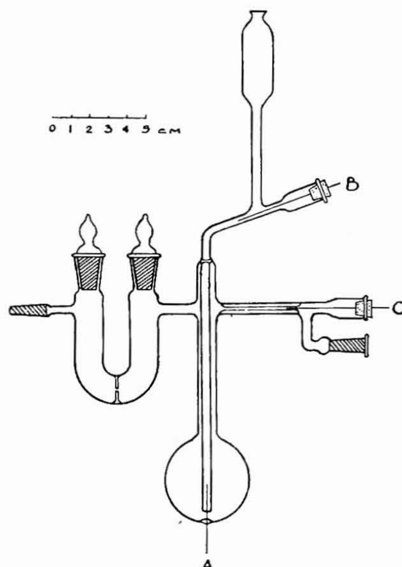


Figure 3. Pressure Regulator

APPARATUS

Balance. Variations in the zero points of the microbalances were largely eliminated by keeping them in an air-conditioned room and by placing aluminum plates (300 × 210 × 25 mm.) in the interior of the cases. The rider and all the weights were made of aluminum and the tare bottles were filled with glass beads. These materials were chosen because their densities were nearer the densities of the samples to be weighed than the heavy metals. Only when the density of the sample differed significantly from that of aluminum were vacuum corrections applied. A significant variation in air density between weighings is not as likely in micro as in macro work because of the shorter lapse of time. The rider and weights were carefully intercalibrated.

Combustion Furnace and Constant-Temperature Chamber. The combustion furnace and constant-temperature chamber, separated by 20 mm. of asbestos, are placed in a porcelain tube 250 mm. long and 70 mm. in diameter (Figure 1.) This is mounted on a Pertinax box which contains all the instruments for control of temperature and automatic regulation—voltage regulators, contact thermometer relay, and rheostats. A voltmeter, ammeter, time switch, and microchronometer are mounted on the front of the box.

Depending on the constancy of the current supply, the constant-temperature chamber is controlled by a simple voltage regulator or contact thermometer. The constant-temperature chamber is made of aluminum and is 60 mm. long and 35 mm. in diameter. There is a central bore for the combustion tube and a parallel bore 8 mm. in diameter for the contact thermometer. The relay does not break the whole circuit but rather short-circuits a small rheostat when the temperature falls below that required.

The constant-temperature chamber and the combustion furnace are connected in series, so that the temperature of the combustion furnace is controlled simultaneously with that of the constant-temperature chamber.

Absolute temperatures are not so important as constancy of temperature. The constant-temperature chamber is operated at about 200° C. and the furnace at about 700° C. The constant-temperature chamber should be held constant within 0.5° C. and the furnace within 2° C.

The combustion tube (Figure 4) is made of Supremax glass and fitted with polished standard-taper ground joints. The pipet-shaped enlargement, 100 mm. long and 22 mm. in diameter, provides space for the sample vapors to mix well with oxygen before entering the combustion zone proper and for substances that detonate.

The combustion tube is held firmly by clamps (Figure 1), so it

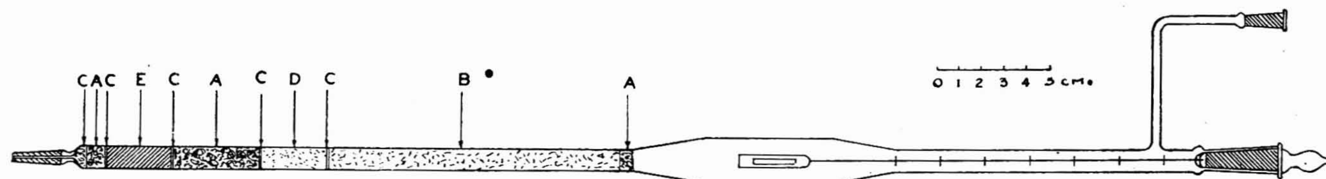


Figure 4. Combustion Tube

A. Silver wool *B.* Copper oxide *C.* Asbestos *D.* Lead chromate *E.* Lead dioxide

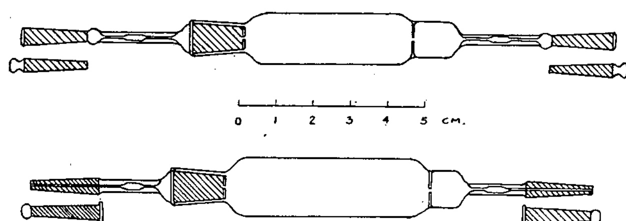


Figure 5. Absorption Tubes

cannot be displaced by removal of the stopper or by the steel spring that holds the absorption tubes in place.

A platinum tube (Figure 2) 7 mm. in diameter and 30 mm. long is fastened to the stopper by a platinum wire 170 mm. long and 1.5 mm. in diameter. The platinum boat or glass capillary is placed in this tube. A window, the size of the platinum boat, is cut in the tube, so the sample can be watched during heating. Seven circular platinum plates, fastened to the platinum wire normal to its axis, divide the back of the combustion tube into seven chambers and prevent the back-diffusion of vapors.

Starting at the furnace and extending 220 mm. toward the stopper (Figure 1) the combustion tube is wound with a chrome-nickel heating tape in such a way as to allow good observation of the sample between the windings. The windings are held in place on the underside of the combustion tube by an asbestos-potassium silicate putty. This wound section is surrounded by a Supremax tube 220 mm. long and 24 mm. in inside diameter.

Automatic Vaporization Apparatus. The automatic vaporization apparatus consists of the pressure regulator (Figure 3) and a circular rheostat driven by an electric motor through a reduction gear. The manometer of the pressure regulator is filled with slightly acidified water and the U-tube with phosphorus pentoxide on pumice, asbestos, and Ascarite. *A* and *B* are platinum contacts. *C* is a steel wire for narrowing the capillary and thus adjusting the sensibility. The rheostat is connected into the circuit of the heating tape. The motor turns the rheostat slowly, decreasing the resistance, thus causing a constantly rising temperature within the vaporization zone. The rate of increase can be regulated further by controlling the speed of the motor with a potentiometer connected into the circuit of the armature coil. A commutator, connected in like manner, permits reversal of the direction of the motor should the sample vaporize too rapidly. The regulation of the speed of the motor and the proportion of the reduction gear should be chosen so that the resistance is cleared in 3 minutes at high speed and in 2 hours at slow speed. The rise in temperature in the vaporization zone should be about 6° C. per minute at low speed. The rheostat is wound with resistance wire of different diameters in such a way as to obtain a linear rise of temperature. A circular rheostat without stops was chosen because it returns to its initial position. A pointer mounted on the axis of the rheostat indicates on a scale the temperature within the vaporization zone at any position of the rheostat.

The vaporization unit can be used in an entirely automatic manner for routine microdeterminations or for precision determinations where the combustion characteristics of the given material are known. When the vaporization is too rapid the pressure regulator acting through a relay turns off the heating system, and, through the commutator, reverses the motor so that the resistance is increased. It remains thus until the excess pressure has been dissipated. If the pressure regulator is adjusted to a high sensibility, this play continues for some time and until the sample is slowly vaporized and burned.

For the precision determination where the combustion characteristics of the material are not known the apparatus is used in a semiautomatic manner by varying the speed of the motor as needed. The art of combustion consists in burning the sample very slowly, allowing it to vaporize far below its boiling or sublimation point. When the pressure in the pressure regulator has considerably decreased, the motor speed is increased, and the vaporization zone brought to red heat.

Liquids are weighed in capillaries of larger than usual size. When the air bubble in the half-filled capillary is heated, the liquid is expelled below its boiling point. In order to obtain a gradual mixing of the vapors with oxygen, the capillary is first put into a quartz tube 35 mm. long and 4 mm. in inside diameter. This is filled up with quartz wool and then introduced, inverted, into the platinum tube.

Hygroscopic samples are weighed in bottles with ground-in stoppers, preferably made of quartz, which are introduced directly into the platinum cylinder.

Filling. The combustion tube filling (Figure 4) consists of the reagents used by Pregl (*10*) but they are much more finely divided and have more effective surfaces.

Copper oxide is formed in the combustion tube. Pure electrolytic copper wire 0.05 mm. in diameter is cut into pieces 5 mm. long. It is washed with benzene, alcohol, and ether and, after drying, is stuffed into the combustion tube compactly. Its complete oxidation takes 12 to 15 hours. The resistance to gas flow is not seriously increased by this transformation. It is not advisable to carry out the oxidation in a separate tube and transfer the copper oxide because the thin pins break too easily.

Silver is used in the form of a very fine wool, and the lead chromate is used in fine grains.

The increase in surface is attended by an increase in the hygroscopicity of the filling. For this reason, not only the lead dioxide but also the rest of the filling must be held at constant temperature; the combustion tube must be closed immediately after each analysis.

Exact hydrogen values can be obtained in the presence of lead dioxide if the temperature and the amount and velocity of the gases passed through it are held constant, and if materials of widely different hydrogen content are not burned consecutively.

Absorption Tubes. The absorption tubes used by Pregl (*10*) were modified slightly in dimensions and provided with ground joints (Figure 5). The joints must not be lubricated, but are ground in with fine emery powder and then polished with rouge in turpentine. (All ground joints on the apparatus are treated in this manner.)

The water tube is made preferably of Supremax glass, so the parts of the joint connecting the water and combustion tubes will have the same coefficient of expansion. The filling is phosphorus pentoxide on pumice. The carbon dioxide tube is filled with Ascarite followed by a short layer of phosphorus pentoxide on pumice, separated by asbestos.

The absorption tubes are held together and to the combustion tube by a single steel spring (Figure 1). To prevent condensation of the larger amounts of moisture, a semicylindrical heater 40 mm. long, cut from a copper tube 7 mm. in diameter, extends from the constant-temperature chamber under the joint and capillaries of the water tube (Figure 1).

If the absorption tubes have capillaries of standard length and not more than 0.2 mm. in inside diameter, and if they are capped (stoppered), they are absolutely constant in weight.

Mariotte Bottle. A modified Mariotte bottle is shown in Figure 6. The 200-cc. measuring cylinders are arranged one above the other (Figure 1) on a rod which can be rotated. By simply changing over the rubber tubing and inverting, it is ready for the next analysis.

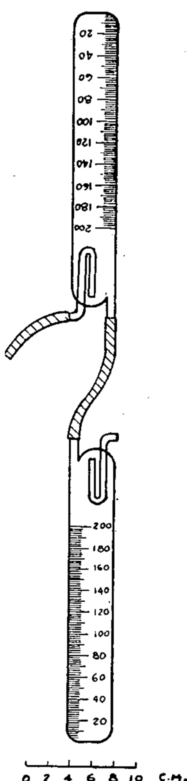


Figure 6. Modified Mariotte Bottle

To obtain accurate hydrogen values, especially when the humidity is high, it is necessary to operate the air supply separate from the oxygen and to pass it through a large drying tower containing Ascarite and phosphorus pentoxide on pumice. The air passes too slowly through the capillary of the pressure regulator (Figure 3). A rapid flow of dry air must stream from the combustion tube when it is opened to

Table I. Analytical Results on Five Compounds

	Sample Mg.	H_2O Mg.	CO_2 Mg.	C %	H %	Theory C %	Theory H %	Deviation C %	Deviation H %
Fluorene	10.593	5.757	36.460	93.928	6.082	93.935	6.065	−0.007	+0.017
	11.235	6.086	38.665	93.914	6.062			−0.021	−0.003
	15.318	8.312	52.721	93.925	6.073			−0.010	+0.008
	14.215	7.717	48.928	93.930	6.075			−0.005	+0.010
			Av.	93.924	6.073			−0.011	+0.008
Benzil	17.863	7.694	52.347	79.970	4.820	79.983	4.795	−0.013	+0.025
	17.431	7.500	51.084	79.976	4.815			−0.007	+0.020
	14.320	6.158	41.975	79.990	4.812			+0.007	+0.017
	15.195	6.532	44.548	80.005	4.811			+0.022	+0.016
			Av.	79.985	4.814			+0.002	+0.019
Salicylic acid	14.993	5.842	33.437	60.860	4.361	60.868	4.379	−0.008	−0.018
	14.150	5.573	31.575	60.893	4.408			+0.025	+0.029
	19.754	7.692	44.046	60.847	4.358			−0.021	−0.021
	15.851	6.207	35.340	60.841	4.382			−0.027	+0.003
			Av.	60.860	4.377			−0.008	−0.002
Acetanilide	12.133	7.265	31.612	71.100	6.701	71.085	6.713	+0.015	−0.012
	13.137	7.878	34.215	71.073	6.711			−0.012	−0.002
	12.704	7.630	33.088	71.075	6.721			−0.010	+0.008
	13.120	7.890	34.172	71.077	6.730			−0.008	+0.017
			Av.	71.081	6.716			−0.004	+0.003
p-Nitrobiphenyl	12.666	5.176	33.584	72.357	4.573	72.349	4.555	+0.008	+0.018
	15.235	6.219	40.386	72.340	4.568			−0.009	+0.013
	16.194	6.601	42.936	72.352	4.562			+0.003	+0.007
	14.718	6.012	39.025	72.357	4.571			+0.008	+0.016
			Av.	72.351	4.568			+0.002	+0.013

C = 12.010.
H = 1.008.

Table II. Automatic Analyses of Micro Samples

	Sample Mg.	H_2O Mg.	CO_2 Mg.	C %	H %	Theory C %	Theory H %	Deviation C %	Deviation H %
Benzene	4.235	2.94	14.31	92.21	7.77	92.25	7.75	−0.04	+0.02
	4.550	3.14	15.37	92.18	7.72			−0.07	−0.03
	5.124	3.57	17.33	92.30	7.79			+0.05	+0.04
	5.655	3.93	19.12	92.27	7.78			+0.02	+0.03
			Av.	92.24	7.77			−0.01	+0.02
Salicylic acid	5.215	2.05	11.64	60.91	4.40	60.87	4.38	+0.04	+0.02
	5.944	2.37	13.26	60.88	4.46			+0.01	+0.08
	4.593	1.81	10.24	60.84	4.41			−0.03	+0.03
	4.458	1.77	9.95	60.91	4.44			+0.04	+0.06
			Av.	60.89	4.43			+0.02	+0.05
Acetanilide	3.976	2.39	10.35	71.04	6.73	71.09	6.71	−0.05	+0.02
	4.644	2.78	12.10	71.10	6.70			+0.01	−0.01
	5.271	3.19	13.74	71.14	6.77			+0.05	+0.06
	5.629	3.39	14.67	71.12	6.74			+0.03	+0.03
			Av.	71.10	6.74			+0.01	+0.03
Picric acid	4.345	0.53	5.01	31.47	1.37	31.45	1.32	+0.02	+0.05
	6.810	0.82	7.86	31.50	1.35			+0.05	+0.03
	4.585	0.57	5.27	31.37	1.39			−0.08	+0.07
	6.223	0.78	7.18	31.49	1.40			+0.04	+0.08
			Av.	31.46	1.38			+0.01	+0.06
Pyridine perchlorate	6.344	1.95	7.78	33.47	3.44	33.44	3.37	+0.03	+0.07
	5.557	1.70	6.80	33.40	3.42			−0.04	+0.05
	7.292	2.21	8.94	33.46	3.39			+0.02	+0.02
	5.152	1.59	6.32	33.47	3.45			+0.03	+0.08
			Av.	33.45	3.42			+0.01	+0.05

prevent introduction of moist room air. (One cubic centimeter of air at 22° C. and a relative humidity of 70% contains 0.014 mg. of water.)

If oxygen and air are not available in requisite purity, a preheater must be used.

The pressure conditions described by Pregl (*10*) are essential for the proper operation of the pressure regulator of the automatic combustion unit. To prevent loss at the connections slight excess suction is applied during the combustion. The air is delivered at higher pressure (greater speed) but it is not necessary to readjust the Mariotte bottle because by this time the concentrations of water and carbon dioxide in the gas stream are very small.

The combustion proper takes 15 to 20 minutes. The rate of oxygen flow is 5 cc. per minute. Air is delivered at a rate of 8 to 10 cc. per minute and 140 to 150 cc. are used. Pregl's weighing procedure (*10*) is followed. A single determination takes about one hour and serial determinations take 45 to 50 minutes.

Precision analytical results for five organic compounds are given in Table I. Routine results on micro samples where fully automatic operation was employed are given in Table II. Even substances which are very volatile, or sublime, or detonate can be burned automatically.

A great number of carbon and hydrogen microdeterminations in various types of organic compounds were performed manually and automatically. The results obtained by the automatic procedure were always as accurate as those obtained manually and usually were more accurate. In the case of very volatile materials and those which sublime, the automatic procedure described above proved much superior to manual operation or the type of automatic combustion employing a small motor-driven furnace.

The automatic procedure described in this paper differs from many others so designated in that the heating rate is controlled directly by the combustion characteristics of the sample rather than by a prearranged schedule set by an operator. The speed of the motor is so adjusted that full temperature will be reached in 15 minutes. If this is too fast the pressure regulator interrupts the heating for a short time. In the precision procedure where larger samples are burned the method becomes semiautomatic in that the operator adjusts the speed of the motor, and thus the rate of increase of temperature, according to the volatility of the sample. The automatic features make the work of the operator easier and, more important, the results obtained are more accurate.

LITERATURE CITED

(1) Baxter, G. P., and Hale, A. H., *J. Am. Chem. Soc.*, 58, 510 (1936).
(2) Berraz, G., *Anales Soc. Ciént. Argentina, Sección Santa Fé*, 9, 9 (1937).
(3) Boetius, M., "Über die Fehlerquellen der mikroanalytischen Bestimmung von C und H nach der Methode von Pregl," Berlin, Verlag Chemie, 1931.
(4) Clark, R. O., and Stillson, G. H., Ind. Eng. Chem., Anal. Ed., 19, 423 (1947).
(5) Hallett, L. T., *Ibid.*, 10, 101 (1938).
(6) Kirner, W. R., *Ibid.*, 10, 342 (1938).
(7) Lieb, H., and Soltys, A., *Mikrochemie*, 20, 59 (1936).
(8) Lindner, J., *Ber.*, 59, 2561, 2806 (1926); 60, 124 (1927); 63, 949, 1123, 1396, 1672 (1930); 64, 1560 (1931); 65, 1696 (1932); 67, 1652 (1934); 76, 701 (1943); *Mikrochemie*, 34, 67 (1948).
(9) Niederl, J. B., and Meadow, J. R., *Mikrochemie*, 9, 350 (1931).
(10) Pregl-Roth, "Quantitative organische Mikroanalyse," Wien, Springer Verlag, 1947; Pregl, F., "Quantitative Organic Microanalysis," Philadelphia, P. Blakiston's Sons, 1937.
(11) Reihlen, H., and Weinbrenner, E., *Chem. Fabrik*, 7, 63 (1934); *Mikrochemie*, 23, 285 (1937/38).
(12) Renoll, M. W., Midgley, Thomas, Jr., and Henne, A. L., Ind. Eng. Chem., Anal. Ed., 9, 566 (1937).
(13) Royer, G. L., Norton, A. R., and Sundberg, O. E., *Ibid.*, 12, 688 (1940).
(14) Tunnicliff, D. D., Peters, E. D., Lykken, Louis, and Tuemmler, F. D., *Ibid.*, 18, 710 (1946).
(15) Wagman, D. D., and Rossini, F. D., *J. Research Natl. Bur. Standards*, 32, 95 (1944).
(16) Zimmermann, W., *Mikrochemie*, 31, 149 (1943).

Received February 3, 1948.

Table of Azeotropes and Nonazeotropes

L. H. HORSLEY, *The Dow Chemical Company, Midland, Mich.*

THIS table of azeotropes and nonazeotropes is a supplement to the table previously published in ANALYTICAL CHEMISTRY (*63*).

It is arranged in a table of binary systems and a table of ternary systems. Individual systems are arranged according to empirical formula. The systems containing inorganic constituents are listed first, using alphabetical order by formula, and then organic compounds in the *Chemical Abstracts* formula index system.

For a given binary system the component with the lower order formula is chosen as the A-component and is shown in bold-faced type. Under each A-component, the B-components are also arranged by formula. A similar arrangement is used for the ternary systems.

A formula index is included at the end of the table and lists under each compound all the systems in which that compound is one of the components.

Table I. Binary Systems

No.	B-Component Formula	B-Component Name	B-Component B.P., ° C.	Azeotropic Data B.P., ° C.	Azeotropic Data Weight % A	Reference
A =	**HBr**	**Hydrobromic Acid**	**− 67**			
1	H_2S	Hydrogen sulfide	−70/480	− 70/420	60.5	*144*
2	H_2S	Hydrogen sulfide	− 86	Nonazeotrope		*94*
3	O_2S	Sulfur dioxide	− 10	Nonazeotrope		*94, 144*
A =	**Br_4Sn**	**Tin Bromide**	**202**			
4	$C_7H_{12}O_4$	Ethyl malonate	198.9	Reacts		*94*
A =	**CF_2O**	**Carbonyl Fluoride**				
5	CF_4O	Trifluoromethyl hypofluorite	− 94.2	− 97.0	10	*69*
A =	**CO_2**	**Carbon Dioxide**	**− 79.1**			
6	N_2O	Nitrous oxide	− 89.8			*94*
7	O_3S	Sulfur trioxide	47			*94*
8	CS_2	Carbon disulfide	46.2	Nonazeotrope		*94*
9	$CHCl_3$	Chloroform	61.2			*94*
10	$C_6H_5NO_3$	*o*-Nitrophenol	214			*94*
A =	**Cl_2**	**Chlorine**	**− 33.5**			
11	S_2Cl_2	Sulfur chloride	138			*94*
12	H_2O	Water	100	Nonazeotrope		*94*
A =	**ClH**	**Hydrochloric Acid**	**− 85**			
13	O_2S	Sulfur dioxide	− 10	Nonazeotrope at 35°		*144*
14	C_3H_6O	Acetone	56.2			*94*
A =	**Cl_3Sb**	**Antimony Chloride**	**220**			
15		Aromatics	200–220	Nonazeotrope		*34, 147*
A =	**Cl_4Si**	**Silicon Chloride**	**56.5**			
16	CH_3NO_2	Nitromethane	101	53.8	94	*127*
17	$C_2H_4Cl_2$	1,1-Dichloroethane	57.4	52.7	63.5	*128*
18	$C_2H_4Cl_2$	1,2-Dichloroethane	83.7	Azeotrope		*128*
19	C_3H_5N	Propionitrile	97	55.6	92	*127*
20	C_6H_{14}	2-Methylpentane	60.4	Nonazeotrope		*128*
21	C_6H_{14}	3-Methylpentane	63.3	Nonazeotrope		*128*
A =	**Cl_4Sn**	**Tin Chloride**	**113.85**			
22	C_3H_5ClO	Epichlorohydrin	116.45	Reacts		*94*
23	C_5H_5N	Pyridine	115.5	Reacts		*94*
24	$C_6H_{12}O_2$	Ethyl butyrate	119.9	Reacts		*94*
A =	**Cu**	**Copper**	**2310**			
25	Pb	Lead	1525			*94*
A =	**FH**	**Hydrofluoric Acid**	**19.4**			
26	CCl_2F_2	Dichlorodifluoromethane	....	20[a]	8[a]	*8*
27	$CHClF_2$	Chlorodifluoromethane	.		1–2.2	*8*
28	$C_4H_{10}O$	Ethyl ether	34.5	74	40	*27*
A =	**HI**	**Hydriodic Acid**	**− 34**			
29	H_2S	Hydrogen sulfide	− 63.5	Nonazeotrope at −60		*94, 144*
A =	**H_2O**	**Water**	**100**			
30	H_2S	Hydrogen sulfide	−63.5	Nonazeotrope		*94*
31	O_2S	Sulfur dioxide	− 10	Nonazeotrope		*94*
32	CHN	Hydrocyanic acid	26	Vapor pressure curve		*94*
33	CH_2Cl_2	Dichloromethane	41.5	38.1	1.5	*4*
34	CH_2O	Formaldehyde	− 21	Nonazeotrope		*94, 117*
35	C_2HCl_3	Trichloroethylene	86.2–86.6	73.6	5.4	*56, 122*
36	$C_2H_4Cl_2$	1,2-Dichloroethane	84	72	19.5	*2, 60*
37	$C_2H_4Cl_2O$	Bis(chloromethyl) ether	106	Azeotrope		*110*
38	C_2H_5Br	Bromoethane	38.4	37	1.3[b]	*94, 107*
39	C_2H_5ClO	2-Chloroethanol	128.7	97.8	57.7	*5, 13, 23, 24*
40	C_2H_5I	Iodoethane	70	66	3–4[b]	*94, 116*
41	C_2H_6	Ethane	− 93			*94*
42	C_3H_5ClO	Chloroacetone	121	Minimum B.P.		*110*

[a] Under unspecified pressure.
[b] Volume per cent.

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	H_2O	**Water** (*Contd.*)	100			
43	C_3H_5ClO	α-Chloropropionaldehyde	86	80.5–81		*108*
44	C_3H_5ClO	Epichlorohydrin	117	88	25	*47*
45	$C_3H_6Cl_2$	1,2-Dichloropropane	97	78	12	*55*
46	$C_3H_6O_2$	Methoxyacetaldehyde	92.3/770	88.8/770	20	*37*
47	$C_3H_6O_3$	Trioxane	114.5	91.4	30	*152*
48	C_3H_7ClO	Propylene chlorohydrin	127.4	95.4	45.8	*23, 24, 26, 70*
49	C_3H_7N	Allylamine	52.9	Nonazeotrope		*135*
50	$C_3H_8O_2$	2-Methoxyethanol	124.5	99.9	77.8	*25*
51	$C_3H_{10}N_2$	1,2-Diaminopropane	119.7	Nonazeotrope		*23, 24*
52	C_4H_4O	1-Butyn-3-one	85	74	35	*140*
53	C_4H_5N	Pyrrole	129.8	93–93.5		*6*
54	$C_4H_6O_2$	Biacetyl	87–88	78.5		*21, 102*
55	C_4H_7Cl	1-Chloro-2-methyl-1-propene	68.1	61.9	7.5	*19*
56	$C_4H_7ClO_2$	4-Chloromethyl-1,3-dioxolane	66–68/40	99		*132*
57	$C_4H_8Cl_2O$	1,3-Dichloro-2-methyl-2-propanol	174	98.3	64.8	*19*
58	$C_4H_8O_2$	1,3-Dioxane	104–105	86.5		*132*
59	$C_4H_8O_3$	Methyl lactate	143.8	99	80	*130*
60	C_4H_9ClO	1-Chloro-2-methyl-2-propanol	126.7	93–94	34	*19*
61	C_4H_9I	1-Iodo-2-methylpropane	122.5	95–96	21[a]	*94, 116*
62	C_4H_9N	Methylallylamine	78.7	78.4	4.1	*135*
63	$C_4H_{10}O_2$	Meso-2,3-butanediol	183–184	Nonazeotrope		*113*
64	$C_4H_{10}O_2$	*l*-2,3-Butanediol		Nonazeotrope		*149*
65	$C_4H_{10}O_2$	Acetaldehyde dimethyl acetal	64.3	61.3	3.6	*7*
66	$C_4H_{10}O_2$	1,2-Dimethoxyethane	83	77.4	10.1	*25, 66, 94*
67	$C_4H_{10}O_2$	Ethoxymethoxymethane	65.91	61.25	4.4	*159*
68	$C_4H_{10}O_2$	1-Methoxy-2-propanol	118	96	48.5	*36*
69	$C_4H_{11}N$	Diethylamine	56			*94*
70	C_5H_7NO	Furfurylamine	144	99	74	*145*
71	$C_5H_8O_2$	Allyl acetate	105	Azeotrope		*110*
72	$C_5H_8O_2$	Methyl methacrylate	99.5	49/200	11.6/200	*157*
73	$C_5H_8O_2$	Methyl methacrylate	99.5	86–92/760		*94*
74	$C_5H_8O_2$	2,4-Pentanedione	138	Heterogeneous		*59*
75	$C_5H_{10}O$	2-Methyltetrahydrofuran	77	Minimum B.P.		*14*
76	$C_5H_{10}O$	Tetrahydropyran		Minimum B.P.		*132*
77	$C_5H_{10}O_2$	4,5-Dimethyl-1,3-dioxolane		Minimum B.P.		*47*
78	$C_5H_{10}O_2$	3-Ethoxy-1,2-epoxypropane	124–126	90–91		*16*
79	$C_5H_{10}O_3$	Methyl β-methoxypropionate	84/100	Azeotrope		*64, 110*
80	$C_5H_{11}Cl$	1-Chloropentane	108.35	82	32.1	*66*
81	$C_5H_{12}O_2$	1,2-Dimethoxypropane	92–93	80		*58*
82	$C_5H_{12}O_3$	1,1,2-Trimethoxyethane	126–127.5	93–94	30	*94, 107*
83	$C_6H_5NO_2$	Nitrobenzene	210.85	98.6	88[a]	*6, 28*
84	C_6H_7N	3-Picoline	144	94.1–94.3/700	61.4/700	*6, 28, 100*
85	C_6H_7N	4-Picoline	145.3	94.6–94.8/700	63.5/700	*6, 28, 33, 100*
86	$C_6H_8O_2$	Vinyl crotonate	132.7/757	91.0/760	24.2	*133*
87	C_6H_{10}	4-Methyl-1,3-pentadiene		67.0	7.5	*129*
88	$C_6H_{10}O$	1-Hexen-5-one	129	Minimum B.P.		*110*
89	$C_6H_{10}O_2$	Crotonyl acetate	129	Minimum B.P.		*110*
90	$C_6H_{11}N$	Diallylamine	110.4	87	22–23	*135*
91	$C_6H_{12}O$	Butyl vinyl ether	93.8	76.7	11.5	*136*
92	$C_6H_{12}O$	Butyl vinyl ether	93.8	Nonazeotrope		*136*
93	$C_6H_{12}O$	2,2-Dimethyltetrahydrofuran	90–92	Minimum B.P.		*59*
94	$C_6H_{12}O$	3-Hexanone	124	Minimum B.P.		*110*
95	$C_6H_{12}O$	2-Methyl-2-pentene-4-ol		94.6	40.8	*129*
96	$C_6H_{14}O_2$	2-Butoxyethanol	171.2	98.8	79.2	*25*
97	$C_6H_{14}O_2$	1,2-Diethoxyethane	123.5	89.4	25	*25, 94*
98	$C_6H_{14}O_2$	Ethoxypropoxymethane	113.7	85.90	18.4	*159*
99	$C_6H_{15}N$	Diisopropylamine	83.86	74.1	9.2	*135*
100	$C_6H_{15}N$	Triethylamine	89.4	75	10	*94, 151*
101	C_7H_7Cl	*p*-Chlorotoluene	163.5	95		*18*
102	C_7H_9N	2,6-Lutidine	144	93.3–93.5/700	51.5/700	*6, 28, 100*
103	$C_7H_{14}O$	4-Heptanone	143	94		*110, 111*
104	$C_7H_{14}O_2$	*sec*-Amyl acetate	133.5	92.0	33.2	*134*
105	$C_7H_{14}O_2$	Butyl propionate	137	Minimum B.P.		*110*
106	$C_7H_{14}O_2$	Enanthic acid	221			*94*
107	$C_7H_{16}O$	Amyl ethyl ether	120	Minimum B.P.		*110*
108	$C_7H_{16}O$	Ethyl isoamyl ether	112	Azeotrope		*110*
109	$C_7H_{16}O_2$	Diisopropoxymethane	129	79–80	12	*94, 150*
110	C_8H_8	Styrene	145	93		*106*
111	C_8H_{10}	Ethylbenzene	60.5/60	33.5/60	33	*11, 106*
112	C_8H_{10}	*m*-Xylene	139	92	35.8	*94, 107, 122*
113	C_8H_{14}	Diisobutylene	101–104	81	87	*134*
114	$C_8H_{15}N$	Dimethallylamine	149.0	94.1	40.3	*135*
115	$C_8H_{16}O$	Allyl isoamyl ether	120	Minimum B.P.		*110*
116	$C_8H_{16}O$	2,2,5,5-Tetramethyltetrahydrofuran	115	Minimum B.P.		*59*
117	$C_8H_{18}O$	Butyl ether	142.6	92.9	28[a]	*110, 111, 112, 118, 158*
118	$C_8H_{18}O$	*sec*-Butyl ether	121	Minimum B.P.		*110*
119	$C_8H_{18}O$	Ethyl hexyl ether	143–144	92.9	29[a]	*111*
120	$C_8H_{18}O_2$	1,1-Dipropoxyethane	147.7	94.7	36.6	*7*
121	$C_8H_{18}O_3$	Bis(2-ethoxyethyl) ether		98.4	78.5	*25*
122	$C_8H_{19}N$	Dibutylamine		Minimum B.P.		*71*
123	$C_{10}H_8$	Naphthalene	218	98.8	84	*107*
124	$C_{10}H_{22}O_2$	Acetaldehyde dibutyl acetal	188.8	98.7	66.3	*7, 138*

[a] Volume per cent.

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**H_2O**	**Water** (*Contd.*)	**100**			
125	$C_{10}H_{22}O_2$	Acetaldehyde diisobutyl acetal	171.3	97.4	52.5	*7*
126	$C_{12}H_{26}O_2$	Acetaldehyde diamyl acetal	225.3	99.8	85.5	*7*
127	$C_{12}H_{26}O_2$	Acetaldehyde diisoamyl acetal	213.6	99.3	78.8	*7*
A =	**H_3N**	**Ammonia**	**−33.6**			
128	C_2H_6O	Methyl ether	−23	−37	42.5	*62*
A =	**O_2S**	**Sulfur Dioxide**	**−10**			
129	C_4H_{10}	Butane	−0.6	−18	63.3	*50, 104*
130	C_4H_{10}	2-Methylpropane	−12.4	−24	..	*50, 104*
A =	**$CClN$**	**Cyanogen Chloride**	**12.5**			
131	CHN	Hydrocyanic acid	26	Nonazeotrope		*54*
A =	**CCl_3NO_2**	**Trichloronitromethane**	**111.83**			
132	C_3H_5I	3-Iodopropene	101.8	Nonazeotrope		*92*
133	$C_3H_6Cl_2$	1,3-Dichloropropane	129.8	Nonazeotrope		*92*
134	C_3H_7ClO	1-Chloro-2-propanol	127.0	<110.8	<96	*92*
135	C_3H_7I	1-Iodopropane	102.4	Nonazeotrope		*92*
136	$C_3H_8O_2$	2-Methoxyethanol	124.5	<110.5	<82	*92*
137	$C_4H_8O_2$	Dioxane	101.35	Nonazeotrope		*92*
138	$C_4H_8O_2$	Isobutyric acid	154.6	Nonazeotrope		*92*
139	C_4H_9I	1-Iodo-2-methylpropane	120.8	Nonazeotrope		*92*
140	$C_4H_{10}O$	*sec*-Butyl alcohol	99.5	96.1	60	*92*
141	$C_4H_{10}O$	*tert*-Butyl alcohol	82.45	82.25	37	*92*
142	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91*
143	$C_5H_{10}O$	Isovaleraldehyde	92.1	Nonazeotrope		*92*
144	$C_5H_{11}Br$	1-Bromo-3-methylbutane	120.65	Nonazeotrope		*92*
145	$C_5H_{12}O$	3-Methyl-2-butanol	112.9	<106.5	<80	*92*
146	$C_5H_{12}O$	2-Pentanol	119.8	108.0	83	*92*
147	$C_5H_{12}O$	3-Pentanol	116.0	<107.3	<82	*92*
148	C_6H_6	Benzene	80.15	Nonazeotrope		*92*
149	C_6H_{10}	Cyclohexene	82.75	Nonazeotrope		*92*
150	C_6H_{12}	Cyclohexane	80.75	Nonazeotrope		*92*
151	$C_6H_{12}O$	Cyclohexanol	160.8	Nonazeotrope		*92*
152	$C_6H_{12}O_2$	Methyl isovalerate	116.5	Nonazeotrope		*92*
153	$C_7H_{14}O$	*o*-Methylcyclohexanol	168.5	Nonazeotrope		*92*
154	$C_7H_{16}O$	*n*-Heptyl alcohol	176.15	Nonazeotrope		*92*
155	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*92*
156	C_8H_{10}	*m*-Xylene	139.2	Nonazeotrope		*92*
157	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	111.0	80	*92*
158	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		*92*
A =	**CCl_4**	**Carbon Tetrachloride**	**76.75**			
159	$C_2H_4Cl_2$	1,1-Dichloroethane	57	Vapor-liquid equilibrium		*68*
160	C_3H_9ClSi	Chlorotrimethylsilane	57.5	Nonazeotrope		*128*
161	$C_4H_8O_2$	Butyric acid	163.5	Nonazeotrope		*105*
162	C_5H_5N	Pyridine	115.5	Nonazeotrope		*94*
163	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
164	C_6H_7N	Aniline	184.35			*94*
165	C_7H_{16}	Heptane	98.45	Vapor pressure data		*94, 139*
A =	**CS_2**	**Carbon Disulfide**	**46.25**			
166	CH_3NO_2	Nitromethane	101.2	44.25	90	*92, 93*
167	$C_2H_4Cl_2O$	Bis(chloromethyl) ether	104	43.1	75	*93*
168	$C_2H_5NO_2$	Nitroethane	114.2	Nonazeotrope		*92*
169	$C_4H_8O_2$	Methyl propionate	79.7	Nonazeotrope		*94*
170	$C_4H_{10}O_2$	Isovaleric acid	176.5	Vapor pressure data		*94*
171	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
172	$C_5H_{10}O$	2-Pentanone	102.35	Nonazeotrope		*90*
173	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
174	$C_6H_5NO_2$	Nitrobenzene	210.85			*94*
175	C_6H_7N	Aniline	184.35			*94*
176	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
177	C_7H_8	Toluene	110.7	Nonazeotrope		*94*
178	C_7H_{16}	Heptane	98.45			*94*
179	$C_9H_{10}O_2$	Ethyl benzoate	213			*94*
180	$C_{10}H_8$	Naphthalene	218			*94*
181	$C_{10}H_{14}O$	Thymol	233			*94*
182	$C_{10}H_{16}O$	Camphor	208.9			*94*
A =	**$CHBrCl_2$**	**Bromodichloromethane**	**90.2**			
183	$C_2H_5NO_2$	Nitroethane	114.2	Nonazeotrope		*92*
184	C_3H_7I	2-Iodopropane	89.45	90.7	50	*87*
185	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
186	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
A =	**$CHBr_3$**	**Bromoform**	**148.3**			
187	$C_2H_2Cl_4$	1,1,2,2-Tetrachloroethane	146.2	145.5	45	*87*
188	C_6H_5Br	Bromobenzene	156.1	Nonazeotrope		*87*
189	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
190	$C_7H_{14}O$	4-Heptanone	143.55	151.0	77	*90*
A =	**$CHCl_3$**	**Chloroform**	**61.2**			
191	CH_2Cl_2	Dichloromethane	41.5	Nonazeotrope		*46*
192	$C_2H_4Cl_2$	1,1-Dichloroethane	57.3	Vapor-liquid equilibrium		*68*
193	C_2H_5Cl	Chloroethane	13.3	Nonazeotrope		*94*
194	C_3H_7Br	1-Bromopropane	71.0	Nonazeotrope		*87*
195	$C_3H_7NO_2$	Propylnitrite	47.75	Nonazeotrope		*88*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$\mathbf{CHCl_3}$	**Chloroform (*Contd.*)**	**61.2**			
196	C_3H_9ClSi	Chlorotrimethylsilane	57.5	Nonazeotrope		*128*
197	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
198	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88*
199	C_5H_5N	Pyridine	115.5			*94*
200	C_6H_5Cl	Chlorobenzene	131.8			*94*
201	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
202	C_6H_7N	Aniline	184.35			*94*
203	C_7H_{16}	Heptane	98.45			*94*
204	C_8H_{10}	*p*-Xylene	138.2			*94*
205	$C_9H_{10}O_2$	Ethyl benzoate	213			*94*
A =	$\mathbf{CH_2Br_2}$	**Dibromomethane**	**79.0**			
206	CH_4O	Methanol	64.7	Azeotrope doubtful		*94*
207	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	98.0	70	*90*
208	$C_5H_{10}O$	2-Pentanone	102.35	Nonazeotrope		*90*
A =	$\mathbf{CH_2ClNO_2}$	**Chloronitromethane**	**122.5**			
209	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91*
210	$C_6H_{14}S$	Isopropyl sulfide	120.5	<119.7	20	*92*
A =	$\mathbf{CH_2Cl_2}$	**Dichloromethane**	**41.5**			
211	C_2H_5Br	1-Bromoethane	38.4	38.1	20	*87*
212	$C_3H_7NO_2$	Isopropyl nitrite	40.1	39.45	53	*88*
A =	$\mathbf{CH_2I_2}$	**Diiodomethane**	**181**			
213	$C_6H_4Cl_2$	*p*-Dichlorobenzene	174.4	171.3	48	*87*
A =	$\mathbf{CH_2O_2}$	**Formic Acid**	**100.7**			
214	$C_2H_5NO_2$	Nitroethane	114.2	Nonazeotrope		*92*
215	$C_4H_{10}S$	Ethyl sulfide	92.2	82.2	35	*93*
216	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	>102.15	<85	*90*
217	$C_5H_{10}O_2$	Isobutyl formate	98.3	Nonazeotrope		*158*
218	C_6H_7N	3-Picoline	143.5	100–125/200		*32, 124*
219	C_6H_7N	4-Picoline	143.1	100–125/200		*32, 124*
220	$C_6H_{12}O$	Pinacone	106.2	>107.1	<24	*90*
221	C_7H_9N	2,6-Lutidine	143	100–125/200		*32, 124*
A =	$\mathbf{CH_3Br}$	**Bromomethane**	**4.5**			
222	CH_4O	Methanol	64.7	3.55	99.45	*156*
223	$C_3H_7NO_2$	Isopropyl nitrite	40.1	Nonazeotrope		*88*
A =	$\mathbf{CH_3I}$	**Iodomethane**	**42.6**			
224	C_5H_5N	Pyridine	115.5			*94*
A =	$\mathbf{CH_3NO_2}$	**Nitromethane**	**101.15**			
225	C_2H_5ClO	2-Chloroethanol	128.6	Nonazeotrope		*92*
226	$C_2H_5NO_3$	Ethyl nitrate	87.70	87.68	1.2	*92*
227	C_2H_6S	Ethanethiol	35.8	Nonazeotrope		*92*
228	C_2H_6S	Methyl sulfide	37.4	Nonazeotrope		*92*
229	$C_3H_6O_2$	Propionic acid	141.3	Nonazeotrope		*92*
230	C_3H_7Cl	1-Chloropropane	46.4	Nonazeotrope		*93*
231	C_3H_7ClO	1-Chloro-2-propanol	127.0	Nonazeotrope		*92*
232	C_3H_7ClO	2-Chloro-1-propanol	133.7	Nonazeotrope		*92*
233	$C_3H_7NO_3$	Propyl nitrate	110.5	100.2	75	*92*
234	C_3H_9ClSi	Chlorotrimethylsilane	57.7	Nonazeotrope		*127*
235	C_4H_8O	2-Butanone	79.6	Nonazeotrope		*90*
236	$C_4H_8O_2$	Dioxane	101.35	100.55	56.5	*92*
237	$C_4H_8O_2$	Methyl propionate	79.85	Nonazeotrope		*92*
238	$C_4H_8O_2$	Propyl formate	80.85	Nonazeotrope		*92*
239	$C_4H_{10}O_2$	2-Ethoxyethanol	135.3	Nonazeotrope		*92*
240	$C_4H_{10}S$	Butanethiol	97.5	< 93.2		*92*
241	$C_4H_{10}S$	Ethyl sulfide	92.1	85.0	30	*92, 93*
242	C_5H_{10}	3-Methyl-1-butene	20.6	Nonazeotrope		*92*
243	C_5H_{10}	Cyclopentane	49.3	< 47.5	> 9	*92*
244	$C_5H_{10}O$	Cyclopentanol	140.85	Nonazeotrope		*92*
245	$C_5H_{10}O_2$	Isopropyl acetate	89.5	< 89.3		*92*
246	$C_5H_{10}O_2$	Methyl isobutyrate	92.5	91.2		*92*
247	$C_5H_{11}Br$	1-Bromo-3-methylbutane	120.65	97.5		*92*
248	$C_5H_{11}Cl$	1-Chloro-3-methylbutane	99.4	88.2	48	*92*
249	C_5H_{12}	2-Methylbutane	27.95	Nonazeotrope		*92*
250	$C_5H_{12}O_2$	2-Propoxyethanol	151.35	Nonazeotrope		*92*
251	C_6H_{10}	Cyclohexene	82.75	< 74.5	<31	*92*
252	C_6H_{10}	1,5-Hexadiene	60.1	< 57.5	<23	*92*
253	$C_6H_{10}S$	Allyl sulfide	139.35	Nonazeotrope		*92*
254	C_6H_{12}	Cyclohexane	80.75	70.2	28	*92*
255	C_6H_{12}	Methylcyclopentane	72.0	64.2	23	*92*
256	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
257	$C_6H_{12}O$	Pinacolone	106.2	<100.5		*90*
258	$C_6H_{12}O_2$	Ethyl butyrate	121.5	Nonazeotrope		*92*
259	$C_6H_{12}O_2$	Ethyl isobutyrate	110.1	100.0	72	*92*
260	C_6H_{14}	2,3-Dimethylbutane	58.0	< 54.5	<26	*92*
261	C_7H_{16}	*n*-Heptane	98.4	80.2	37	*92*
262	C_8H_8	Styrene	145.8	Nonazeotrope		*92*
263	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*92*
264	C_8H_{10}	*m*-Xylene	139.2	Nonazeotrope		*92*
265	C_8H_{10}	*o*-Xylene	144.3	Nonazeotrope		*92*
266	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	90.2	50	*92*
267	C_8H_{18}	2,5-Dimethylhexane	109.4	85.5	43	*92*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**CH_3NO_2**	**Nitromethane (*Contd.*)**	**101.15**			
268	C_8H_{18}	*n*-Octane	125.75	92.0	53	*92*
269	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		*92*
270	C_9H_{12}	Cumene	152.8	Nonazeotrope		*92*
271	C_9H_{12}	Mesitylene	164.6	Nonazeotrope		*92*
272	C_nH_{2n+2}	Paraffins	90–118	75–90		*51*
A =	**CH_4O**	**Methanol**	**64.7**			
273	$C_3H_4Cl_2$	1,2-Dichloro-1-propene	76.8–77.0	56.5–56.8	25	*66*
274	$C_3H_8O_2$	2-Methoxyethanol	124	Nonazeotrope		*137*
275	$C_4H_4Cl_2$	2,3-Dichloro-1,3-butadiene	98	61.5/760	50.0	*154*
276	C_4H_4S	Thiophene	84	< 59.55	<55	*93*
277	C_4H_{10}	Butane	0.6			*94*
278	$C_4H_{10}O_2$	Ethoxymethoxymethane	65.90	57.1	25.3	*159*
279	$C_4H_{11}N$	Isobutylamine	68.0	Reacts		*84, 98*
280	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91, 94*
281	C_5H_6O	2-Methylfuran	63.7	51.5	22.3	*120*
282	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
283	$C_5H_{11}Cl$	1-Chloropentane	108.35	Nonazeotrope		*64*
284	$C_5H_{14}OSi$	Methoxymethyltrimethylsilane	83	60	36[a]	*142*
285	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
286	$C_{10}H_{14}O$	Thymol	233			*94*
A =	**CH_5N**	**Methylamine**	**−6.5**			
287	C_5H_{10}	Amylenes		Minimum B.P.		*40*
A =	**C_2Cl_4**	**Tetrachloroethylene**	**120.8**			
288	C_5H_5N	Pyridine	115.4	112.85	51.5	*91*
289	C_5H_8O	Cyclopentanone	130.65	120.1	86	*90*
290	$C_6H_{12}O$	3-Hexanone	123.3	118.15	55	*90*
A =	**C_2HCl_3**	**Trichloroethylene**	**86.95**			
291	C_2H_3N	Acetonitrile	81.6	74.6/778	71	*119*
292	C_3H_6O	Acetone	56.15	Nonazeotrope		*90*
293	$C_4H_8O_2$	Butyric acid	162.5	Nonazeotrope		*106*
294	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
295	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
A =	**$C_2HCl_3O_2$**	**Trichloroacetic Acid**	**197.55**			
296	$C_2H_4O_2$	Methyl formate	31.9	Nonazeotrope		*94*
297	$C_4H_{10}O$	Ethyl ether	34.6	Nonazeotrope		*94*
298	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
299	C_7H_8O	*p*-Cresol	201.7	Reacts		*78*
300	$C_7H_8O_2$	Guaiacol	205.05	Reacts		*78*
A =	**C_2HCl_5**	**Pentachloroethane**	**161.95**			
301	$C_5H_8O_2$	2,4-Pentanedione	169.5	<159.4	>40	*94*
302	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
303	$C_6H_{12}O_3$	Propyl lactate	171.7	Nonazeotrope		*94*
304	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
305	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	169.0	35	*90*
A =	**$C_2H_2Cl_2O_2$**	**Dichloroacetic Acid**	**190**			
306	$C_2H_4O_2$	Methyl formate	31.9	Nonazeotrope		*94*
307	$C_4H_{10}O$	Ethyl ether	34.6	Nonazeotrope		*94*
308	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
A =	**$C_2H_2Cl_4$**	**1,1,2,2-Tetrachloroethane**	**146.35**			
309	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
310	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
A =	**$C_2H_3BrO_2$**	**Bromoacetic Acid**	**208**			
311	$C_{11}H_{20}O$	Methyl terpineol ether	216	Reacts		*94*
A =	**$C_2H_3ClO_2$**	**Chloroacetic Acid**	**189.35**			
312	$C_2H_4O_2$	Methyl formate	31.9	Nonazeotrope		*94*
313	$C_4H_{10}O$	Ethyl ether	34.6	Nonazeotrope		*94*
314	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
315	$C_{11}H_{20}O$	Isobornyl methyl ether	192.2	Reacts		*94*
A =	**C_2H_3N**	**Acetonitrile**	**81.6**			
316	C_3H_6O	Acetone	56.4	Nonazeotrope		*119*
A =	**C_2H_4**	**Ethylene**	**−103.9**			
317	C_2H_6	Ethane	−88.3	Nonazeotrope		*29*
A =	**$C_2H_4Br_2$**	**1,1-Dibromoethane**	**110**			
318	C_4H_5N	Pyrrol	130.0	Nonazeotrope		*91*
319	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
A =	**$C_2H_4Br_2$**	**1,2-Dibromoethane**	**131.5**			
320	$C_2H_4Cl_2$	1,2-Dichloroethane	83.7	Nonazeotrope		*94*
321	$C_3H_7NO_2$	1-Nitropropane	75/113	75/133.0	73	*74*
322	$C_3H_7NO_2$	1-Nitropropane	120/550.2	120/612.7	72	*74*
323	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
324	C_8H_8	Styrene	68/60	Nonazeotrope		*11*
A =	**$C_2H_4Cl_2$**	**1,1-Dichloroethane**	**83.7**			
325	$C_2H_4Cl_2$	1,2-Dichloroethane	83.7	Vapor-liquid equilibrium		*68*
326	C_3H_9ClSi	Chlorotrimethylsilane	57.7	56.4	..	*128*

[a] Volume per cent.

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., °C.	Azeotropic Data B.P., °C.	Weight % A	Reference
A =	**$C_2H_4Cl_2$**	**1,2-Dichloroethane**	**83.7**			
327	$C_4H_8O_2$	Butyric acid	162	Nonazeotrope		*105*
328	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
A =	**$C_2H_4Cl_2O$**	**Bis(chloromethyl) Ether**	**104**			
329	C_3H_7Cl	1-Chloropropane	46.4	Nonazeotrope		*93*
A =	**$C_2H_4O_2$**	**Acetic acid**	**118.5**			
330	$C_2H_5NO_2$	Nitroethane	114.2	112.4	30	*92*
331	$C_3H_6Br_2$	1,2-Dibromopropane	140.5	116.0	70	*93*
332	$C_4H_6O_3$	Methylpyruvate	137.5	Nonazeotrope		*90*
333	$C_4H_8O_2$	Butyric acid	163.5	Vapor pressure data		*94*
334	C_5H_8O	Cyclopentanone	130.65	Nonazeotrope		*90*
335	C_6H_7N	3-Picoline	144	152.5	30.4	*32, 33, 124*
336	C_6H_7N	4-Picoline	145.3	154.3	30.3	*32, 33, 124*
337	$C_6H_{10}S$	Allyl sulfide	139	116.55	78.5	*93*
338	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90*
339	$C_6H_{14}S$	Isopropyl sulfide	120	111.5	48	*93*
340	$C_7H_6O_2$	Benzoic acid	249.5			*94*
341	$C_7H_6O_3$	Salicylic acid	211/20			*94*
342	C_7H_9N	2,6-Lutidine	144	148	27.8	*32, 33, 124*
343	$C_7H_{14}O_2$	Amyl acetate	149	Nonazeotrope		*112*
344	$C_8H_{14}O_4$	Meso-2,3-butanediol diacetate	190–193	Nonazeotrope		*113*
345	$C_8H_{16}O_2$	Methyl isoamyl acetate		Nonazeotrope		*109*
346	$C_{12}H_{11}N$	Diphenylamine	302			*94*
347	$C_{13}H_{10}O$	Benzophenone	305			*94*
A =	**$C_2H_4O_2$**	**Methyl Formate**	**31.9**			
348	$C_2H_5NO_2$	Ethyl nitrite	17.4	Nonazeotrope		*87, 88*
349	C_2H_6S	Methyl sulfide	37.2	29.0	62	*93*
350	$C_3H_7NO_2$	Isopropyl nitrite	40.1	Nonazeotrope		*87, 88*
351	$C_3H_7NO_2$	Propyl nitrite	47.75	Nonazeotrope		*87, 88*
352	C_5H_6	Cyclopentadiene	41.0	Minimum B.P.		*45*
353	C_5H_8	1,3-Pentadiene	42.5	Minimum B.P.		*45*
A =	**C_2H_5Br**	**Bromoethane**	**38.4**			
354	$C_4H_8O_2$	Butyric acid	163.5	Vapor pressure data		*94*
355	C_5H_5N	Pyridine	115.5			*94*
356	$C_6H_{12}O_2$	Caproic acid	204.5			*94*
357	$C_9H_{10}O_2$	Ethyl benzoate	213			*94*
A =	**C_2H_5BrO**	**2-Bromoethanol**	**150.2**			
358	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
359	$C_9H_{18}O$	2,6-Dimethyl 4-heptanone	168.0	Nonazeotrope		*90*
A =	**C_2H_5ClO**	**2-Chloroethanol**	**128.8**			
360	$C_2H_5NO_2$	Nitroethane	114.2	Nonazeotrope		*92*
361	$C_3H_6Br_2$	1,2-Dibromopropane	140.5	126.0		*93*
362	$C_5H_{11}Br$	1-Bromo-3-methylbutane	120.3	113.0	24	*93*
363	C_6H_5Br	Bromobenzene	156.1	127.45		*97*
364	$C_6H_{10}O$	Mesityl oxide	129.45	130.2	33	*90*
365	$C_6H_{12}O$	2-Hexanone	127.2	129.0	75	*90*
366	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
367	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
368	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90*
369	$C_6H_{13}Br$	1-Bromohexane	156.5	126.5		*97*
370	$C_6H_{14}S$	Isopropyl sulfide	120	115.5	30	*93*
371	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
372	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
373	C_8H_{18}	2,5-Dimethylhexane	109.4	101.0		*97*
A =	**C_2H_5ClO**	**Chloromethyl Methyl Ether**	**59.15**			
374	C_4H_8O	2-Butanone	79.6	Nonazeotrope		*90*
A =	**C_2H_5I**	**Iodoethane**	**72.3**			
375	C_3H_5Br	3-Bromopropene	70.5	Nonazeotrope		*87*
A =	**C_2H_5NO**	**Acetamide**	**221.2**			
377	C_2H_7NO	2-Aminoethanol	170.8	Nonazeotrope		*89*
378	$C_4H_{11}NO$	2,2′-Iminodiethanol	268.0	Nonazeotrope		*89*
379	$C_5H_4O_2$	2-Furaldehyde	161.45	Reacts		*78*
380	$C_5H_8O_3$	Levulinic acid	252	Nonazeotrope		*90*
381	$C_6H_4ClNO_2$	*m*-Chloronitrobenzene	235.5	212.5	50	*92*
382	$C_6H_4ClNO_2$	*o*-Chloronitrobenzene	246.0	216.0	60	*92*
383	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
384	$C_6H_8N_2$	*o*-Phenylenediamine	258.6	Nonazeotrope		*89*
385	$C_6H_{15}NO$	2-Diethylaminoethanol	162.2	Nonazeotrope		*89*
386	$C_7H_5Cl_3$	α,α,α-Trichlorotoluene	220.9	Reacts		*78*
387	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	210.8	42	*92*
388	C_7H_9N	Methylaniline	196.25	193.8	14	*89*
389	C_7H_9N	*m*-Toluidine	203.1	200.95	14	*89*
390	C_7H_9N	*p*-Toluidine	200.55	198.7	12	*89*
391	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
392	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
393	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	<209.5	21	*89*
394	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	<213.5	<29	*89*
395	$C_8H_{11}N$	Ethylaniline	205.5	199.0	18	*89*
396	$C_8H_{11}NO$	*o*-Phenetidine	232.5	216.0	55	*89*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., °C.	Azeotropic Data B.P., °C.	Weight % A	Reference
A =	C_2H_5NO	**Acetamide (*Contd.*)**	221.2			
397	$C_8H_{11}NO$	*p*-Phenetidine	249.9	Nonazeotrope		89
398	$C_8H_{14}O$	Methylheptenone	173.2	Nonazeotrope		90
399	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		90
400	C_9H_7N	Quinoline	237.3	Nonazeotrope		91
401	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	194.0	22	89
402	$C_9H_{14}O$	Phorone	197.8	194.8	12	90
403	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		90
404	$C_{10}H_9N$	1-Naphthylamine	300.8	Nonazeotrope		89
405	$C_{10}H_{16}O$	Camphor	209.1	199.8	23	90
406	$C_{10}H_{16}O$	Carvenone	234.5	213.0	44	90
407	$C_{10}H_{16}O$	Fenchone	193.6	<192.8	> 5	90
A =	$C_2H_5NO_2$	**Ethyl Nitrite**	17.4			
408	C_2H_6S	Methyl sufide	37.4	Nonazeotrope		88
409	C_3H_5Cl	2-Chloropropene	22.65	Nonazeotrope		88
410	C_3H_8O	Isopropyl alcohol	82.35	Minimum B.P.		98
411	C_4H_4O	Furan	31.7	Nonazeotrope		88
412	C_4H_{10}	Butane	0.6	Nonazeotrope		88
413	C_5H_{10}	Cyclopentane	49.3	Nonazeotrope		88
414	C_5H_{10}	2-Methyl-2-butene	37.15	Nonazeotrope		88
415	$C_5H_{12}O$	Ethyl propyl ether	38.85	Nonazeotrope		88
A =	$C_2H_5NO_2$	**Nitroethane**	114.2			
416	$C_2H_5NO_3$	Ethyl nitrate	87.7	Nonazeotrope		92
417	C_3H_7ClO	1-Chloro-2-propanol	127.0	Nonazeotrope		92
418	$C_3H_7NO_3$	Propyl nitrate	110.5	<109.6	>21	92
419	$C_4H_8O_2$	Dioxane	101.35	Nonazeotrope		92
420	C_4H_9Br	1-Bromobutane	101.5	96.0	25	92
421	C_4H_9Br	1-Bromo-2-methylpropane	91.4	89.5	10	92
422	C_4H_9Cl	1-Chlorobutane	78.5	Nonazeotrope		92
423	$C_5H_{10}O_2$	Propyl acetate	101.6	Nonazeotrope		92
424	$C_5H_{11}Br$	1-Bromo-3-methylbutane	120.65	<108.5	>55	92
425	$C_5H_{12}O$	Amyl alcohol	138.2	<137.8	>83	92
426	$C_5H_{12}O_2$	2-Propoxyethanol	151.35	Nonazeotrope		92
427	C_6H_6	Benzene	80.15	Nonazeotrope		92
428	C_6H_{12}	Methylcyclopentane	72.0	71.2	4	92
429	$C_6H_{12}O_2$	Butyl acetate	126.0	Nonazeotrope		92
430	$C_6H_{12}O_2$	Ethyl butyrate	121.5	<113.7	>73	92
431	$C_6H_{12}O_2$	Ethyl isobutyrate	110.1	108.5	27	92
432	$C_6H_{12}O_2$	Isobutyl acetate	117.4	112.5	60	92
433	$C_6H_{14}S$	Isopropyl sulfide	120.5	<110.9	>60	92
434	C_7H_{14}	Methylcyclohexane	101.15	90.8	30	92
435	C_nH_{2n+2}	Paraffins	107–110	82–104	..	30
436	C_7H_{16}	*n*-Heptane	98.4	89.2	28	92
437	C_8H_{10}	*m*-Xylene	139.2	Nonazeotrope		92
438	C_8H_{18}	2,5-Dimethylhexane	109.4	< 96.9	>62	92
A =	$C_2H_5NO_3$	**Ethyl Nitrate**	87.68			
439	$C_3H_6O_3$	Methyl carbonate	90.25	Nonazeotrope		87
440	C_4H_8O	2-Butanone	79.6	Nonazeotrope		90
A =	C_2H_6	**Ethane**	− 88.3			
441	$C_4H_{10}O$	Isobutyl alcohol	108	Nonazeotrope		94
442	$C_5H_{12}O$	Isoamyl alcohol	131.8			94
A =	$C_2H_6Cl_2Si$	**Dichlorodimethylsilane**				
443	C_7H_{16}	2-Methylhexane	90.1	Nonazeotrope		128
444	C_7H_{16}	3-Methylhexane	91.96	Nonazeotrope		128
A =	C_2H_6O	**Ethyl Alcohol**	78.3			
445	C_4H_4S	Thiophene	84	70.0	45	93
446	C_4H_6	1,3-Butadiene	− 4.5	Nonazeotrope		20
447	$C_4H_6O_2$	Biacetyl	88	74.5	53	90, 102
448	$C_4H_7ClO_2$	Ethyl chloroacetate	143.5	Nonazeotrope		22
449	C_4H_8O	Ethyl vinyl ether	35.5	Nonazeotrope		136
450	$C_4H_{10}O_2$	2-Ethoxyethanol	133	Nonazeotrope		3
451	$C_4H_{10}O_2$	Ethoxymethoxymethane	65.90	63.95	13.3	159
452	$C_4H_{11}ClSi$	Chloromethyltrimethylsilane	97	72	..	142
453	C_5H_5N	Pyridine	115.4	Nonazeotrope		91, 94
454	$C_5H_{10}O$	Allyl ethyl ether	63–65	60.5	..	99
455	$C_5H_{11}Cl$	1-Chloropentane	108.35	72.5	..	64
456	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		92
457	C_6H_7N	Aniline	184.35			94
458	C_6H_{10}	1-Hexyne	70.2	62.8	23.2	61
459	C_6H_{10}	3-Hexyne	80.5	67.5	34.4	61
460	$C_6H_{12}O$	(1-Methylallyl) ethyl ether	76.65	69	..	99
461	$C_6H_{12}O$	*trans*-2-Butenyl ethyl ether	100.45	77.5	..	99
462	$C_6H_{12}O$	*cis*-2-Butenyl ethyl ether	100.3	76.2	..	99
463	$C_6H_{14}O_2$	Ethoxypropoxymethane	113.7	Nonazeotrope		159
464	$C_6H_{16}OSi$	Ethoxymethyltrimethylsilane	102	74	..	142
465	C_7H_{12}	1-Heptyne	99.5	74.2	54.6	61
466	C_7H_{12}	5-Methyl-1-hexyne	90.8	71.0	39.8	61
467	C_8H_{18}	2,2,4-Trimethylpentane	25/96.1	30.4	Liquid vapor	72, 73
468	$C_9H_{10}O_2$	Ethyl benzoate	213			94
A =	C_2H_6O	**Methyl Ether**	− 21			
469	C_3H_9N	Trimethylamine	3.5	Nonazeotrope		62

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$C_2H_6O_2$	**Glycol**	**197.4**			
471	$C_4H_8O_2$	Dioxane	101.4	Nonazeotrope		*35*
472	$C_5H_{12}O_3$	2-(2-Methoxyethoxy)ethanol	194.2	192	30	*25*
473	$C_6H_4ClNO_2$	*m*-Chloronitrobenzene	235.5	192.5	53	*92*
474	$C_6H_4ClNO_2$	*o*-Chloronitrobenzene	246.0	193.5	68	*92*
475	$C_6H_8N_2$	*o*-Phenylenediamine	258.6	Nonazeotrope		*89*
476	$C_6H_{10}O_2$	2,5-Hexanedione	191.3	<180.5	<45	*90*
477	$C_6H_{10}O_4$	Ethyl oxalate	185.0	Reacts		*94*
478	$C_6H_{10}O_4$	Methyl succinate	195	Reacts		*94*
479	$C_7H_5Cl_3$	α,α,α-Trichlorotoluene	220.9	Reacts		*78*
480	C_7H_9NO	*o*-Anisidine	219.0	<193.5	<59	*89*
481	$C_7H_{12}O_4$	Ethyl malonate	198.9	Reacts		*94*
482	$C_7H_{16}O$	Heptyl alcohol	176.15	174.1	17	*87*
483	$C_8H_8O_2$	Benzyl formate	202.3	Reacts		*78*
484	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	188.6	47	*89*
485	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	<189.0	<91.6	*89*
486	$C_8H_{14}O_4$	Ethyl succinate	217.25	Reacts		*78*
487	$C_8H_{18}O_2$	2-(2-Butoxyethoxy)ethanol	230.4	196.2	72.5	*25*
488	$C_8H_{18}O_3$	Bis(2-ethoxyethyl) ether		178.0	26.1	*25*
489	C_9H_7N	Quinoline	237.3	196.35	79.5	*91*
490	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	182.0	47	*89*
491	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	164.2	35	*90*
492	$C_{10}H_{18}O$	Menthone	209.5	<190.0	<62	*90*
493	$C_{10}H_{18}O$	β-Terpineol	210.5	188.4	50	*87*
494	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	188.45	46	*95*
A =	C_2H_6S	**Ethanethiol**	**36.2**			
495	C_5H_8	Isoprene	34.1	Reacts		*94*
A =	C_2H_6S	**Methyl Sulfide**	**37.4**			
496	$C_3H_7NO_2$	Propyl nitrite	47.75	Nonazeotrope		*88*
497	$C_3H_8O_2$	Methylal	42.25	35.7		*93*
A =	$C_2H_6SO_4$	**Methyl Sulfate**	**188.4**			
498	C_6H_6O	Phenol	181.5	Reacts		*94*
499	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	185.8	63	*87*
A =	C_2H_7N	**Ethylamine**	**16.55**			
500	C_4H_4O	Furan	31.7	Nonazeotrope		*89*
501	$C_4H_{10}O$	Ethyl ether	34.6	Nonazeotrope		*89*
502	$C_4H_{10}O$	Methyl propyl ether	38.95	Nonazeotrope		*89*
503	C_5H_{10}	3-Methyl-1-butene	20.6	< 15.4	>54	*89*
503a	C_5H_{12}	2-Methylbutane	27.95	Nonazeotrope		*89*
A =	C_2H_7NO	**2-Aminoethanol**	**170.8**			
504	C_3H_7NO	Propionamide	222.2	Nonazeotrope		*89*
505	$C_4H_{10}O_2$	2-Ethoxyethanol	135.3	Nonazeotrope		*89*
506	C_5H_8O	Cyclopentanone	130.65	Nonazeotrope		*89*
507	$C_5H_{12}O_2$	2-Propoxyethanol	151.35	Nonazeotrope		*89*
508	$C_5H_{12}O_3$	2-(2-Methoxyethoxy)ethanol	192.95	Nonazeotrope		*89*
509	$C_6H_4Cl_2$	*o*-Dichlorobenzene	179.5	157.3	40	*89*
510	C_6H_5Br	Bromobenzene	156.1	145.0	22	*89*
511	C_6H_5Cl	Chlorobenzene	131.75	128.55	13.5	*89, 93, 141*
512	C_6H_5I	Iodotoluene	188.45	161.0	45	*89*
513	C_6H_6	Benzene	80.15	Nonazeotrope		*89*
514	C_6H_6O	Phenol	182.2	Nonazeotrope		*89*
515	C_6H_7N	Aniline	184.35	170.3	90	*89*
516	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*89*
517	$C_6H_{10}S$	Allyl sulfide	139	137.2	8	*93*
518	C_6H_{12}	Cyclohexane	80.75	Nonazeotrope		*89*
519	C_6H_{14}	Hexane	68.8	Nonazeotrope		*89*
520	$C_6H_{14}O_2$	2-Butoxyethanol	171.15	166.95	43	*89*
521	C_7H_7Br	*m*-Bromotoluene	184.3	159.3	44	*89*
522	C_7H_7Br	*o*-Bromotoluene	181.5	157.8	4	*89*
523	C_7H_7Cl	*o*-Chlorotoluene	159.2	146.5	26	*89*
524	C_7H_7Cl	*p*-Chlorotoluene	162.4	148.2	28	*89*
525	C_7H_8O	Aniso	153.85	145.75	25.5	*89*
526	C_7H_8O	*o*-Cresol	191.1	Nonazeotrope		*89*
527	C_7H_8O	*p*-Cresol	201.7	Nonazeotrope		*89*
528	C_7H_9N	Methylaniline	196.25	167.5	70	*89*
529	C_7H_9N	*o*-Toluidine	200.35	Nonazeotrope		*89*
530	C_7H_{14}	Methylcyclohexane	101.15	<100.5	<10	*89*
531	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*89*
532	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*89*
533	C_8H_{10}	Ethylbenzene	136.15	131.0	15	*89*
534	C_8H_{10}	*m*-Xylene	139.2	133.0	18	*89*
535	C_8H_{10}	*o*-Xylene	144.3	<138.0	20	*89*
536	$C_8H_{10}O$	Benzyl methyl ether	167.8	150.5	28	*89*
537	$C_8H_{10}O$	*p*-Methylanisole	177.05	154.5	37	*89*
538	$C_8H_{10}O$	Phenetole	170.45	151.0	30	*89, 97*
539	$C_8H_{11}N$	Dimethylaniline	194.15	163.5	55	*89*
540	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
541	C_8H_{18}	*n*-Octane	125.75	<123.0	<16	*89*
542	$C_8H_{18}O$	Butyl ether	142.4	136.5	16	*89*
543	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		*89*
544	$C_8H_{18}S$	Isobutyl sulfide	172.0	156.0	33	*93*
545	C_9H_{12}	Mesitylene	164.6	148.5	30	*89*
546	C_9H_{12}	Propylbenzene	159.3	<147.0	<30	*89*

Table I. Binary Systems (*Continued*)

	B-Component			Azeotropic Data		
No.	Formula	Name	B.P., ° C.	B.P., ° C.	Weight % A	Reference
A =	**C_2H_7NO**	**2-Aminoethanol** (*Contd.*)	**170.8**			
547	$C_9H_{12}O$	Benzyl ethyl ether	185.0	159.8	45	*89*
548	$C_9H_{12}O$	Phenyl propyl ether	190.5	162.5	55	*89*
549	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	161.0	50	*89*
550	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	<169.0	>75	*89*
551	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*89*
552	$C_{10}H_{14}$	Butylbenzene	183.1	<158.5	<48	*89*
553	$C_{10}H_{14}$	Cymene	176.7	154.7	37	*89*
554	$C_{10}H_{15}N$	Diethylaniline	217.05	<169.0	>82	*89*
555	$C_{10}H_{16}$	Camphene	159.6	144.0	28	*89*
556	$C_{10}H_{16}$	*α*-Pinene	155.8	142.0	25	*89*
557	$C_{10}H_{16}$	*α*-Terpinene	173.4	<154.0	<36	*89*
558	$C_{10}H_{16}$	Dipentene	177.7	153.0	37	*89*
559	$C_{10}H_{22}O$	Amyl ether	187.5	<160.0	<50	*89*
560	$C_{11}H_{10}$	1-Methylnaphthalene	244.6	Nonazeotrope		*89*
561	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*89*
562	$C_{11}H_{20}O$	Isobornyl methyl ether	192.4	<165.0	<62	*89*
563	$C_{13}H_{12}$	Diphenylmethane	265.4	Nonazeotrope		*89*
A =	**$C_2H_8N_2$**	**Ethylenediamine**	**116.5**			
564	$C_3H_8O_2$	2-Methoxyethanol	124.5	130.0	31-32	*26*
A =	**$C_3H_3Cl_3O_2$**	**Methyl Trichloroacetate**	**152**			
565	$C_5H_{10}O_3$	Ethyl lactate	155	Azeotrope doubtful		*94*
A =	**$C_3H_4Cl_2$**	**1,3-Dichloropropene**				
566	C_3H_5Cl	3-Chloropropene	45.7	Nonazeotrope		*155*
A =	**$C_3H_4O_3$**	**Pyruvic Acid**	**166.8**			
567	$C_3H_6O_2$	Propionic acid	141.3	Nonazeotrope		*90*
568	$C_5H_{10}O_3$	2-Methoxyethyl acetate	144.6	Nonazeotrope		*90*
569	C_6H_5Br	Bromobenzene	156.1	147.0	34	*90*
570	C_6H_6	Benzene	80.15	Nonazeotrope		*90*
571	$C_6H_{12}O_3$	2-Ethoxyethyl acetate	156.8	Nonazeotrope		*90*
572	C_7H_7Cl	*o*-Chlorotoluene	159.2	149.5	37	*90*
573	C_7H_7Cl	*p*-Chlorotoluene	162.4	151.5	40	*90*
574	C_7H_8	Toluene	110.75	110.05	7.5	*90*
575	C_7H_8O	Anisole	153.85	148.5	28	*90*
576	C_8H_{10}	Ethylbenzene	136.15	130.5	22	*90*
577	C_8H_{10}	*o*-Xylene	144.3	137.0	28	*90*
578	$C_8H_{18}O$	Butyl ether	142.4	138.0	15	*90*
579	C_9H_{12}	Cumene	152.8	143.0	33	*90*
580	C_9H_{12}	Mesitylene	164.6	151.2	40	*90*
581	C_9H_{12}	Propylbenzene	159.3	147.6	37	*90*
A =	**C_3H_5Br**	**3-Bromopropene**	**70.8**			
582	C_3H_6O	Acetone	56.15	56.05	8	*90*
583	C_4H_8O	2-Butanone	79.6	Nonazeotrope		*90*
584	C_4H_9Cl	1-Chloro-2-methylpropane	68.85	68.75	15	*87*
A =	**C_3H_5BrO**	**Epibromohydrin**	**138.5**			
585	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
A =	**$C_3H_5BrO_2$**	***α*-Bromopropionic Acid**	**205.5**			
586	$C_6H_5NO_2$	Nitrobenzene	210.75	203.3	60	*92*
A =	**C_3H_5Cl**	**2-Chloropropene**	**22.65**			
587	C_3H_5Cl	3-Chloropropene	45.7	Nonazeotrope		*155*
588	$C_3H_7NO_2$	Isopropyl nitrite	40.1	Nonazeotrope		*88*
A =	**C_3H_5Cl**	**3-Chloropropene**	**45.15**			
589	C_3H_6O	Acetone	56.15	44.6	90	*90*
590	C_3H_7Cl	1-Chloropropane	46.6	Nonazeotrope		*87*
A =	**C_3H_5ClO**	**1-Chloro-2-Propanone**	**119.7**			
591	C_3H_8O	Isopropyl alcohol	82.4	Nonazeotrope		*90*
592	$C_4H_{10}O$	Butyl alcohol	117.8	112.5	57	*90*
593	$C_4H_{10}O$	*sec*-Butyl alcohol	99.5	Nonazeotrope		*90*
594	$C_5H_{10}O$	Cyclopentanol	140.85	Nonazeotrope		*90*
595	$C_5H_{12}O$	Amyl alcohol	138.2	Nonazeotrope		*90*
596	$C_5H_{12}O$	*tert*-Amyl alcohol	102.35	Nonazeotrope		*90*
597	$C_5H_{12}O$	2-Pentanol	119.8	<116.0	<68	*90*
598	C_7H_{14}	Methylcyclohexane	101.15	<100.5	..	*90*
599	$C_7H_{14}O_2$	Ethyl isovalerate	134.7	Nonazeotrope		*90*
600	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*90*
A =	**C_3H_5ClO**	**Epichlorohydrin**	**116.4**			
601	C_4H_5N	Pyrrole	130.5	Reacts		*94*
602	C_5H_5N	Pyridine	115.5	Reacts		*94*
603	$C_5H_{10}O$	3-Pentanone	102.05	Nonazeotrope		*90*
604	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
A =	**$C_3H_5ClO_2$**	**Methyl Chloroacetate**	**129.95**			
605	C_5H_8O	Cyclopentanone	130.65	<129.6		*90*
606	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
607	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
608	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
A =	**C_3H_5I**	**3-Iodopropene**	**102.0**			
609	C_3H_8O	Isopropyl alcohol	82.45	~ 79	~58	*94*
610	$C_5H_{11}Cl$	1-Chloro-3-methylbutane	99.4	Nonazeotrope		*87*
611	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	96.0		*88*

Table I. Binary Systems (*Continued*)

No.	B-Component			Azeotropic Data		
	Formula	Name	B.P., ° C.	B.P., ° C.	Weight % A	Reference
A =	C_3H_5N	**Propionitrile**	**97.1**			
612	C_3H_9ClSi	Chlorotrimethylsilane	57.7	Nonazeotrope		*127*
613	C_7H_8	Toluene	110.7	Minimum B.P.		*76*
A =	$C_3H_5N_3O_9$	**Nitroglycerin**				
614	C_3H_6O	Acetone	56.15	Nonazeotrope		*94, 103*
A =	$C_3H_6Br_2$	**1,2-Dibromopropane**	**141.6**			
615	$C_3H_6O_2$	Propionic acid	141.3	134.5	67	*93*
616	C_4H_5N	Pyrrole	130	Nonazeotrope		*93*
617	$C_4H_{10}O_2$	2-Ethoxyethanol	135.3	132.5	50	*93*
618	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
619	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
620	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
A =	$C_3H_6Cl_2$	**1,2-Dichloropropane**	**97**			
621	C_3H_8O	Isopropyl alcohol	82.4		50	*49*
622	$C_4H_8O_2$	Butyric acid	162.4	Nonazeotrope		*105*
A =	$C_3H_6Cl_2$	**2,2-Dichloropropane**	**70.3**			
623	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
A =	$C_3H_6Cl_2O$	**1,3-Dichloro-2-propanol**	**174.5**			
624	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
625	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
626	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	177.5	>85	*90*
A =	$C_3H_6Cl_2O$	**2,3-Dichloro-1-propanol**	**183**			
627	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
628	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
629	$C_8H_{16}O$	2-Octanone	172.85	184.0		*90*
A =	C_3H_6O	**Acetone**	**56.35**			
630	C_3H_6O	Allyl alcohol	96.85	Nonazeotrope		*90*
631	C_3H_7I	2-Iodopropane	89.45	Nonazeotrope		*90*
632	C_3H_8O	*n*-Propyl alcohol	97.2	Nonazeotrope		*90*
633	C_4H_8O	Butyraldehyde	75.2	Nonazeotrope		*90*
634	C_4H_8O	Isobutyraldehyde	63.5	Nonazeotrope		*90*
635	C_4H_9Cl	2-Chlorobutane	68.25	55.75	80	*90*
636	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88, 90*
637	$C_4H_{10}O$	Butyl alcohol	117.7	Nonazeotrope		*17, 49*
638	$C_4H_{10}O$	Isobutyl alcohol	108.0	Nonazeotrope		*90*
639	$C_4H_{11}N$	Butylamine	77.8	Nonazeotrope		*89*
640	C_5H_8	3-Methyl-1,2-butadiene	40.8	35.3	27	*90*
641	C_5H_{10}	Cyclopentane	49.3	41.0	36	*90*
642	$C_5H_{12}O$	*tert*-Amyl alcohol	102.35	Nonazeotrope		*90*
643	$C_5H_{12}O_2$	Diethoxymethane	87.95	Nonazeotrope		*90*
644	C_6H_5F	Fluorobenzene	84.9	Nonazeotrope		*90*
645	C_6H_7N	Aniline	184.35			*94*
646	C_6H_{12}	Methylcyclopentane	72.0	50.3	57	*90*
647	C_6H_{14}	2,3-Dimethylbutane	58.0	46.3	42	*90*
648	$C_6H_{14}O$	Isopropyl ether	69.0	54.2	61	*46*
649	$C_6H_{14}O$	Propyl ether	90.1	Nonazeotrope		*90*
650	$C_6H_{15}N$	Triethylamine	89.35	Nonazeotrope		*89*
651	C_7H_6O	Benzoic acid	249.5			*94*
652	C_7H_{14}	Methylcyclohexane	101.15	Nonazeotrope		*90*
653	C_8H_{18}	2,5-Dimethyhexane	109.4	Nonazeotrope		*90*
654	$C_9H_{10}O_2$	Ethyl benzoate	213			*94*
A =	C_3H_6O	**Allyl Alcohol**	**97.0**			
655	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91*
656	$C_5H_{10}O$	2-Pentanone	102.35	96.0	70	*90*
A =	C_3H_6O	**Propionaldehyde**	**48.7**			
657	C_4H_8O	Cyclopropyl methyl ether	44.73	43	..	*135*
A =	C_3H_6O	**Propylene Oxide**	**35**			
658	C_5H_{10}	Cyclopentane	49.3	Minimum B.P. azeotrope		*153*
659	C_5H_{10}	Pentenes		Minimum B.P. azeotrope		*153*
660	C_5H_{12}	Pentanes		Minimum B.P. azeotrope		*153*
661	C_6H_{12}	Cyclohexane	80.75	Minimum B.P. azeotrope		*153*
662	C_6H_{12}	Hexenes		Minimum B P. azeotrope		*153*
663	C_6H_{14}	Hexanes		Minimum B.P. azeotrope		*153*
A =	$C_3H_6O_2$	**1,3-Dioxolane**	**75**			
664	C_6H_6	Benzene	80.2	74	85	*76*
A =	$C_3H_6O_2$	**Ethyl Formate**	**54.15**			
665	$C_3H_7NO_2$	Isopropyl nitrite	40.1	Nonazeotrope		*87, 88*
666	$C_3H_7NO_2$	Propyl nitrite	47.75	47.4	12	*87, 88*
667	$C_9H_{10}O_2$	Ethyl benzoate	213	Vapor pressure data		*94*
668	C_9H_{12}	Pseudocumene	169	Vapor pressure data		*94*
A =	$C_3H_6O_2$	**Methyl Acetate**	**57.0**			
669	$C_3H_7NO_2$	Isopropyl nitrite	40.1	Nonazeotrope		*88*
670	$C_3H_7NO_2$	Propyl nitrite	47.75	Nonazeotrope		*87, 88*
671	$C_4H_8O_2$	Ethyl acetate	77.05			*94*
672	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88*
673	$C_5H_{10}O_2$	Propyl acetate	101.55			*94*
674	C_6H_5Cl	Chlorobenzene	131.8			*94*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	B-Component Name	B-Component B.P., ° C.	Azeotropic Data B.P., ° C.	Azeotropic Data Weight % A	Azeotropic Data Reference
A =	**$C_3H_6O_2$**	**Propionic Acid**	**141.3**			
675	$C_4H_6O_3$	Methyl pyruvate	137.5	<137.2	>75	*90*
676	$C_5H_8O_3$	Ethyl pyruvate	155.5	Nonazeotrope		*90*
677	C_5H_8O	Cyclopentanone	130.65	Nonazeotrope		*90*
678	$C_5H_{11}NO_3$	Isoamyl nitrate	~149.6	138.4	59	*82*
679	C_6H_7N	3-Picoline	143.5	122/212	48.5	*32, 33, 124*
680	C_6H_7N	4-Picoline	143.1	124/212	48.1	*32, 33, 124*
681	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
682	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
683	$C_6H_{12}O$	2-Hexanone	127.2	Nonazeotrope		*90*
684	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
685	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
686	$C_6H_{13}Br$	1-Bromohexane	156.5	139.0	..	*97*
687	C_7H_9N	2,6-Lutidine	143	119/212	48.8	*32, 33, 124*
688	C_nH_x	Hydrocarbons	138-140	134	67	*123*
689	$C_8H_{16}O_2$	Amyl propionate		Nonazeotrope		*123*
A =	**$C_3H_6O_3$**	**Methyl Carbonate**	**90.25**			
690	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
691	$C_5H_{10}O_2$	Methyl isobutyrate	92.5	Nonazeotrope		*87*
692	$C_6H_{10}O$	Mesityl oxide	129.45	126.45	94	*90*
A =	**$C_3H_6O_3$**	**Trioxane**	**114.5**			
693	C_8H_{10}	Xylene	140	Minimum B.P.		*76*
694	C_nH_{2n+2}	Paraffins	94-115	Minimum B.P		*75*
A =	**C_3H_7Br**	**2-Bromopropane**	**59.35**			
695	C_4H_8O	2-Butanone	79.6	Nonazeotrope		*90*
A =	**C_3H_7Cl**	**1-Chloropropane**	**46.65**			
696	$C_4H_8O_2$	Ethyl acetate	77.05	Nonazeotrope		*93*
697	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88, 93*
698	$C_4H_{10}O$	*tert*-Butyl alcohol	82.55	Nonazeotrope		*93*
699	$C_4H_{10}O$	Ethyl ether	34.5	Nonazeotrope		*93*
700	C_5H_{12}	Pentane	36	<34.8	<32	*93*
A =	**C_3H_7ClO**	**1-Chloro-2-propanol**	**127.0**			
701	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
702	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
A =	**C_3H_7I**	**1-Iodopropane**	**102.4**			
703	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
704	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	< 96.7	..	*88*
A =	**C_3H_7I**	**2-Iodopropane**	**89.35**			
705	C_4H_8O	2-Butanone	79.6	Nonazeotrope		*90*
A =	**C_3H_7NO**	**Propionamide**	**222.2**			
706	$C_5H_8O_3$	Levulinic acid	252	Nonazeotrope		*90*
707	$C_6H_4ClNO_2$	*m*-Chloronitrobenzene	235.5	216.5	>48	*92*
708	$C_6H_4ClNO_2$	*o*-Chloronitrobenzene	246.0	<220.6	>54	*92*
709	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
710	$C_6H_8N_2$	*o*-Phenylenediamine	258.6	Nonazeotrope		*89*
711	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	214.5	44	*92*
712	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
713	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
714	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
715	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	<212.0	<27	*89*
716	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	220.5	28	*89*
717	$C_8H_{11}N$	Ethylaniline	205.5	<204.0	>12	*89*
718	$C_8H_{11}NO$	*o*-Phenetidine	232.5	<222.0	..	*89*
719	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
720	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
721	$C_9H_{10}O$	Propiophenone	217.7	207.0	28	*90*
722	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	182.5	..	*89*
723	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	199.0	20	*89*
724	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
725	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
726	$C_{10}H_9N$	1-Naphthylamine	300.8	Nonazeotrope		*89*
727	$C_{10}H_{16}O$	Camphor	209.1	203.5	17	*90*
A =	**$C_3H_7NO_2$**	**Ethyl Carbamate**	**185.25**			
728	$C_6H_4Cl_2$	*p*-Dichlorobenzene	174.35	167.0	24.2	*93*
729	$C_6H_5NO_2$	Nitrobenzene	210.75	184.95	88	*92*
730	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	Nonazeotrope		*92*
731	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	Nonazeotrope		*92*
732	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	Nonazeotrope		*92*
733	C_8H_8O	Acetophenone	202.0	184.85	86	*90*
734	$C_8H_{14}O$	Methylheptenone	173.2	171.5	30	*90*
735	$C_8H_{16}O$	2-Octanone	172.85	171.5	28	*90*
736	$C_8H_{18}S$	Isobutyl sulfide	172.0	166.5	23	*93*
737	$C_9H_{10}O$	*p*-Methylacetophenone	226.35	Nonazeotrope		*90*
738	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*90*
739	$C_9H_{14}O$	Phorone	197.8	<184.5	<82	*90*
740	$C_{10}H_{16}O$	Camphor	209.1	184.85	84	*90*
741	$C_{10}H_{16}O$	Fenchone	193.6	<182.0	<75	*90*
A =	**$C_3H_7NO_2$**	**Isopropyl Nitrite**	**40.0**			
742	$C_3H_7NO_2$	Propyl nitrite	47.75	Nonazeotrope		*88*
743	C_4H_4O	Furan	31.7	Nonazeotrope		*88*
744	$C_4H_{10}O$	Methyl propyl ether	38.85	< 37.5	33	*88*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic data B.P., ° C.	Weight % A	Reference
A =	$C_3H_7NO_2$	**Isopropyl Nitrite (*Contd.*)**	**40.0**			
745	C_5H_{10}	Cyclopentane	49.3	< 39.9	<92	*88*
746	C_5H_{10}	2-Methyl-2-butene	37.1	35.5	38	*88*
747	C_5H_{10}	3-Methyl-1-butene	20.6	Nonazeotrope		*88*
748	C_6H_{10}	Biallyl	60.1	Nonazeotrope		*88*
749	C_6H_{14}	2,3-Dimethylbutane	58.0	Nonazeotrope		*88*
A =	$C_3H_7NO_2$	**1-Nitropropane**	**130.5**			
750	C_8H_8	Styrene	68/60	Nonazeotrope		*11*
751	C_8H_{10}	Ethylbenzene	60.5/60	56.4/60	61	*11*
A =	$C_3H_7NO_2$	**2-Nitropropane**	**120**			
752	C_nH_{2n+2}	Paraffins	107–110	96–108		*30*
A =	$C_3H_7NO_2$	**Propyl Nitrite**	**47.75**			
753	C_5H_{10}	Cyclopentane	49.3	45.5	54	*88*
754	$C_5H_{12}O$	Ethyl propyl ether	63.85	Nonazeotrope		*88*
755	C_6H_{14}	2,3-Dimethylbutane	58.0	Nonazeotrope		*88*
A =	C_3H_8O	**Isopropyl Alcohol**	**82.45**			
756	$C_4H_6O_2$	Biacetyl	88	77.3	~60[a]	*90, 102*
757	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
758	$C_5H_{10}O$	3-Pentanone	102.05	Nonazeotrope		*90*
759	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90*
A =	C_3H_8O	**Propyl Alcohol**	**97.25**			
760	$C_4H_6O_2$	Biacetyl	87.5	85.0	25	*90*
761	C_4H_8S	Tetrahydrothiophene	118.8	96.5	90	*93*
762	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91, 94*
763	$C_5H_9ClO_2$	Propyl chloroacetate	162.3	Nonazeotrope		*22*
764	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	93.5	35	*90*
765	$C_5H_{12}O_2$	Diethoxymethane	88.0	86.15	11	*159*
766	$C_6H_{14}O_2$	Ethoxypropoxymethane	113.7	Nonazeotrope		*159*
767	$C_8H_{18}O_2$	1,1-Dipropoxyethane	147.7	Nonazeotrope		*7*
A =	$C_3H_8O_2$	**2-Methoxyethanol**	**124**			
768	C_4H_5N	Pyrrole	130.0	Nonazeotrope		*91*
769	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91*
770	$C_5H_{12}O_3$	2-(2-Methoxyethoxy)ethanol	193.2	Nonazeotrope		*137*
771	C_6H_5Cl	Chlorobenzene	131	119.45	47.5	*93*
772	$C_6H_{10}O$	Mesityl oxide	129.45	122.5	59	*90*
773	$C_6H_{10}S$	Allyl sulfide	139	122.5	75	*93*
774	$C_6H_{12}O$	2-Hexanone	127.2	<121.5	<56	*90*
775	$C_6H_{12}O$	3-Hexanone	123.3	<119.5	<43	*90*
776	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	114.2	25	*90*
A =	$C_3H_8O_2$	**Methylal**	**42.15**			
777	C_3H_9N	Propylamine	49.7	Nonazeotrope		*89*
778	C_5H_{10}	1-Pentene	30.1	29.8	26[a]	*126*
779	C_5H_{10}	2-Pentene	36.5	34.9	29[a]	*126*
A =	$C_3H_8O_2$	**1,2-Propanediol**	**188.5**			
781	C_6H_7N	Aniline	184.35	179.5	43	*89*
782	C_7H_9N	Methylaniline	196.25	<181.0	>46	*89*
783	C_8H_8O	Acetophenone	202.0	<183.5	..	*90*
784	$C_8H_{11}N$	Dimethylaniline	194.05	<177.0	>45	*89*
785	$C_8H_{16}O$	2-Octanone	172.85	<169.5	..	*90*
786	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	<174.0	37	*89*
787	$C_{10}H_{16}O$	Camphor	209.1	<185.0	..	*90*
788	$C_{10}H_{18}O$	Menthone	209.5	<185.0	<85	*90*
A =	$C_3H_8O_3$	**Glycerol**	**290.0**			
789	$C_6H_4ClNO_2$	*m*-Chloronitrobenzene	235.5	232.2	10	*92*
790	$C_6H_4ClNO_2$	*o*-Chloronitrobenzene	246.0	242.1	15?	*92*
791	$C_6H_4ClNO_2$	*p*-Chloronitrobenzene	239.1	235.6	13	*92*
792	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
793	C_9H_{12}	3-Phenylpropanol	235.6	Nonazeotrope		*87*
794	$C_{10}H_{10}O_2$	Methyl cinnamate	261.9	Reacts		*78*
795	$C_{11}H_{12}O_2$	Ethyl cinnamate	271.5	Reacts		*79*
A =	C_3H_8S	**1-Propanethiol**	**67.5**			
796	C_5H_8	3-Methyl-1,2-butadiene	40.8	Reacts		*94*
797	C_6H_{10}	Biallyl	60.2	Reacts		*94*
A =	$C_3H_9BO_3$	**Methyl Borate**	**68.7**			
798	$C_4H_8O_2$	Ethyl acetate	77.1	Nonazeotrope		*87*
799	$C_4H_8O_2$	Isopropyl formate	68.8	< 67.0	<58	*87*
800	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*87, 88*
801	$C_4H_9NO_2$	Isobutyl nitrite	67.1	< 66.9	..	*87, 88, 94*
A =	C_3H_9ClSi	**Chlorotrimethylsilane**	**57.7**			
802	C_6H_{14}	2-Methylpentane	60.4	56.4	65	*128*
803	C_6H_{14}	3-Methylpentane	63.3	57.3	70[a]	*128*
A =	C_3H_9N	**Propylamine**	**49.7**			
804	C_4H_8O	2-Butanone	79.6	Nonazeotrope		*89*
805	$C_4H_{10}O$	Ethyl ether	34.6	Nonazeotrope		*89*
806	C_5H_{10}	Cyclopentane	49.3	47.0	52	*89*
807	C_5H_{12}	2-Methylbutane	27.95	Nonazeotrope		*89, 94*
808	C_6H_{14}	2,3-Dimethylbutane	58.0	Nonazeotrope		*89*

[a] Volume per cent.

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	B-Component Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Azeotropic Data Weight % A	Reference
A =	**C_3H_9N**	**Trimethylamine**	**3.5**			
809	C_4H_8	1-Butene	−6	Nonazeotrope		*62*
810	C_4H_8	2-Methylpropene	−6	Nonazeotrope		*62*
811	C_4H_{10}	*n*-Butane	0	Nonazeotrope		*62*
812	C_4H_{10}	2-Methylpropane	−10	Nonazeotrope		*62*
A =	**C_4H_4S**	**Thiophene**	**84.7**			
813	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
814	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88*
815	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
A =	**$C_4H_5ClO_2$**	**α-Chlorocrotonic Acid**	**212.5**			
816	$C_6H_5NO_2$	Nitrobenzene	210.75	<208.0	>30	*92*
817	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	<211.2	>72	*92*
A =	**C_4H_5N**	**Pyrrole**	**130.5**			
818	$C_4H_{10}O$	Butyl alcohol	117.8	Nonazeotrope		*91*
819	$C_4H_{10}S$	Ethyl sulfide	92.1	Nonazeotrope		*91*
820	$C_5H_{10}O$	Cyclopentanol	140.85	Nonazeotrope		*91*
821	$C_5H_{12}O$	Amyl alcohol	138.2	Nonazeotrope		*91*
822	$C_5H_{12}O$	Isoamyl alcohol	131.9	<129.4	>21	*91*
823	$C_5H_{12}O$	2-Pentanol	119.8	Nonazeotrope		*91*
824	$C_5H_{12}O_2$	2-Propoxyethanol	151.35	Nonazeotrope		*91*
825	C_6H_5Br	Bromobenzene	156.1	Nonazeotrope		*91*
826	$C_6H_{14}S$	Isopropyl sulfide	120.5	117.5	20	*91*
827	$C_6H_{14}S$	Propyl sulfide	140.8	127.5	65	*91, 93*
828	C_7H_7Cl	*o*-Chlorotoluene	159.2	Nonazeotrope		*91*
829	C_7H_8	Toluene	110.75	Nonazeotrope		*91*
830	C_8H_{10}	Xylenes	140	Minimum B.P.		*76*
831	C_8H_{18}	*n*-Octane	125.75	<124.3	<36	*91*
A =	**C_4H_6**	**1,3-Butadiene**	**−4.5**			
832	$C_4H_{10}O$	Ethyl ether	34.5	Nonazeotrope		*20*
A =	**C_4H_6O**	**Crotonaldehyde**	**102.25**			
833	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
A =	**$C_4H_6O_2$**	**Allyl Formate**	**80.0**			
834	$C_4H_9NO_2$	Butyl nitrite	78.2	< 77.0	>30	*87, 88*
A =	**$C_4H_6O_2$**	**Biacetyl**	**87.5**			
835	$C_5H_{12}O$	Isoamyl alcohol	131.9	Nonazeotrope		*90*
836	C_6H_6	Benzene	80	79.3	~55[a]	*102*
A =	**$C_4H_6O_2$**	**Methacrylic Acid**				
837	$C_5H_8O_2$	Methyl methacrylate		Nonazeotrope		*157*
A =	**$C_4H_6O_3$**	**Acetic Anhydride**	**138**			
838	C_7H_{14}	Methylcyclohexane	101	99	~18	*48*
839	C_7H_{16}	*n*-Heptane	98.4	Azeotrope		*48*
840	C_8H_{16}	Ethylcyclohexane	131	118	~37	*48*
841	C_8H_{18}	*n*-Octane	125.8	Azeotrope		*48*
842	C_9H_{20}	*n*-Nonane	150	Azeotrope		*48*
843	$C_{10}H_{22}$	*n*-Decane	173	Azeotrope		*48*
844	$C_{11}H_{24}$	*n*-Undecane	194.5	Azeotrope		*48*
A =	**$C_4H_6O_3$**	**Methyl Pyruvate**	**137.5**			
845	$C_4H_8O_2$	Isobutyric acid	154.6	Nonazeotrope		*90*
846	C_4H_9I	1-Iodobutane	130.4	<127.0	..	*90*
847	$C_5H_8O_2$	2,4-Pentanedione	137.7	<136.2	..	*90*
848	$C_5H_{10}O_2$	Propyl acetate	101.6	Nonazeotrope		*90*
849	$C_5H_{11}I$	1-Iodo-3-methylbutane	147.65	<136.0	..	*90*
850	C_6H_5Br	Bromobenzene	156.1	Nonazeotrope		*90*
851	C_6H_5Cl	Chlorobenzene	131.75	129.0	30	*90*
852	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
853	$C_6H_{12}O$	2-Hexanone	127.2	Nonazeotrope		*90*
854	$C_6H_{12}O_2$	Isobutyl acetate	117.4	Nonazeotrope		*90*
855	$C_6H_{14}O$	Propyl ether	90.1	Nonazeotrope		*90*
856	C_7H_8O	Anisole	153.85	Nonazeotrope		*90*
857	$C_7H_{14}O_2$	Ethyl isovalerate	134.7	<132.0	..	*90*
858	$C_7H_{14}O_2$	Isoamyl acetate	142.1	135.0	65	*90*
859	C_8H_{10}	*m*-Xylene	139.2	130.0	50	*90*
860	C_8H_{16}	*m*-Dimethylcyclohexane	120.7	<117.0	..	*90*
861	$C_8H_{18}O$	Butyl ether	142.4	130.2	..	*90*
862	$C_8H_{18}O$	Isobutyl ether	122.3	<121.5	..	*90*
863	$C_{10}H_{16}$	Camphene	159.6	<135.2	..	*90*
864	$C_{10}H_{16}$	α-Pinene	155.8	<134.5	..	*90*
A =	**$C_4H_6O_4$**	**Methyl Oxalate**	**164.45**			
865	$C_8H_{16}O_2$	Butyl butyrate	166.4	160.5	58	*87*
866	$C_8H_{16}O_2$	Ethyl caproate	167.7	161.0	60	*87*
867	$C_8H_{16}O_2$	Isoamyl propionate	160.7	157.5	38	*87*
868	$C_8H_{16}O_2$	Isobutyl butyrate	156.9	<155.5	>23	*87*
869	$C_8H_{16}O_2$	Propyl isovalerate	155.7	<154.5	>20	*87*
870	$C_9H_{18}O_2$	Isoamyl isobutyrate	169.8	161.0	65	*87*
871	$C_{10}H_{16}$	Terpinylene	175	~155	<80	*94*
872	$C_{10}H_{20}O_2$	Isoamyl isovalerate	171.2	162.2	70	*87*
873	$C_{12}H_{22}O_4$	Isoamyl oxalate	172.7	Doubtful		*94*

[a] Volume per cent.

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**$C_4H_7BrO_2$**	**Ethyl Bromoacetate**	**158.2**			
874	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
A =	**$C_4H_7ClO_2$**	**Ethyl Chloroacetate**	**143.5**			
875	C_5H_8O	Cyclopentanone	130.65	Nonazeotrope		*90*
876	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
877	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
878	$C_6H_{12}O$	2-Hexanone	127.2	Nonazeotrope		*90*
879	$C_7H_{14}O$	4-Heptanone	143.55	142.75	47	*90*
A	**$C_4H_8Cl_2O$**	**Bis(2-Chloroethyl) Ether**	**178.65**			
880	$C_5H_8O_3$	Methyl acetoacetate	169.5	Nonazeotrope		*90*
881	$C_6H_{10}O_3$	Ethyl acetoacetate	180.4	Nonazeotrope		*90*
882	C_7H_7Br	*o*-Bromotoluene	181.4	<177.9	>63	*93*
883	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
884	$C_8H_{18}S$	Butyl sulfide	185.0	178.4	88	*93*
A =	**C_4H_8O**	**2-Butanone**	**79.6**			
885	C_4H_8O	Isobutyraldehyde	63.5	Nonazeotrope		*90*
886	$C_4H_8O_2$	Dioxane	101.35	Nonazeotrope		*90*
887	C_4H_9Br	2-Bromobutane	91.2	Nonazeotrope		*90*
888	C_4H_9Cl	2-Chlorobutane	68.25	Nonazeotrope		*90*
889	$C_4H_9NO_2$	Butyl nitrite	78.2	76.7	30	*88, 90*
890	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88, 90*
891	$C_4H_{10}O$	*n*-Butyl alcohol	117.8	Nonazeotrope		*90*
892	$C_4H_{10}O$	Isobutyl alcohol	108.0	Nonazeotrope		*90*
893	$C_4H_{11}N$	Butylamine	77.8	74.0	35	*89*
894	$C_5H_{10}O$	Isovaleraldehyde	92.1	Nonazeotrope		*90*
895	$C_5H_{12}O_2$	Diethoxymethane	87.95	Nonazeotrope		*90*
896	C_6H_5F	Fluorobenzene	84.9	77.3	75	*90*
897	C_6H_{10}	Cyclohexene	82.75	73.0	47	*90*
898	C_6H_{14}	2,3-Dimethylbutane	58.0	56.0	15	*90*
899	$C_6H_{15}N$	Dipropylamine	109.2	Nonazeotrope		*89*
900	C_7F_{16}	Perfluoroheptane	81.6	62–63	..	*44*
A =	**C_4H_8O**	**1-Butene-3-ol**				
901	$C_4H_{10}O_2$	2,3-Butanediol		Nonazeotrope		*113*
A =	**C_4H_8O**	**Butyraldehyde**	**75.7**			
902	C_7H_{16}	Paraffins	75–80	~ 61	..	*57*
A =	**C_4H_8O**	**Isobutylaldehyde**	**63**			
903	C_6H_6	Benzene	81	Nonazeotrope		*57*
904	C_7H_{16}	Paraffins	75–80	~ 50	..	*57*
A =	**$C_4H_8O_2$**	**Butyric Acid**	**162.45**			
905	$C_5H_8O_3$	Ethyl pyruvate	155.5	Nonazeotrope		*90*
906	C_6H_{10}	Cyclohexene	82.75	Nonazeotrope		*105*
907	$C_6H_{10}O_3$	Ethyl acetoacetate	180.4	Nonazeotrope		*90*
908	C_6H_{12}	Cyclohexane	80.75	Nonazeotrope		*105*
909	C_7H_{14}	Methylcyclohexane	101.8	Nonazeotrope		*105*
910	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
911	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	65.7/10	63.3/10	34/10	*10*
912	$C_8H_{14}O$	Methylheptenone	173.2	Nonazeotrope		*90*
913	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
914	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	**$C_4H_8O_2$**	***m*-Dioxane**	**105**			
915	C_7H_8	Toluene	110.7	....	85	*76*
A =	**$C_4H_8O_2$**	***p*-Dioxane**	**101.4**			
916	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91*
917	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
918	$C_6H_{10}O$	Cyclohexanone	156.7	Nonazeotrope		*35*
919	C_nH_{2n+2}	Paraffins	109.5–110.5	96.6–98.9	..	*39*
A =	**$C_4H_8O_2$**	**Ethyl Acetate**	**77.15**			
920	$C_4H_9NO_2$	Butyl nitrite	78.2	76.3	71	*87, 88*
921	$C_4H_9NO_2$	Isobutyl nitrite	67.1	Nonazeotrope		*88*
922	$C_4H_{10}O$	Isobutyl alcohol	108.0	Vapor pressure data		*94*
923	C_5H_5N	Pyridine	115.5			*94*
A =	**$C_4H_8O_2$**	**Isobutyric Acid**	**154.35**			
924	$C_4H_{10}O$	Ethyl ether	34.06	Vapor pressure data		*94*
925	$C_5H_8O_3$	Ethyl pyruvate	155.5	153.0	60	*90*
926	$C_5H_8O_3$	Methyl acetoacetate	169.5	Nonazeotrope		*90*
927	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
928	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
929	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	**$C_4H_8O_2$**	**Isopropyl Formate**	**68.8**			
930	$C_4H_9NO_2$	Isobutyl nitrite	67.1	65.5	40	*87, 88*
A =	**$C_4H_8O_2$**	**Methyl Propionate**	**79.7**			
931	$C_4H_9NO_2$	Butyl nitrite	78.2	77.7	12	*87, 88*
A =	**$C_4H_8O_2$**	**Propyl Formate**	**80.8**			
932	$C_4H_9NO_2$	Butyl nitrite	78.2	76.8	35	*87, 88*
A =	**$C_4H_8O_3$**	**Glycol Monoacetate**	**190.9**			
933	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
934	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
935	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	References
A =	$C_4H_8O_3$	**Methyl Lactate**	**143.8**			
936	C_5H_8O	Cyclopentanone	130.65	Nonazeotrope		*90*
937	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
938	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
939	$C_7H_{14}O$	4-Heptanone	143.55	142.7	47	*90*
A =	C_4H_8S	**Tetrahydrothiophene**	**118.8**			
940	C_5H_5N	Pyridine	115.4	113.5	45	*91*
A =	C_4H_9Br	**1-Bromobutane**	**100.35**			
941	C_4H_9Cl	1-Chlorobutane		Nonazeotrope		*139*
942	$C_5H_{10}O$	2-Pentanone	102.35	100.1	63	*90*
943	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
944	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
945	$C_6H_{12}O$	Pinacolone	106.2	101.1	86	*86, 90*
946	$C_6H_{12}O_2$	Ethyl isobutyrate	110.1	Nonazeotrope		*85*
947	C_7H_{16}	Heptane	98.45	96.7	50	*81, 139*
A =	C_4H_9Br	**2-Bromobutane**	**91.2**			
948	C_4H_9Br	1-Bromo-2-methylpropane	91.4	Nonazeotrope		*87*
949	$C_5H_{10}O$	3-Pentanone	102.05	Nonazeotrope		*90*
950	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
A =	C_4H_9Br	**1-Bromo-2-methylpropane**	**91.3**			
951	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
952	$C_4H_{10}O$	*tert*-Butyl alcohol	82.5	Minimum B.P.		*148*
A =	C_4H_9Cl	**1-Chlorobutane**	**78.05**			
953	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
954	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
955	C_7H_{16}	Heptane		Nonazeotrope		*139*
A =	C_4H_9Cl	**2-Chlorobutane**	**68.25**			
956	$C_4H_9NO_2$	Butyl nitrite	78.2	Nonazeotrope		*88*
957	$C_4H_9NO_2$	Isobutyl nitrite	67.1	66.2	38	*88*
958	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
A =	C_4H_9Cl	**1-Chloro-2-methylpropane**	**68.85**			
959	C_5H_5N	Pyridine	115.5			*94*
960	C_7H_{16}	Heptane	98.45			*94*
A =	C_4H_9Cl	**2-Chloro-2-methylpropane**	**51.6**			
961	$C_4H_{10}O$	*tert*-Butyl alcohol	82.5	Nonazeotrope		*148*
A =	C_4H_9I	**1-Iodobutane**	**130.4**			
962	C_5H_8O	Cyclopentanone	130.65	129.0	60	*90*
963	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
A =	C_4H_9N	**Pyrrolidine**				
964	C_6H_6	Benzene	80	Minimum B.P.		*76*
A =	$C_4H_9NO_2$	**Butyl Nitrite**	**77.8**			
965	$C_4H_{10}S$	Ethyl sulfide	92.1	Nonazeotrope		*88*
966	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*88, 90*
967	$C_5H_{10}O_2$	Isopropyl acetate	89.5	Nonazeotrope		*88*
968	$C_5H_{12}O_2$	Diethoxymethane	87.95	Nonazeotrope		*88*
969	C_6H_5F	Fluorobenzene	84.9	Nonazeotrope		*88*
970	$C_6H_{14}O$	Propyl ether	90.1	Nonazeotrope		*88*
971	C_7H_{14}	Methylcyclohexane	101.15	Nonazeotrope		*88*
972	C_7H_{16}	Heptane	98.4	Nonazeotrope		*88*
A =	$C_4H_9NO_2$	**Isobutyl Nitrite**	**67.1**			
973	$C_4H_{10}O_2$	Acetaldehyde dimethyl acetal	64.3	Nonazeotrope		*88*
974	C_5H_{10}	Cyclopentane	49.3	Nonazeotrope		*88*
975	$C_5H_{12}O$	Ethyl propyl ether	63.85	< 63.7	5	*88*
976	C_6H_6	Benzene	80.15	Nonazeotrope		*88*
A =	$C_4H_9NO_3$	**Isobutyl Nitrate**	**122.9**			
977	$C_5H_{10}O_3$	Ethyl carbonate	126.5	Nonazeotrope		*87*
978	$C_6H_{12}O_2$	Isoamyl formate	123.8	<122.0	>54	*87*
979	$C_6H_{12}O_2$	Propyl propionate	123.0	<121.7	>41	*87*
A =	$C_4H_{10}O$	**Butyl Alcohol**	**117.75**			
980	C_5H_{10}	2-Methyl-2-butene	37.75	Nonazeotrope		*43*
981	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
982	$C_5H_{10}O$	2-Pentanone	102.35	Nonazeotrope		*90*
983	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
984	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
985	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
986	$C_6H_{11}ClO_2$	Butyl chloroacetate	181.9	Nonazeotrope		*22*
987	$C_6H_{12}O$	Butyl vinyl ether	93.8	93.3	7.75	*41, 136*
988	$C_6H_{12}O$	2-Hexanone	127.2	Nonazeotrope		*90*
989	$C_6H_{12}O$	3-Hexanone	123.3	117.2	80	*90*
990	$C_6H_{14}S$	Isopropyl sulfide	120.5	112.0	45	*93*
991	$C_8H_{16}O_2$	Butyl butyrate	166	Nonazeotrope		*109*
992	$C_{10}H_{22}O_2$	Acetaldehyde dibutyl acetal	187.8	Nonazeotrope		*7, 31*
A =	$C_4H_{10}O$	***sec*-Butyl Alcohol**	**99.5**			
993	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
994	$C_6H_{12}O$	Pinacolone	106.2	99.1	84	*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$C_4H_{10}O$	***sec*-Butyl Alcohol (*Contd.*)**	**99.5**			
995	C_7H_{14}	Methylcyclohexane	100.8	89.9	41	*9*
996	C_8H_8	Styrene	68/60	45/60	96	*11*
997	C_8H_{10}	Ethylbenzene	60.5/60	44/60	84	*11*
A =	$C_4H_{10}O$	***tert*-Butyl Alcohol**	**82.55**			
998	$C_5H_{10}O$	3-Pentanone	102.05	Nonazeotrope		*90*
999	C_8H_8	Styrene	68/60	Nonazeotrope		*11*
1000	C_8H_{10}	Ethylbenzene	60.5/60	28/60	95	*11*
A =	$C_4H_{10}O$	**Ethyl Ether**	**34.6**			
1001	C_5H_5N	Pyridine	115.5			*94*
1002	$C_6H_{15}N$	Triethylamine	89.35	Nonazeotrope		*89*
1003	C_9H_{12}	Pseudocumene	169	Vapor pressure data		*94*
1004	$C_{14}H_{10}$	Anthracene				*94*
A =	$C_4H_{10}O$	**Isobutyl Alcohol**	**108.0**			
1005	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*90*
1006	$C_6H_{11}ClO_2$	Isobutyl chloroacetate	97.8	Nonazeotrope		*22*
1007	$C_6H_{12}O$	2-Hexanone	127.2	Nonazeotrope		*90*
1008	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
1009	$C_6H_{12}O$	Isobutyl vinyl ether	83.0	82.7	6.2	*136*
1010	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	107.85	91	*90*
1011	$C_6H_{14}S$	Isopropyl sulfide	120.5	105.8	73	*93*
1012	$C_9H_{20}O_2$	Diisobutoxy methane	163.8	Nonazeotrope		*52*
1013	$C_{10}H_{22}O_2$	Acetaldehyde diisobutylacetal	171.3	Nonazeotrope		*7*
A =	$C_4H_{10}O$	**Methyl Propyl Ether**	**38.8**			
1014	$C_4H_{11}N$	Diethylamine	55.9	Nonazeotrope		*89*
A =	$C_4H_{10}O_2$	**Acetaldehyde Dimethyl Acetal**	**64.3**			
1015	$C_4H_{11}N$	Diethylamine	55.9	Nonazeotrope		*89*
A =	$C_4H_{10}O_2$	**2-Ethoxyethanol**	**135.3**			
1016	C_5H_5N	Pyridine	115.4	Nonazeotrope		*91*
1017	C_5H_8O	Cyclopentanone	130.65	<130.2	<27	*90*
1018	$C_6H_{10}O$	Mesityl oxide	129.45	128.9	18	*90*
1019	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
1020	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
1021	$C_6H_{12}O_2$	Butyl acetate	124.8	125.8	35.7	*25*
1022	$C_6H_{14}O_2$	1,2-Diethoxyethane	123.1	121.0	3.1	*25*
1023	$C_6H_{14}S$	Propyl sulfide	140.8	130.2	52	*93*
1024	$C_6H_{15}NO$	2-Diethylaminoethanol	162.2	Nonazeotrope		*89*
1025	C_7H_8	Toluene	110.75	110.15	..	*97*
1026	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
1027	C_7H_{16}	Heptane	98.4	96.5	..	*97*
1028	C_8H_8	Styrene	145	Minimum B.P.		*115*
1029	C_8H_{10}	Ethylbenzene	136	Minimum B.P.		*115*
1030	$C_8H_{18}O$	Butyl ether	131	127.0	50.0	*25*
A =	$C_4H_{10}O_2$	**1-Methoxy-2-propanol**	**118–119**			
1031	C_7H_8	Toluene	110.7	106.5/750	30	*36*
A =	$C_4H_{10}O_3$	**Diethylene Glycol**	**245.5**			
1032	$C_6H_4ClNO_2$	*m*-Chloronitrobenzene	235.5	228.2	32	*92*
1033	$C_6H_4ClNO_2$	*o*-Chloronitrobenzene	246.0	233.5	41	*92*
1034	$C_6H_4ClNO_2$	*p*-Chloronitrobenzene	239.1	229.5	34	*92*
1035	$C_6H_5NO_2$	Nitrobenzene	210.75	210.0	10	*92*
1036	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	224.2	25	*92*
1037	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	218.2	17.5	*92*
1038	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	228.75	35	*92*
1039	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1040	C_9H_7N	Quinoline	237.3	233.6	29	*91*
1041	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
A =	$C_4H_{10}S$	**2-Methyl-1-propanethiol**	**88**			
1042	C_6H_8	1,3-Cyclohexadiene	80.8	Reacts		*94*
1043	C_6H_8	1,4-Cyclohexadiene	85.6	Reacts		*94*
1044	C_6H_{10}	Cyclohexene	82.75	Reacts		*94*
A =	$C_4H_{11}N$	**Butylamine**	**77.8**			
1045	C_6H_{12}	Cyclohexane	80.75	76.5	60	*89*
1046	C_6H_{12}	Methylcyclopentane	72.0	< 77.5	..	*89*
A =	$C_4H_{11}N$	**Diethylamine**	**55.9**			
1047	C_5H_{10}	2-Methyl-2-butene	37.1	Nonazeotrope		*89*
1048	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*89*
1049	$C_5H_{12}O$	Ethyl propyl ether	63.85	Nonazeotrope		*80, 89*
1050	C_6H_{12}	Methylcyclopentane	72.0	Nonazeotrope		*89*
1051	C_6H_{14}	2,3-Dimethylbutane	58.0	<55.0	<62	*89*
A =	$C_4H_{11}N$	**Isobutylamine**	**68.5**			
1052	C_5H_{10}	Cyclopentane	49.3	Nonazeotrope		*89*
1053	$C_5H_{10}O$	3-Methyl-2-butanone	95.4	Nonazeotrope		*89*
1054	C_6H_6	Benzene	80.15	Nonazeotrope		*89*
1055	C_6H_{12}	Cyclohexane	80.75	Nonazeotrope		*89*
A =	$C_4H_{11}NO$	**2-Amino-2-methyl-1-propanol**	**165.4/760**			
1056	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	59.0/10	46/10	*10*
A =	$C_5H_4O_2$	**2-Furaldehyde**	**161.5**			
1057	$C_5H_8O_3$	Methyl acetoacetate	~169.5	Reacts		*94*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	B-Component Name	B-Component B.P., ° C.	Azeotropic Data B.P., ° C.	Azeotropic Data Weight % A	Reference
A =	C_5H_5N	**Pyridine**	**115.5**			
1058	$C_5H_{12}O$	Amyl alcohol	138.2	Nonazeotrope		*91*
1059	$C_5H_{12}O$	*tert*-Amyl alcohol	102.35	Nonazeotrope		*91*
1060	$C_5H_{12}O$	Isoamyl alcohol	131.9	Nonazeotrope		*91*
1061	$C_5H_{12}O$	3-Pentanol	116.0	117.4	45	*91*
1062	C_6H_6	Benzene	80.15	Nonazeotrope		*91, 94*
1063	C_6H_7N	Aniline	184.35			*94*
1064	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90, 91*
1065	C_6H_{12}	Cyclohexane	80.75	Nonazeotrope		*91*
1066	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90, 91*
1067	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90, 91*
1068	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	114.9	60	*90, 91*
1069	$C_6H_{12}O_2$	Isobutyl acetate	117.4	114.5	..	*91*
1070	$C_6H_{12}O_2$	Propyl propionate	123.0	Nonazeotrope		*91*
1071	$C_6H_{14}O$	Propyl ether	90.1	Nonazeotrope		*91*
1072	$C_6H_{14}S$	Isopropyl sulfide	120.5	<114.5	<72	*91*
1073	C_7H_{14}	Methylcyclohexane	100	Minimum B.P.		*38*
1074	C_7H_{16}	*n*-Heptane	98.4	<97.0	<14	*91, 94*
1075	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*91*
1076	C_8H_{10}	*m*-Xylene	139.2	Nonazeotrope		*91*
1077	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	<111.0	..	*91*
1078	C_8H_{18}	2,5-Dimethylhexane	109.4	<105.5	<40	*91*
1079	C_8H_{18}	*n*-Octane	125.75	<112.8	<90	*91*
1080	C_8H_{18}	2,2,4-Trimethylpentane	99.3	95.75	23.4	*91*
1081	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		*91*
A =	$C_5H_6O_2$	**Furfuryl Alcohol**	**169.35**			
1082	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	60.5/10	32/10	*10*
1083	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
A =	C_5H_8O	**Cyclopentanone**	**130.65**			
1084	$C_5H_{10}O_3$	Ethyl carbonate	126.5	Nonazeotrope		*90*
1085	$C_5H_{11}Br$	1-Bromo-3-methylbutane	120.65	Nonazeotrope		*90*
1086	$C_5H_{12}O$	Isoamyl alcohol	131.9	<130.0	>58	*80*
1087	$C_5H_{12}O$	2-Pentanol	119.8	Nonazeotrope		*90*
1088	C_6H_5Cl	Chlorobenzene	131.75	Nonazeotrope		*90*
1089	$C_6H_{12}O_2$	Butyl acetate	126.0	Nonazeotrope		*90*
1090	$C_6H_{12}O_2$	Isoamyl formate	123.8	Nonazeotrope		*90*
1091	C_7H_8	Toluene	110.75	Nonazeotrope		*90*
1092	$C_7H_{14}O_2$	Ethyl isovalerate	134.7	Nonazeotrope		*90*
1093	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*90*
1094	C_8H_{16}	*m*-Dimethylcyclohexane	120.7	118.0	20	*90*
A =	$C_5H_8O_2$	**2,4-Pentanedione**	**138**			
1095	$C_5H_{10}O$	Cyclopentanol	140.85	<135.5	>68	*90*
1096	$C_5H_{12}O$	Isoamyl alcohol	131.9	<130.0	>35	*90, 94*
1097	C_6H_5Br	Bromobenzene	156.15	154.7	~10	*94*
1098	C_6H_5I	Iodobenzene	188.55	~169	>90	*94*
1099	C_7H_7Cl	α-Chlorotoluene	179.35	~167.5	<80	*94*
A =	$C_5H_8O_3$	**Ethyl Pyruvate**	**155.5**			
1100	C_6H_5Br	Bromobenzene	156.1	149.5	48	*90*
1101	C_6H_5Cl	Chlorobenzene	131.75	Nonazeotrope		*90*
1102	$C_6H_{10}O$	Cyclohexanone	155.7	153.5	..	*90*
1103	$C_6H_{12}O_2$	Butyl acetate	126.0	Nonazeotrope		*90*
1104	C_7H_7Br	*o*-Bromotoluene	181.5	Nonazeotrope		*90*
1105	C_7H_7Cl	*o*-Chlorotoluene	159.2	151.5	52	*90*
1106	C_7H_7Cl	*p*-Chlorotoluene	162.4	153.2	58	*90*
1107	C_7H_8O	Anisole	153.85	148.0	50	*90*
1108	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
1109	$C_7H_{14}O_2$	Butyl propionate	146.8	<145.5	>23	*90*
1110	$C_7H_{14}O_2$	Ethyl isovalerate	134.7	Nonazeotrope		*90*
1111	C_8H_{10}	*m*-Xylene	139.2	137.2	30	*90*
1112	$C_8H_{10}O$	Phenetole	170.45	Nonazeotrope		*90*
1113	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
1114	$C_8H_{16}O_2$	Isoamyl propionate	160.7	153.0	67	*90*
1115	$C_8H_{16}O_2$	Isobutyl isobutyrate	148.6	147.0	33	*90*
1116	$C_8H_{16}O_2$	Propyl isovalerate	155.7	<151.8	..	*90*
1117	$C_8H_{18}O$	Isobutyl ether	142.4	140.4	..	*90*
1118	C_9H_{12}	Cumene	152.8	146.2	45	*90*
1119	C_9H_{12}	Mesitylene	164.6	<151.5	..	*90*
1120	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
1121	$C_{10}H_{16}$	Camphene	159.6	<148.0	..	*90*
1122	$C_{10}H_{16}$	α-Pinene	155.8	<147.0	..	*90*
1123	$C_{10}H_{18}O$	Cineol	176.35	Nonazeotrope		*90*
A =	$C_5H_8O_3$	**Levulinic Acid**	**251**			
1124	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*90*
1125	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	229.5	15	*90*
1126	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	221.55	4	*90*
1127	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	236.4	22	*90*
1128	$C_7H_{14}O_2$	Enanthic acid	222.0	Nonazeotrope		*90*
1129	$C_8H_8O_3$	Methyl salicylate	222.95	222.75	6	*90*
1130	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*90*
1131	$C_8H_{12}O_4$	Ethyl maleate	223.3	Nonazeotrope		*90*
1132	$C_8H_{16}O_2$	Caprylic acid	238.5	Nonazeotrope		*90*
1133	$C_9H_{10}O_3$	Ethyl salicylate	233.8	230.5	18	*90*
1134	$C_{10}H_8$	Naphthalene	218.0	216.7	11	*90*
1135	$C_{10}H_{10}O_2$	Safrole	235.9	232.5	17	*90*
1136	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	Nonazeotrope		*90*
1137	$C_{12}H_{18}$	1,3,5-Triethylbenzene	215.5	214.0	11	*90*
1138	$C_{12}H_{22}O$	Bornyl ethyl ether	204.9	Nonazeotrope		*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A	$C_5H_8O_3$	**Methyl Acetoacetate**	**169.5**			
1139	$C_5H_{10}O_2$	Valeric acid	186.35	Nonazeotrope		*90*
1140	$C_6H_4Cl_2$	*p*-Dichlorobenzene	174.4	167.2	33	*90*
1141	C_6H_6O	Phenol	181.5	Reacts		*94*
1142	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
1143	C_7H_6O	Benzaldehyde	179.2	Reacts		*94*
1144	C_7H_7Cl	*o*-Chlorotoluene	159.2	<158.2	>16	*90*
1145	C_7H_7Cl	*p*-Chlorotoluene	162.4	160.0	26	*90*
1146	C_7H_8O	Anisole	153.85	Nonazeotrope		*90*
1147	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	60.0/10	52/10	*90*
1148	$C_8H_{10}O$	Benzyl methyl ether	167.8	<160.0	>47	*90*
1149	$C_8H_{10}O$	Phenetole	170.45	<163.5	>52	*90*
1150	$C_8H_{14}O$	Methylheptenone	173.2	167.7	..	*90*
1151	$C_8H_{16}O$	2-Octanone	172.85	168.5	..	*90*
1152	$C_8H_{16}O_2$	Ethyl caproate	167.7	164.0	55	*90*
1153	$C_8H_{16}O_2$	Isoamyl propionate	160.7	<159.5	>20	*90*
1154	$C_8H_{16}O_2$	Isobutyl isobutyrate	148.6	Nonazeotrope		*90*
1155	$C_8H_{18}O$	Butyl ether	142.4	Nonazeotrope		*90*
1156	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	<166.8	..	*90*
1157	$C_9H_{18}O_2$	Isoamyl butyrate	181.05	<168.5	>75	*90*
1158	$C_9H_{18}O_2$	Isobutyl isovalerate	171.2	165.0	60	*90*
1159	$C_{10}H_{14}$	*p*-Cymene	176.7	165.0	56	*90*
1160	$C_{10}H_{16}$	Camphene	159.6	152.8	40	*90*
1161	$C_{10}H_{18}$	Dipentene	177.7	162.3	61	*90*
1162	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	Nonazeotrope		*90*
1163	$C_{10}H_{22}O$	Amyl ether	187.5	Nonazeotrope		*90*
1164	$C_{10}H_{22}O$	Isoamyl ether	173.2	160.5	60	*90*
A =	$C_5H_8O_4$	**Methyl Malonate**	**181.5**			
1165	C_6H_6O	Phenol	181.5	Reacts		*94*
1166	C_6H_7N	Aniline	184.35	Reacts		*94*
1167	$C_6H_{10}O_4$	Ethyl oxalate	185.65	Nonazeotrope		*87*
1168	$C_6H_{10}O_4$	Glycol diacetate	186.3	Nonazeotrope		*87*
1169	C_7H_8O	*o*-Cresol	190.8	Reacts		*94*
1170	C_7H_8O	*p*-Cresol	201.8	Reacts		*94*
1171	C_8H_8O	Acetophenone	202.0	201.0	39	*90*
1172	$C_8H_{14}O$	Methylheptenone	173.2	Nonazeotrope		*90*
1173	$C_8H_{18}O$	Octyl alcohol	195.15	Reacts		*79*
1174	$C_8H_{18}O$	*sec*-Octyl alcohol	178.05	Reacts		*94*
1175	$C_9H_{18}O_2$	Butyl isovalerate	177.6	175.0	30	*87*
1176	$C_9H_{18}O_2$	Isoamyl butyrate	181.05	<177.2	>39	*87*
1177	$C_9H_{18}O_2$	Isobutyl isovalerate	171.2	<170.5	>17	*87*
1178	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	<180.8	>75	*87*
A =	C_5H_{10}	**2-Methyl-2-butene**	**37.15**			
1179	C_6H_6	Benzene	80.2			*94*
1180	C_9H_{12}	Pseudocumene	169			*94*
A =	C_5H_{10}	**Amylene**	**37**			
1181	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92, 94*
1182	C_6H_7N	Aniline	184.35	Nonazeotrope		*94*
1183	$C_{10}H_{16}$	Pinene	~156			*94*
A =	$C_5H_{10}O$	**Cyclopentanol**	**140.85**			
1184	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
1185	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
A =	$C_5H_{10}O$	**Isovaleraldehyde**	**92.3**			
1186	$C_5H_{10}O$	3-Pentanone	102.05	Nonazeotrope		*90*
A =	$C_5H_{10}O$	**3-Methyl-2-butanone**	**95.4**			
1187	$C_5H_{10}O_2$	Ethyl propionate	99.1	Nonazeotrope		*90*
1188	$C_5H_{11}Cl$	1-Chloro-3-methylbutane	99.4	95.0	65	*90*
1189	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	94.0	50	*88, 90*
A =	$C_5H_{10}O$	**2-Pentanone**	**102.25**			
1190	$C_5H_{10}O_2$	Methyl isobutyrate	92.5	Nonazeotrope		*90*
1191	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	96.5	20	*88, 90*
1192	$C_5H_{12}O$	*tert*-Amyl alcohol	102.35	100.9	58	*90*
1193	C_6H_{12}	Cyclohexane	80.75	79.8	5	*90*
1194	C_7H_{16}	Heptane	98.4	93.2	34	*90*
A =	$C_5H_{10}O$	**3-Pentanone**	**101.7**			
1195	$C_5H_{11}Cl$	1-Chloro-3-methylbutane	99.4	98.5	25	*90*
1196	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	96.45	21	*88, 90*
1197	$C_5H_{12}O$	Isoamyl alcohol	131.9	Nonazeotrope		*90*
1198	$C_5H_{12}O$	2-Pentanol	119.8	Nonazeotrope		*90*
1199	$C_5H_{12}O$	3-Pentanol	116.0	Nonazeotrope		*90*
1200	C_6H_{12}	Methylcyclopentane	72.0	Nonazeotrope		*90*
1201	C_6H_{14}	Hexane	68.8	Nonazeotrope		*90*
1202	$C_6H_{14}O$	Propyl ether	90.1	Nonazeotrope		*90*
1203	$C_6H_{15}N$	Dipropylamine	109.2	<101.0	<82	*89*
1204	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	100.5	83	*90*
A =	$C_5H_{10}O_2$	**Ethyl Propionate**	**99.15**			
1205	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90*
A =	$C_5H_{10}O_2$	**Isobutyl Formate**	**97.9**			
1206	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	95.5	43	*87, 88*
1207	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$C_5H_{10}O_2$	**Isopropyl Acetate**	**90.8**			
1208	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*87, 88*
A =	$C_5H_{10}O_2$	**Isovaleric Acid**	**176.5**			
1209	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*90*
1210	$C_6H_{10}O_3$	Ethyl acetoacetate	180.4	176.1	77	*90*
1211	$C_8H_{14}O$	Methylheptenone	173.2	Nonazeotrope		*90*
1212	$C_8H_{18}S$	Butyl sulfide	185.0	175	73	*93*
1213	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	$C_5H_{10}O_2$	**Methyl Isobutyrate**	**92.3**			
1214	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*87, 88*
A =	$C_5H_{10}O_2$	**Propyl Acetate**	**101.55**			
1215	$C_5H_{11}NO_2$	Isoamyl nitrite	97.15	Nonazeotrope		*88*
A =	$C_5H_{10}O_2$	**Tetrahydrofurfuryl Alcohol**	**72.1/10**			
1216	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	63.0/10	29.5/10	*10*
A =	$C_5H_{10}O_2$	**Valeric Acid**	**186.35**			
1217	$C_6H_{10}O_3$	Ethyl acetoacetate	180.4	Nonazeotrope		*90*
1218	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1219	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
1220	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
A =	$C_5H_{10}O_3$	**Ethyl Carbonate**	**126.0**			
1221	$C_6H_{12}O$	3-Hexanone	123.3	Nonazeotrope		*90*
A =	$C_5H_{10}O_3$	**Ethyl Lactate**	**153.9**			
1222	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
1223	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	$C_5H_{11}Br$	**1-Bromo-3-methylbutane**	**120.3**			
1224	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
1225	$C_6H_{12}O$	3-Hexanone	123.3	119.8	45	*90, 93*
1226	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	115.6	30	*90, 93*
A =	$C_5H_{11}Br$	**1-Bromopentane**	**130.0**			
1227	C_7H_8	Toluene	110.7	Nonazeotrope		*125*
A =	$C_5H_{11}I$	**1-Iodo-3-methylbutane**	**147.65**			
1228	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
1229	$C_7H_{14}O$	4-Heptanone	143.55	143.0	35	*90*
A =	$C_5H_{11}N$	**Piperidine**	**105.7**			
1230	C_7H_{14}	Methylcyclohexane	100	Minimum B.P.		*38*
A =	$C_5H_{11}NO_2$	**Ethyl *N*-Ethylaminoformate**				
1231	$C_6H_4Cl_2$	*p*-Dichlorobenzene	174.35	167.0	24.2	*93*
1232	$C_8H_{18}S$	Isobutyl sulfide	172.0	166.5	23	*93*
A =	$C_5H_{11}NO_2$	**Isoamyl Nitrite**	**97.15**			
1233	$C_5H_{12}O_2$	Diethoxymethane	87.95	Nonazeotrope		*88*
1234	C_6H_{12}	Methylcyclopentane	72.0	Nonazeotrope		*88*
1235	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*88, 90*
1236	$C_6H_{14}O$	Propyl ether	90.1	Nonazeotrope		*88*
1237	C_8H_{16}	*m*-Dimethylcyclohexane	120.7	Nonazeotrope		*88*
1238	C_8H_{18}	2,5-Dimethylhexane	109.4	Nonazeotrope		*88*
A =	$C_5H_{11}NO_3$	**Isoamyl Nitrate**	**149.6**			
1239	$C_7H_{14}O_2$	Methyl caproate	149.8	148.5	55	*87*
1240	$C_8H_{16}O_2$	Isobutyl butyrate	156.9	Nonazeotrope		*87*
1241	$C_8H_{16}O_2$	Isobutyl isobutyrate	148.6	<147.5	<40	*87*
A =	C_5H_{12}	**2-Methylbutane**	**27.95**			
1242	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92, 94*
1243	$C_9H_{10}O_2$	Ethyl benzoate	213	Vapor pressure data		*94*
A =	C_5H_{12}	**Pentane**	**36.15**			
1244	C_6H_{14}	Hexane	68.95			*94*
1245	C_7H_{16}	Heptane	98.45			*94*
1246	C_8H_{18}	Octane	125			*94*
A =	$C_5H_{12}O$	**Amyl Alcohol**	**137.8**			
1247	C_8H_{10}	Ethylbenzene	60.5/60	57.5/60	20	*11*
1248	$C_{10}H_{22}O$	Amyl ether	188	Nonazeotrope		*118*
1249	$C_{12}H_{26}O_2$	Acetaldehyde diamyl acetal	225.3	Nonazeotrope		*7*
A =	$C_5H_{12}O$	**Ethyl Propyl Ether**	**63.6**			
1250	$C_6H_{15}N$	Triethylamine	89.35	Nonazeotrope		*89*
A =	$C_5H_{12}O$	**Isoamyl Alcohol**	**131.3**			
1251	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
1252	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	Nonazeotrope		*90*
1253	$C_7H_{13}ClO_2$	Isoamyl chloroacetate	195.2	Nonazeotrope		*22*
1254	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
1255	$C_7H_{14}O$	Isoamyl vinyl ether	112.6	112.1	12	*136*
1256	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
1257	$C_{12}H_{26}O_2$	Acetaldehyde diisoamyl acetal	213.6	Nonazeotrope		*7*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	B-Component Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**$C_5H_{12}O$**	**2-Methyl-1-butanol**	**70/60**			
1258	C_8H_8	Styrene	68/60	60/60	52	*11*
1259	C_8H_{10}	Ethylbenzene	60.5/60	56/60	33	*11*
A =	**$C_5H_{12}O$**	**3-Methyl-2-butanol**	**61/60**			
1260	C_8H_{10}	Ethylbenzene	60.5/60	51/60	62/60	*11*
A =	**$C_5H_{12}O$**	**2-Pentanol**	**119.3**			
1261	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
1262	$C_6H_{12}O$	2-Hexanone	127.2	Nonazeotrope		*90*
1263	C_8H_8	Styrene	68/60	60/60	69	*11*
1264	C_8H_{10}	Ethylbenzene	60.5/60	54/60	50	*11*
A =	**$C_5H_{12}O$**	**3-Pentanol**	**116.0**			
1265	$C_6H_{12}O$	4-Methyl-2-pentanone	116.05	<115.0	>35	*90*
1266	C_8H_{10}	Ethylbenzene	60.5/60	51/60	50	*11*
A =	**$C_5H_{12}O_2$**	**Diethoxymethane**	**87.95**			
1267	C_6H_6	Benzene	80.15	Nonazeotrope		*97*
1268	$C_6H_{15}N$	Triethylamine	89.35	86.8	..	*89*
1269	C_7H_{16}	*n*-Heptane	98.4	87.8	..	*97*
A =	**$C_5H_{12}O_2$**	**2-Propoxyethanol**	**151.35**			
1270	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
1271	$C_6H_{15}NO$	2-Diethylaminoethanol	162.2	Nonazeotrope		*89*
1272	C_7H_9N	Benzylamine	185.0	Nonazeotrope		*89*
1273	$C_7H_{14}O$	4-Heptanone	143.55	Nonazeotrope		*90*
1274	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		*90*
1275	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
1276	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	**$C_5H_{12}O_3$**	**2-(2-Methoxyethoxy)ethanol**	**193.2**			
1277	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
1278	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
1279	$C_6H_{11}NO_2$	Nitrocyclohexane	205.3	<192.7	..	*92*
1280	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	Nonazeotrope		*92*
1281	C_7H_9N	Methylaniline	196.25	190.0	60	*89*
1282	C_8H_8O	Acetophenone	202.0	191.9	80	*90*
1283	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
1284	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	<183.0	..	*89*
1285	$C_9H_{14}O$	Phorone	197.8	190.5	<75	*90*
1286	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
1287	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
A =	**$C_5H_{12}S$**	**3-Methyl-1-butanethiol**	**~120**			
1288	$C_6H_{10}O$	1-Hexene-5-one	129	Reacts		*94*
A =	**$C_6H_3Cl_3$**	**1,3,5-Trichlorobenzene**	**208.4**			
1289	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	Nonazeotrope		*92*
1290	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1291	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
A =	**C_6H_4BrCl**	***p*-Bromochlorobenzene**	**196.4**			
1292	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
1293	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1294	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.13	Nonazeotrope		*89*
1295	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1296	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
A =	**$C_6H_4Br_2$**	***p*-Dibromobenzene**	**220.25**			
1297	$C_6H_4ClNO_2$	*m*-Chloronitrobenzene	235.5	Nonazeotrope		*92*
1298	$C_6H_4ClNO_2$	*p*-Chloronitrobenzene	239.1	Nonazeotrope		*92*
1299	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
1300	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1301	$C_8H_{11}N$	Ethylaniline	205.5	Nonazeotrope		*89*
1302	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
1303	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1304	$C_{10}H_{18}O$	α-Terpineol	217.8	Reacts		*78*
A =	**$C_6H_4ClNO_2$**	***m*-Chloronitrobenzene**	**235.5**			
1305	$C_6H_6O_2$	Pyrocatechol	245.9	Nonazeotrope		*92*
1306	$C_6H_{14}O_2$	Dipropylene glycol	229.2	<227.0	..	*92*
1307	$C_7H_5Cl_3$	α,α,α-Trichlorotoluene	220.8	Nonazeotrope		*92*
1308	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	Nonazeotrope		*92*
1309	$C_7H_{14}O_2$	Enanthic acid	222.0	<221.5	..	*92*
1310	$C_8H_8O_3$	Methylsalicylate	222.95	Nonazeotrope		*92*
1311	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*92*
1312	$C_8H_{10}O$	*p*-Ethylphenol	220.0	Nonazeotrope		*92*
1313	$C_8H_{11}NO$	*o*-Phenetidine	232.5	Nonazeotrope		*89*
1314	$C_8H_{11}NO$	*p*-Phenetidine	249.9	Nonazeotrope		*89*
1315	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91, 92*
1316	$C_9H_{10}O$	Cinnamyl alcohol	257.0	Nonazeotrope		*92*
1317	$C_9H_{10}O_3$	Ethyl salicylate	233.8	Nonazeotrope		*92*
1318	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*92*
1319	$C_{10}H_{12}O_2$	Propyl benzoate	230.85	Nonazeotrope		*92*
1320	$C_{10}H_{14}O$	Carvacrol	237.85	<235.4	..	*92*
1321	$C_{10}H_{14}O$	Thymol	232.9	Nonazeotrope		*92*
1322	$C_{11}H_{10}$	1-Methylnaphthalene	244.6	Nonazeotrope		*92*
1323	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	<231.8	..	*92*
1324	$C_{12}H_{20}O_2$	Bornyl acetate	227.6	Nonazeotrope		*92*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**$C_6H_4ClNO_2$**	***o*-Chloronitrobenzene**	**230**			
1325	$C_6H_6O_2$	Resorcinol	281.4	Nonazeotrope		*92*
1326	$C_6H_{14}O_4$	Triethylene glycol	288.7	Nonazeotrope		*92*
1327	$C_7H_6O_2$	Benzoic acid	250.8	243.0	67	*92*
1328	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	Nonazeotrope		*92*
1329	$C_7H_{14}O_2$	Enanthic acid	222.0	Nonazeotrope		*92*
1330	$C_8H_{11}NO$	*o*-Phenetidine	232.5	Nonazeotrope		*89*
1331	$C_8H_{11}NO$	*p*-Phenetidine	249.9	Nonazeotrope		*89*
1332	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91, 92*
1333	$C_{10}H_7Cl$	1-Chloronaphthalene	262.7	Nonazeotrope		*92*
1334	$C_{10}H_{10}O_2$	Isosafrole	252.0	Nonazeotrope		*92*
1335	$C_{10}H_{10}O_2$	Safrole	235.9	Nonazeotrope		*92*
1336	$C_{10}H_{14}O$	Carvacrol	237.85	Nonazeotrope		*92*
1337	$C_{10}H_{14}O$	Thymol	232.9	Nonazeotrope		*92*
1338	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*92*
1339	$C_{11}H_{14}O_2$	Butyl benzoate	249.5	Nonazeotrope		*92*
1340	$C_{11}H_{14}O_2$	Isobutyl benzoate	241.9	Nonazeotrope		*92*
1341	$C_{12}H_{16}O_3$	Isoamyl salicylate	277.5	Nonazeotrope		*92*
A =	**$C_6H_4ClNO_2$**	***p*-Chloronitrobenzene**	**239.1**			
1342	$C_6H_{14}O_3$	Dipropylene glycol	229.2	<228.3	<89	*92*
1343	C_7H_8O	Benzyl alcohol	205.25	Nonazeotrope		*92*
1344	$C_7H_{16}O_4$	2-[2-(2-Methoxyethoxy)-ethoxy]ethanol	245.25	<234.0	..	*92*
1345	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*92*
1346	$C_8H_{16}O_2$	Caprylic acid	238.5	<235.5	..	*92*
1347	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91, 92*
1348	C_9H_8O	Cinnamaldehyde	253.5	Nonazeotrope		*92*
1349	$C_9H_{10}O$	Cinnamyl alcohol	257.0	Nonazeotrope		*92*
1350	$C_{10}H_9N$	Quinaldine	246.5	Nonazeotrope		*92*
1351	$C_{10}H_{14}O$	Carvacrol	237.85	237.4	.	*92*
1352	$C_{11}H_{10}$	1-Methylnaphthalene	244.6	Nonazeotrope		*92*
1353	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*92*
1354	$C_{11}H_{14}O_2$	Butyl benzoate	249.5	Nonazeotrope		*92*
1355	$C_{12}H_{10}$	Diphenyl	256.1	Nonazeotrope		*92*
A =	**$C_6H_4Cl_2$**	***o*-Dichlorobenzene**	**179.5**			
1356	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
1357	C_6H_7N	Aniline	184.35	77.4	70	*89*
1358	$C_6H_{10}O_3$	Ethyl acetoacetate	180.4	175.5	58	*90*
1359	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1360	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1361	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
A =	**$C_6H_4Cl_2$**	***p*-Dichlorobenzene**	**174.35**			
1362	$C_6H_{14}O_2$	2-Butoxyethanol	171.25	168.3	48	*93*
1363	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1364	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1365	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	**C_6H_5Br**	**Bromobenzene**	**156.15**			
1366	C_6H_5F	Fluorobenzene	85.2	Vapor pressure data		*94*
1367	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
A =	**C_6H_5Cl**	**Chlorobenzene**	**131.9**			
1368	C_6H_5F	Fluorobenzene	85.2	Vapor pressure data		*94*
1369	C_6H_5I	Iodobenzene	188.55			*94*
1370	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
1371	$C_6H_{10}O$	Mesityl oxide	129.45	Nonazeotrope		*90*
A =	**C_6H_5ClO**	***o*-Chlorophenol**	**175.5**			
1372	C_6H_7N	3-Picoline	143.5	178–184/760	..	*124*
1373	C_6H_7N	4-Picoline	143.1	178–184	..	*124*
1374	C_7H_7Br	α-Bromotoluene	~198.5	Reacts		*94*
1375	C_7H_7Cl	α-Chlorotoluene	179.35	Reacts		*94*
1376	C_7H_9N	2,6-Lutidine	143	178–184/760	..	*124*
A =	**C_6H_5ClO**	***p*-Chlorophenol**	**219.75**			
1377	$C_7H_5Cl_3$	α,α,α-Trichlorotoluene	220.9	Reacts		*78*
1378	$C_7H_6Cl_2$	α,α-Dichlorotoluene	265.1	Reacts		*94*
1379	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	Nonazeotrope		*92*
1380	C_7H_8O	Benzyl alcohol	205.2	Reacts		*78*
1381	$C_9H_{10}O$	Propiophenone	217.7	230.3	..	*90*
1382	$C_{10}H_{14}O$	Carvone	231.0	238.3	<45	*90*
1383	$C_{10}H_{16}O$	Camphor	209.1	227.5	>75	*90*
A =	**C_6H_5F**	**Fluorobenzene**	**85.2**			
1384	C_6H_5I	Iodobenzene	188.55	Vapor pressure data		*94*
A =	**C_6H_5I**	**Iodobenzene**	**188.55**			
1385	$C_6H_5NO_2$	Nitrobenzene	210.75	Nonazeotrope		*92*
1386	C_7H_7Br	*m*-Bromotoluene	184.3	Nonazeotrope		*87*
1387	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
1388	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1389	$C_8H_{11}N$	Ethylaniline	205.5	Nonazeotrope		*89*
1390	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
A =	**$C_6H_5NO_2$**	**Nitrobenzene**	**210.75**			
1391	$C_6H_5NO_3$	*o*-Nitrophenol	217.2	Nonazeotrope		*92*
1392	C_6H_6	Benzene	80.15	Nonazeotrope		*92, 94*
1393	C_6H_7N	Aniline	184.35	Nonazeotrope		*89*
1394	$C_6H_8O_4$	Methyl maleate	204.05	203.9	7	*92*
1395	$C_6H_{14}O$	*n*-Hexanol	157.85	Nonazeotrope		*92*
1396	$C_6H_{14}O_2$	2-Butoxyethanol	171.15	Nonazeotrope		*92*

Table I. Binary Systems (*Continued*)

No.	B-Component: Formula	Name	B.P., ° C.	Azeotropic Data: B.P., ° C.	Weight % A	Reference
A =	$C_6H_5NO_2$	**Nitrobenzene** (*Contd.*)	**210.75**			
1397	C_7H_6O	Benzaldehyde	179.2	Nonazeotrope		*92*
1398	C_7H_8	Toluene	110.7	Nonazeotrope		*92, 94*
1399	C_7H_9N	Benzylamine	185.0	Nonazeotrope		*89*
1400	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1401	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
1402	C_7H_9N	*o*-Toluidine	200.35	Nonazeotrope		*89*
1403	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1404	$C_7H_{12}O_4$	Ethyl malonate	199.35	Nonazeotrope		*92*
1405	$C_7H_{14}O_2$	Enanthic acid	222.0	<209.5	<88	*92*
1406	$C_7H_{16}O_4$	2-[2-(2-Methoxyethoxy)ethoxy]ethanol	245.25	Nonazeotrope		*92*
1407	$C_8H_8O_2$	Phenyl acetate	215.3	Nonazeotrope		*92*
1408	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*92*
1409	$C_8H_{10}O$	*p*-Ethylphenol	220.0	Nonazeotrope		*92*
1410	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1411	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1412	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	Nonazeotrope		*89*
1413	$C_8H_{11}N$	Ethylaniline	205.5	Nonazeotrope		*89*
1414	$C_8H_{12}O_4$	Ethyl fumarate	217.85	Nonazeotrope		*92*
1415	$C_8H_{12}O_4$	Ethyl maleate	223.3	Nonazeotrope		*92*
1416	$C_8H_{14}O_4$	Propyl oxalate	214.2	210.0	..	*92*
1417	$C_8H_{16}O_2$	Caprylic acid	238.5	Nonazeotrope		*92*
1418	$C_8H_{16}O_3$	Isoamyl lactate	202.4	Nonazeotrope		*92*
1419	$C_9H_{10}O$	Cinnamyl alcohol	257.0	Nonazeotrope		*92*
1420	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	<210	..	*89*
1421	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
1422	$C_{10}H_{16}O$	Pulegone	223.8	Nonazeotrope		*90*
1423	$C_{10}H_{18}O$	β-Terpineol	210.5	204.8	50	*92*
1424	$C_{10}H_{22}S$	Isoamyl sulfide	214.8	209.5	<93	*92*
1425	$C_{11}H_{16}O$	Methyl thymol ether	216.5	<209.2	<82	*92*
1426	$C_{12}H_{22}O$	Bornyl ethyl ether	204.9	203.0	30	*92*
1427	$C_{12}H_{22}O$	Ethyl isobornyl ether	203.8	202.5?	25?	*92*
A =	$C_6H_5NO_3$	***o*-Nitrophenol**	**217.25**			
1428	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1429	$C_9H_{10}O$	*p*-Methylacetophenone	226.35	Nonazeotrope		*90*
1430	$C_9H_{10}O$	Phorone	197.8	Nonazeotrope		*90*
1431	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
A =	C_6H_6	**Benzene**	**80.2**			
1432	C_6H_7N	Aniline	184.35	Nonazeotrope		*89, 94*
1433	$C_6H_{12}O$	Pinacolone	106.2	Nonazeotrope		*90*
1434	$C_6H_{15}N$	Triethylamine	89.35	Nonazeotrope		*89*
1435	C_7H_{16}	2,2-Dimethylpentane	....	75.85	46.3	*12*
1436	C_8H_{18}	Octane	125.8			*94*
1437	$C_9H_{10}O_2$	Ethyl benzoate	213	Vapor pressure data		*94*
1438	$C_{10}H_8$	Naphthalene	218.1			*94*
A =	C_6H_6O	**Phenol**	**182.2**			
1439	$C_6H_{10}O_3$	Ethyl acetoacetate	180.7	Reacts		*94*
1440	$C_7H_6Cl_2$	α,α-Dichlorotoluene	205.1	Reacts		*94*
1441	C_7H_7Br	α-Bromotoluene	198.5	Reacts		*94*
1442	C_7H_7Cl	α-Chlorotoluene	179.35	Reacts		*94*
1443	C_7H_9N	Benzylamine	185.0	196.8	45	*89*
1444	$C_7H_{12}O_4$	Ethyl malonate	198.6	Reacts		*94*
1445	$C_8H_{11}N$	Ethylaniline	205.5	Nonazeotrope		*89*
1446	$C_8H_{18}S$	Butyl sulfide	185	177.5	45	*93*
1447	$C_8H_{18}S$	Isobutyl sulfide	172	<170.5	<28	*93*
1448	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*90*
1449	$C_9H_{14}O$	Phorone	197.8	198.8	18	*90*
1450	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	183.4	80	*89*
A =	$C_6H_6O_2$	**Pyrocatechol**	**245.9**			
1451	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	Nonazeotrope		*92*
1452	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*87*
1453	$C_8H_{11}NO$	*o*-Phenetidine	232.5	246.0	92	*83, 89*
1454	$C_8H_{11}NO$	*p*-Phenetidine	249.9	253.8	34	*83, 89*
1455	$C_{10}H_{14}O$	Thymol	232.9	232.2	17	*87*
A =	$C_6H_6O_2$	**Resorcinol**	**281.4**			
1456	$C_8H_{11}NO$	*o*-Phenetidine	232.5	Nonazeotrope		*89*
1457	$C_{12}H_{16}O_2$	Isoamyl benzoate	262.0	Nonazeotrope		*81*
A =	C_6H_6S	**Benzenethiol**	**170**			
1458	$C_{10}H_{16}$	Camphene	~158	Reacts		*94*
1459	$C_{10}H_{16}$	α-Phellandrene	171.5	Reacts		*94*
1460	$C_{10}H_{16}$	α-Pinene	155.8	Reacts		*94*
1461	$C_{10}H_{18}$	Menthene	170.8	Reacts		*94*
A =	C_6H_7N	**Aniline**	**184.35**			
1462		Aromatic hydrocarbons	160–175	Minimum B.P.		*34*
1463	C_nH_{2n+2}	Paraffins	160–175	Minimum B.P.		*34*
1464	$C_6H_{10}O$	Cyclohexanone	155.7	Nonazeotrope		*89*
1465	$C_6H_{11}NO_2$	Nitrocyclohexane	205.4	Nonazeotrope		*89*
1466	C_6H_{12}	Cyclohexane	80.75	Nonazeotrope		*89, 94*
1467	C_6H_{14}	*n*-Hexane	68.8	Nonazeotrope		*89, 94*
1468	$C_6H_{14}O_2$	2-Butoxyethanol	171.15	Nonazeotrope		*89*
1469	$C_6H_{15}NO$	2-Diethylaminoethanol	162.2	Nonazeotrope		*89*
1470	C_7H_6O	Benzaldehyde	179.2	Reacts		*94*
1471	C_7H_7Br	α-Bromotoluene	198.5	Reacts		*94*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	C_6H_7N	**Aniline (*Contd.*)**	**184.35**			
1472	C_7H_7Br	*m*-Bromotoluene	184.3	179.9	39	*89*
1473	C_7H_7Cl	α-Chlorotoluene	179.35	Reacts		*94*
1474	C_7H_7Cl	*o*-Chlorotoluene	159.2	Nonazeotrope		*89*
1475	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	Nonazeotrope		*89*
1476	C_7H_8	Toluene	110.75	Nonazeotrope		*89*
1477	$C_7H_8O_2$	Guaiacol	205.05	Nonazeotrope		*89*
1478	C_7H_{14}	Methylcyclohexane	101.15	Nonazeotrope		*89*
1479	C_7H_{16}	Heptane	98.4	Nonazeotrope		*89, 94*
1480	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*89*
1481	C_8H_{10}	*o*-Xylene	144.3	Nonazeotrope		*89*
1482	C_8H_{10}	*p*-Xylene	138.45	Nonazeotrope		*89*
1483	$C_8H_{10}O$	Benzyl methyl ether	167.8	Nonazeotrope		*89*
1484	$C_8H_{10}O_2$	*o*-Ethoxyphenol	216.5	Nonazeotrope		*89*
1485	$C_8H_{10}O_2$	Veratrole	206.8	Nonazeotrope		*89*
1486	$C_8H_{14}O$	Methylheptenone	173.2	Reacts		*78*
1487	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	Nonazeotrope		*89*
1488	C_8H_{18}	Octane	125.75	Nonazeotrope		*89*
1489	$C_8H_{18}O$	Butyl ether	142.4	Nonazeotrope		*89*
1490	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		*89*
1491	C_9H_{12}	Cumene	152.8	Nonazeotrope		*89*
1492	$C_9H_{12}O$	Benzyl ethyl ether	185.0	179.8	51	*89*
1493	$C_9H_{12}O$	Phenyl propyl ether	190.5	<183.5	<82	*89*
1494	$C_{10}H_{14}$	Butylbenzene	183.1	177.8	46	*89*
1495	$C_{10}H_{16}$	β-Pinene	163.8	161.8	23	*89*
1496	$C_{10}H_{16}$	α-Terpinene	173.4	169.5	32	*89*
1497	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*89*
1498	$C_{10}H_{18}$	Dipentene	177.7	171.3	39	*89*
1499	$C_{10}H_{18}$	*d*-Menthene	170.8	<167.5	<34	*89*
1500	$C_{10}H_{18}O$	β-Terpineol	210.75	Nonazeotrope		*89*
1501	$C_{10}H_{22}$	*n*-Decane	173.3	<169.5	<36	*89*
1502	$C_{10}H_{22}$	2,7-Dimethyloctane	160.1	<159.5	<22	*77, 89*
1503	$C_{10}H_{22}O$	Amyl ether	187.5	177.5	55	*89*
1504	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*89*
1505	$C_{11}H_{20}O$	Isobornyl methyl ether	192.4	<183.8	<80	*89, 94*
A =	C_6H_7N	**3-Picoline**	**144**			
1506	C_7H_8	Toluene	110.7	Nonazeotrope		*33*
1507	C_8H_{18}	2,3,4-Trimethylpentane		Nonazeotrope		*33*
A =	C_6H_7N	**4-Picoline**	**145.3**			
1508	C_7H_8	Toluene	110.7	Nonazeotrope		*33*
1509	C_8H_{18}	2,3,4-Trimethylpentane		Nonazeotrope		*33*
A =	$C_6H_8N_2$	***o*-Phenylenediamine**	**158.6**			
1510	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	Nonazeotrope		*89*
1511	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	Nonazeotrope		*89*
1512	$C_7H_8O_2$	*m*-Methoxyphenol	243.8	Nonazeotrope		*89*
1513	$C_8H_{10}O$	Phenethyl alcohol	219.4	Nonazeotrope		*89*
1514	$C_9H_{12}O$	3-Phenylpropanol	235.6	Nonazeotrope		*89*
1515	$C_{10}H_8O$	1-Naphthol	288.0	Nonazeotrope		*89*
1516	$C_{10}H_{10}O_2$	Isosafrole	252.0	249.2	30	*89*
1517	$C_{10}H_{10}O_2$	Safrole	235.9	Nonazeotrope		*89*
1518	$C_{10}H_{12}O$	Anethole	235.7	Nonazeotrope		*89*
1519	$C_{10}H_{12}O_2$	Eugenol	254.8	Nonazeotrope		*89*
1520	$C_{10}H_{20}O$	Menthol	216.3	Nonazeotrope		*89*
1521	$C_{11}H_{10}$	1-Methylnaphthalene	244.6	<243.0	<17	*89*
1522	$C_{11}H_{14}O_2$	1-Allyl-3,4-dimethylbenzene	254.7	250.5	38	*89*
1523	$C_{11}H_{14}O_2$	1,2-Dimethoxy-4-propenylbenzene	270.5	Nonazeotrope		*89*
1524	$C_{12}H_{10}$	Acenaphthene	277.9	<258.0	..	*89*
1525	$C_{12}H_{10}$	Diphenyl	256.1	249.7	37	*89*
1526	$C_{13}H_{12}$	Diphenylmethane	265.4	254.0	70	*89*
1527	$C_{14}H_{11}$	1,2-Diphenylethane	284.5	Nonazeotrope		*89*
A =	$C_6H_8O_4$	**Methyl Fumarate**	**193.25**			
1528	$C_6H_{10}O_4$	Ethyl oxalate	185.65	Nonazeotrope		*87*
1529	$C_6H_{10}O_4$	Glycol diacetate	186.3	Nonazeotrope		*87*
1530	$C_7H_{12}O_4$	Ethyl malonate	199.35	Nonazeotrope		*87*
1531	$C_8H_8O_2$	Methyl benzoate	199.4	Nonazeotrope		*87*
1532	$C_9H_{18}O_2$	Methyl caprylate	192.9	189.4	46	*87*
A =	$C_6H_8O_4$	**Methyl Maleate**	**204.05**			
1533	$C_8H_8O_2$	Methyl benzoate	199.4	198.95	25	*87*
1534	$C_9H_{10}O_2$	Ethyl benzoate	212.5	Nonazeotrope		*87*
1535	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	190.65	25	*87*
A =	$C_6H_{10}O$	**Cyclohexanone**	**156.7**			
1536	$C_6H_{12}O_3$	Propyl lactate	171.7	Nonazeotrope		*90*
1537	$C_7H_{14}O$	Methylcyclohexanol	168.5	Nonazeotrope		*90*
1538	$C_7H_{14}O_2$	Methyl caproate	149.7	Nonazeotrope		*90*
1539	$C_8H_{16}O_2$	Butyl butyrate	166.4	Nonazeotrope		*90*
1540	C_9H_{12}	Cumene	152.8	152.0	65	*90*
1541	$C_{10}H_{16}$	β-Pinene	163.8	152.2	65	*90*
1542	$C_{10}H_{16}$	α-Terpinene	173.4	Nonazeotrope		*90*
A =	$C_6H_{10}O$	**Mesityl Oxide**	**130.5**			
1543	$C_6H_{12}O_2$	Propyl propionate	123.0	Nonazeotrope		*90*
1544	C_7H_{14}	Methyl cyclohexane	101.15	Nonazeotrope		*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$C_6H_{10}O$	**Mesityl Oxide** (*Contd.*)	**130.5**			
1545	$C_7H_{14}O_2$	Isobutyl propionate	134.0	Nonazeotrope		*90*
1546	C_8H_{16}	*m*-Dimethylcyclohexane	120.7	118.0	25	*90*
1547	$C_8H_{16}O_2$	Propyl isovalerate	134.7	Nonazeotrope		*90*
1548	$C_8H_{18}O$	Butyl ether	142.4	Nonazeotrope		*90*
A =	$C_6H_{10}O_2$	**2,5-Hexanedione**	**75.4/10**			
1549	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	66.0/10	24/10	*10*
1550	$C_8H_{18}O$	Octyl alcohol	195.2	<190.0	>65	*90*
A =	$C_6H_{10}O_3$	**Ethyl Acetoacetate**	**180.7**			
1551	$C_6H_{10}O_4$	Ethyl oxalate	185.65	Nonazeotrope		*90*
1552	$C_6H_{12}O_2$	Isocaproic acid	199.5	Nonazeotrope		*90*
1553	C_7H_6O	Benzoic acid	179.2	Reacts		*94*
1554	C_7H_8O	Anisole	153.85	Nonazeotrope		*90*
1555	C_7H_8O	*o*-Cresol	190.8	Reacts		*94*
1556	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1557	$C_8H_8O_2$	Phenyl acetate	195.7	Nonazeotrope		*90*
1558	C_8H_{10}	*o*-Xylene	144.3	Nonazeotrope		*90*
1559	$C_8H_{10}O$	*p*-Methylanisole	177.05	175.7	30	*90, 97*
1560	$C_8H_{10}O_2$	Veratrole	206.8	Nonazeotrope		*90*
1561	$C_8H_{16}O_2$	Butyl butyrate	166.4	Nonazeotrope		*90*
1562	$C_8H_{16}O_2$	Isoamyl propionate	160.7	Nonazeotrope		*90*
1563	$C_8H_{18}O$	Butyl ether	142.4	Nonazeotrope		*90*
1564	C_9H_{12}	Propylbenzene	159.3	158.3	24	*90*
1565	$C_9H_{12}O$	Benzyl ethyl ether	185.0	175.5	>75	*90*
1566	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
1567	$C_9H_{18}O_2$	Isoamyl isobutyrate	169.8	169.0	20	*90*
1568	$C_9H_{18}O_2$	Isobutyl isovalerate	171.2	170.2	25	*90*
1569	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*90*
1570	$C_{10}H_{14}$	Butylbenzene	183.1	174.0	52	*90*
1571	$C_{10}H_{16}$	α-Terpinene	173.4	166.6	40	*90*
1572	$C_{10}H_{16}O$	Fenchone	193.6	Nonazeotrope		*90*
1573	$C_{10}H_{18}$	Dipentene	177.7	169.05	43	*90*
1574	$C_{10}H_{18}$	*d*-Menthene	170.8	164.9	..	*90*
1575	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	179.5	77	*90*
1576	$C_{10}H_{22}O$	Amyl ether	187.5	174.5	70	*90*
1577	$C_{11}H_{20}O$	Isobornyl methyl ether	192.4	<179.0	..	*90*
A =	$C_6H_{10}O_4$	**Ethyl Oxalate**	**185.65**			
1577a	$C_6H_{10}O_4$	Methylaniline	196.25	Reacts		*94*
1578	$C_9H_{18}O_2$	Butyl isovalerate	177.6	176.3	25	*87*
1579	$C_9H_{18}O_2$	Ethyl enanthate	188.7	183.0	60	*87*
1580	$C_9H_{18}O_2$	Isobutyl isovalerate	185.65	Nonazeotrope		*87*
1581	$C_9H_{18}O_2$	Methyl caprylate	192.9	184.2	70	*87*
1582	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	184.1	69	*87*
A =	$C_6H_{10}O_4$	**Glycol Diacetate**	**186.3**			
1583	$C_9H_{18}O_2$	Butyl isovalerate	177.6	<177.0	>15	*87*
1584	$C_9H_{18}O_2$	Isoamyl butyrate	181.05	179.0	38	*87*
1585	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	184.6	75	*87*
A =	$C_6H_{10}O_4$	**Methyl Succinate**	**195.5**			
1586	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
1587	$C_9H_{18}O_3$	Isobutyl carbonate	190.3	Nonazeotrope		*87*
1588	$C_{10}H_{20}O_2$	Ethyl caprylate	208.35	Nonazeotrope		*87*
1589	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	191.0	30	*87*
A =	$C_6H_{11}NO_2$	**Nitrocyclohexane**	**205.3**			
1590	C_7H_6O	Benzaldehyde	179.2	Nonazeotrope		*92*
1591	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1592	C_7H_9N	*m*-Toluidine	203.1	<203.0	>.4	*89*
1593	C_7H_9N	*o*-Toluidine	200.35	Nonazeotrope		*89*
1594	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1595	$C_8H_{11}N$	Ethylaniline	205.5	<204.8	..	*89*
1596	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
A =	C_6H_{12}	**Methylcyclopentane**	**71.8**			
1597	$C_6H_{15}N$	Triethylamine	89.35	Nonazeotrope		*89*
A =	$C_6H_{12}O$	**Cyclohexanol**	**160.65**			
1598	$C_8H_{10}O$	Benzyl methyl ether	170.5	Minimum B.P.		*135*
1599	$C_8H_{11}N$	Dimethylaniline	194.05	Nonazeotrope		*89*
1600	$C_8H_{14}O$	Methylheptenone	173.2	Nonazeotrope		*90*
1601	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
1602	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
1603	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	$C_6H_{12}O$	**2-Hexanone**	**127.2**			
1604	$C_6H_{12}O_2$	Isoamyl formate	123.8	Nonazeotrope		*90*
1605	$C_7H_{14}O_2$	Propyl isobutyrate	134.0	Nonazeotrope		*90*
A =	$C_6H_{12}O$	**3-Hexanone**	**123.3**			
1606	$C_6H_{12}O_2$	Butyl acetate	126.0	123.1	..	*90*
1607	$C_6H_{12}O_2$	Ethyl butyrate	121.5	Nonazeotrope		*90*
1608	$C_6H_{12}O_2$	Isoamyl formate	123.8	123.0	50	*90*
1609	$C_6H_{12}O_2$	Isobutyl acetate	117.4	Nonazeotrope		*90*
1610	$C_6H_{12}O_2$	Methyl isovalerate	116.5	Nonazeotrope		*90*
1611	$C_6H_{12}O_2$	Propyl propionate	123.0	122.5	40	*90*
1612	$C_6H_{14}S$	Isopropyl sulfide	120.5	119.0	32	*93*
1613	$C_6H_{15}BO_3$	Ethyl borate	118.6	116.7	28	*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$C_6H_{12}O$	**3-Hexanone** (*Contd.*)	123.3			
1614	$C_6H_{15}N$	Dipropylamine	109.2	Nonazeotrope		89
1615	C_7H_8	Toluene	110.75	Nonazeotrope		90
1616	C_7H_{16}	*n*-Heptane	98.4	Nonazeotrope		90
1617	C_8H_{10}	*m*-Xylene	139.2	Nonazeotrope		90
1618	C_8H_{16}	*m*-Dimethylcyclohexane	120.7	116.0	37	90
A =	$C_6H_{12}O$	**4-Methyl-2-pentanone**	116.05			
1619	$C_6H_{12}O_2$	Ethyl butyrate	121.5	Nonazeotrope		90
1620	$C_6H_{12}O_2$	Ethyl isobutyrate	110.1	Nonazeotrope		90
1621	$C_6H_{12}O_2$	Isobutyl acetate	117.4	115.6		90
1622	$C_6H_{12}O_2$	Isopropyl propionate	110.5	Nonazeotrope		90
1623	$C_6H_{12}O_2$	Methyl isovalerate	116.5	115.6	55	90
1624	$C_6H_{14}S$	Isopropyl sulfide	120.5	114.9	72	93
1625	$C_6H_{15}N$	Dipropylamine	109.2	<105.5	<32	89
1626	C_7H_8	Toluene	110.75	110.7	3	90
1627	C_7H_{14}	Methylcyclohexane	101.15	<100.1	<20	90
1628	C_7H_{16}	Heptane	98.4	97.5	13	90
1629	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		90
1630	C_8H_{16}	*m*-Dimethylcyclohexane	120.7	112.0	53	90
1631	C_8H_{18}	*n*-Octane	125.75	113.4	65	90
A =	$C_6H_{12}O$	**Pinacolone**	106.2			
1632	$C_6H_{12}O_2$	Ethyl isobutyrate	110.1	Nonazeotrope		90
1933	$C_6H_{12}O_2$	Isopropyl propionate	110.5	Nonazeotrope		90
1634	C_6H_{14}	Hexane	68.8	Nonazeotrope		90
1635	C_7H_8	Toluene	110.75	106.0	85	90
1636	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	104.0	75	90
A =	$C_6H_{12}O_2$	**Caproic Acid**	204.5			
1637	$C_7H_6O_2$	Benzoic acid	249.5	....	..	94
1638	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	Nonazeotrope		92
1639	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		90
1640	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		90
A =	$C_6H_{12}O_2$	**4-Hydroxy-4-methyl-2-pentanone**	61.6/10			
1641	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	59.0/10	58/10	10
A =	$C_6H_{12}O_3$	**Propyl Lactate**	171.7			
1641a	$C_6H_{12}O_3$	Propyl lactate	171.7	171.2	~22	94
1642	$C_8H_{16}O$	2-Octanone	172.85	<171.4	<75	90
A =	$C_6H_{13}ClO_2$	**Chloroacetaldehyde Diethylacetal**	156.8			
1643	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		90
A =	C_6H_{14}	***n*-Hexane**	68.95			
1644	$C_6H_{15}N$	Triethylamine	89.35	Nonazeotrope		89
A =	$C_6H_{14}O$	**2-Ethylbutanol**	55.6/10			
1645	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	65.5/10	54.9/10	74/10	10
A =	$C_6H_{14}O$	***n*-Hexyl Alcohol**	157.85			
1646	$C_7H_{14}O$	5-Methyl-2-hexanone	144.2	Nonazeotrope		90
1647	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	62.0/10	43/10	10
1648	$C_8H_{11}N$	Dimethylaniline	194.05	Nonazeotrope		89
1649	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		90
1650	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		89
1651	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		90
A =	$C_6H_{14}O$	**Propyl Ether**	90.55			
1652	$C_6H_{15}N$	Dipropylamine	109.2	Nonazeotrope		89
1653	$C_6H_{15}N$	Triethylamine	89.35	< 88.5	..	89
A =	$C_6H_{14}O_2$	**Acetaldehyde Diethyl Aceta**	103.55			
1654	$C_6H_{15}N$	Dipropylamine	109.2	Nonazeotrope		89
A =	$C_6H_{14}O_2$	**2-Butoxyethanol**	171.25			
1655	$C_6H_{15}NO$	2-Diethylaminoethanol	162.2	Nonazeotrope		89
1656	C_7H_9N	Benzylamine	185.0	Nonazeotrope		89
1657	C_7H_9N	Methylaniline	196.25	Nonazeotrope		89
1658	$C_7H_{14}O_3$	1,3-Butanediol methyl ether acetate	171.75	170.1	53	96
1659	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	62.5/10	37/10	10
1660	$C_8H_{10}O$	Phenetole	170.45	167.1	..	97
1661	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		89
1662	$C_8H_{18}S$	Isobutyl sulfide	172	163.8	42	93
1663	C_9H_7N	Quinoline	237.3	Nonazeotrope		91
1664	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	170.95	88	89
1665	$C_{10}H_{22}O_2$	Acetaldehyde dibutyl acetal	240	170.6	42.0	25
A =	$C_6H_{14}O_2$	**Pinacol**	174.35			
1666	$C_8H_{11}N$	Dimethylaniline	194.05	<169.5	>60	89
A =	$C_6H_{14}O_3$	**Dipropylene Glycol**	229.2			
1667	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	216.9	>21	92
1668	$C_7H_7NO_2$	*p*-Nitrotoluene	238.9	225.0	62?	92
A =	$C_6H_{15}N$	**Dipropylamine**	109.2			
1669	C_7H_8	Toluene	110.75	<108.5	>53	89
1670	C_7H_{16}	*n*-Heptane	98.4	Nonazeotrope		89
1671	C_8H_{16}	1,3-Dimethylcyclohexane	120.7	Nonazeotrope		89
1672	C_8H_{18}	2,4-Dimethylhexane	109.4	<108.0	<54	89
1673	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		89

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	B-Component Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	$C_6H_{15}N$	**Triethylamine**	89.35			
1674	C_7H_8O	Anisole	153.85	148.0	19	*89*
1675	C_7H_{14}	Methylcyclohexane	101.15	Nonazeotrope		*89*
1676	C_7H_{16}	*n*-Heptane	98.4	Nonazeotrope		*89*
A =	$C_6H_{15}NO$	**2-Diethylaminoethanol**	162.2			
1676a	C_7H_8O	Anisole	153.85	<148.0	>19	*89*
1677	C_7H_8O	*o*-Cresol	191.1	Nonazeotrope		*89*
1678	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1679	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	57.0/10	91	*10*
1680	$C_8H_{11}N$	Dimethylaniline	194.15	<160.5	>58	*89*
1681	$C_8H_{18}O$	Isobutyl ether	122.3	Nonazeotrope		*89*
1682	$C_{10}H_{22}O$	Isoamyl ether	173.2	<156.5	>58	*89*
A =	$C_7H_5Cl_3$	**α,α,α-Trichlorotoluene**	220.9			
1683	C_7H_8O	Benzyl alcohol	205.2	Reacts		*78*
1684	$C_7H_8O_2$	Guaiacol	205.05	Reacts		*78*
1685	$C_{10}H_7Cl$	α-Chloronaphthalene	262.7	Nonazeotrope		*84*
A =	$C_7H_6Cl_2$	**α,α-Dichlorotoluene**	205.1			
1686	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	Nonazeotrope		*92*
1687	C_7H_8O	Benzyl alcohol	205.5	182?	..	*94*
1688	C_7H_8O	*m*-Cresol	202.8	Reacts		*94*
1689	C_7H_8O	*o*-Cresol	190.8	Reacts		*94*
1690	C_7H_8O	*p*-Cresol	201.8	Reacts		*94*
1691	C_7H_9N	Methylaniline	196.1	Reacts		*94*
1692	C_7H_9N	*p*-Toluidine	200.3	Reacts		*94*
1693	$C_8H_{11}N$	Ethylaniline	206.3	Reacts		*94*
1694	$C_{10}H_{18}O$	Menthone	207	Azeotrope doubtful		*94*
A =	C_7H_6O	**Benzaldehyde**	179.2			
1695	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	63.5/10	57/10	*10*
1696	$C_8H_{11}N$	Dimethylaniline	194.05	Reacts		*94*
1697	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
1698	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	$C_7H_6O_2$	**Benzoic Acid**	250.5			
1699	$C_7H_7NO_2$	*m*-Nitrotoluene	230.8	Nonazeotrope		*92*
A =	C_7H_7Br	**α-Bromotoluene**	181.4			
1700	C_7H_8O	*o*-Cresol	190.8	Reacts		*94*
1701	C_7H_8O	*p*-Cresol	201.8	Reacts		*94*
1702	C_7H_9N	Methylaniline	196.1	Reacts		*94*
1703	C_7H_9N	*p*-Toluidine	200.3	Reacts		*94*
A =	C_7H_7Br	***m*-Bromotoluene**	184.3			
1704	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1705	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1706	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
1707	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
A =	C_7H_7Br	***o*-Bromotoluene**	181.4			
1708	C_7H_9N	*m*-Toluidine	200.55	Nonazeotrope		*89*
1709	C_7H_9N	*o*-Toluidine	200.35	Nonazeotrope		*89*
1710	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1711	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
A =	C_7H_7Br	***p*-Bromotoluene**	185			
1712	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
A =	C_7H_7Cl	**α-Chlorotoluene**	179.35			
1713	C_7H_8O	*o*-Cresol	190.8	Reacts		*94*
1714	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1715	$C_8H_{11}N$	Dimethylaniline	194.05	Reacts		*94*
A =	C_7H_7Cl	***o*-Chlorotoluene**	159.3			
1717	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	C_7H_7Cl	***p*-Chlorotoluene**	162.4			
1718	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
1719	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	C_7H_7I	***p*-Iodotoluene**	212			
1720	$C_7H_7NO_2$	*o*-Nitrotoluene	221.75	Nonazeotrope		*92*
1721	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
1722	C_7H_9N	*o*-Toluidine	200.35	Nonazeotrope		*89*
1723	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1724	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1725	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
1726	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*90*
A =	$C_7H_7NO_2$	***m*-Nitrotoluene**	230.8			
1727	$C_7H_{14}O_2$	Enanthic acid	222.0	220.0	30	*92*
1728	$C_7H_{16}O_4$	2-[2-(2-Methoxyethoxy)-ethoxy]ethanol	245.25	226.4	77	*92*
1729	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*92*
1730	$C_8H_{10}O$	*p*-Ethylphenol	220.0	Nonazeotrope		*92*
1731	$C_8H_{11}NO$	*o*-Phenetidine	232.5	233.0	30	*89*
1732	$C_8H_{11}NO$	*p*-Phenetidine	249.9	Nonazeotrope		*89*
1733	$C_8H_{12}O_4$	Ethyl fumarate	217.85	Nonazeotrope		*92*
1734	$C_8H_{12}O_4$	Ethyl maleate	223.3	Nonazeotrope		*92*
1735	$C_8H_{14}O_4$	Ethyl succinate	217.25	Nonazeotrope		*92*
1736	$C_8H_{16}O_2$	Caprylic acid	238.5	<229.8	<80	*92*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**$C_7H_7NO_2$**	***m*-Nitrotoluene (*Contd.*)**	**230.8**			
1737	$C_8H_{18}O_3$	2-(2-Butoxyethoxy)ethanol	231.2	<229.0	<70	*92*
1738	C_9H_7N	Quinoline	237.6	Nonazeotrope		*92*
1739	$C_9H_{10}O$	Cinnamyl alcohol	257.0	Nonazeotrope		*92*
1740	$C_9H_{10}O_2$	Benzyl acetate	215.0	Nonazeotrope		*92*
1741	$C_{10}H_{12}O_2$	Propyl benzoate	230.85	230.0	48	*92*
1742	$C_{10}H_{14}O$	Carvacrol	237.85	Nonazeotrope		*92*
1743	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
1744	$C_{10}H_{20}O$	Citronellol	224.4	223.2	>26	*92*
1745	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*92*
1746	$C_{11}H_{14}O_2$	Ethyl β-phenylpropionate	248.1	Nonazeotrope		*92*
1747	$C_{11}H_{14}O_2$	Isobutyl benzoate	241.9	Nonazeotrope		*92*
1748	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
1749	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	<230.2	>56	*92*
1750	$C_{12}H_{20}O_2$	Bornyl acetate	227.6	<226.5	>28	*92*
A =	**$C_7H_7NO_2$**	***o*-Nitrotoluene**	**221.85**			
1751	C_7H_9N	Methylaniline	196.25	Nonazeotrope		*89*
1752	C_7H_9N	*o*-Toluidine	200.35	Nonazeotrope		*89*
1753	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1754	$C_7H_{14}O_2$	Enanthic acid	222.0	<218.0	<60	*92*
1755	$C_7H_{16}O_4$	2-[2-(2-Methoxyethoxy)ethoxy]ethanol	245.25	<220.8	88	*92*
1756	$C_8H_8O_2$	Phenyl acetate	228.75	Nonazeotrope		*92*
1757	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*92*
1758	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1759	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	Nonazeotrope		*89*
1760	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1761	$C_8H_{11}N$	Ethylaniline	205.5	Nonazeotrope		*89*
1762	$C_8H_{12}O_4$	Ethyl fumarate	217.85	Nonazeotrope		*92*
1763	$C_8H_{12}O_4$	Ethyl maleate	223.3	221.0	62	*92*
1764	$C_8H_{14}O_4$	Ethyl succinate	217.25	<217.1	..	*92*
1765	C_9H_7N	Quinoline	237.3	Nonazeotrope		*92*
1766	$C_9H_{10}O$	Cinnamyl alcohol	257.0	Nonazeotrope		*92*
1767	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1768	$C_{10}H_{14}O$	Carvacrol	237.85	Nonazeotrope		*92*
1769	$C_{10}H_{17}Cl$	Bornyl chloride	207.5	Nonazeotrope		*92*
1770	$C_{10}H_{18}O$	Citronellal	208.0	Nonazeotrope		*92*
1771	$C_{10}H_{18}O$	β-Terpineol	210.5	209.7	10	*92*
1772	$C_{10}H_{20}O_2$	Methyl pelargonate	213.8	Nonazeotrope		*92*
1773	$C_{11}H_{10}$	1-Methylnaphthalene	244.6	Nonazeotrope		*92*
1774	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*92*
1775	$C_{11}H_{20}O$	Methyl α-terpineol ether	216.2	215.0	15?	*92*
A =	**$C_7H_7NO_2$**	***p*-Nitrotoluene**	**238.8**			
1776	$C_7H_{16}O_4$	2-[2-(2-Methoxyethoxy)ethoxy]ethanol	245.25	231.2	61	*92*
1777	$C_8H_8O_2$	Phenylacetic acid	266.8	Nonazeotrope		*92*
1778	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*92*
1779	C_9H_7N	Quinoline	237.3	237.2	8	*91, 92*
1780	$C_9H_{12}O_2$	2-Benzyloxyethanol	265.2	Nonazeotrope		*92*
1781	$C_{10}H_7Cl$	1-Chloronaphthalene	262.7	Nonazeotrope		*92*
1782	$C_{10}H_{12}O_2$	Eugenol	254.8	Nonazeotrope		*92*
1783	$C_{10}H_{14}O$	Carvacrol	237.85	237.7	>25	*92*
1784	$C_{10}H_{18}O$	Borneol	215.0	Nonazeotrope		*92*
1785	$C_{10}H_{18}O$	β-Terpineol	210.5	Nonazeotrope		*92*
1786	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*92*
1787	$C_{11}H_{14}O_2$	Ethyl β-phenylpropionate	248.1	Nonazeotrope		*92*
1788	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
1789	$C_{12}H_{10}$	Diphenyl	256.1	Nonazeotrope		*92*
1790	$C_{12}H_{10}O$	Diphenyl ether	259.0	Nonazeotrope		*92*
1791	$C_{12}H_{16}O_3$	Isoamyl salicylate	277.5	Nonazeotrope		*92*
A =	**C_7H_8**	**Toluene**	**110.75**			
1792	C_7H_9N	2,6-Lutidine	144	Nonazeotrope		*33*
1793	C_7H_{14}	Methylcyclohexane	100.85	Nonazeotrope		*121*
1794	C_7H_{16}	*n*-Heptane	98.45	Nonazeotrope		*15, 94*
1795	C_8H_{10}	*m*-Xylene	139.0			*94*
1796	C_8H_{10}	*p*-Xylene				*94*
1797	C_8H_{18}	*n*-Octane	125.4	Nonazeotrope		*15*
A =	**C_7H_8O**	**Anisole**	**153.85**			
1797a	$C_7H_{16}O_3$	Ethyl orthoformate	145.75	Nonazeotrope		*87*
1798	$C_8H_{18}O$	Butyl ether	142.4	Nonazeotrope		*87*
1799	$C_8H_{19}N$	Diisobutylamine	138.5	Nonazeotrope		*89*
A =	**C_7H_8O**	**Benzyl Alcohol**	**205.2**			
1800	C_7H_9NO	*o*-Anisidine	219.0	Nonazeotrope		*89*
1801	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1802	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	Nonazeotrope		*89*
1803	$C_8H_{11}NO$	*o*-Phenetidine	232.5	Nonazeotrope		*89*
1804	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
1805	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*90*
1806	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	202.8	58	*89*
A =	**C_7H_8O**	***m*-Cresol**	**202.2**			
1807	C_7H_8O	*p*-Cresol	200.9/738	Nonazeotrope		*53*
1808	C_7H_9N	Benzylamine	185.0	>207.2	<94	*89*
1809	C_7H_9N	*m*-Toluidine	203.1	205.5	53	*89*
1810	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., °C.	Azeotropic Data B.P., °C.	Weight % A	Reference
A =	**C_7H_8O**	***o*-Cresol**	**191.1**			
1811	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
1812	$C_7H_{12}O_4$	Ethyl malonate	198.9	Reacts		*94*
1813	$C_7H_{14}O_3$	1,3-Butanediol methyl ether acetate	171.75	194.1	68	*96*
1814	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1815	$C_9H_{14}O$	Phorone	197.8	201.3	35	*90*
1816	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
1817	$C_{10}H_{15}N$	Diethylaniline	217.95	Nonazeotrope		*89*
1818	$C_{10}H_{16}O$	Fenchone	193.6	199.6	43	*90*
A =	**C_7H_8O**	***p*-Cresol**	**201.7**			
1819	C_7H_9N	Benzylamine	185.0	>206.5	<95	*89*
1820	C_7H_9N	*m*-Toluidine	203.1	204.9	47	*89*
1821	$C_7H_{12}O_4$	Ethyl malonate	198.9	Reacts		*94*
1822	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1823	$C_8H_{14}O_4$	Ethyl succinate	216.5	Reacts		*94*
1824	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1825	$C_9H_{14}O$	Phorone	197.8	206.0	55	*90*
1826	$C_{10}H_{16}$	Terpinene	180.5	~179		*94*
1827	$C_{10}H_{16}$	Terpinolene	185	183	~15	*94*
A =	**$C_7H_8O_2$**	**Guaiacol**	**205.1**			
1828	C_7H_9N	*m*-Toluidine	203.1	Nonazeotrope		*89*
1829	C_7H_9N	*p*-Toluidine	200.55	Nonazeotrope		*89*
1830	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1831	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.35	Nonazeotrope		*89*
A =	**$C_7H_8O_2$**	***m*-Methoxyphenol**	**244**			
1832	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
A =	**C_7H_8S**	**α-Toluenethiol**	**194.8**			
1833	$C_{10}H_{16}$	Terpinolene	185	Reacts		*94*
A =	**C_7H_9N**	**Benzylamine**	**185.0**			
1834	$C_8H_{10}O$	Benzyl methyl ether	167.8	Nonazeotrope		*89*
1835	$C_8H_{10}O$	Methyl *p*-methylanisole	177.05	Nonazeotrope		*89*
1836	$C_8H_{10}O$	Phenetole	170.45	Nonazeotrope		*89*
1837	$C_{10}H_{18}O$	Cineole	176.35	175.6	16.5	*89*
1838	$C_{10}H_{22}O$	Amyl ether	187.5	<180.0	<67	*89*
1839	$C_{10}H_{22}O$	Isoamyl ether	173.2	170.4	23	*89*
A =	**C_7H_9N**	**2,6-Lutidine**	**144**			
1840	C_8H_{18}	2,3,4-Trimethylpentane	133	Nonazeotrope		*33*
A =	**C_7H_9N**	**Methylaniline**	**196.25**			
1841	C_7H_9N	*o*-Toluidine	200.3	Nonazeotrope		*87*
1843	$C_7H_{16}O$	*n*-Heptyl alcohol	176.75	Nonazeotrope		*89*
1844	$C_8H_{10}O$	Methyl *p*-methylanisole	177.05	Nonazeotrope		*89*
1845	$C_8H_{10}O_2$	*o*-Ethoxyphenol	216.5	Nonazeotrope		*89*
1846	C_9H_8	Indene	182.6	Nonazeotrope		*89*
1847	C_9H_{12}	Mesitylene	164.6	Nonazeotrope		*89*
1848	$C_{10}H_{14}$	Cymene	176.7	Nonazeotrope		*89*
1849	$C_{10}H_{16}$	Camphene	159.6	Nonazeotrope		*89*
1850	$C_{10}H_{16}$	α-Pinene	155.8	Nonazeotrope		*89*
1851	$C_{10}H_{16}$	β-Pinene	163.8	Nonazeotrope		*89*
1852	$C_{10}H_{16}$	α-Terpinene	173.4	Nonazeotrope		*89*
1853	$C_{10}H_{16}$	Dipentene	177.7	<177.2	<11	*89*
1854	$C_{10}H_{18}O$	Cineole	176.35	Nonazeotrope		*89*
1855	$C_{10}H_{18}O$	β-Terpineol	210.5	Nonazeotrope		*89*
1856	$C_{10}H_{22}O$	Isoamyl ether	173.2	Nonazeotrope		*89*
1857	$C_{12}H_{18}$	1,3,5-Triethylbenzene	215.5	Nonazeotrope		*89*
1858	$C_{12}H_{22}O$	Ethyl isobornyl ether	203.8	Nonazeotrope		*89*
A =	**C_7H_9N**	***m*-Toluidine**	**203.3**			
1859	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*89*
1860	$C_8H_{10}O$	*p*-Ethylphenol	218.8	Nonazeotrope		*89*
1861	$C_8H_{10}O_2$	*o*-Ethoxyphenol	216.5	Nonazeotrope		*89*
1862	$C_8H_{18}O$	*n*-Octyl alcohol	195.2	Nonazeotrope		*89*
1863	$C_8H_{18}O$	*sec*-Octyl alcohol	180.4	Nonazeotrope		*89*
1864	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*89*
1865	$C_{10}H_{14}$	Butylbenzene	183.1	Nonazeotrope		*89*
1866	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*89*
1867	$C_{10}H_{16}O$	Pulegone	223.8	Nonazeotrope		*89*
1868	$C_{10}H_{18}O$	α-Terpineol	218.25	Nonazeotrope		*89*
1869	$C_{11}H_{20}O$	Methyl α-terpineol ether	216.2	Nonazeotrope		*89*
1870	$C_{12}H_{22}O$	Ethyl isobornyl ether	203.8	<201.0	<60	*89*
A =	**C_7H_9N**	***o*-Toluidine**	**200.3**			
1871	$C_7H_{12}O_4$	Ethyl malonate	198.9	Reacts		*94*
1872	$C_7H_{16}O$	*n*-Heptyl alcohol	176.15	Nonazeotrope		*89*
1873	$C_8H_{10}O$	Phenethyl alcohol	219.4	Nonazeotrope		*89*
1874	$C_8H_{18}O$	*sec*-Octyl alcohol	180.4	Nonazeotrope		*89*
1875	C_9H_8	Indene	182.6	Nonazeotrope		*89*
1876	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*89*
1877	$C_{10}H_{14}$	Butylbenzene	183.1	Nonazeotrope		*89*
1878	$C_{10}H_{14}$	Cymene	176.7	Nonazeotrope		*89*
1879	$C_{10}H_{18}O$	β-Terpineol	210.75	Nonazeotrope		*89*
1880	$C_{10}H_{20}O$	Menthol	216.3	Nonazeotrope		*89*
A =	**C_7H_9N**	***p*-Toluidine**	**200.3**			
1881	$C_8H_{18}O$	*sec*-Octyl alcohol	180.4	Nonazeotrope		*89*
1882	C_9H_8	Indene	182.6	Nonazeotrope		*89*
1883	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*89*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., °C.	Azeotropic Data B.P., °C.	Weight % A	Reference
A =	C_7H_9N	***p*-Toluidine (*Contd.*)**	**200.3**			
1884	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*89*
1885	$C_{10}H_{16}$	Terpinolene	184.6	<183.5	..	*89*
A =	C_7H_9NO	***o*-Anisidine**	**219.0**			
1886	$C_{10}H_{20}O$	Menthol	216.3	<216.0	..	*89*
A =	$C_7H_{12}O_4$	**Ethyl Malonate**	**199.35**			
1887	$C_8H_8O_2$	Benzyl formate	203.0	<198.2	..	*87*
1888	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*90*
1889	$C_9H_{14}O$	Phorone	197.8	<197.65	<47	*90*
1890	$C_9H_{18}O_2$	Methyl caprylate	192.9	191.9	26	*87*
1891	$C_9H_{18}O_3$	Isobutyl carbonate	190.3	Nonazeotrope		*87*
1892	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
1893	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	191.75	30	*87*
A =	$C_7H_{14}O$	**4-Heptanone**	**143.55**			
1894	$C_7H_{14}O_2$	Butyl propionate	146.8	Nonazeotrope		*90*
1895	$C_7H_{14}O_2$	Ethyl *n*-valerate	145.15	Nonazeotrope		*90*
1896	C_8H_{10}	*m*-Xylene	139.2	139.0	10	*90*
1897	C_9H_{12}	Cumene	152.8	Nonazeotrope		*90*
1898	C_9H_{12}	Propylbenzene	159.3	Nonazeotrope		*90*
1899	$C_{10}H_{16}$	Camphene	159.6	142.5	95	*90*
A =	$C_7H_{14}O$	***o*-Methylcyclohexanol**	**168.5**			
1900	$C_8H_{11}N$	Dimethylaniline	194.05	Nonazeotrope		*89*
1901	$C_8H_{14}O$	Methylheptenone	173.2	Nonazeotrope		*90*
1902	$C_8H_{16}O$	2-Octanone	172.85	Nonazeotrope		*89*
1903	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*90*
1904	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	167.5	40	*90*
A =	$C_7H_{14}O$	**5-Methyl-2-hexanone**	**144.2**			
1905	$C_7H_{14}O_2$	Butyl propionate	146.8	Nonazeotrope		*90*
1906	$C_7H_{14}O_2$	Isoamyl acetate	142.1	141.8	18	*90*
1907	$C_7H_{14}O_2$	Isobutyl propionate	137.5	Nonazeotrope		*90*
1908	$C_7H_{14}O_2$	Propyl butyrate	143.7	143.3	35	*90*
1909	C_8H_{10}	Ethylbenzene	136.15	Nonazeotrope		*90*
1910	C_8H_{10}	*o*-Xylene	144.3	143.0	42	*90*
1911	$C_8H_{16}O_2$	Isobutyl isobutyrate	148.6	Nonazeotrope		*90*
1912	C_9H_{12}	Cumene	152.8	Nonazeotrope		*90*
1913	$C_{10}H_{16}$	α-Pinene	155.8	102.0	75	*90*
A =	$C_7H_{14}O_2$	**Amyl Acetate**	**149.0**			
1914	$C_8H_{16}O_2$	Isobutyl isobutyrate	148.6	<148.5	>10	*87*
A =	$C_7H_{14}O_2$	**Enanthic Acid**	**222.0**			
1915	C_8H_8O	Acetophenone	202.0	Nonazeotrope		*90*
1916	$C_9H_{10}O$	*p*-Methylacetophenone	226.35	<221.2	>70	*90*
1917	$C_9H_{10}O$	Propiophenone	217.7	216.5	20	*90*
1918	$C_{10}H_{14}O$	Carvone	231.0	Nonazeotrope		*90*
A =	$C_7H_{14}O_2$	**Isobutyl Propionate**	**134.0**			
1919	C_8H_8	Styrene	68/60	Nonazeotrope		*11*
A =	$C_7H_{14}O_3$	**1,3-Butanediol Methyl Ether Acetate**	**171.75**			
1920	$C_9H_{18}O_2$	Isobutyl isovalerate	171.2	170.35	47	*96*
A =	$C_7H_{16}O$	***n*-Heptyl Alcohol**	**176.5**			
1921	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	175.5	82	*89*
1922	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
A =	$C_7H_{16}O$	**2-Heptanol**	**65.4/10**			
1923	C_8H_9Cl	*o,m,p*-Chloroethylbenzene	67.5/10	61.4/10	43/10	*10*
A =	$C_7H_{16}O_4$	**2-[2-(2-Methoxyethoxy)ethoxy]ethanol**	**245.25**			
1925	C_9H_7N	Quinoline	237.3	235.55	22	*91*
A =	C_8H_8O	**Acetophenone**	**202**			
1926	$C_8H_{10}O$	3,4-Xylenol	226.8	Nonazeotrope		*90*
1927	$C_8H_{10}O$	*p*-Ethylphenol	218.8	219.5	15	*90*
1928	$C_8H_{10}O_2$	*o*-Ethoxyphenol	216.5	Nonazeotrope		*90*
1929	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1930	$C_8H_{14}O_4$	Propyl oxalate	214.2	Nonazeotrope		*90*
1931	$C_8H_{18}O$	*sec*-Octyl alcohol	180.4	Nonazeotrope		*90*
1932	$C_9H_{10}O_2$	Ethyl benzoate	212.5	Nonazeotrope		*90*
1933	$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine	185.3	Nonazeotrope		*89*
1934	$C_{10}H_{18}O$	β-Terpineol	210.5	Nonazeotrope		*90*
1935	$C_{10}H_{20}O_2$	Methyl pelargonate	213.8	Nonazeotrope		*90*
A =	$C_8H_8O_2$	**Benzyl Formate**	**202.3**			
1936	$C_8H_8O_2$	Methyl benzoate	199.4	Nonazeotrope		*87*
A =	$C_8H_8O_2$	**Methyl Benzoate**	**199.55**			
1937	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
1938	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
1939	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	Nonazeotrope		*87*
A =	$C_8H_8O_3$	**Methyl Salicylate**	**222.3**			
1941	C_9H_7N	Quinoline	237.3	Nonazeotrope		*91*
1942	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*90*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**C_8H_{10}**	***m*-Xylene**	**139.0**			
1943	$C_8H_{19}N$	Diisobutylamine	138.5	137.5	49	*89*
A =	**$C_8H_{10}O$**	***p*-Ethylphenol**	**218.8**			
1944	$C_8H_{11}N$	Ethylaniline	217.05	214.0	60	*89*
1945	$C_8H_{11}NO$	*o*-Phenetidine	232.5	Nonazeotrope		*89*
1946	$C_9H_{10}O$	*p*-Methylacetophenone	226.35	229.5	30	*90*
1947	$C_9H_{10}O$	Propiophenone	217.7	224.5	..	*90*
1948	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1949	$C_{10}H_{15}N$	Diethylaniline	217.05	214.0	60	*89*
A =	**$C_8H_{10}O$**	***p*-Methylanisole**	**175.3**			
1950	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1951	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	**$C_8H_{10}O$**	**Phenethyl Alcohol**	**219.4**			
1952	$C_8H_{11}N$	Dimethylaniline	194.05	Nonazeotrope		*89*
1953	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1954	$C_8H_{11}N$	3,4-Dimethylaniline	225.5	Nonazeotrope		*89*
1955	$C_8H_{11}NO$	*o*-Phenetidine	232.5	Nonazeotrope		*89*
1956	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	208.5	30	*89*
1957	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
A =	**$C_8H_{10}O$**	**Phenetole**	**171.5**			
1958	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1959	$C_9H_{13}N$	Dimethyl-*o*-toluidine	185.35	Nonazeotrope		*89*
1960	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	**$C_8H_{10}O$**	**3,4-Xylenol**	**226.8**			
1961	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1962	$C_8H_{11}N$	Ethylaniline	205.5	Nonazeotrope		*89*
1963	$C_8H_{11}NO$	*o*-Phenetidine	232.5	232.65	8	*89*
1964	$C_8H_{11}NO$	*p*-Phenetidine	249.9	Nonazeotrope		*89*
1965	$C_9H_{10}O$	Propiophenone	217.7	228.5	67	*90*
1966	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1967	$C_{10}H_{14}O$	Thymol	232.9	Nonazeotrope		*87*
1968	$C_{10}H_{15}N$	Diethylaniline	217.5	217.0	8	*89*
A =	**$C_8H_{10}O_2$**	***o*-Ethoxyphenol**	**216.5**			
1969	$C_8H_{11}N$	Dimethylaniline	194.15	Nonazeotrope		*89*
1970	$C_8H_{11}N$	2,4-Dimethylaniline	214.0	Nonazeotrope		*89*
1971	$C_9H_{10}O$	Propiophenone	217.7	218.3		*90*
1972	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
1973	$C_{10}H_{15}N$	Diethylaniline	217.05	<216.2	>57	*78, 89*
1974	$C_{10}H_{16}O$	Pulegone	223.8	Nonazeotrope		*90*
A =	**$C_8H_{10}O_2$**	**Veratrole**	**205.5**			
1975	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
A =	**$C_8H_{11}N$**	**Dimethylaniline**	**194.15**			
1976	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*89*
1977	C_9H_{12}	Mesitylene	164.6	Nonazeotrope		*89*
1978	C_9H_{12}	Propylbenzene	159.3	Nonazeotrope		*89*
1979	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*89*
1980	$C_{10}H_{14}$	Cymene	176.7	Nonazeotrope		*89*
1981	$C_{10}H_{16}$	α-Pinene	155.8	Nonazeotrope		*89*
1982	$C_{10}H_{16}$	β-Pinene	163.8	Nonazeotrope		*89*
1983	$C_{10}H_{16}$	α-Terpinene	173.4	Nonazeotrope		*89*
1984	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*89*
1985	$C_{10}H_{18}$	Dipentene	177.7	Nonazeotrope		*89*
1986	$C_{10}H_{20}O$	Cintronellol	224.4	Nonazeotrope		*89*
1987	$C_{10}H_{22}O$	Amyl ether	187.5	<187.0	<27	*89*
1988	$C_{10}H_{22}O$	Isoamyl ether	173.2	Nonazeotrope		*89*
1989	$C_{12}H_{22}O$	Bornyl ethyl ether	204.9	Nonazeotrope		*89*
A =	**$C_8H_{11}N$**	**2,4-Dimethylaniline**	**214.0**			
1990	$C_8H_{18}O$	*n*-Octyl alcohol	195.2	Nonazeotrope		*89*
1991	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*89*
1992	$C_{10}H_{14}O$	Thymol	232.9	Nonazeotrope		*89*
1993	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*89*
1994	$C_{10}H_{20}O$	Menthol	216.3	213.5	70	*89*
1995	$C_{12}H_{18}$	1,3,5-Triethylbenzene	215.5	212.5	51	*89*
A =	**$C_8H_{11}N$**	**3,4-Dimethylaniline**	**225.5**			
1996	$C_9H_{12}O$	3-Phenylpropanol	235.6	Nonazeotrope		*89*
1997	$C_{10}H_{18}$	Naphthalene	218.0	Nonazeotrope		*89*
1998	$C_{10}H_{20}O$	Citronellol	224.4	223.5	40	*89*
1999	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*89*
A =	**$C_8H_{11}N$**	**Ethylaniline**	**205.5**			
2000	$C_8H_{18}O$	*sec*-Octyl alcohol	180.4	Nonazeotrope		*89*
2001	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*89*
2002	$C_{10}H_{15}N$	Diethylaniline	216.5			*94*
2003	$C_{10}H_{16}$	Terpinolene	184.6	Nonazeotrope		*89*
2004	$C_{10}H_{20}O$	Citronellol	224.4	Nonazeotrope		*89*
2005	$C_{10}H_{22}O$	*n*-Decyl alcohol	232.8	Nonazeotrope		*89*
2006	$C_{11}H_{20}O$	Isobornyl methyl ether	192.4	Nonazeotrope		*89*
2007	$C_{12}H_{22}O$	Bornyl ethyl ether	204.9	<203.0	<48	*89*
A =	**$C_8H_{11}NO$**	***o*-Phenetidine**	**232.5**			
2008	$C_9H_{12}O$	3-Phenylpropanol	235.6	Nonazeotrope		*89*
2009	$C_{10}H_{12}O$	Anethole	235.7	232.25	75	*89*

Table I. Binary Systems (*Continued*)

No.	B-Component Formula	Name	B.P., ° C.	Azeotropic Data B.P., ° C.	Weight % A	Reference
A =	**$C_8H_{11}NO$**	***o*-Phenetidine** (*Contd.*)	**232.5**			
2010	$C_{10}H_{14}O$	Carvacrol	237.85	238.0	13	*89*
2011	$C_{10}H_{18}O$	α-Terpineol	218.85	Nonazeotrope		*89*
2012	$C_{10}H_{20}O$	Menthol	216.3	Nonazeotrope		*89*
2013	$C_{10}H_{22}O$	*n*-Decyl alcohol	232.8	232.0	>52	*89*
2014	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*89*
2015	$C_{12}H_{18}$	1,3,5-Triethylbenzene	215.5	Nonazeotrope		*89*
A =	**$C_8H_{11}NO$**	***p*-Phenetidine**	**249.9**			
2016	$C_9H_{10}O$	Cinnamyl alcohol	257.0	Nonazeotrope		*89*
2017	$C_9H_{12}O$	3-Phenylpropanol	235.6	Nonazeotrope		*89*
2018	$C_{10}H_{12}O$	Anethole	235.7	Nonazeotrope		*89*
2019	$C_{10}H_{14}O$	Carvacrol	237.85	Nonazeotrope		*89*
2020	$C_{10}H_{14}O$	Carvone	231.0	Nonazeotrope		*89*
2021	$C_{10}H_{16}O$	Carvenone	234.5	Nonazeotrope		*89*
2022	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	240.85	15	*89*
2023	$C_{11}H_{14}O_2$	1,2-Dimethoxy-4-propenylbenzene	270.5	Nonazeotrope		*89*
2024	$C_{12}H_{16}O_3$	Isoamyl salicylate	277.5	Nonazeotrope		*89*
A =	**$C_8H_{12}O_4$**	**Ethyl Fumarate**	**217.85**			
2025	$C_9H_{10}O$	*p*-Methylacetophenone	226.35	Nonazeotrope		*90*
2026	$C_9H_{10}O$	Propiophenone	217.7	216.8	53	*90*
2027	$C_9H_{10}O_2$	Benzyl acetate	215.0	Nonazeotrope		*87*
2028	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
2029	$C_{10}H_{16}O$	Pulegone	223.8	Nonazeotrope		*90*
2030	$C_{10}H_{20}O_2$	Methyl pelargonate	213.8	Nonazeotrope		*87*
2031	$C_{12}H_{20}O_2$	Bornyl acetate	227.6	Nonazeotrope		*87*
A =	**$C_8H_{12}O_4$**	**Ethyl Maleate**	**223.3**			
2032	$C_9H_{10}O$	*p*-Methylacetophenone	226.35	223.15	88	*90*
2033	$C_9H_{10}O$	Propiophenone	217.7	Nonazeotrope		*90*
2034	$C_9H_{10}O_2$	Benzyl acetate	215.0	Nonazeotrope		*87*
2035	$C_{10}H_{14}O$	Carvone	231.0	Nonazeotrope		*90*
2036	$C_{10}H_{16}O$	Pulegone	223.9	223.8	53	*90*
A =	**$C_8H_{14}O$**	**Methylheptenone**	**173.2**			
2037	$C_8H_{18}O$	Octyl alcohol	195.2	Nonazeotrope		*90*
2038	$C_{10}H_{14}$	Butylbenzene	183.1	Nonazeotrope		*90*
2039	$C_{10}H_{14}$	*p*-Cymene	176.7	172.7	72	*90*
2040	$C_{10}H_{16}$	α-Terpinene	173.4	170.0	42	*90*
2041	$C_{10}H_{18}$	Dipentene	177.7	170.9	52.5	*90*
A =	**$C_8H_{14}O_4$**	**Ethyl Succinate**	**217.25**			
2042	$C_{10}H_{12}O_2$	Ethyl α-toluate	228.75	Nonazeotrope		*87*
2043	$C_{10}H_{18}O$	Geraniol	229.7	Reacts		*78*
2044	$C_{10}H_{20}O_2$	Methyl pelargonate	213.8	212.5	..	*87*
2045	$C_{11}H_{22}O_2$	Ethyl pelargonate	227	Nonazeotrope		*87*
2046	$C_{12}H_{20}O_2$	Bornyl acetate	227.6	Nonazeotrope		*87*
A =	**$C_8H_{14}O_4$**	**Propyl Oxalate**	**214**			
2047	$C_9H_{10}O_2$	Benzyl acetate	215.0	<212.5	..	*87*
A =	**$C_8H_{16}O$**	**2-Octanone**	**174.1**			
2048	$C_8H_{16}O_2$	Butyl butyrate	166.4	Nonazeotrope		*90*
2049	$C_8H_{16}O_2$	Hexyl acetate	171.5	171.4?	..	*90*
2050	C_9H_{12}	Mesitylene	164.6	Nonazeotrope		*90*
2051	C_9H_{12}	Pseudocumene	168.2	168.0	..	*90*
2052	$C_{10}H_{16}$	α-Terpinene	173.4	169.0	42	*90*
2053	$C_{10}H_{18}$	Dipentene	177.7	170.0	55	*90*
A =	**$C_8H_{16}O_2$**	**Butyl Butyrate**	**166.4**			
2054	$C_8H_{20}SiO_4$	Ethyl silicate	168.8	Nonazeotrope		*87*
2055	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	**$C_8H_{16}O_2$**	**Ethyl Caproate**	**167.8**			
2056	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	167.5	60	*90*
A =	**$C_8H_{16}O_2$**	**Isoamyl Propionate**	**160.3**			
2057	$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	168.0	Nonazeotrope		*90*
A =	**$C_8H_{16}O_3$**	**Isoamyl Lactate**	**202.4**			
2058	$C_9H_{14}O$	Phorone	197.8	Nonazeotrope		*90*
2059	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
A =	**C_8H_{18}**	***n*-Octane**	**125.8**			
2060	C_8H_{18}	2,2,4-Trimethylpentane	99.2	Nonazeotrope		*15*
A =	**$C_8H_{18}O$**	**Isobutyl Ether**	**122.3**			
2061	$C_8H_{19}N$	Diisobutylamine	138.5	Nonazeotrope		*89*
A =	**$C_8H_{18}O$**	**Octyl Alcohol**	**195.2**			
2062	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*90*
2063	$C_{10}H_{18}O$	Menthone	209.5	Nonazeotrope		*90*
A =	**$C_8H_{18}O$**	***sec*-Octyl Alcohol**	**180.4●**			
2064	$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine	210.2	Nonazeotrope		*89*
2065	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
A =	**$C_8H_{18}O_3$**	**2-[2-Butoxy)ethoxy]ethanol**	**231.2**			
2066	C_9H_7N	Quinoline	237.3	<229.5	>56	*91*
A =	**$C_8H_{18}S$**	**Isobutyl Sulfide**				
2067	$C_{10}H_{22}O$	Isoamyl ether	....	171.0	62	*93*

Table I. Binary Systems (*Continued*)

No.	B-Component			Azeotropic Data		
	Formula	Name	B.P., ° C.	B.P., ° C.	Weight % A	Reference
A =	**$C_8H_{20}SiO_4$**	**Ethyl Silicate**	**168.8**			
2068	$C_9H_{18}O_2$	Isobutyl isovalerate	171.2	168.75	93	*87*
A =	**C_9H_7N**	**Quinoline**	**237.3**			
2069	$C_9H_{10}O_3$	Ethyl salicylate	233.8	Nonazeotrope		*91*
2070	$C_9H_{12}O_2$	2-Benzyloxyethanol	265.2	Nonazeotrope		*91*
2071	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*91*
2072	$C_{10}H_{10}O_2$	Safrole	235.9	235.15	27	*91*
2073	$C_{10}H_{10}O_2$	Isosafrole	252.0	Nonazeotrope		*91*
2074	$C_{10}H_{12}O$	Anethole	235.7	234.7	30	*91*
2075	$C_{10}H_{20}O$	Menthol	216.3	Nonazeotrope		*91*
2076	$C_{11}H_{10}$	α-Methylnaphthalene	244.6	Nonazeotrope		*91*
2077	$C_{11}H_{10}$	β-Methylnaphthalene	241.15	237.25	93	*91*
2078	$C_{12}H_{10}$	Diphenyl	256.1	Nonazeotrope		*91*
2079	$C_{12}H_{16}O_3$	Isoamyl salicylate	277.5	Nonazeotrope		*91*
A =	**C_9H_8**	**Indene**	**182.6**			
2080	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	**$C_9H_{10}O$**	**Cinnamyl Alcohol**	**257.0**			
2081	$C_{10}H_{14}O$	Carvone	231.0	Nonazeotrope		*90*
2082	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
A =	**$C_9H_{10}O$**	***p*-Methylacetophenone**	**226.3**			
2083	$C_{10}H_{12}O$	Anethole	235.7	Nonazeotrope		*90*
2084	$C_{10}H_{12}O_2$	Ethyl α-toluate	228.75	226.2	75	*90*
2085	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
2086	$C_{10}H_{20}O$	Citronellol	224.4	223.7	32	*90*
2087	$C_{11}H_{20}O$	Methyl terpenyl ether	216.2	Nonazeotrope		*90*
2088	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	Nonazeotrope		*90*
A =	**$C_9H_{10}O$**	**Propiophenone**	**217.7**			
2089	$C_{10}H_{15}N$	Diethylaniline	217.05	<216.6	<47	*89*
2090	$C_{10}H_{20}O_2$	Methyl pelargonate	213.8	Nonazeotrope		*90*
2091	$C_{12}H_{18}$	1,3,5-Triethylbenzene	215.5	215.4	25	*90*
A =	**$C_9H_{10}O_2$**	**Benzyl Acetate**	**214.9**			
2092	$C_{10}H_{16}O$	Pulegone	223.8	Nonazeotrope		*90*
A =	**$C_9H_{10}O_2$**	**Ethyl Benzoate**	**212.4**			
2093	$C_9H_{10}O_2$	Methyl α-toluate	215.3	Nonazeotrope		*87*
2094	$C_{10}H_{15}N$	Diethylaniline	216.1	Reacts		*94*
A =	**$C_9H_{10}O_2$**	**Methyl α-Toluate**	**215.3**			
2095	$C_{10}H_{16}O$	Pulegone	223.6	Nonazeotrope		*90*
A =	**$C_9H_{10}O_3$**	**Ethyl Salicylate**	**233.7**			
2096	$C_{10}H_{16}O$	Pulegone	223.8	Nonazeotrope		*90*
A =	**C_9H_{12}**	**Mesitylene**	**164.6**			
2097	$C_9H_{13}N$	N,N-Dimethyl-o-toluidine	185.3	Nonazeotrope		*89*
A =	**$C_9H_{12}O$**	**3-Phenylpropanol**	**235.6**			
2098	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
A =	**$C_9H_{13}N$**	***N,N*-Dimethyl-*o*-toluidine**	**185.3**			
2099	$C_{10}H_8$	Naphthalene	218.0	Nonazeotrope		*89*
2100	$C_{10}H_{14}$	Cymene	176.7	Nonazeotrope		*89*
2101	$C_{10}H_{16}$	Camphene	159.5	Nonazeotrope		*89*
2102	$C_{10}H_{16}$	α-Pinene	155.8	Nonazeotrope		*89*
2103	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*89*
2104	$C_{10}H_{18}O$	Borneol	215.0	Nonazeotrope		*89*
2105	$C_{10}H_{18}O$	β-Terpineol	210.5	Nonazeotrope		*89*
2106	$C_{11}H_{20}O$	Isobornyl methyl ether	192.4	Nonazeotrope		*89*
A =	**$C_9H_{13}N$**	***N,N*-Dimethyl-*p*-toluidine**	**210.2**			
2107	$C_{10}H_{18}O$	Geraniol	229.6	Nonazeotrope		*89*
2108	$C_{10}H_{22}O$	*n*-Decyl alcohol	232.8	Nonazeotrope		*89*
A =	**$C_9H_{14}O$**	**Phorone**	**197.8**			
2109	$C_9H_{18}O_2$	Methyl caprylate	192.9	Nonazeotrope		*90*
A =	**$C_9H_{18}O$**	**2,6-Dimethyl-4-heptanone**	**168.0**			
2110	$C_9H_{18}O_2$	Isoamyl isobutyrate	169.8	Nonazeotrope		*90*
2111	$C_9H_{18}O_2$	Isobutyl isovalerate	172.2	Nonazeotrope		*90*
A =	**$C_9H_{18}O_2$**	**Methyl Caprylate**	**192.9**			
2112	$C_{10}H_{20}O_2$	Isoamyl isovalerate	192.7	192.5	47	*87*
A =	**$C_{10}H_8O$**	**1-Naphthol**	**288.0**			
2113	$C_{10}H_9N$	1-Naphthylamine	200.8	Nonazeotrope		*89*
2114	$C_{10}H_9N$	2-Naphthylamine	306.1	Nonazeotrope		*89*
2115	$C_{12}H_{11}N$	Diphenylamine	275	Azeotrope		*94*
A =	**$C_{10}H_9N$**	**1-Naphthylamine**	**300.8**			
2116	$C_{12}H_{10}$	Acenaphthene	277.9	Nonazeotrope		*89*
2117	$C_{13}H_{12}O$	Benzyl phenyl ether	286.5	Nonazeotrope		*89*
2118	$C_{14}H_{14}$	1,2-Diphenylethane	284.5	Nonazeotrope		*89*
A =	**$C_{10}H_{10}O_2$**	**Isosafrole**	**252.1**			
2119	$C_{11}H_{17}N$	Isoamylaniline	256.0	<250.0	>64	*89*

Table I. Binary Systems (*Continued*)

No.	B-Component			Azeotropic Data		
	Formula	Name	B.P., ° C.	B.P., ° C.	Weight % A	Reference
A =	$C_{10}H_{10}O_2$	**Safrole**	**235.9**			
2120	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
A =	$C_{10}H_{10}O_4$	**Methyl Phthalate**	**283.2**			
2121	$C_{11}H_{12}O_2$	Ethyl cinnamate	272.0	Nonazeotrope		*87*
A =	$C_{10}H_{12}O$	**Anethole**	**235.7**			
2122	$C_{10}H_{14}O$	Carvone	231.0	Nonazeotrope		*90*
2123	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
A =	$C_{10}H_{12}O_2$	**Eugenol**	**255.0**			
2124	$C_{11}H_{17}N$	Isoamylaniline	256.0	<254.5	..	*89*
A =	$C_{10}H_{12}O_2$	**Propyl Benzoate**	**230.85**			
2125	$C_{10}H_{16}O$	Carvenone	234.5	Nonazeotrope		*90*
2126	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	<230.8	..	*87*
A =	$C_{10}H_{14}$	**Cymene**	**176.7**			
2127	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	$C_{10}H_{14}O$	**Carvacrol**	**237.85**			
2128	$C_{10}H_{14}O$	Carvone	231.0	242.2	58	*90*
2129	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
2130	$C_{10}H_{16}O$	Pulegone	223.8	238.4	..	*90*
2131	$C_{11}H_{17}N$	Isoamylaniline	256.0	Nonazeotrope		*89*
A =	$C_{10}H_{14}O$	**Carvone**	**231.0**			
2132	$C_{10}H_{15}N$	Diethylaniline	217.05	Nonazeotrope		*89*
2133	$C_{10}H_{18}O$	Geraniol	229.6	229.2	40	*90*
2134	$C_{10}H_{20}O$	Menthol	216.3	Nonazeotrope		*90*
2135	$C_{11}H_{10}$	2-Methylnaphthalene	241.15	Nonazeotrope		*90*
2136	$C_{11}H_{14}O_2$	Isobutyl benzoate	241.9	Nonazeotrope		*90*
A =	$C_{10}H_{15}N$	**Diethylaniline**	**217.05**			
2137	$C_{10}H_{16}O$	Camphor	209.1	Nonazeotrope		*89*
2138	$C_{10}H_{16}O$	Citral	226	Reacts		*94*
2139	$C_{10}H_{18}O$	β-Terpineol	210.5	Nonazeotrope		*89*
2140	$C_{11}H_{10}$	2-Methylnaphthalene	241.5	Nonazeotrope		*89*
2141	$C_{11}H_{20}O$	Methyl α-terpinyl ether	216.2	<215.0	<48	*89*
2142	$C_{12}H_{22}O$	Ethyl isobornyl ether	203.8	Nonazeotrope		*89*
A =	$C_{10}H_{16}$	**Camphene**	**159.6**			
2143	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	$C_{10}H_{16}O$	**Camphor**	**208.9**			
2144	$C_{10}H_{18}O$	Citronellal	208.0	207.5	..	*90*
A =	$C_{10}H_{16}O$	**Carvenone**	**234.5**			
2145	$C_{11}H_{14}O_2$	Isobutyl benzoate	241.9	Nonazeotrope		*90*
2146	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	Nonazeotrope		[illegible]
A =	$C_{10}H_{16}O$	**Pulegone**	**221.5**			
2147	$C_{11}H_{22}O_3$	Isoamyl carbonate	232.2	[illegible]		*90*
2148	$C_{12}H_{20}O_2$	Bornyl acetate	227.6	Nonazeotrope		*90*
A =	$C_{10}H_{18}$	**Dipentene**	**177.7**			
2149	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	$C_{10}H_{18}O$	**Cineole**	**176.35**			
2150	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	$C_{10}H_{18}O_4$	**Propyl Succinate**	**250.5**			
2151	$C_{11}H_{14}O_2$	Butyl benzoate	249.0	Nonazeotrope		*87*
A =	$C_{10}H_{22}O$	**Isoamyl Ether**	**173.2**			
2152	$C_{10}H_{23}N$	Diisoamylamine	188.2	Nonazeotrope		*89*
A =	$C_{11}H_{12}O_2$	**Ethyl Cinnamate**	**272.0**			
2153	$C_{12}H_{22}O_4$	Isoamyl oxalate	268.0	<267.5	>21	*87*
A =	$C_{11}H_{14}O_2$	**1-Allyl-3,4-dimethoxybenzene**	**254.7**			
2154	$C_{11}H_{17}N$	Isoamylaniline	256.0	250.5	58	*89*

[End of Table I]

Table II. Ternary Systems

	A-Component			B-Component			C-Component			Azeotropic Data				
No.	Formula	Name	B.P., ° C.	Formula	Name	B.P., ° C.	Formula	Name	B.P., ° C.	B.P., ° C.	Weight % A	Weight % B	Weight % C	Reference
2155	BrH	Hydrobromic acid	-67	H_2O	Water	100	C_6H_5Cl	Chlorobenzene	131.8	105	10.4	11.0	78.6	36
2155a	HF	Hydrofluoric acid	19.4	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	103	30	10	60	27
2156	HNO_3	Nitric acid	86	H_2O	Water	100	O_3S	Sulfur trioxide	47		Vapor pressure data			94
2157	H_2O	Water	100	H_3N	Ammonia	−33.5	$C_3H_8O_3$	Glycerol	~290					94
2158	H_2O	Water	100	CCl_4	Carbon tetrachloride	76.75	C_2H_3N	Acetonitrile	81.6	60	...	...	...	119
2159	H_2O	Water	100	CCl_4	Carbon tetrachloride	76.75	C_3H_6O	Acetone	57		Nonazeotrope			1
2160	H_2O	Water	100	CCl_4	Carbon tetrachloride	76.75	$C_4H_{10}O$	*tert*-Butyl alcohol	82.55	64.7	3.1	85.0	11.9	1
2161	H_2O	Water	100	CS_2	Carbon disulfide	46.25	CH_4O	Methanol	64.7		Nonazeotrope			1
2162	H_2O	Water	100	CS_2	Carbon disulfide	46.25	C_2H_3N	Acetonitrile	81.6	39	...	...	...	119
2163	H_2O	Water	100	$CHCl_3$	Chloroform	61.2	C_2H_3N	Acetonitrile	81.6		Minimum B.P.			119
2164	H_2O	Water	100	$CHCl_3$	Chloroform	61.2	C_3H_6O	Acetone	57	60.4?	40	57.6	38.4	122
2165	H_2O	Water	100	CH_2Cl_2	Dichloromethane	41.5	C_2H_6O	Ethyl alcohol	78.3		Nonazeotrope			4
2166	H_2O	Water	100	CH_2O_2	Formic acid	100.75	C_8H_{10}	*m*-Xylene	139.0	97.5?	10.6	40.4	49.0	122
2167	H_2O	Water	100	CH_4O	Methanol	64.7	$C_3H_5ClO_2$	Methyl chloroacetate	131.4	67.85	5.26	81.20	13.54	22
2168	H_2O	Water	100	CH_4O	Methanol	64.7	$C_3H_8O_2$	Methylal	42.3		Nonazeotrope			52
2169	H_2O	Water	100	CH_4O	Methanol	64.7	$C_4H_{10}O$	Isobutyl alcohol	108.0		Nonazeotrope			67
2170	H_2O	Water	100	CH_4O	Methanol	64.7	$C_4H_{10}O_2$	Acetaldehyde dimethyl acetal	64.3		Nonazeotrope			7
2171	H_2O	Water	100	CH_4O	Methanol	64.7	$C_4H_{10}O_2$	Ethoxymethoxymethane	65.90		Nonazeotrope			159
2172	H_2O	Water	100	C_2Cl_4	Tetrachloroethylene	120.8	C_2H_3N	Acetonitrile	81.6	72	...	...	...	119
2173	H_2O	Water	100	C_2HCl_3	Trichloroethylene	86.95	C_2H_3N	Acetonitrile	81.6	67	6.4	73.1	20.5	119
2174	H_2O	Water	100	$C_2H_2Cl_4$	Tetrachloroethane	146.35	C_2H_3N	Acetonitrile	81.6		Nonazeotrope			119
2175	H_2O	Water	100	C_2H_3N	Acetonitrile	81.6	C_3H_6O	Acetone	57		Nonazeotrope			119
2176	H_2O	Water	100	C_2H_3N	Acetonitrile	81.6	$C_4H_8O_2$	Ethyl acetate	77.05	70	...	...	...	119
2177	H_2O	Water	100	C_2H_3N	Acetonitrile	81.6	$C_5H_{10}O_2$	Propyl acetate	101.6	74	...	...	...	119
2178	H_2O	Water	100	C_2H_3N	Acetonitrile	81.6	$C_6H_{12}O_2$	Butyl acetate	124.8		Nonazeotrope			119
2179	H_2O	Water	100	C_2H_3N	Acetonitrile	81.6	C_6H_6	Benzene	80.2	66	8.2	23.3	68.5	119
2180	H_2O	Water	100	C_2H_3N	Acetonitrile	81.6	C_7H_8	Toluene	110.7	73	...	...	...	119
2181	H_2O	Water	100	$C_2H_4O_2$	Acetic acid	118.5	C_7H_8	Toluene	110.7		Nonazeotrope			94
2182	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_4H_6O_2$	Biacetyl	88		Nonazeotrope?			102
2183	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_4H_7ClO_2$	Ethyl chloroacetate	143.5	81.35	17.5	61.7	20.8	22
2184	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_4H_{10}O_2$	2-Ethoxyethanol	133		Nonazeotrope			3
2185	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_4H_{10}O_2$	Ethoxymethoxymethane	65.90		Nonazeotrope			159
2186	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	C_6H_{10}	1-Hexyne	70.2	59.9	...	...	...	61
2187	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	C_6H_{10}	3-Hexyne	80.5	64.4	...	...	...	61
2188	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_6H_{14}O_2$	Acetal	103.6	77.8	11.4	27.6	61.0	7
2189	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_6H_{14}O_2$	Ethoxypropoxymethane	113.7		Nonazeotrope			159
2190	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	$C_6H_{15}N$	Triethylamine	89.4	74.7	9	13	78	94, 151
2191	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	C_7H_{12}	1-Heptyne	99.5	71.0	...	...	...	61
2192	H_2O	Water	100	C_2H_6O	Ethyl alcohol	78.3	C_7H_{12}	5-Methyl-1-hexyne	90.8	69.0	...	...	...	61
2193	H_2O	Water	100	$C_2H_6O_2$	Glycol	197.4	$C_4H_8O_2$	Dioxane	101.4		Nonazeotrope			35
2194	H_2O	Water	100	C_3H_6O	Acetone	57	C_5H_8	Isoprene	34.8	32.5	0.4	7.6	92.0	114
2195	H_2O	Water	100	C_3H_6O	Acetone	57	C_6H_6O	Phenol	181.5		Nonazeotrope			94, 131
2196	H_2O	Water	100	C_3H_8O	Isopropyl alcohol	82.44	C_4H_8O	2-Butanone	79.6		Nonazeotrope			1
2197	H_2O	Water	100	C_3H_8O	Propyl alcohol	97.2	C_4H_8O	2-Butanone	79.6		Nonazeotrope			1
2198	H_2O	Water	100	C_3H_8O	Propyl alcohol	97.2	$C_5H_9ClO_2$	Propyl chloroacetate	162.3	88.6	25.25	58.27	16.48	22
2199	H_2O	Water	100	C_3H_8O	Propyl alcohol	97.2	$C_5H_{12}O_2$	Diethoxymethane	87.5		Nonazeotrope			159
2200	H_2O	Water	100	C_3H_8O	Propyl alcohol	97.2	$C_6H_{14}O_2$	Ethoxypropoxymethane	113.7	83.8	17.6	22.9	59.5	159
2201	H_2O	Water	100	C_3H_8O	Propyl alcohol	97.2	$C_8H_{18}O_2$	Acetaldehyde dipropyl acetal	147.7	87.6	27.4	51.6	21.	7
2202	H_2O	Water	100	C_4H_6O	Crotonaldehyde	102.15	C_7H_8	Toluene	110.7	85.3	...	...	...	146
2203	H_2O	Water	100	C_4H_6O	Crotonaldehyde	102.15	C_nH_{2n+2}	Paraffins	100–110	80–85	...	...	...	146
2204	H_2O	Water	100	C_4H_8O	2-Butanone	79.6	$C_4H_{10}O$	*tert*-Butyl alcohol	82.55		Nonazeotrope			1
2205	H_2O	Water	100	C_4H_8O	Butyraldehyde	75.7	C_7H_{16}	Heptanes	75–80	~57	...	...	...	57
2206	H_2O	Water	100	C_4H_8O	Isobutyraldehyde	63	C_7H_{16}	Heptanes	75–80	48	...	...	...	57
2207	H_2O	Water	100	C_4H_9Cl	1-Chloro-2-methylpropane	68.85	$C_4H_{10}O$	*tert*-Butyl alcohol	82.55	62	...	...	...	94
2208	H_2O	Water	100	$C_4H_{10}O$	Butyl alcohol	117.4	$C_6H_{11}ClO_2$	Butyl chloroacetate	181.9	93.1	41.8	50.3	7.9	22
2209	H_2O	Water	100	$C_4H_{10}O$	Butyl alcohol	117.4	$C_9H_{20}O_2$	Dibutoxymethane	181.8		Nonazeotrope			52, 158

2210	H_2O	Water	100	$C_4H_{10}O$	Butyl alcohol	117.4	$C_{10}H_{22}O_2$	Acetaldehyde dibutyl acetal	188.8	Nonazeotrope				7
2211	H_2O	Water	100	$C_4H_{10}O$	*sec*-Butyl alcohol	99.53	$C_8H_{18}O$	Butyl ether	141	86.5	...	...	...	42
2212	H_2O	Water	100	$C_4H_{10}O$	*sec*-Butyl alcohol	99.53	$C_8H_{18}O$	*sec*-Butyl ether	118	83-84	...	...	...	42
2213	H_2O	Water	100	$C_4H_{10}O$	Ethyl ether	34.5	C_6H_{15}	Triethylamine	89.4		...	...	...	94
2214	H_2O	Water	100	$C_4H_{10}O$	Isobutyl alcohol	108	C_6H_6	Benzene	80.2	Nonazeotrope				94, 160
2215	H_2O	Water	100	$C_4H_{10}O$	Isobutyl alcohol	107.4	$C_6H_{11}ClO_2$	Isobutyl chloroacetate	174.4	90.2	33.64	53.1	13.26	22
2216	H_2O	Water	100	$C_4H_{10}O$	Isobutyl alcohol	108	$C_8H_{18}O$	Butyl ether	141.9	89	...	...	...	118
2217	H_2O	Water	100	$C_4H_{10}O$	Isobutyl alcohol	108	$C_8H_{18}O$	Isobutyl ether	122.2	85.4	...	...	...	118
2218	H_2O	Water	100	$C_4H_{10}O$	Isobutyl alcohol	107.5	$C_9H_{20}O_2$	Diisobutoxymethane	163.8	Nonazeotrope				52, 158
2219	H_2O	Water	100	$C_4H_{10}O$	Isobutyl alcohol	107.8	$C_{10}H_{22}O_2$	Acetaldehyde diisobutyl acetal	171.3	Nonazeotrope				7
2220	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_6H_8	Cyclohexadiene		Minimum B.P.				143
2221	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_6H_{10}	Cyclohexene	82.75	Minimum B.P.				143
2222	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_6H_{12}	Cyclohexane	80.75	Minimum B.P.				143
2223	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_7H_{10}	Methylcyclohexadiene		Minimum B.P.				143
2224	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_7H_{14}	1,1-Dimethylcyclopentane		Minimum B.P.				143
2225	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_7H_{14}	1,2-Dimethylcyclopentane		Minimum B.P.				143
2226	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_7H_{14}	1,3-Dimethylcyclopentane		Minimum B.P.				143
2227	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_7H_{16}	*n*-Heptane	98.45	Minimum B.P.				143
2228	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_7H_{16}	3-Methylhexane	91.8	Minimum B.P.				143
2229	H_2O	Water	100	C_5H_5N	Pyridine	115.5	C_8H_{14}	Diisobutylene		Minimum B.P.				143
2230	H_2O	Water	100	$C_5H_{12}O$	Amyl alcohol	137.2	$C_{11}H_{24}O_2$	Diamyloxymethane	221.6	Nonazeotrope				52, 158
2231	H_2O	Water	100	$C_5H_{12}O$	Amyl alcohol	137.5	$C_{12}H_{26}O_2$	Acetaldehyde diamyl acetal	225.3	Nonazeotrope				7
2232	H_2O	Water	100	$C_5H_{12}O$	Isoamyl alcohol	131.3	C_6H_6	Benzene	80.2	Nonazeotrope				160
2233	H_2O	Water	100	$C_5H_{12}O$	Isoamyl alcohol	131.3	$C_7H_{13}ClO_2$	Isoamyl chloroacetate	195.2	95.4	46.2	47.3	6.5	22
2234	H_2O	Water	100	$C_5H_{12}O$	Isoamyl alcohol	131.6	$C_{12}H_{26}O_2$	Acetaldehyde diisoamyl acetal	213.6	Nonazeotrope				7
2235	H_2O	Water	100	$C_6H_5NO_2$	Nitrobenzene	210.85	C_6H_6	Benzene	80.2					94
2236	H_2O	Water	100	$C_6H_5NO_2$	Nitrobenzene	210.85	C_6H_7N	Aniline	184.35					94
2237	H_2O	Water	100	$C_6H_5NO_2$	Nitrobenzene	210.85	C_7H_8	Toluene	110.7					94
2238	H_2O	Water	100	$C_6H_5NO_2$	Nitrobenzene	210.85	C_8H_{10}	Xylene						94
2239	H_2O	Water	100	$C_6H_5NO_2$	Nitrobenzene	210.85	$C_{10}H_{16}$	α-Pinene	155.8					94
2240	H_2O	Water	100	C_6H_6	Benzene	80.2	C_7H_8	Toluene	110.7					94
2241	H_2O	Water	100	C_6H_6O	Phenol	181.5	C_6H_7N	Aniline	184.35					94
2242	H_2O	Water	100	C_6H_6O	Phenol	181.5	$C_6H_{15}N$	Triethylamine	89.4					94
2243	H_2O	Water	100	$C_6H_{12}O$	2-Methyl-2-pentene-4-ol		$C_8H_{14}O$	2,4,6-Trimethyl-5,6-dihydro-1,2-pyran		90.7	27.0	9.7	63.3	129
2244	H_2O	Water	100	$C_6H_{12}O_2$	Isoamyl formate	123.6	$C_7H_{14}O_2$	Isoamyl acetate	138.8					94
2245	H_3N	Ammonia	−33	C_2H_6O	Methyl ether	−21	C_3H_9N	Trimethylamine	3.5					
2246	H_3N	Ammonia	−33	C_3H_9N	Trimethylamine	3.5	C_4H_8	1-Butene	−6	Nonazeotrope				62
2247	H_3N	Ammonia	−33	C_3H_9N	Trimethylamine	3.5	C_4H_8	2-Methylpropene	−6	Nonazeotrope				62
2248	H_3N	Ammonia	−33.	C_3H_9N	Trimethylamine	3.5	C_4H_{10}	Butane	0	Nonazeotrope				62
2249	H_3N	Ammonia	−33	C_3H_9N	Trimethylamine	3.5	C_4H_{10}	2-Methylpropane	−10	Nonazeotrope				62
2250	CCl_4	Carbon tetrachloride	76.75	CH_4O	Methanol	64.7	C_6H_6	Benzene	80.2	Nonazeotrope				62
2251	CCl_4	Carbon tetrachloride	76.75	$C_4H_8O_2$	Ethyl acetate	77.05	C_6H_5Cl	Chlorobenzene	131.8					94
2252	CS_2	Carbon disulfide	46.25	CH_4O	Methanol	64.7	C_6H_6	Benzene	80.2					94
2253	$CHCl_3$	Chloroform	61	CH_2Cl_2	Dichloromethane	40.0	C_3H_6O	Acetone	57	Nonazeotrope				46
2254	$CHCl_3$	Chloroform	61	CH_4O	Methanol	64.7	C_3H_6O	Acetone	57	57.5	47	23	30	46
2255	$CHCl_3$	Chloroform	61.2	C_2H_5Cl	Chloroethane	13.3	C_2H_6O	Ethyl alcohol	78.3					94
2256	CH_2Cl_2	Dichloromethane	40.0	CH_4O	Methanol	64.7	C_3H_6O	Acetone	57	Nonazeotrope				46, 56
2257	CH_4O	Methanol	64.7	C_6H_6	Benzene	80.2	C_7H_8	Toluene	110.7					94
2258	C_2HCl_5	Pentachloroethane	161.95	$C_4H_6O_4$	Methyl oxalate	163.3	$C_6H_{12}O$	Cyclohexanol	160.65					94
2259	C_2H_4O	Acetaldehyde	20.2	$C_2H_4O_2$	Acetic acid	118.5	C_3H_6O	Acetone	56.25					94
2260	C_3H_6O	Acetone	57	C_7H_8	Toluene	110.4	C_7H_{14}	Methylcyclohexane	100.8	Liquid-vapor equilibrium				15
2261	$C_3H_6O_2$	Methyl acetate	57.1	$C_4H_8O_2$	Ethyl acetate	77.05	$C_5H_{10}O_2$	Propyl acetate	101.6					94
2262	C_3H_8O	Propyl alcohol	97.2	$C_5H_{11}Br$	1-Bromo-3-methylbutane	120.2	$C_6H_{12}O_2$	Ethyl butyrate	119.9					94
2263	$C_4H_6O_4$	Methyl oxalate	163.3	$C_6H_{12}O$	Cyclohexanol	160.65	$C_{10}H_{16}$	*d*-Limonene	177.8	Reacts				94
2264	$C_4H_8O_2$	Ethyl acetate	77.1	$C_4H_{10}O$	Butyl alcohol	117.7	C_7H_8	Toluene	110.7	Nonazeotrope				101
2265	C_5H_5N	Pyridine	115.3	$C_5H_{11}N$	Piperidine	105.8	C_8H_{14}	Diisobutylene	102.5	98.6	...	...	...	38
2266	C_6H_7N	Aniline	184.35	$C_6H_{10}O_4$	Ethyl oxalate	185	C_7H_7Br	*o*-Bromotoluene	181.75	Reacts				94
2267	C_6H_7N	Aniline	184.35	$C_6H_{10}O_4$	Ethyl oxalate	185	C_7H_7Br	*p*-Bromotoluene	185	Reacts				94
2268	C_6H_7N	Aniline	184.35	$C_6H_{10}O_4$	Ethyl oxalate	185	$C_{10}H_{16}$	*d*-Limonene	177.8	Reacts				94
2269	C_6H_7N	Aniline	184.35	$C_6H_{10}O_4$	Ethyl oxalate	185	$C_{10}H_{16}$	Terpinene	180.5	Reacts				94
2270	C_7H_7Cl	α-Chlorotoluene	179.35	$C_7H_{14}O_3$	Isobutyl lactate	182.15	$C_{10}H_{16}$	Terpinene	180.5	Azeotrope doubtful				94
2271	C_7H_8	Toluene	110.4	C_7H_{14}	Methylcyclohexane	100.8	C_7H_{16}	*n*-Heptane	98.4	Liquid-vapor equilibrium				15
2272	$C_7H_{14}O_3$	Isobutyl lactate	182.15	$C_8H_{18}O$	*sec*-Octyl alcohol	178.7	$C_{10}H_{16}$	*d*-Limonene	177.8	Reacts				94

Table III. Formula Index

The following index lists all compounds appearing in the azeotropic tables, including the numbers of the systems in which each compound appears.

Formula	Name and System Nos.
BrH	Hydrobromic acid. B.p., −67 1–3, 2155
Br_4Sn	Tin bromide. B.p., 202 4
CF_2O	Carbonyl fluoride 5
CO_2	Carbon dioxide. B.p., −79.1 6–10
ClH	Hydrochloric acid. B.p., −85 13, 14
Cl_2	Chlorine. B.p., −33.5 11, 12
Cl_2S_2	Sulfur chloride. B.p., 138 11
Cl_3Sb	Antimony chloride. B.p., 220 15
Cl_4Si	Silicon chloride. B.p., 56.5 16–21
Cl_4Sn	Tin chloride. B.p., 113.85 22–24
Cu	Copper. B.p., 2310 25
FH	Hydrofluoric acid. B.p., 19.4 26–28, 2155a
HI	Hydroiodic acid. B.p., −34 29
HNO_3	Nitric acid. B.p., 86 2156
H_2O	Water. B.p., 100 12, 30–127, 2155–2244
H_2S	Hydrogen sulfide. B.p., −59.6 1, 2, 29, 30
H_3N	Ammonia. B.p., −33 128, 2157, 2245–2249
N_2O	Nitrous oxide. B.p., −90.7 6
O_2S	Sulfur dioxide. B.p., −10 3, 13, 31, 129, 130
O_3S	Sulfur trioxide. B.p., 47 7, 2156
Pb	Lead. B.p., 1525 25
$CClN$	Cyanogen chloride. B.p., 12.5 131
CCl_2F_2	Dichlorodifluoromethane 26
CCl_3NO_2	Trichloronitromethane. B.p., 111.85 132–158
CCl_4	Carbon tetrachloride. B.p., 76.75 159–165, 2158–2160, 2250, 2251
CF_4O	Trifluoromethyl hypofluorite. B.p., −94.2 5
CS_2	Carbon disulfide. B.p., 46.25 8, 166–182, 2161, 2162, 2252
$CHBrCl_2$	Bromodichloromethane. B.p., 90.2 183–186
$CHBr_3$	Bromoform. B.p., 148.3 187–190
$CHClF_2$	Chlorodifluoromethane 27
$CHCl_3$	Chloroform. B.p., 61 9, 191–205, 2163, 2164, 2253–2255
CHN	Hydrocyanic acid. B.p., 26 32, 131
CH_2Br_2	Dibromomethane. B.p., 97 206–208
CH_2ClNO_2	Chloronitromethane. B.p., 122.5 209, 210
CH_2Cl_2	Dichloromethane. B.p., 40.0 33, 191, 211, 212, 2165, 2253, 2256
CH_2I_2	Diiodomethane. B.p., 181 213
CH_2O	Formaldehyde. B.p., −21 34
CH_2O_2	Formic acid. B.p., 100.75 214–221, 2166
CH_3Br	Bromomethane. B.p., 4.5 222, 223
CH_3I	Iodomethane. B.p., 42.6 224
CH_3NO_2	Nitromethane. B.p., 101 16, 166, 225–272
CH_4O	Methanol. B.p., 64.7 206, 222, 273–284, 2161, 2167–2171, 2250, 2252, 2254, 2256, 2257
CH_5N	Methylamine. B.p., −6.5 287
C_2Cl_4	Tetrachloroethylene. B.p., 120.8 288–290, 2172
C_2HCl_3	Trichloroethylene. B.p., 86.95 35, 291–295, 2173
$C_2HCl_3O_2$	Trichloroacetic acid. B.p., 197.55 296–300
C_2HCl_5	Pentachloroethane. B.p., 161.95 301–305, 2258
$C_2H_2Cl_2O_2$	Dichloroacetic acid. B.p., 190 306–308
$C_2H_2Cl_4$	1,1,2,2-Tetrachloroethane. B.p., 146.35 187, 309, 310, 2174
$C_2H_3BrO_2$	Bromoacetic acid. B.p., 208 311
$C_2H_3ClO_2$	Chloroacetic acid. B.p., 189.35 312–315
C_2H_3N	Acetonitrile. B.p., 81.6 291, 316, 2158, 2162, 2163, 2171–2180
C_2H_4	Ethylene. B.p., −103.9 317
$C_2H_4Br_2$	1,1-Dibromoethane. B.p., 110 318, 319
$C_2H_4Br_2$	1,2-Dibromoethane. B.p., 131.5 320–324
$C_2H_4Cl_2$	1,1-Dichloroethane. B.p., 57.3 17, 159, 192, 325, 326
$C_2H_4Cl_2$	1,2-Dichloroethane. B.p., 83.7 18, 36, 320, 325, 327, 328
$C_2H_4Cl_2O$	Bis(chloromethyl) ether. B.p., 106 37, 167, 329
C_2H_4O	Acetaldehyde. B.p., 20.2 2259
$C_2H_4O_2$	Acetic acid. B.p., 118 330–347, 2181, 2259
$C_2H_4O_2$	Methyl formate. B.p., 31.9 296, 306, 312, 348–353
C_2H_5Br	Bromoethane. B.p., 38.4 38, 211, 354–357
C_2H_5BrO	2-Bromoethanol. B.p., 150.2 358, 359
C_2H_5Cl	Chloroethane. B.p., 13.3 193, 2255
C_2H_5ClO	2-Chloroethanol. B.p., 128.8 39, 225, 360–373
C_2H_5ClO	Chloromethyl methyl ether. B.p., 59.15 374
C_2H_5I	Iodoethane. B.p., 72.3 40, 375
C_2H_5NO	Acetamide. B.p., 222 377–407
$C_2H_5NO_2$	Ethyl nitrite. B.p., 17.4 348, 408–415
$C_2H_5NO_2$	Nitroethane. B.p., 114.2 168, 183, 214, 330, 360, 416–438
$C_2H_5NO_3$	Ethyl nitrate. B.p., 87.68 226, 416, 439, 440
C_2H_6	Ethane. B.p., −88.3 41, 317, 441, 442
$C_2H_6Cl_2Si$	Dichlorodimethylsilane 443, 444
C_2H_6O	Ethyl alcohol. B.p., 78.3 445–468, 2155a, 2165, 2182–2192, 2255
C_2H_6O	Methyl ether. B.p., −21 128, 469, 2245
$C_2H_6O_2$	Glycol. B.p., 197.4 470–494, 2193
C_2H_6S	Ethanethiol. B.p., 36.2 227, 495
C_2H_6S	Methyl sulfide. B.p., 37.2 228, 349, 408, 496, 497
$C_2H_6SO_4$	Methyl sulfate. B.p., 188.4 498, 499
C_2H_7N	Ethylamine. B.p., 16.55 500–503
C_2H_7NO	2-Aminoethanol. B.p., 172 377, 504–563
$C_2H_8N_2$	Ethylenediamine. B.p., 116.5 564
$C_3H_3Cl_3O_2$	Methyl trichloroacetate. B.p., 152 565
$C_3H_4Cl_2$	1,2-Dichloro-1-propene. B.p., 77 273
$C_3H_4Cl_2$	1,3-Dichloropropene 566
$C_3H_4O_3$	Pyruvic acid. B.p., 166.8 567–581
C_3H_5Br	3-Bromopropene. B.p., 70.8 375, 582–584
C_3H_5BrO	Epibromohydrin. B.p., 138.5 585
$C_3H_5BrO_2$	α-Bromopropionic acid. B.p., 205.5 386
C_3H_5Cl	2-Chloropropene. B.p., 22.65 409, 587, 588
C_3H_5Cl	3-Chloropropene. B.p., 45.7 566, 587, 589, 590
C_3H_5ClO	1-Chloro-2-propanone. B.p., 119.7 42, 591–600
C_3H_5ClO	α-Chloropropionaldehyde. B.p., 86 43
C_3H_5ClO	Epichlorohydrin. B.p., 116.4 22, 44, 601–604
$C_3H_5ClO_2$	Methyl chloroacetate. B.p., 131.4 605–608, 2167
C_3H_5I	3-Iodopropene. B.p., 102.0 132, 609–611
C_3H_5N	Propionitrile. B.p., 97 19, 612, 613
$C_3H_5N_3O_9$	Nitroglycerin 614
$C_3H_6Br_2$	1,2-Dibromopropane. B.p., 141.6 331, 361, 615–620
$C_3H_6Cl_2$	1,2-Dichloropropane. B.p., 97 45, 621, 622
$C_3H_6Cl_2$	1,3-Dichloropropane. B.p., 129.8 133
$C_3H_6Cl_2$	2,2-Dichloropropane. B.p., 69.8 623

Table III. Formula Index (*Continued*)

Formula	Name and System Nos.
$C_3H_6Cl_2O$	1,3-Dichloro-2-propanol. B.p., 174.5 624–626
$C_3H_6Cl_2O$	2,3-Dichloro-1-propanol. B.p., 183 627–629
C_3H_6O	Acetone. B.p., 56.4 14, 292, 316, 582, 589, 614, 630–654, 2159, 2164, 2175, 2194, 2195, 2253, 2254, 2256, 2259, 2260
C_3H_6O	Allyl alcohol. B.p., 96.85 630, 655, 656
C_3H_6O	Propionaldehyde. B.p., 48.7 657
C_3H_6O	Propylene oxide. B.p., 35 658–663
$C_3H_6O_2$	1,3-Dioxolane. B.p., 75 664
$C_3H_6O_2$	Ethyl formate. B.p., 54.1 665–668
$C_3H_6O_2$	Methoxyacetaldehyde. B.p., 92 46
$C_3H_6O_2$	Methyl acetate. B.p., 57.1 669–674, 2261
$C_3H_6O_2$	Propionic acid. B.p., 140.7 229, 567, 615, 675–689
$C_3H_6O_3$	Methyl carbonate. B.p., 90.35 439, 690–692
$C_3H_6O_3$	Trioxane. B.p., 114.5 47, 693, 694
C_3H_7Br	1-Bromopropane. B.p., 71.0 194
C_3H_7Br	2-Bromopropane. B.p., 59.35 695
C_3H_7Cl	1-Chloropropane. B.p., 46.4 230, 329, 590, 696–700
C_3H_7ClO	1-Chloro-2-propanol B.p., 127 48, 134, 231, 417, 701, 702
C_3H_7ClO	2-Chloro-1-propanol. B.p., 133.7 232
C_3H_7I	1-Iodopropane. B.p., 102.4 135, 703, 704
C_3H_7I	2-Iodopropane. B.p., 89.35 184, 631, 705
C_3H_7N	Allylamine. B.p., 52.9 49
C_3H_7NO	Propionamide. B.p., 222.1 504, 706–727
$C_3H_7NO_2$	Ethyl carbamate. B.p., 185.25 728–741
$C_3H_7NO_2$	Isopropyl nitrite. B.p., 40.0 212, 223, 350, 588, 665, 669, 742–**749**
$C_3H_7NO_2$	1-Nitropropane. B.p., 130.5 321, 322, 750, 751
$C_3H_7NO_2$	2-Nitropropane. B.p., 120 752
$C_3H_7NO_2$	Propyl nitrite. B.p., 47.75 195, 351, 496, 666, 670, 742, **753–755**
$C_3H_7NO_3$	Propyl nitrate B.p., 110.5 233, 418
C_3H_8O	Isopropyl alcohol. B.p., 82.44 410, 591, 609, 621, 756–759, 2196
C_3H_8O	Propyl alcohol. B.p., 97.2 760–767, 2197–2201, 2262
$C_3H_8O_2$	2-Methoxyethanol. B.p., 124 50, 136, 274, 564, 768–776
$C_3H_8O_2$	Methylal. B.p., 42.25 497, 777–779, 2168
$C_3H_8O_2$	1,2-Propanediol. B.p., 188.5 780–788
$C_3H_8O_3$	Glycerol. B.p., 290 789–795, 2157
C_3H_8S	1-Propanethiol. B.p., 67.5 796, 797
$C_3H_9BO_3$	Methyl borate. B.p., 68.7 798–801
C_3H_9ClSi	Chlorotrimethylsilane. B.p., **57.5** 160, 196, 234, 326, 612, 802, 803
C_3H_9N	Propylamine. B.p., 49.7 777, 804–808
C_3H_9N	Trimethylamine. B.p., 3.5 469, 809–812, 2245–2249
$C_3H_{10}N_2$	1,2-Propanediamine. B.p., **119.7** 51
$C_4H_4Cl_2$	2,3-Dichloro-1,3-butadiene. **B.p., 98** 275
C_4H_4O	1-Butyne-3-one. B.p., 85 52
C_4H_4O	Furan. B.p., 31.7 411, 500, 743
C_4H_4S	Thiophene. B.p., 84 276, 445, 813–815
$C_4H_5ClO_2$	α-Chlorocrotonic acid. **B.p., 212.5** 816, 817
C_4H_5N	Pyrrole. B.p., 130.5 53, 318, 601, 616, 818–831
C_4H_6	1,3-Butadiene. B.p., −4.5 446, 832
C_4H_6O	Crotonaldehyde. B.p., 102.15 833, 2202, 2203
$C_4H_6O_2$	Allyl formate. B.p., 80.0 834
$C_4H_6O_2$	Biacetyl. B.p., 87.5 54, 447, 756, 835, 836, 2182
$C_4H_6O_2$	Methacrylic acid 837
$C_4H_6O_3$	Acetic anhydride. B.p., 138 838–844
$C_4H_6O_3$	Methyl pyruvate. B.p., **137.5** 332, 675, 845–864
$C_4H_6O_4$	Methyl oxalate. B.p., **164.2** 865–873, 2258, 2263
$C_4H_7BrO_2$	Ethyl bromoacetate. **B.p., 158.2** **874**
C_4H_7Cl	1-Chloro-2-methyl-1-propene. B.p., 68.1 55
$C_4H_7ClO_2$	4-Chloromethyl-1,3-dioxolane 56
$C_4H_7ClO_2$	Ethyl chloroacetate. B.p., 143.5 448, 875–879, 2183
C_4H_8	1-Butene. B.p., −6 809, 2246
C_4H_8	2-Methylpropene. B.p., −6 810, 2247
$C_4H_8Cl_2O$	Bis-2-(chloroethyl) ether. B.p., 178 880–884
$C_4H_8Cl_2O$	1,3-Dichloro-2-methyl-2-propanol. B.p., 174 57
C_4H_8O	2-Butanone. B.p., 79.6 235, 374, 440, 583, 695, 705, 804, 885–900, 2196, **2197**, 2204
C_4H_8O	1-Butene-3-ol 901
C_4H_8O	Butyraldehyde. B.p., 75.7 633, 902, 2205
C_4H_8O	Cyclopropyl methyl ether. B.p., 44.73 657
C_4H_8O	Ethyl vinyl ether. B.p., 35.5 449
C_4H_8O	Isobutyraldehyde. B.p., 63 634, 885, 903, 904, 2206
$C_4H_8O_2$	Butyric acid. B.p., 162.45 161, 293, 327, 333, 354, 622, 905–914
$C_4H_8O_2$	1,3-Dioxane. B.p., 104 58, 915
$C_4H_8O_2$	1,4-Dioxane. B.p., 101.3 137, 236, 419, 471, 886, 916–919, 2193
$C_4H_8O_2$	Ethyl acetate. B.p., 77.05 671, 696, 798, 920–923, 2176, 2251, 2261, 2264
$C_4H_8O_2$	Isobutyric acid. B.p., 154.35 138, 845, 924–929
$C_4H_8O_2$	Isopropyl formate. B.p., 68.8 799, 930
$C_4H_8O_2$	Methyl propionate. B.p., 79.85 172, 237, 931
$C_4H_8O_2$	Propyl formate. B.p., 80.85 238, 932
$C_4H_8O_3$	Glycol monoacetate. B.p., 190.9 933–935
$C_4H_8O_3$	Methyl lactate. B.p., 143.8 59, 936–939
C_4H_8S	Tetrahydrothiophene. B.p., 118.8 761, 940
C_4H_9Br	1-Bromobutane. B.p., 103.5 420, 941–947
C_4H_9Br	2-Bromobutane. B.p., 91.2 887, 948–950
C_4H_9Br	1-Bromo-2-methylpropane. B.p., 91.4 421, 948, 951, 952
C_4H_9Cl	1-Chlorobutane. B.p., 77.9 422, 941, 953–955
C_4H_9Cl	2-Chlorobutane. B.p., 68.25 635, 888, 956–958
C_4H_9Cl	1-Chloro-2-methylpropane. B.p., 68.8 584, 959, 960, 2207
C_4H_9Cl	2-Chloro-2-methylpropane. B.p., 50.8 961
C_4H_9ClO	1-Chloro-2-methyl-2-propanol. B.p., 126.7 60
C_4H_9I	1-Iodobutane. B.p., 130.4 846, 962, 963
C_4H_9I	1-Iodo-2-methylpropane. B.p., 122.5 61, 139
C_4H_9N	2-Methylallylamine. B.p., 78.7 62
C_4H_9N	Pyrrolidine. B.p., 87.5 964
$C_4H_9NO_2$	Butyl nitrite. B.p., 77.8 185, 197, 294, 623, 800, 813, 834, 889, 920, **931, 932, 951,** 956, 965–972
$C_4H_9NO_2$	Isobutyl nitrite. B.p., 67.1 198, 636, 672, 697, 801, 814, 890, 921, 930, **957, 973–976**
$C_4H_9NO_3$	Isobutyl nitrate. B.p., 122.9 977–979
C_4H_{10}	Butane. B.p., 0 129, 277, 412, 811, 2248
C_4H_{10}	2-Methylpropane. B.p., −10 130, 812, 2249
$C_4H_{10}O$	Butyl alcohol. B.p., 117.75 592, 637, 818, 891, 980–992, 2208–2210, 2264
$C_4H_{10}O$	*sec*-Butyl alcohol. B.p., 99.6 140, 593, 993–997, 2211, 2212
$C_4H_{10}O$	*tert*-Butyl alcohol. B.p., 82.55 141, 698, 952, 961, 998–1000, 2160, 2204, 2207
$C_4H_{10}O$	Ethyl ether. B.p., 34.5 28, 297, 307, 313, 501, 699, 805, 832, 924, **1001–1004,** 2213
$C_4H_{10}O$	Isobutyl alcohol. B.p., 108 441, 638, 892, 922, 1005–1013, 2169, 2214–2219
$C_4H_{10}O$	Methyl propyl ether. B.p., 38.9 502, 744, 1014
$C_4H_{10}O_2$	Acetaldehyde dimethyl acetal. B.p., 64.3 65, 973, 1015
$C_4H_{10}O_2$	*l*-2,3-Butanediol 64
$C_4H_{10}O_2$	Meso-2,3-butanediol. B.p., 183–184 63, 901
$C_4H_{10}O_2$	1,2-Dimethoxyethane. B.p., 83 66, 2170
$C_4H_{10}O_2$	2-Ethoxyethanol. B.p., 133 239, 450, 505, 617, 1016–1030, 2184
$C_4H_{10}O_2$	Ethoxymethoxymethane. B.p., 65.91 67, 278, 451, 2171, 2185

Table III. Formula Index (*Continued*)

Formula	Name and System Nos.
$C_4H_{10}O_2$	1-Methoxy-2-propanol. B.p., 119 68, 1031
$C_4H_{10}O_3$	Diethylene glycol. B.p., 245.5 1031–1041
$C_4H_{10}S$	1-Butanethiol. B.p., 97.5 240
$C_4H_{10}S$	Ethyl sulfide. B.p., 92.2 215, 241, 819, 965
$C_4H_{10}S$	2-Methyl-1-propanethiol. B.p., 88 1042–1044
$C_4H_{11}ClSi$	Chloromethyltrimethylsilane. B.p., 97 452
$C_4H_{11}N$	Butylamine. B.p., 77.8 639, 893, 1045, 1046
$C_4H_{11}N$	Diethylamine. B.p., 55.9 69, 1014, 1015, 1047–1051
$C_4H_{11}N$	Isobutylamine. B.p., 68.5 279, 1052–1055
$C_4H_{11}NO$	2-Amino-2-methyl-1-propanol. B.p., 165.4 1056
$C_4H_{11}NO_2$	2,2′-Iminodiethanol. B.p., 268 378
$C_5H_4O_2$	2-Furaldehyde. B.p., 161.45 379, 1057
C_5H_5N	Pyridine. B.p., 115.5 23, 142, 162, 199, 209, 224, 280, 288, 355, 453, 602, 655, 769, 916, 923, 940, 959, 1001, 1016, 1058–1081, 2220–2229, 2265
C_5H_6	Cyclopentadiene. B.p., 41 352
C_5H_6O	2-Methylfuran. B.p., 63.7 281
$C_5H_6O_2$	Furfuryl alcohol. B.p., 169.35 1082, 1083
C_5H_7NO	Furfurylamine. B.p., 144 70
C_5H_8	Isoprene. B.p., 34.5 495, 2194
C_5H_8	3-Methyl-1,2-butadiene. B.p., 408 640, 796
C_5H_8	Piperylene. B.p., 42.5 353
C_5H_8O	Cyclopentanone. B.p., 129 289, 334, 506, 605, 677, 875, 936, 962, 1017, 1084–1094
$C_5H_8O_2$	Allyl acetate. B.p., 105 71
$C_5H_8O_2$	Methyl methacrylate. B.p., 99.5 72, 73, 837
$C_5H_8O_2$	2,4-Pentanedione. B.p., 138 74, 301, 847, 1095–1099
$C_5H_8O_3$	Ethyl pyruvate. B.p., 155.5 676, 905, 925, 1100–1123
$C_5H_8O_3$	Levulinic acid. B.p., 251 380, 706, 1124–1138
$C_5H_8O_3$	Methyl acetoacetate. B.p., 169.5 880, 926, 1057, 1139–1164
$C_5H_8O_4$	Methyl malonate. B.p., 181.4 1165–1178
$C_5H_9ClO_2$	Propyl chloroacetate. B.p., 162.3 2198
C_5H_{10}	Amylenes 290, 659
C_5H_{10}	Cyclopentane. B.p., 49.3 243, 413, 641, 658, 745, 753, 806, 974, 1048
C_5H_{10}	2-Methyl-2-butene. B.p., 37.75 414, 746, 980, 1047, 1179, 1180
C_5H_{10}	3-Methyl-1-butene. B.p., 22.5 242, 503, 747
$C_5H_{10}O$	Allyl ethyl ether. B.p., 64 454
$C_5H_{10}O$	Cyclopentanol. B.p., 140.85 244, 594, 820, 1095, 1184, 1185
$C_5H_{10}O$	Isovaleraldehyde. B.p., 92.1 143, 894, 1186
$C_5H_{10}O$	3-Methyl-2-butanone. B.p., 94 169, 207, 216, 282, 295, 690, 703, 757, 8[illegible]3, 966, 981, 1005, 1048, 1053, 1187–1189
$C_5H_{10}O$	2-Pentanone. B.p., 102.25 170, 208, 656, 942, 982, 998, 1190–1194
$C_5H_{10}O$	3-Pentanone. B.p., 102.2 603, 758, 949, 1186, 1195–1204
$C_5H_{10}O$	Tetrahydro-2-methylfuran. B.p., 77 75
$C_5H_{10}O$	Tetrahydropyran 76
$C_5H_{10}O_2$	4,5-Dimethyl-1,3-dioxolane 77
$C_5H_{10}O_2$	3-Ethoxy-1,2-epoxypropane. B.p., 125 78
$C_5H_{10}O_2$	Ethyl propionate. B.p., 99.15 1187, 1205
$C_5H_{10}O_2$	Isobutyl formate. B.p., 98.3 217, 1206, 1207
$C_5H_{10}O_2$	Isopropyl acetate. B.p., 91.0 245, 967, 1208
$C_5H_{10}O_2$	Isovaleric acid. B.p., 176.5 171, 1209–1213
$C_5H_{10}O_2$	Methyl isobutyrate. B.p., 92.3 246, 691, 1190, 1214
$C_5H_{10}O_2$	Propyl acetate. B.p., 101.6 423, 673, 848, 1215, 2177, 2261
$C_5H_{10}O_2$	Tetrahydrofurfuryl alcohol 1216
$C_5H_{10}O_2$	Valeric acid. B.p., 187 1139, 1217–1220
$C_5H_{10}O_3$	Ethyl carbonate. B.p., 126 977, 1084, 1221
$C_5H_{10}O_3$	Ethyl lactate. B.p., 153.9 565, 1222, 1223
$C_5H_{10}O_3$	2-Methoxyethyl acetate. B.p., 144.6 568
$C_5H_{10}O_3$	Methyl β-methoxypropionate 79
$C_5H_{11}Br$	1-Bromo-3-methylbutane. B.p., 120.3 144, 247, 362, 424, 1085, 1224–1226, 2262
$C_5H_{11}Br$	1-Bromopentane. B.p., 130 1227
$C_5H_{11}Cl$	1-Chloro-3-methylbutane. B.p., 99.4 248, 610, 1188, 1195
$C_5H_{11}Cl$	1-Chloropentane. B.p., 108.35 80, 283, 455
$C_5H_{11}I$	1-Iodo-3-methylbutane. B.p., 147.65 849, 1228, 1229
$C_5H_{11}N$	Piperidine. B.p., 105.7 1230, 2265
$C_5H_{11}NO_2$	Ethyl *N*-ethylaminoformate 1231, 1232
$C_5H_{11}NO_2$	Isoamyl nitrite. B.p., 97.15 163, 173, 328, 611, 678, 704, 815, 917, 950, 953, 1189, 1191, 1196, 1206, 1208, 1214, 1215, 1233–1238
$C_5H_{11}NO_3$	Isoamyl nitrate. B.p., 149.6 1239–1241
C_5H_{12}	2-Methylbutane. B.p., 27.95 249, 503a, 807, 1242, 1243
C_5H_{12}	Pentane. B.p., 36.15 660, 700, 1244–1246
$C_5H_{12}O$	Amyl alcohol. B.p., 137.8 425, 595, 821, 1058, 1247–1249, 2230, 2231
$C_5H_{12}O$	*tert*-Amyl alcohol. B.p., 101.7 596, 642, 1059, 1192
$C_5H_{12}O$	Ethyl propyl ether. B.p., 63.6 415, 754, 975, 1049, 1250
$C_5H_{12}O$	Isoamyl alcohol. B.p., 131.3 442, 822, 835, 1060, 1086, 1096, 1197, 1251–1257, 2232–2234
$C_5H_{12}O$	3-Methyl-2-butanol. B.p., 112.9 145, 1260
$C_5H_{12}O$	2-Methyl-1-butanol 1258, 1259
$C_5H_{12}O$	2-Pentanol. B.p., 119.3 146, 597, 823, 1087, 1198, 1261–1264
$C_5H_{12}O$	3-Pentanol. B.p., 116.0 147, 1061, 1199, 1265, 1266
$C_5H_{12}O_2$	Diethoxymethane. B.p., 87.5 643, 895, 968, 1253, 1267, 1268, 1269, 2199
$C_5H_{12}O_2$	1,2-Dimethoxypropane. B.p., 92 81
$C_5H_{12}O_2$	2-Propoxyethanol. B.p., 151.35 250, 426, 507, 824, 1270–1276
$C_5H_{12}O_3$	2-(2-Methoxyethoxy)ethanol. B.p., 193.2 472, 508, 770, 1277–1287
$C_5H_{12}O_3$	1,1,2-Trimethoxyethane. B.p., 126 82
$C_5H_{12}S$	3-Methyl-1-butanethiol. B.p., 120 1288
$C_5H_{14}OSi$	Methoxymethyltrimethylsilane. B.p., 83 284
$C_6H_3Cl_3$	1,3,5-Trichlorobenzene. B.p., 208.4 1289–1291
C_6H_4BrCl	*p*-Bromochlorobenzene. B.p., 196.4 1292–1296
$C_6H_4Br_2$	*p*-Dibromobenzene. B.p., 220.25 1297–1304
$C_6H_4ClNO_2$	*m*-Chloronitrobenzene. B.p., 235.5 381, 473, 707, 789, 1032, 1297, 1305–1324
$C_6H_4ClNO_2$	*o*-Chloronitrobenzene. B.p., 230 382, 474, 708, 790, 1033, 1325–1341
$C_6H_4ClNO_2$	*p*-Chloronitrobenzene. B.p., 239.1 791, 1034, 1298, 1342–1355
$C_6H_4Cl_2$	*o*-Dichlorobenzene. B.p., 179.5 509, 1356–1361
$C_6H_4Cl_2$	*p*-Dichlorobenzene. B.p., 174.35 213, 728, 1140, 1231, 1362–1365
C_6H_5Br	Bromobenzene. B.p., 156 188, 363, 510, 569, 825, 850, 1097, 1100, 1366, 1367
C_6H_5Cl	Chlorobenzene. B.p., 131.8 200, 511, 674, 851, 1088, 1101, 1368–1371, 2155, 2251
C_6H_5ClO	*o*-Chlorophenol. B.p., 15.75 1372–1376
C_6H_5ClO	*p*-Chlorophenol. B.p., 219.75 1377–1383
C_6H_5F	Fluorobenzene. B.p., 85.15 644, 896, 969, 1366, 1368, 1384
C_6H_5I	Iodobenzene. B.p., 188.55 512, 1098, 1369, 1384–1390
$C_6H_5NO_2$	Nitrobenzene. B.p., 210.75 83, 174, 189, 201, 285, 298, 302, 308, 309, 314, 323, 456, 586, 729, 816, 933, 943, 954, 958, 983, 993, 1035, 1124, 1181, 1242, 1277, 1356, 1370, 1385, 1391–1427, 2235–2239
$C_6H_5NO_3$	*o*-Nitrophenol. B.p., 217.65 10, 1391, 1428–1431
C_6H_6	Benzene. B.p., 80.2 148, 427, 513, 570, 664, 836, 903, 964, 976, 1054, 1062, 1179, 1267, 1392, 1432–1438, 2179, 2214, 2232, 2235, 2240, 2250, 2252, 2257
C_6H_6O	Phenol. B.p., 182.2 498, 514, 1141, 1165, 1439–1450, 2195, 2241, 2242
$C_6H_6O_2$	Pyrocatechol. B.p., 245.9 1305, 1451–1455
$C_6H_6O_2$	Resorcinol. B.p., 281.4 1325, 1456, 1457
C_6H_6S	Benzenethiol. B.p., 170 1458–1461
C_6H_7N	Aniline. B.p., 184.35 164, 175, 202, 310, 383, 457, 515, 645, 709, 984, 1063, 1166, 1182, 1184, 1251, 1270, 1278, 1292, 1357, 1367, 1393, 1432, 1462–1505, 2236, 2241, 2266–2269
C_6H_7N	3-Picoline. B.p., 143.5 84, 218, 335, 679, 1372, 1506, 1507
C_6H_7N	4-Picoline. B.p., 143.1 85, 219, 336, 680, 1373, 1508, 1509

Table III. Formula Index (*Continued*)

Formula	Name and System Nos.
C_6H_8	1,3-Cyclohexadiene. B.p., 80.8 1042, 2220
C_6H_8	1,4-Cyclohexadiene. B.p., 85.6 1043
$C_6H_8N_2$	*o*-Phenylenediamine. B.p., 158.6 384, 475, 710, 1510–1527
$C_6H_8O_2$	Vinyl crotonate. B.p., 132.7 86
$C_6H_8O_4$	Methyl fumarate. B.p., 193.25 1528–1532
$C_6H_8O_4$	Methyl maleate. B.p., 204.05 1394, 1533–1535
C_6H_{10}	Cyclohexene. B.p., 82.75 149, 251, 879, 906, 1044, 2221
C_6H_{10}	Biallyl. B.p., 60.2 252, 748, 797
C_6H_{10}	1-Hexyne. B.p., 70.2 458, 2186
C_6H_{10}	3-Hexyne. B.p., 80.5 459, 2187
C_6H_{10}	4-Methyl-1,3-pentadiene 87
$C_6H_{10}O$	Cyclohexanone. B.p., 156.7 358, 516, 624, 627, 681, 876, 918, 937, 1102, 1142, 1209, 1464, 1536–1542
$C_6H_{10}O$	1-Hexene-5-one. B.p., 129 88, 1288
$C_6H_{10}O$	Mesityl oxide. B.p., 130.5 364, 585, 604, 618, 682, 692, 852, 877, 938, 985, 1018, 1064, 1185, 1224, 1228, 1261, 1371, 1543–1548
$C_6H_{10}O_2$	Crotonyl acetate. B.p., 129 89
$C_6H_{10}O_2$	2,5-Hexanedione. B.p., 191.3 476, 1549, 1550
$C_6H_{10}O_3$	Ethyl acetoacetate. B.p., 180.7 881, 907, 1210, 1217, 1358, 1439, 1551–1577
$C_6H_{10}O_4$	Ethyl oxalate. B.p., 185.65 477, 1167, 1528, 1551, 1577a–1852, 2266–2269
$C_6H_{10}O_4$	Glycol diacetate. B.p., 186.3 1168, 1529, 1583–1585
$C_6H_{10}O_4$	Methyl succinate. B.p., 195 478, 1586–1589
$C_6H_{10}S$	Allyl sulfide. B.p., 139 253, 337, 517
$C_6H_{11}ClO_2$	Butyl chloroacetate. B.p., 175 986, 1006, 2208
$C_6H_{11}ClO_2$	Isobutyl chloroacetate. B.p., 174.4 2215
$C_6H_{11}N$	Diallylamine. B.p., 110.4 90
$C_6H_{11}NO_2$	Nitrocyclohexane. B.p., 205.3 1279, 1465, 1590–1596
C_6H_{12}	Cyclohexane. B.p., 80.75 150, 254, 518, 661, 908, 1045, 1055, 1065, 1193, 1466, 2222
C_6H_{12}	Hexenes 662
C_6H_{12}	Methylcyclopentane. B.p., 71.8 255, 428, 646, 1046, 1050, 1200, 1234, 1597
$C_6H_{12}O$	*cis*-2-Butenyl ethyl ether. B.p., 100.3 462
$C_6H_{12}O$	*trans*-2-Butenyl ethyl ether. B.p., 100.45 461
$C_6H_{12}O$	Butyl vinyl ether. B.p., 93.8 91, 92, 987
$C_6H_{12}O$	Cyclohexanol. B.p., 160.8 151, 1598–1603, 2258, 2263
$C_6H_{12}O$	2,2-Dimethyltetrahydrofuran. B.p., 91 93
$C_6H_{12}O$	2-Hexanone. B.p., 127.5 365, 683, 853, 878, 988, 1007, 1262, 1604, 1605
$C_6H_{12}O$	3-Hexanone. B.p., 124 94, 290, 366, 606, 684, 701, 963, 989, 1008, 1019, 1067, 1221, 1225, 1606–1618
$C_6H_{12}O$	Isobutyl vinyl ether. B.p., 83.0 1009
$C_6H_{12}O$	1-Methylallyl ethyl ether. B.p., 83.0 460
$C_6H_{12}O$	4-Methyl-2-pentanone. B.p., 117 176, 186, 256, 319, 367, 607, 685, 702, 944, 1010, 1020, 1068, 1226, 1252, 1265, 1619–1631
$C_6H_{12}O$	2-Methyl-2-pentene-4-ol 95, 2243
$C_6H_{12}O$	Pinacolone. B.p., 106.2 220, 257, 338, 368, 759, 945, 944, 1066, 1205, 1207, 1235, 1632–1636
$C_6H_{12}O_2$	Butyl acetate. B.p., 124.8 429, 1021, 1089, 1103, 1606, 2178
$C_6H_{12}O_2$	Caproic acid. B.p., 204.5 356, 1637–1640
$C_6H_{12}O_2$	Ethyl butyrate. B.p., 119.9 24, 258, 430, 1607, 1619, 2262
$C_6H_{12}O_2$	Ethyl isobutyrate. B.p., 110.1 259, 431, 946, 1620, 1632
$C_6H_{12}O_2$	4-Hydroxy-4-methyl-2-pentanone. B.p., 165 1641
$C_6H_{12}O_2$	Isoamyl formate. B.p., 123.6 978, 1090, 1604, 1608, 2244
$C_6H_{12}O_2$	Isobutyl acetate. B.p., 118 432, 854, 1069, 1609, 1621
$C_6H_{12}O_2$	Isocaproic acid. B.p., 199.5 1552
$C_6H_{12}O_2$	Isopropyl propionate. B.p., 110.5 1622, 1633
$C_6H_{12}O_2$	Methyl isovalerate. B.p., 116.3 152, 1610, 1623
$C_6H_{12}O_2$	Propyl propionate. B.p., 123.0 1611
$C_5H_{12}O_3$	2-Ethoxyethyl acetate. B.p., 156.8 571
$C_6H_{12}O_3$	Propyl lactate. B.p., 171.7 303, 1536, 1641a, 1442
$C_6H_{13}Br$	1-Bromohexane. B.p., 156.5 369, 686
$C_6H_{13}ClO_2$	Chloroacetaldehyde diethyl acetal. B.p., 156.8 1643
C_6H_{14}	2,3-Dimethylbutane. B.p., 58.0 260, 647, 749, 808, 898, 1051
C_6H_{14}	Hexane. B.p., 68.95 519, 663, 1201, 1245, 1467, 1634, 1644
C_6H_{14}	2-Methylpentane. B.p., 60.2 20, 802
C_6H_{14}	3-Methylpentane. B.p., 63.2 21, 803
$C_6H_{14}O$	2-Ethylbutanol. B.p., 148.9 1645
$C_6H_{14}O$	Hexyl alcohol. B.p., 157.8 1395, 1646–1651
$C_6H_{14}O$	Isopropyl ether. B.p., 69.0 648
$C_6H_{14}O$	Propyl ether. B.p., 90.55 649, 855, 970, 1071, 1202, 1236, 1652, 1653
$C_6H_{14}O_2$	Acetal. B.p., 103.55 1654, 2188
$C_6H_{14}O_2$	2-Butoxyethanol. B.p., 171.25 96, 520, 1362, 1396, 1468, 1655–1665
$C_6H_{14}O_2$	1,2-Diethoxyethane. B.p., 123.1 97, 1022
$C_6H_{14}O_2$	Ethoxypropoxymethane. B.p., 113.7 98, 463, 2189, 2200
$C_6H_{14}O_2$	Pinacol. B.p., 174.35 1666
$C_6H_{14}O_3$	Dipropylene glycol. B.p., 229.2 1306, 1342, 1667, 1668
$C_6H_{14}O_2$	Triethylene glycol. B.p., 288.7 1326
$C_6H_{14}S$	Isopropyl sulfide. B.p., 120.5 210, 339, 370, 433, 826, 990, 1011, 1072, 1612, 1624
$C_6H_{14}S$	Propyl sulfide. B.p., 140.8 827, 1023
$C_6H_{15}BO_3$	Ethyl borate. B.p., 118.6 1613
$C_6H_{15}N$	Diisopropylamine. B.p., 83.86 99
$C_6H_{15}N$	Dipropylamine. B.p., 109.2 899, 1203, 1614, 1625, 1652, 1654, 1669–1673
$C_6H_{15}N$	Triethylamine. B.p., 89.4 100, 650, 1002, 1250, 1268, 1434, 1597, 1644, 1653, 1674–1676, 2190, 2213, 2242
$C_6H_{15}NO$	2-Diethylaminoethanol. B.p., 162.2 385, 1024, 1271, 1469, 1655, 1676a–1682
$C_6H_{16}O_2Si$	Ethoxymethyltrimethylsilane. B.p., 102 464
C_7F_{16}	Perfluoroheptane. B.p., 81.6 900
$C_7H_5Cl_3$	α,α,α-Trichlorotoluene. B.p., 220.9 386, 479, 1307, 1377, 1683–1685
$C_7H_6Cl_2$	α,α-Dichlorotoluene. B.p., 205.2 1378, 1440, 1686–1694
C_7H_6O	Benzaldehyde. B.p., 179.2 1143, 1397, 1470, 1590, 1695–1698
$C_7H_6O_2$	Benzoic acid. B.p., 250.5 340, 651, 1327, 1553, 1637, 1699
$C_7H_6O_3$	Salicylic acid 341
C_7H_7Br	α-Bromotoluene. B.p., 198.5 1374, 1441, 1471, 1700–1703
C_7H_7Br	*m*-Bromotoluene. B.p., 183.8 521, 1386, 1472, 1704–1707
C_7H_7Br	*o*-Bromotoluene. B.p., 181.4 522, 882, 1104, 1708–1711, 2266
C_7H_7Br	*p*-Bromotoluene. B.p., 185 1712, 2267
C_7H_7Cl	α-Chlorotoluene. B.p., 179.35 1099, 1375, 1442, 1473, 1713–1716, 2270
C_7H_7Cl	*o*-Chlorotoluene. B.p., 159.3 523, 572, 828, 1105, 1144, 1474, 1717
C_7H_7Cl	*p*-Chlorotoluene. B.p., 162.4 101, 524, 573, 1106, 1145, 1718, 1719
C_7H_7I	*p*-Iodotoluene. B.p., 212 1720–1726
$C_7H_7NO_2$	*m*-Nitrotoluene. B.p., 230.8 387, 711, 730, 1036, 1125, 1308, 1379, 1451, 1510, 1699, 1727–1750
$C_7H_7NO_2$	*o*-Nitrotoluene. B.p., 221.85 731, 817, 1037, 1126, 1280, 1289, 1475, 1667, 1686, 1720, 1751–1775
$C_7H_7NO_2$	*p*-Nitrotoluene. B.p., 238.8 732, 1038, 1127, 1328, 1511, 1638, 1668, 1776–1791
C_7H_8	Toluene. B.p., 110.7 177, 574, 613, 829, 915, 1025, 1031, 1091, 1227, 1398, 1476, 1506, 1508, 1615, 1626, 1635, 1669, 1792–1797, 2180, 2181, 2202, 2237, 2240, 2257, 2260, 2264, 2271
C_7H_8O	Anisole. B.p., 153.85 525, 575, 856, 1107, 1146, 1554, 1674, 1676a, 1797a, 1798, 1799
C_7H_8O	Benzyl alcohol. B.p., 205.2 1343, 1380, 1683, 1687, 1800–1806
C_7H_8O	*m*-Cresol. B.p., 202.8 1688, 1807–1810
C_7H_8O	*o*-Cresol. B.p., 191.1 526, 1169, 1555, 1677, 1689, 1700, 1713, 1811–1818
C_7H_8O	*p*-Cresol. B.p., 201.7 299, 527, 1170, 1690, 1701, 1808, 1819–1827
$C_7H_8O_2$	Guaiacol. B.p., 205.1 300, 1477, 1684
$C_7H_8O_2$	*m*-Methoxyphenol 1512, 1832
C_7H_8S	α-Toluenethiol. B.p., 194.8 1833
C_7H_9N	Benzylamine. B.p., 185.0 1272, 1399, 1443, 1656, 1808, 1819, 1834–1839
$C_7H\ N$	2,6-Lutidine. B.p., 143 102, 221, 342, 687, 1376, 1792, 1840

Table III. Formula Index (*Continued*)

Formula	Name and System Nos.
C_7H_9N	Methylaniline. B.p., 196.1 388, 528, 712, 1281, 1290, 1359, 1363, 1400, 1591, 1657, 1678, 1691, 1702, 1704, 1751, 1841–1858
C_7H_9N	*m*-Toluidine. B.p., 203.3 389, 713, 1299, 1387, 1401, 1592, 1593, 1708, 1721, 1809, 1811, 1820, 1828, 1859–1870
C_7H_9N	*o*-Toluidine. B.p., 200.3 529, 1402, 1709, 1722, 1752, 1841, 1871–1880
C_7H_9N	*p*-Toluidine. B.p., 202.3 390, 714, 1300, 1388, 1403, 1692, 1703, 1710, 1712, 1723, 1753, 1829, 1881–1885
C_7H_9NO	*o*-Anisidine. B.p., 219.0 480, 1800, 1886
C_7H_{10}	Methylcyclohexadiene 2223
C_7H_{12}	1-Heptyne. B.p., 99.5 465, 2191
C_7H_{12}	5-Methyl-1-hexyne. B.p., 90.8 466, 2192
$C_7H_{12}O_4$	Ethyl malonate. B.p., 198.1 4, 481, 1404, 1444, 1530, 1812, 1821, 1871, 1887–1893
$C_7H_{13}ClO_2$	Isoamyl chloroacetate. B.p., 190 1253, 2233
C_7H_{14}	1,1-Dimethylcyclopentane 2224
C_7H_{14}	1,2-Dimethylcyclopentane 2225
C_7H_{14}	1,3-Dimethylcyclopentane 2226
C_7H_{14}	Methylcyclohexane. B.p., 101.8 434, 530, 598, 652, 838, 909, 971, 995, 1073, 1230, 1478, 1544, 1627, 1675, 1793, 2260, 2271
$C_7H_{14}O$	4-Heptanone. B.p., 143.55 103, 190, 371, 391, 531, 608, 619, 879, 927, 939, 1229, 1254, 1273, 1894–1899
$C_7H_{14}O$	Isoamyl vinyl ether. B.p., 112.6 1255
$C_7H_{14}O$	*o*-Methylcyclohexanol. B.p., 168.5 153, 1537, 1900–1904
$C_7H_{14}O$	5-Methyl-2-hexanone. B.p., 144.2 372, 392, 620, 910, 928, 1026, 1108, 1222, 1256, 1274, 1646, 1905–1913
$C_7H_{14}O_2$	Amyl acetate. B.p., 149.0 343, 1914
$C_7H_{14}O_2$	*sec*-Amyl acetate. B.p., 133.5 104
$C_7H_{14}O_2$	Butyl propionate. B.p., 146.5 105, 1109, 1894, 1905
$C_7H_{14}O_2$	Enanthic acid. B.p., 221 106, 1128, 1309, 1329, 1405, 1727, 1754, 1915–1918
$C_7H_{14}O_2$	Ethyl isovalerate. B.p., 134.7 599, 857, 1092, 1110
$C_7H_{14}O_2$	Ethyl valerate. B.p., 145.15 1895
$C_7H_{14}O_2$	Isoamyl acetate. B.p., 142.1 858, 1906, 2244
$C_7H_{14}O_2$	Isobutyl propionate. B.p., 136.9 1545, 1907, 1919
$C_7H_{14}O_2$	Methyl caproate. B.p., 149.6 1239, 1538
$C_7H_{14}O_2$	Propyl butyrate. B.p., 143.7 1908
$C_7H_{14}O_2$	Propyl isobutyrate. B.p., 134.0 1605
$C_7H_{14}O_3$	1,3-Butanediol methyl ether acetate. B.p., 171.75 1658, 1813, 1920
$C_7H_{14}O_3$	Isobutyl lactate. B.p., 178.7 2270, 2272
C_7H_{16}	2,2-Dimethylpentane. B.p., 79.1 1435
C_7H_{16}	Heptane. B.p., 98.45 165, 178, 203, 261, 436, 839, 947, 955, 960, 972, 1027, 1074, 1194, 1245, 1269, 1474, 1616, 1628, 1670, 1676, 1794, 2205, 2206, 2227, 2271
C_7H_{16}	2-Methylhexane. B.p., 90.0 443
C_7H_{16}	3-Methylhexane. B.p., 91.8 444, 2228
$C_7H_{16}O$	Amyl ethyl ether. B.p., 120 107
$C_7H_{16}O$	Ethyl isoamyl ether. B.p., 112 108
$C_7H_{16}O$	Heptyl alcohol. B.p., 176.5 154, 482, 1843, 1872, 1921, 1922
$C_7H_{16}O$	*sec*-Heptyl alcohol. B.p., 65.4/10 1923
$C_7H_{16}O_2$	Diisopropoxymethane. B.p., 129.0 109
$C_7H_{16}O_3$	Ethyl orthoformate. B.p., 145.75 1797a
$C_7H_{16}O_4$	2-[2-(2-Methoxyethoxy)ethoxy]ethanol. B.p., 245.25 1344, 1406, 1728, 1755, 1776, 1925
C_8H_8	Styrene. B.p., 145.8 110, 262, 324, 750, 996, 999, 1028, 1258, 1263, 1919
C_8H_8O	Acetophenone. B.p., 202 532, 625, 628, 733, 934, 1039, 1171, 1218, 1282, 1293, 1428, 1556, 1714, 1915, 1926–1935
$C_8H_8O_2$	Benzyl formate. B.p., 202.3 483, 1887, 1936
$C_8H_8O_2$	Methyl benzoate. B.p., 199.55 1531, 1533, 1936, 1937–1939
$C_8H_8O_2$	Phenyl acetate. B.p., 195.55 1407, 1557, 1756
$C_8H_8O_2$	Phenylacetic acid. B.p., 266.8 1777
$C_8H_8O_3$	Methyl salicylate. B.p., 222.3 1129, 1310, 1941, 1942
C_8H_9Cl	*o,m,p*-Chloroethylbenzene 911, 1056, 1082, 1147, 1216, 1549, 1641, 1645, 1647, 1659, 1679, 1695, 1923
C_8H_{10}	Ethylbenzene. B.p., 136.15 111, 155, 263, 533, 576, 600, 751, 997, 1000, 1029, 1075, 1093, 1247, 1259, 1260, 1264, 1266, 1480, 1629, 1909
C_8H_{10}	*m*-Xylene. B.p., 139.0 112, 156, 264, 437, 534, 693, 830, 859, 1076, 1111, 1617, 1795, 1896, 1943, 2166, 2238
C_8H_{10}	*o*-Xylene. B.p., 143.6 265, 535, 577, 1481, 1558, 1910
C_8H_{10}	*p*-Xylene. B.p., 138.4 204, 1482, 1796
$C_8H_{10}O$	Benzyl methyl ether. B.p., 170.5 536, 1148, 1483, 1598, 1834
$C_8H_{10}O$	*p*-Ethylphenol. B.p., 220 1312, 1409, 1730, 1860, 1927, 1944–1949
$C_8H_{10}O$	*p*-Methylanisole. B.p., 175.3 537, 1559, 1835, 1844, 1950, 1951
$C_8H_{10}O$	Phenethyl alcohol. B.p., 219.4 1513, 1873, 1952–1957
$C_8H_{10}O$	Phenetole. B.p., 171.5 538, 1112, 1149, 1660, 1836, 1958–1960
$C_8H_{10}O$	3,4-Xylenol. B.p., 226.8 1130, 1311, 1345, 1408, 1452, 1729, 1757, 1778, 1859, 1926, 1961–1968
$C_8H_{10}O_2$	*o*-Ethoxyphenol. B.p., 216.5 1484, 1845, 1861, 1928, 1969–1974
$C_8H_{10}O_2$	Veratrole. B.p., 205.5 1485, 1560, 1975
$C_8H_{11}N$	*N,N*-Dimethylaniline. B.p., 194.05 539, 784, 1291, 1360, 1364, 1410, 1594, 1599, 1648, 1661, 1666, 1680, 1696, 1705, 1715, 1724, 1758, 1900, 1950, 1952, 1958, 1969, 1976–1989
$C_8H_{11}O$	2,4-Dimethylaniline. B.p., 214.0 393, 484, 540, 715 1411, 1760, 1801, 1814, 1822, 1830, 1929, 1953, 1961, 1970, 1990–1995
$C_8H_{11}N$	3,4-Dimethylaniline. B.p., 225.5 394, 485, 716, 1412, 1759, 1802, 1954, 1996–1999
$C_8H_{11}N$	Ethylaniline. B.p., 205.5 395, 717, 1301, 1389, 1413, 1445, 1595, 1693, 1761, 1944, 1962, 2000–2007
$C_8H_{11}NO$	*o*-Phenetidine. B.p., 232.5 396, 718, 1313, 1330, 1453, 1456, 1731, 1803, 1945, 1955, 1963, 2008–2015
$C_8H_{11}NO$	*p*-Phenetidine. B.p., 249.9 397, 1314, 1331, 1454, 1732, 1964, 2016–2024
$C_8H_{12}O_4$	Ethyl fumarate. B.p., 217.85 1414, 1733, 1762, 2025–2031
$C_8H_{12}O_4$	Ethyl maleate. B.p., 223.3 1131, 1415, 1734, 1763, 2032–2036
C_8H_{14}	Diisobutylene 113, 2229, 2265
$C_8H_{14}O$	6-Methyl-5-hepten-2-one. B.p., 173.2 398, 734, 912, 1150, 1172, 1211, 1486, 1600, 1901, 2037–2041
$C_8H_{14}O$	2,4,6-Trimethyl-5,6-dihydro-1,2-pyran 2243
$C_8H_{14}O_4$	Meso-2,3-butanediol diacetate. B.p., 190 344
$C_8H_{14}O_4$	Ethyl succinate. B.p., 217.25 1764, 1823, 2042–2046
$C_8H_{14}O_4$	Propyl oxalate. B.p., 212.0 1416, 1930, 2047
$C_8H_{15}N$	Dimethallylamine. B.p., 149 114
C_8H_{16}	1,3-Dimethylcyclohexane. B.p., 120.5 157, 266, 860, 1077, 1094, 1204, 1237, 1487, 1546, 1618, 1630, 1636, 1671
C_8H_{16}	Ethylcyclohexane. B.p., 131 840
$C_8H_{16}O$	Allyl isoamyl ether. B.p., 120 115
$C_8H_{16}O$	2-Octanone. B.p., 174.1 399, 629, 719, 735, 785, 874, 883, 913, 1113, 1151, 1219, 1601, 1642, 1643, 1649, 1706, 1888, 1902, 2048–2053
$C_8H_{16}O$	2,2,5,5-Tetramethyltetrahydrofuran. B.p., 115 116
$C_8H_{16}O_2$	Amyl propionate 689
$C_8H_{16}O_2$	Butyl butyrate. B.p., 166.4 865, 991, 1539, 1561, 2048, 2054, 2055
$C_8H_{16}O_2$	Caprylic acid. B.p., 237.5 1135, 1346, 1417, 1736
$C_8H_{16}O_2$	Ethyl caproate. B.p., 167.7 866, 1152, 2056
$C_8H_{16}O_2$	Hexyl acetate. B.p., 171.5 2049
$C_8H_{16}O_2$	Isoamyl propionate. B.p., 160.3 867, 1114, 1153, 1562, 2057
$C_8H_{16}O_2$	Isobutyl butyrate. B.p., 156.8 868, 1240
$C_8H_{16}O_2$	Isobutyl isobutyrate. B.p., 147.3 1115, 1154, 1241, 1911
$C_8H_{16}O_2$	Methyl isoamyl acetate. 345
$C_8H_{16}O_2$	Propyl isovalerate. B.p., 155.7 869, 1116, 1547
$C_8H_{16}O_3$	Isoamyl lactate. B.p., 202.4 1418, 2058, 2059
C_8H_{18}	2,4-Dimethylhexane. B.p., 109.4 1672
C_8H_{18}	2,5-Dimethylhexane. B.p., 109.2 267, 373, 438, 653, 1078, 1238
C_8H_{18}	*n*-Octane. B.p., 125.8 268, 541, 831, 841, 1079, 1246, 1436, 1488, 1631, 1797, 2060
C_8H_{18}	2,2,4-Trimethylpentane. B.p., 113.6 467, 1080, 2060
C_8H_{18}	2,3,4-Trimethylpentane. B.p., 113 1507, 1509, 1840
$C_8H_{18}O$	Butyl ether. B.p., 141 117, 542, 578, 861, 1030, 1155, 1489, 1548, 1563, 1798, 2211, 2216

Table III. Formula Index (*Continued*)

Formula	Name and System Nos.
$C_8H_{18}O$	*sec*-Butyl ether. B.p., 121 118, 2212
$C_8H_{18}O$	Ethyl hexyl ether. B.p., 143 119
$C_8H_{18}O$	Isobutyl ether. B.p., 122.2 158, 269, 543, 862, 1081, 1117, 1490, 1673, 1681, 2061, 2217
$C_8H_{18}O$	Octyl alcohol. B.p., 195.15 1173, 1550, 1862, 2037, 2062, 2063
$C_8H_{18}O$	*sec*-Octyl alcohol. B.p., 179 1174, 1863, 1874, 1881, 1931, 2000, 2064, 2065, 2272
$C_8H_{18}O_2$	Acetaldehyde dipropyl acetal. B.p., 147.7 120
$C_8H_{18}O_3$	Bis(2-ethoxyethyl) ether 121, 488
$C_8H_{18}O_3$	2-(2-Butoxyethoxy)ethanol. B.p., 230.4 487, 1737, 2066
$C_8H_{18}S$	Butyl sulfide. B.p., 185.0 884, 1212, 1446
$C_8H_{18}S$	Isobutyl sulfide. B.p., 172.0 544, 736, 1232, 1447, 1662, 2067
$C_8H_{19}N$	Dibutylamine 122
$C_8H_{19}N$	Diisobutylamine. B.p., 138.5 1799, 1943, 2061
$C_8H_{20}SiO$	Ethyl silicate. B.p., 168.8 2054, 2068
C_9H_7N	Quinoline. B.p., 238.5 400, 489, 720, 792, 1040, 1083, 1283, 1302, 1315, 1332, 1347, 1663, 1725, 1738, 1765, 1779, 1804, 1925, 1941, 2066, 2069–2079
C_9H_8	Indene. B.p., 182.6 1846, 1875, 1882, 2080
C_9H_8O	Cinnamaldehyde. B.p., 253.5 1348
$C_9H_{10}O$	Cinnamyl alcohol. B.p., 257.0 1316, 1349, 1419, 1739, 1766, 2016, 2081, 2082
$C_9H_{10}O$	*p*-Methylacetophenone. B.p., 226.35 737, 1429, 1916, 1946, 2025, 2032, 2083–2088
$C_9H_{10}O$	Propiophenone. B.p., 217.7 721, 738, 1381, 1448, 1639, 1726, 1805, 1876, 1883, 1917, 1942, 1947, 1965, 1971, 1976, 1991, 2001, 2026, 2033, 2089–2091
$C_9H_{10}O_2$	Benzyl acetate. B.p., 214.9 1740, 2027, 2034, 2047, 2092
$C_9H_{10}O_2$	Ethyl benzoate. B.p., 212.4 179, 205, 357, 468, 654, 667, 1243, 1437, 1534, 1932, 2093, 2094
$C_9H_{10}O_2$	Methyl α-toluate. B.p., 215.3 2093, 2095
$C_9H_{10}O_3$	Ethyl salicylate. B.p., 233.7 1133, 1317, 2069, 2096
C_9H_{12}	Cumene. B.p., 152.4 270, 579, 1118, 1491, 1540, 1897, 1912
C_9H_{12}	Mesitylene. B.p., 164.6 271, 545, 580, 1119, 1847, 1977, 2050, 2097
C_9H_{12}	Propylbenzene. B.p., 158.9 546, 581, 1564, 1898, 1978
C_9H_{12}	Pseudocumene. B.p., 169 668, 1003, 1180, 2051
$C_9H_{12}O$	Benzyl ethyl ether. B.p., 185.0 547, 1492, 1565
$C_9H_{12}O$	3-Phenylpropanol. B.p., 235.6 793, 1514, 1996, 2008, 2017, 2098
$C_9H_{12}O$	Phenyl propyl ether. B.p., 190.2 548, 1493
$C_9H_{12}O_2$	2-Benzyloxyethanol. B.p., 265.2 1780, 2070
$C_9H_{13}N$	*N,N*-Dimethyl-*o*-toluidine. B.p., 185.3 304, 549, 722, 786, 1275, 1284, 1294, 1361, 1390, 1596, 1602, 1650, 1664, 1831, 1903, 1921, 1933, 1959, 2097, 2099–2106
$C_9H_{13}N$	*N,N*-Dimethyl-*p*-toluidine. B.p., 210.2 401, 490, 550, 723, 1295, 1303, 1420, 1767, 1806, 1810, 1824, 1948, 1956, 1966, 1972, 2064, 2107, 2108
$C_9H_{14}O$	Phorone. B.p., 198.2 402, 724, 739, 935, 1220, 1285, 1296, 1421, 1430, 1449, 1586, 1640, 1697, 1815, 1825, 1889, 1937, 2058, 2109
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone. B.p., 164 305, 359, 402, 491, 626, 725, 914, 929, 1120, 1156, 1213, 1223, 1276, 1365, 1450, 1566, 1603, 1651, 1698, 1717, 1719, 1816, 1904, 2055, 2056, 2057, 2110, 2111
$C_9H_{18}O_2$	Butyl isovalerate. B.p., 177.6 1175, 1578, 1583
$C_9H_{18}O_2$	Ethyl enanthate. B.p., 188.7 1579
$C_9H_{18}O_2$	Isoamyl butyrate. B.p., 178.5 1157, 1176, 1584
$C_9H_{18}O_2$	Isoamyl isobutyrate. B.p., 168.9 870, 1567, 2110
$C_9H_{18}O_2$	Isobutyl isovalerate. B.p., 168.7 1158, 1177, 1568, 1580, 1920, 2068, 2111
$C_9H_{18}O_2$	Methyl caprylate. B.p., 192.9 1532, 1581, 1890, 2109, 2112
$C_9H_{18}O_3$	Isobutyl carbonate. B.p., 190.3 1587, 1891
C_9H_{20}	Nonane. B.p., 150.7 842
$C_9H_{20}O_2$	Dibutoxymethane. B.p., 181.8 2209
$C_9H_{20}O_2$	Diisobutoxymethane. B.p., 163.8 1012, 2219
$C_{10}H_7Cl$	1-Chloronaphthalene. B.p., 262.7 1333, 1685, 1781
$C_{10}H_8$	Naphthalene. B.p., 218 123, 180, 551, 1134, 1318, 1438, 1569, 1864, **1884, 1979,** 1997, 2071, 2099
$C_{10}H_8O$	1-Naphthol. B.p., 288.5 1515, 2113–2115
$C_{10}H_9N$	1-Naphthylamine. B.p., 300.8 404, 726, 2113, 2116–2118
$C_{10}H_9N$	2-Naphthylamine. B.p., 306.1 2114
$C_{10}H_9N$	Quinaldine. B.p., 246.5 1350
$C_{10}H_{10}O_2$	Isosafrole. B.p., 252.1 1334, 1516, 2073, 2119
$C_{10}H_{10}O_2$	Methyl cinnamate. B.p., 261.9 294
$C_{10}H_{10}O_2$	Safrole. B.p., 235.9 1135, 1335, 1517, 2072, 2120
$C_{10}H_{10}O_4$	Methyl phthalate. B.p., 283.2 2121
$C_{10}H_{12}O$	Anethole. B.p., 233.8 1518, 2009, 2018, 2074, 2083, 2122, 2123
$C_{10}H_{12}O_2$	Ethyl α-toluate. B.p., 228.75 2042, 2084
$C_{10}H_{12}O_2$	Eugenol. B.p., 255 1519, 1782, 2124
$C_{10}H_{12}O_2$	Propyl benzoate. B.p., 230.85 1319, 1741, 2125, 2126
$C_{10}H_{14}$	Butylbenzene. B.p., 183.1 552, 1494, 1570, 1865, 1877, 2038
$C_{10}H_{14}$	Cymene. B.p., 176.7 553, 1159, 1848, 1878, 1980, 2039, 2100, 2127
$C_{10}H_{14}O$	Carvacrol. B.p., 237.85 1320, 1336, 1351, 1742, 1768, 1783, 2010, 2019, 2128–2131
$C_{10}H_{14}O$	Carvone. B.p., 230.95 1382, 1917, 2020, 2035, 2081, 2122, 2128, 2132–2136
$C_{10}H_{14}O$	Thymol. B.p., 232.8 181, 286, 1321, 1337, 1455, 1967, 1992
$C_{10}H_{15}N$	Diethylaniline. B.p., 217.05 554, 1286, 1743, 1817, 1922, 1949, 1968, 1973, 1975, 2002, 2065, 2082, 2085, 2089, 2094, 2123, 2129, 2132, 2137–2142
$C_{10}H_{16}$	Camphene. B.p., 159.6 555, 863, 1121, 1160, 1458, 1849, 1899, 2101, 2143
$C_{10}H_{16}$	α-Phellandrene. B.p., 171.5 1459
$C_{10}H_{16}$	*d*-Limonene. B.p., 177.8 2263, 2268, 2272
$C_{10}H_{16}$	α-Pinene. B.p., 155.8 556, 864, 1122, 1183, 1460, 1850, 1913, 1981, 2102, 2239
$C_{10}H_{16}$	β-Pinene. B.p., 164 1495, 1541, 1851, 1982
$C_{10}H_{16}$	α-Terpinene. B.p., 173.3 557, 1496, 1542, 1571, 1826, 1852, 1983, 2040, 2052, 2269, 2270
$C_{10}H_{16}$	Terpinolene. B.p., 185 1827, 1885, 2003
$C_{10}H_{16}$	Terpinylene. B.p., 175 871
$C_{10}H_{16}O$	Camphor. B.p., 209.1 182, 405, 727, 740, 787, 1041, 1287, 1383, 1431, 1497, 1866, 1892, 1938, 1984, 1993, 2028, 2059, 2062, 2103, 2137, 2144
$C_{10}H_{16}O$	Carvenone. B.p., 234.0 406, 2021, 2125, 2145, 2146
$C_{10}H_{16}O$	Citral. B.p., 226 2138
$C_{10}H_{16}O$	Fenchone. B.p., 193 407, 741, 1572, 1818
$C_{10}H_{16}O$	Pulegone. B.p., 224 1422, 1867, 1974, 2029, 2036, 2092, 2095, 2096, 2130, 2147, 2148
$C_{10}H_{17}Cl$	Bornyl chloride. B.p., 207.5 1769
$C_{10}H_{18}$	Dipentene. B.p. 177.7 558, 1161, 1498, 1573, 1853, 1985, 2041, 2053, 2149
$C_{10}H_{18}$	*d*-Menthene. B.p., 170.8 1461, 1499, 1574
$C_{10}H_{18}O$	Borneol B.p., 215.0 1784, 2104
$C_{10}H_{18}O$	Cineole. B.p., 176.35 1123, 1837, 1854, 2150
$C_{10}H_{18}O$	Citronellal B.p., 208.0 1770, 2144
$C_{10}H_{18}O$	Geraniol. B.p., 229.7 2043, 2107, 2133
$C_{10}H_{18}O$	Menthone. B.p., 207 492, 788, 1694, 2063
$C_0H_{18}O$	α-Terpineol. B.p., 217.8 1304, 1868, 2011
$C_{10}H_{18}O$	β-Terpineol. B.p., 210.5 493, 1423, 1500, 1771, 1784, 1855, 1879, 1934, 2105, 2139
$C_{10}H_{18}O_4$	Propyl succinate. B.p., 250.5 2151
$C_{10}H_{20}O$	Citronellol. B.p., 224.5 1744, 1986, 1998, 2004, 2086
$C_{10}H_{20}O$	Menthol. B.p., 216.4 1520, 1880, 1886, 1994, 2020, 2075, 2134
$C_{10}H_{20}O_2$	Ethyl caprylate. B.p., 208.35 1588
$C_{10}H_{20}O_2$	Isoamyl isovalerate. B.p., 193.5 499, 872, 1162, 1178, 1535, 1575, 1582, 1585, 1589, 1893, 1939, 2112
$C_{10}H_{20}O_2$	Methyl pelargonate. B.p., 213.8 1772, 1935, 2030, 2044, 2090
$C_{10}H_{22}$	Decane. B.p., 173.3 843, 1501
$C_{10}H_{22}$	2,7-Dimethyloctane. B.p., 160.25 1502
$C_{10}H_{22}O$	Amyl ether. B.p., 190 559, 1163, 1248, 1503, 1576, 1838, 1987
$C_{10}H_{22}O$	Decyl alcohol. B.p., 232.8 2005, 2013, 2108
$C_{10}H_{22}O$	Isoamyl ether. B.p., 172.6 1164, 1682, 1839, 1856, 1988, 2067, 2152
$C_{10}H_{22}O_2$	Acetaldehyde dibutyl acetal. B.p., 188.8 124, 992, 1665, 2210

Table III. Formula Index (*Continued*)

Formula	Name and System Nos.
$C_{10}H_{22}O_2$	Acetaldehyde diisobutyl acetal. B.p., 171.3 125, 1013, 2219
$C_{10}H_{22}S$	Isoamyl sulfide. B.p., 214.8 1424
$C_{10}H_{23}N$	Diisoamylamine. B.p., 188.2 1951, 1960, 2080, 2127, 2143, 2149, 2150, 2152
$C_{11}H_{10}$	1-Methylnaphthalene. B.p., 245.1 560, 1322, 1352, 1521, 1773, 2076
$C_{11}H_{10}$	2-Methylnaphthalene. B.p., 241.15 561, 1338, 1353, 1504, 1745, 1774, 1786, 1999, 2014, 2022, 2077, 2135, 2140
$C_{11}H_{12}O_4$	Ethyl cinnamate. B.p., 271.5 795, 2121, 2153
$C_{11}H_{14}O_2$	1-Allyl-3,4-dimethylbenzene. B.p., 255.0 1522, 2154
$C_{11}H_{14}O_2$	Butyl benzoate. B.p., 249.8 1339, 1354, 2151
$C_{11}H_{14}O_2$	1,2-Dimethyl-4-propenylbenzene. B.p., 270.5 1523, 2023
$C_{11}H_{14}O_2$	Ethyl β-phenylpropionate. B.p., 248.1 1746, 1787
$C_{11}H_{14}O_2$	Isobutyl benzoate B.p., 242.15 1340, 1747, 2136, 2145
$C_{11}H_{16}O$	Methyl thymol ether. B.p., 216.5 1425
$C_{11}H_{17}N$	Isoamylaniline. B.p., 256 1748, 1788, 1832, 1957, 2098, 2119, 2120, 2124, 2131, 2154
$C_{11}H_{20}O$	Isobornyl methyl ether. B.p., 192.2 315, 562, 1505, 1577, 2006, 2106
$C_{11}H_{20}O$	Methyl terpineol ether. B.p., 216.2 311, 1775, 1869, 2087, 2141
$C_{11}H_{22}O_2$	Ethyl pelargonate. B.p., 227 2045
$C_{11}H_{22}O_3$	Isoamyl carbonate. B.p., 232.2 494, 1136, 1323, 1749, 2088, 2126, 2146, 2147
$C_{11}H_{24}$	Undecane. B.p., 194.5 844
$C_{11}H_{24}O_2$	Diamyloxymethane. B.p., 221.6 2230
$C_{12}H_{10}$	Acenaphthene. B.p., 277.9 1524, 2116
$C_{12}H_{10}$	Diphenyl. B.p., 255.9 1355, 1525, 1789, 2078
$C_{12}H_{10}O$	Phenyl ether. B.p., 259.0 1790
$C_{12}H_{11}N$	Diphenylamine. B.p., 302 346, 2115
$C_{12}H_{16}O_2$	Isoamyl benzoate. B.p., 262.3 1457
$C_{12}H_{16}O_3$	Isoamyl salicylate. B.p., 279 1341, 1791, 2024, 2079
$C_{12}H_{18}$	Triethylbenzene. B.p., 215.5 1137, 1857, 1995, 2015, 2091
$C_{12}H_{20}O_2$	Bornyl acetate. B.p., 227.6 1324, 1750, 2031, 2046, 2148
$C_{12}H_{22}O$	Bornyl ethyl ether. B.p., 204.9 1138, 1426, 1989, 2007
$C_{12}H_{22}O$	Ethyl isobornyl ether. B.p., 203.5 1427, 1858, 1870, 2142
$C_{12}H_{22}O_4$	Isoamyl oxalate. B.p., 268.0 873, 2153
$C_{12}H_{26}O_2$	Acetaldehyde diamyl acetal. B.p., 225.3 126, 1249, 2231
$C_{12}H_{26}O_2$	Acetaldehyde diisoamyl acetal. B.p., 213.6 127, 1257, 2234
$C_{13}H_{10}O$	Benzophenone 347
$C_{13}H_{12}$	Diphenylmethane. B.p., 265.6 563, 1526
$C_{13}H_{12}O$	Benzyl phenyl ether. B.p., 286.5 2117
$C_{14}H_{10}$	Anthracene 1004
$C_{14}H_{14}$	1,2-Diphenylethane. B.p., 284.5 1527, 2118

BIBLIOGRAPHY

(1) Atkins, *J. Chem. Soc.*, **117**, 218 (1920).
(2) Bahr and Zieler, *Z. angew. chem.*, **43**, 286 (1930).
(3) Baker *et al.*, *Ind. Eng. Chem.*, **31**, 1260, 1263 (1939).
(4) Bakowski and Treszczanowicz, *Przemsyl Chem.*, **22**, 211 (1938).
(5) Bancelin and Rivat, *Bull. soc. chim.*, (4) **25**, 552 (1909).
(6) Baney, U. S. Patent 2,425,220 (1947).
(7) Beduwe, *Bull. soc. chim. Belg.*, **34**, 41 (1925).
(8) Benning, U. S. Patents 2,450,414–15 (1948).
(9) Berg and Harrison, *Trans. Am. Inst. Chem. Engrs.*, **43**, 487 (1947).
(10) Berg and Harrison, U. S. Patent 2,442,229 (1948).
(11) Berg, Harrison, and Montgomery, *Ind. Eng. Chem.*, **38**, 1149 (1946).
(12) Birch, Collis, and Lowry, *Nature*, **158**, 60 (1946).
(13) Bozza and Gallarati, *Giorn. chim. ind. applicata*, **13**, 163 (1931).
(14) Bremner, Jones, and Coats, Brit. Patent 592,919 (1947).
(15) Bromiley and Quiggle, *Ind. Eng. Chem.*, **25**, 1136 (1933).
(16) Brooks, U. S. Patent 2,436,286 (1948).
(17) Brunjes and Furnas, *Ind. Eng. Chem.*, **27**, 396 (1935).
(18) Buchheim, Ger. Patent 616,596; *Chem. Zentr.*, **1935**, II, 3703.
(19) Burgin, *Ind. Eng. Chem.*, **33**, 386 (1941).
(20) Bushmakin and Kuchinskaya, *Sintet. Kauchuk*, No. 5, 3 (1936).
(21) Calder and Fleer, U. S. Patents 2,401,335–6 (1946).
(22) Calices and Hannotte, *Ing. chim.*, **20**, 1 (1936).
(23) Carbide & Carbon Chemicals Corp., Catalog, 11th ed., 1942.
(24) *Ibid.*, 12th ed., 1945.
(25) Carbide & Carbon Chemicals Corp., "Cellosolve and Carbitol Solvents," Jan. 1, 1947.
(26) Carbide & Carbon Chemicals Corp., *Chem. Inds.*, **33**, 521 (1933).
(27) Carnell, U. S. Patent 2,430,388 (1947).
(28) Ceslak and Karnatz, Brit. Patent 580,048 (1946).
(29) Churchill, Collamore, and Katz, *Oil Gas J.*, **41**, 33 (Aug. 6, 1942).
(30) Clark, U. S. Patent 2,385,610 (1945).
(31) Conner, Elving, and Steingiser, *Ind. Eng. Chem.*, **40**, 497 (1948).
(32) Coulson, Brit. Patent 585,108 (1947).
(33) Coulson and Jones, *J. Soc. Chem. Ind.*, **65**, 169 (1946).
(34) Deansley, U. S. Patent 2,290,636 (1942).
(35) de Mol, *Ing. chim.*, **22**, 362 (1938).
(36) Dow Chemical Co., unpublished data.
(37) Drake, U. S. Patent 2,170,854 (1939).
(38) Engel, *Ibid.*, 2,363,159 (1940).
(39) *Ibid.*, 2,376,870 (1945).
(40) Engs, *Ibid.*, 2,414,639 (1947).
(41) Evans, Brit. Patent 479,675 (1946).
(42) Evans, U. S. Patent 2,140,694 (1938).
(43) Evans and Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).
(44) Evans and Hass, U. S. Patent 2,442,589 (1948).
(45) Evans, Morris, and Shokal, *Ibid.*, 2,426,821 (1947).
(46) Ewell and Welch, *Ind. Eng. Chem.*, **37**, 1224 (1945).
(47) Fairborne, *J. Chem. Soc.*, **1932**, 1965.
(48) Fisher and Fein, U. S. Patent 2,438,278 (1948).
(49) Fordyce and Simonsen, *Ind. Eng. Chem.*, **41**, 104 (1949).
(50) Frey, U. S. Patent 2,186,524 (1940).
(51) Geckler and Fragen, *Ibid.*, 2,316,126 (1943).
(52) Ghysels, *Bull. soc. chim. Belg.*, **33**, 57 (1924).
(53) Goldblum, Martin, and Young, *Ind. Eng. Chem.*, **39**, 1474 (1947).
(54) Gordon and Benson, *Can. J. Research*, **24B**, 285 (1946).
(55) Gordon and Bright, U. S. Patent 2,171,549 (1939).
(56) Gowing-Scopes, *Analyst*, **39**, 6 (1914).
(57) Greenburg, U. S. Patent 2,313,536 (1943).
(58) Gresham and Brooks, *Ibid.*, 2,449,470 (1948).
(59) Guinot and Chassaing, *Ibid.*, 2,437,519 (1948).
(60) Hammond, *Ibid.*, 2,356,785 (1944).
(61) Hennion and Groebner, *J. Am. Chem. Soc.*, **70**, 426 (1948).
(62) Herold, Wustrow, and Wetzel, U. S. Patent 2,091,636 (1937).
(63) Horsley, L. H., ANAL. CHEM., **19**, 503 (1947).
(64) Huntress, "Organic Chlorine Compounds," pp. 588, 1038. New York, John Wiley & Sons, Inc., 1948.
(65) Huntress and Sanchez-Nieva, *J. Am. Chem. Soc.*, **70**, 2813, (1948).
(66) Izard, U. S. Patent 2,061,732 (1936).
(67) Janecke, *Z. physik. Chem.*, **164**, 401 (1933).
(68) Kaplan and Monakhova, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2499 (1937).
(69) Kellogg and Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).
(70) Kireev, Kaplan, and Zlobin, *J. Applied Chem.* (*U.S.S.R.*), **7**, 1333 (1934).
(71) Kodak, Ltd., Brit. Patent 501,927 (1939).
(72) Kretschmer, Abstracts of Papers, Div. of Physical and Inorganic Chemistry, 112th Meeting, AM. CHEM. SOC., New York, 1947.
(73) Kretschmer, Nowakowska, and Wiebe, *J. Am. Chem. Soc.*, **70**, 1785 (1948).
(74) Lacker and Hunt, *Ibid.*, **63**, 1752 (1941).
(74) Lake, U. S. Patent 2,432,771 (1947).
(76) Lake and Stribley, *Ibid.*, 2,439,777 (1948).
(77) Lecat, *Ann. soc. sci. Bruxelles*, **47B**, 108 (1927).
(78) *Ibid.*, **47B**, 149 (1927).
(79) *Ibid.*, **48B**, I, 13 (1928).
(80) *Ibid.*, **48B**, II, 54 (1928).
(81) *Ibid.*, **48B**, II, 113 (1928).
(82) *Ibid.*, **49B**, 17 (1929).
(83) *Ibid.*, **49B**, 119 (1929).
(84) *Ibid.*, **50B**, 21 (1930).
(85) *Ibid.*, **56B**, 41 (1936).
(86) *Ibid.*, **56B**, 221 (1936).
(87) *Ibid.*, **60**, 155 (1946).
(88) *Ibid.*, **60**, 163 (1946).
(89) *Ibid.*, **60**, 169 (1946).

(90) *Ibid.*, **60**, 228 (1946).
(91) *Ibid.*, **61**, 63 (1947).
(92) *Ibid.*, **61**, 79 (1947).
(93) *Ibid.*, **61**, 148 (1947).
(94) Lecat, "Azeotropisme," Brussels, Henri Lamertin, 1918.
(95) Lecat, *Compt. rend.*, **217**, 242 (1943).
(96) *Ibid.*, **222**, 733, 882, 1488 (1946).
(97) *Ibid.*, **223**, 286 (1946).
(98) Lecat, *Z. anorg. allgem. Chem.*, **186**, 119 (1929).
(99) Lepingle, *Bull. soc. chim.*, **39**, 864 (1926).
(100) Lidstone, *J. Chem. Soc.*, **1940**, 241.
(101) Litkenhous, Van Arsdale, and Hutchison, *J. Phys. Chem.*, **44**, 377 (1940).
(102) McDermott, F. A., private communication.
(103) Marshall, *J. Chem. Soc.*, **89**, 1351 (1906).
(104) Matuszak and Frey, IND. ENG. CHEM., ANAL. ED., **9**, 111 (1937).
(105) Nadeau and Fisher, U. S. Patent 2,165,298 (1939).
(106) Natta, *Ibid.*, 2,308,229 (1943).
(107) Naumann, *Ber.*, **10**, 1421, 1819, 2099 (1877).
(108) Oddo, *Gazz. chim. ital.*, **41**, II, 232 (1911).
(109) Othmer, *Ind. Eng. Chem.*, **35**, 614 (1943).
(110) Othmer, U. S. Patent 2,050,234 (1936).
(111) *Ibid.*, 2,170,834 (1939).
(112) *Ibid.*, 2,395,010 (1946).
(113) Othmer, Schlechter, and Kosyalka, *Ind. Eng. Chem.*, **37**, 895 (1945).
(114) Patterson, U. S. Patent 2,407,997 (1946).
(115) Petry, *Ibid.*, 2,411,106 (1946).
(116) Pierre, *Compt. rend.*, **74**, 224 (1872).
(117) Piret and Hall, *Ind. Eng. Chem.*, **40**, 661 (1948).
(118) Popelier, *Bull. soc. sci. Belg.*, **32**, 179 (1923).
(119) Pratt, Preprint, *Trans. Inst. Chem. Engrs.* (*London*) (March 1947).
(120) Pryanishnikov and Genin, *J. Applied Chem.* (*U.S.S.R.*), **13**, 140 (1940).
(121) Quiggle and Fenske, *J. Am. Chem. Soc.*, **59**, 1829 (1937).
(122) Reinders and Minjer, *Rec. trav. chim.*, **66**, 552, 564, 573 (1947).
(123) Richards and Guinot, U. S. Patent 1,915,002 (1933).
(124) Riethof, *Ibid.*, 2,413,649–51 (1946).
(125) Robinson, "Elements of Fractional Distillation," p. 230, New York, McGraw-Hill Book Co., 1930.
(126) Sandberg and Patterson, U. S. Patent 2,428,815 (1947).
(127) Sauer and Hadsell, *J. Am. Chem. Soc.*, **70**, 4258 (1948).
(128) Sauer, Schreiber, and Hadsell, *Ibid.*, **70**, 4254 (1948).
(129) Schelling and Anderson, U. S. Patent 2,422,802 (1947).
(130) Schopmeyer and Arnold, *Ibid.*, 2,350,370 (1944).
(131) Schreinmakers, *Z. physik. Chem.*, **39**, 485; **40**, 440 (1902).
(132) Senkus, U. S. Patent 2,406,713 (1946).
(133) Shawinigan Chemicals, Ltd., Dept. Chem. Divd., "*Report on* Vinyl Crotonate," (1948).
(134) Shell Chemical Corp., "Organic Chemicals Manufactured by Shell," 1939.
(135) Shell Development Co., Data Sheet, 1946.
(136) Shostakovskiĭ and Prilezhaeva, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1129 (1947).
(137) Simonetta and Barakan, *Gazz. chim. ital.*, **77**, 105 (1947).
(138) Smith, U. S. Patent 2,385,546 (1945).
(139) Smyth and Engel, *J. Am. Chem. Soc.*, **51**, 2646 (1929).
(140) Société des usines chimiques Rhône-Poulenc, Brit. Patent 595,738 (1947).
(141) Speck, U. S. Patent 2,449,152 (1948).
(142) Speier, *J. Am. Chem. Soc.*, **70**, 4142 (1948).
(143) Stasse, U. S. Patent 2,363,158 (1944).
(144) Steel and Bagstor, *J. Chem. Soc.*, **97**, 2607 (1910).
(145) Stengel and O'Loughton, U. S. Patent 2,315,139 (1943).
(146) Sullivan, *Ibid.*, 2,265,220 (1941).
(147) Sutherland, *Ibid.*, 2,290,654 (1942).
(148) Timmermans, *J. chim. phys.*, **31**, 98 (1934).
(149) Tomkins, Wheat, and Stranks, *Can. J. Research*, **26F**, 168 (1948).
(150) Trillat and Cambies, *Compt. rend.*, **118**, 1277 (1894).
(151) Tyerman, Brit. Patent 590,713 (1947).
(152) Walker and Carlisle, *Chem. Eng. News*, **21**, 1250 (1943).
(153) Welling, U. S. Patent 2,386,375 (1945).
(154) Willert, *Ibid.*, 2,445,738 (1948).
(155) Williams, *Trans. Am. Inst. Chem. Engrs.*, **37**, 157 (1941).
(156) Williams and Meeker, ANAL. CHEM., **20**, 733 (1948).
(157) Woods, *J. Soc. Chem. Ind.*, **66**, 26 (1947).
(158) Wuyts, *Bull. soc. chim. Belg.*, **33**, 178 (1924).
(159) Wuyts and Docquier, *Ibid.*, **44**, 297 (1935).
(160) Young and Fortey, *J. Chem. Soc.*, **81**, 739 (1942).

RECEIVED February 21, 1949.

NOTES ON ANALYTICAL PROCEDURES...

High Temperature Bath Made from Aluminum Shavings

STEPHEN DJANG
Michigan State College, East Lansing, Mich.

THE need for a high temperature bath for refluxing aqueous solutions led to the work presented in this paper. Because of their high conductivity of heat, aluminum shavings were used in construction of the bath.

A copper box which contains aluminum turnings about the size of rice granules is placed on top of a copper plate 0.6 cm. (0.25 inch) thick and fastened by screws. The copper plate is heated by three electric elements and the heat is regulated and controlled by a thermoregulator, which is located in the center of the bath (Figure 1).

Because of the high conductivity of copper, a uniform temperature bath can be constructed. The copper plate must be thick enough to diffuse sufficient heat to the entire unit. The entire bath is enclosed in a box of Transite, so that the uniform temperature of the bath can be preserved. The space between the copper box and the Transite wall measures 2.5 cm. (1 inch) and is filled with rock wool as insulator. The bath is covered with individual Transite covers with notches to accommodate the necks of the flasks.

The inside of the bath is 40 inches in length, 6 inches in width, and 4.5 inches in depth. Eight 300-ml. round-bottomed flasks can be set in a row. The flasks are placed in metal cups, which are 236-ml. (8-ounce) aluminum measuring cups with handles removed. If flasks break, the solution is trapped in the cups (Figure 1). The flasks are cushioned in the cups with Chore-girl copper ribbon material which retains its form. Aluminum shavings were not satisfactory because they did not retain a definite form to accommodate the shape of the flasks. However, the bath can be operated without the use of metal cups.

In packing the bath the eight metal cups with their contents are placed on the bottom of the box (Figures 1 and 2). Then the aluminum shavings are poured in to a depth of 0.75 inch, evenly distributed but not pressed or tamped. Two aluminum bars, 39 inches long and 0.5 inch in diameter, are laid on top of the aluminum shavings in front and in back of the metal cups but not touching the cups or the side walls of the bath. After all are in position, the bath is filled with aluminum shavings up to 1 inch from the top. The aluminum bars are used as heat conductors (Figures 2 and 3).

The bath was tested for 50 hours of continuous operation at 200° C. Recordings at five different positions in the bath showed that the fluctuation of temperature at all positions was the same, ±1.5° C. (Table I). It was demonstrated that the temperature of the bath was even and constant at various positions in the bath when the thermoregulator was set at 200° C.

When the thermoregulator was set at temperatures ranging from 30° to 250° C. for 12-hour periods, the bath held the given temperature throughout the period tested. The author was in-

Table I. Temperature Variations at Five Positions in the Bath

Time, Min.	Thermo-regulator Pilot Light	1 ° C.	2 ° C.	3 ° C.	4 ° C.	5 ° C.
0	Off	201	203	201	202	201
2	Off	201	203	201	202.5	201
4	Off	201	203	201	203	201
6	On	201	202	200	202	200
8	On	200	201	199	200	200
10	On	199	200	198	200	199
12	On	198	200	198	200	199
14	On	199	200.5	198	200	199.5
16	On	199.5	201	198	200	200
18	On	200	201	199	200.5	200.5
20	Off	200	201	200	201	201
22	Off	200	202	200	201.5	201
24	Off	200.5	203	200.5	202	201.5
26	Off	200.5	203	201	202	200
28	Off	200.5	202	200.5	202	200
30	Off	200	202	200.5	201	199
32	Off	200	202	200	200.5	199
34	On	200	201	199.5	200	199
36	On	199	200	198.5	200	199.5
38	On	198.5	200	198.5	200	199
40	On	198.5	200	198	200	199
42	On	198.5	200	198	200	199
44	Off	199	201	199	200	200
46	Off	199	201	199.5	200	200
48	Off	200	202	200	201	200.5
50	Off	200	202	200	201	201
52	Off	200	202	200	201	200.5
54	Off	200	201.5	200	200.5	200.5
56	Off	199.5	201	199.5	200	200
58	On	198.5	200	199	200	199.5
60	On	198	200	199.5	199.5	199
Highest reading		201	203	201	203	201
Lowest reading		198	200	198	200	199
Range or variation		3	3	3	3	2
Fluctuation		±1.5	±1.5	±1.5	±1.5	±1

terested in securing a bath which was constant at temperatures between 150° and 250° C. and compiled detailed data only at 200° C. Temperatures higher than 250° C. could be secured by adding more heating elements.

The bath so constructed is especially useful at or above 100° C. for refluxing samples for long periods. Aluminum shavings are noncorrosive and always appear clean. Below 100° C.

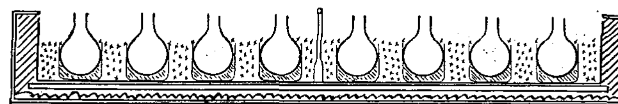
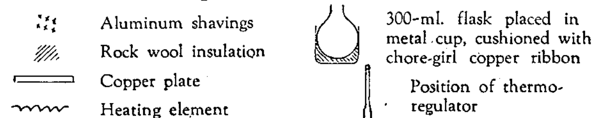


Figure 1. Front section view



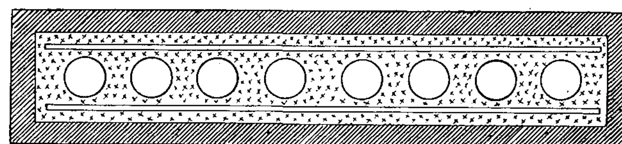
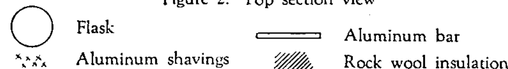


Figure 2. Top section view



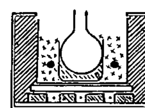
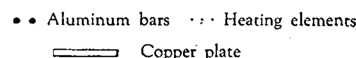


Figure 3. End section view



the shaving bath has one advantage over a water bath: no liquid escapes by evaporation. There is no danger from fumes as with acids or organic liquids; hence this bath is safer for the operator and avoids contamination of samples.

The cost of the material, except the thermoregulator, for building the bath is between $12 and $15. The thermoregulator is manufactured by Fenwal, Inc., Ashland, Mass. An aluminum plate 0.375 inch thick, 40 inches by 6 inches, weighing 10 pounds may be used instead of copper (cost $3). Aluminum shavings are obtainable at machine shops at 10 cents per pound.

Received April 28, 1948.

Detection of Persulfate in Acid Solution

GEORGE L. CLARK and TSONG-CHI TSO
University of Illinois, Urbana, Ill.

THE common reagents that are relatively sensitive and simple in use for persulfate ($S_2O_8^{--}$) detection are aniline, benzidine, 2,7-diaminofluorene, and Zwikker reagent. The first three reagents show color changes due to oxidation of the reagent by persulfate ion, while the last one gives definite and highly typical crystals after reaction with persulfate. All four reagents are very sensitive in neutral solution when used according to the directions in analytical books.

For detection of persulfate in strong acid solutions, the situation is different. The authors have studied the behavior of these four reagents in both neutral and acid solutions of various strengths. Some modifications of the method using two of the reagents have been developed for detection of persulfate in acid solutions. This is of particular importance in the case of persulfuric acid formation at the anode during charging of storage batteries at temperatures as low as −65° F., at which the acid is far more stable than at room temperatures, with resulting solution of lead dioxide and gradual disintegration of the positive plates.

Zwikker Reagent (4 ml. of 10% copper sulfate, 1 ml. of pyridine, and 5 ml. of water) forms specific prismatic crystals with persulfate in neutral solution. The limit of dilution is found in this work to be 1 to 5000 (1 part of persulfate in 5000 parts of neutral solution), but that found by Berisso (*1*) was 1 to 10,000 and that by Wagenaar (*4*) was 1 to 1000. In a 10 *N* solution of sulfuric acid, no crystals are formed in high concentration of persulfate. In 5 *N* or lower acid solutions, crystals of exactly the same form as in neutral solutions are obtained, the limit of dilution varying with the strength of acid (Table I).

Therefore, to test for persulfate ion in acid solution with Zwikker reagent, the sample solution must be diluted before the reagent is added. To prevent the decomposition of persulfate by heat of dilution, the solution should be kept cold during dilution.

2,7-Diaminofluorene (*3*, *7*) is synthesized by nitration of fluorene, followed by reduction of the nitration product with tin and hydrochloric acid. Crystals of 2, 7-diaminofluorene hydrochloride are obtained on precipitating the tin with hydrogen sulfide and evaporating the solution. Usually, an aqueous solution of 2,7-diaminofluorene or its hydrochloride is used for the detection of persulfate. In neutral solution, potassium persulfate gives a distinct blue coloration at a dilution of 1 to 200,000 with a 1% solution of the reagent.

Table I. Limit of Dilution with Zwikker Reagent

Acid Normality in Persulfate Solution	Sensitivity
10	$S_2O_8^{--}$ not detectable in all concentrations
5	1 part $S_2O_8^{--}$ detectable in 500 parts solution
2	1 part $S_2O_8^{--}$ detectable in 1000 parts solution
1	1 part $S_2O_8^{--}$ detectable in 2000 parts solution
0.5	1 part $S_2O_8^{--}$ detectable in 2000 parts solution
0.0	1 part $S_2O_8^{--}$ detectable in 5000 parts solution

The aqueous solution of 2,7-diaminofluorene or its hydrochloride cannot be used in testing acid samples, because a white precipitate is formed on acidification. But if a 1% solution of the reagent or its hydrochloride in concentrated sulfuric acid is used instead of a neutral solution, a clear green coloration is produced by a persulfate solution of any acid strength. The dilution limit is 1 part of potassium persulfate in 10,000.

Aniline (5). According to Lenz and Richter (2), the reagent is prepared by diluting 5 grams of 20% sulfuric acid to 100 ml., adding 10 grams of pure aniline, and filtering after shaking violently. By boiling with an equal volume of persulfate solution, a brown color is developed.

The authors have found that, on boiling, a neutral solution of persulfate at a dilution of 1 to 20,000 gives a yellow coloration. In acid solution the dilution limit is 1 part of potassium persulfate in 2000, in which case a rose coloration is developed.

Benzidine (6). A dilute acetic acid solution of benzidine gives a blue coloration with persulfate solution. The limit of dilution in neutral solution is 1 to 100,000. It cannot be used for samples in strong acid solution because it forms a precipitate on mixing.

SUMMARY

Four kinds of reagents for persulfate detection in neutral solution have been tested in strong acid solution. Benzidine cannot be used in strong acid solution, whereas aniline can be used in acid solution as well as in neutral solution, but with less sensitivity. Zwikker reagent forms the same crystalline precipitate in acid solution as in neutral solution, but previous dilution before adding the reagent is necessary if the sample solution is above 5 N in acid. The most sensitive reagent for detection of persulfate in acid solution is 2,7-diaminofluorene in concentrated sulfuric aid instead of in aqueous solution; one part of persulfate in 10,000 of solution may be detected easily, in contrast with 1 to 2000 for the other two reagents.

LITERATURE CITED

(1) Berisso, Benjamin, *Pubs. inst. invest. microquím., Univ. nacl. litoral* (Rosario, Argentina), 7, 25–32 (1943).
(2) Lenz, W., and Richter, E., *Z. anal. Chem.*, 50, 537–44 (1911).
(3) Schmidt, J., and Hinderer, W., *Ber.*, 65B, 87–90 (1932).
(4) Wagenaar, G. H., *Pharm. Weekblad*, 77, 465 (1940).
(5) Welcher, F. J., "Organic Analytical Reagents," Vol. 2, p. 270, New York, D. Van Nostrand Co., 1947.
(6) *Ibid.*, p. 322.
(7) *Ibid.*, p. 339.

RECEIVED October 14, 1948. From research work carried out under contract with the United States Army Signal Corps Engineering Laboratory, published by permission.

Apparatus for Measuring Gas Absorption or Evolution during Organic Reactions

Catalytic Hydrogenation, Dehydrogenation, and Zerewitinoff Determination

MILTON ORCHIN AND IRVING WENDER
Office of Synthetic Liquid Fuels, Bureau of Mines, Bruceton, Pa.

REACTIONS involving the absorption or evolution of gases are common in the organic laboratory. The measurement and analysis of the gases are desirable, for such information often provides valuable clues concerning the course, speed, and stoichiometry of a reaction. The authors have used the apparatus shown in Figure 1 successfully for three different types of reaction: Zerewitinoff determination of active hydrogen, catalytic hydrogenation, and catalytic dehydrogenation. The size of the apparatus permits its use not only for analytical purposes but for preparative purposes as well.

ZEREWITINOFF METHOD FOR DETERMINATION OF ACTIVE HYDROGEN

Figure 1 represents certain additions and modifications to the usual apparatus for the Zerewitinoff determination of active hydrogen. It features the convenience of magnetic stirring and the use of a serum stopper for the injection of liquids. The preparation of the necessary reagents and the standard precautions to be taken are described elsewhere (2, 4).

After the system is flushed with nitrogen, the sample is weighed into the flask shown in place in Figure 1 and dry pyridine is added. Stirring is started, and an excess of methyl magnesium iodide in n-butyl ether is injected into the reaction chamber through the serum stopper by means of a syringe fitted with a stainless-steel needle. The mercury is lowered immediately, so that a slight negative pressure is maintained within the system while the methane is being generated. Using 1-naphthol, 98% of the theoretical amount of methane was obtained.

A white film of basic magnesium salt collects immediately below the neoprene stopper during a determination. The apparatus is easily cleaned by removing the neoprene stopper and the reaction flask and inserting pipe cleaners moistened successively with dilute hydrochloric acid, ethanol, and acetone.

The sampling system has been used for collecting gases for analysis and for obtaining samples of pure gaseous hydrocarbons. The injection of butyl magnesium chloride into heavy water, for example, yields a deuterated butane.

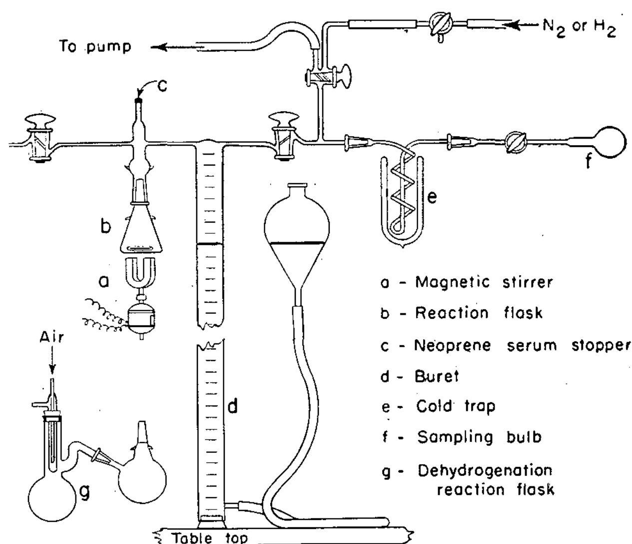


Figure 1. Apparatus for Measuring and Sampling Gases

QUANTITATIVE CATALYTIC HYDROGENATION

When the apparatus is used for hydrogenation, the Erlenmeyer flask described by Noller and Barusch (3) is used as the reaction flask. The apparatus and procedure then resemble those described by Joshel (1). To follow pressure changes and to facilitate leveling the buret, it is convenient to attach a small open-end manometer to the stopcock on the extreme left by means of rubber tubing. When p-nitrotoluene was hydrogenated with platinum oxide catalyst in this apparatus, the amount of hydrogen absorbed was 99% of the theoretical.

CATALYTIC DEHYDROGENATION

The reaction flask for the dehydrogenation is shown in *g*, Figure 1.

With the loaded reaction flask in place, the system is flushed with nitrogen, and the organic compound plus catalyst (palladium charcoal) is heated by means of a salt bath to a temperature at which there is rapid gas evolution or gentle boiling. The evolved gases are collected and measured.

A sample of *p*-cyclohexylanisole was quantitatively dehydrogenated in this apparatus. Because the nature of the evolved gas was of interest, a sample was taken by evacuating the sampling system, closing the stopcock to the pump, and slowly opening the stopcock to the buret. Mass spectrometric analysis of the gas sample showed a small quantity of methanol present, but no methane. This indicated that a portion of the evolved hydrogen was used for hydrogenolysis of the aromatic carbon-to-oxygen bond. This was confirmed by the isolation and identification of a small quantity of diphenyl in the reaction products. To keep traces of the more volatile compounds formed in the reaction flask from entering the sample bulb, it is probably better to use liquid nitrogen in the Dewar in place of the dry ice–acetone mixture which was used in this experiment. The rate of flow through the cold trap may be reduced by placing a negative pressure in the buret before the system is opened to the evacuated gas-sampling bulb.

The authors have used 25-ml. and 50-ml. reaction flasks and a 500-ml. buret in these three determinations, but there is no reason why the scale of the apparatus cannot be reduced for semimicro work. The apparatus can be used, of course, for any reaction in which the measurement of gas absorption or evolution is desirable. Thus, the quantity of oxygen absorbed by coal, the determination of lithium aluminum hydride, and the extent of reduction by this reagent can be measured in such an apparatus.

ACKNOWLEDGMENT

The authors are indebted to Charles Siple for the drawing.

LITERATURE CITED

(1) Joshel, L. M., Ind. Eng. Chem., Anal. Ed., 15, 590 (1943).
(2) Niederl, J. B., and Niederl, V., "Organic Quantitative Microanalysis," p. 263, New York, John Wiley & Sons, Inc., 1946.
(3) Noller, C. R., and Barusch, M. R., Ind. Eng. Chem., Anal. Ed., 14, 907 (1942).
(4) Pregl, F., and Grant, J., "Quantitative Organic Microanalysis," 4th English ed., p. 134, Philadelphia, Blakiston Co., 1945.

Received October 19, 1948.

All-Glass Filtration Apparatus for Radioactive Tracer Experiments

JACOB SACKS
Brookhaven National Laboratory, Upton, L. I., N. Y.

THE extensive use of radioactive isotopes in tracer experiments has resulted in the development of numerous specialized techniques for preparing the sample for measurement. Where the isotope can be obtained as a precipitate, this is filtered off on some device that serves as a sample holder for the radioactivity measurement. The apparatus described by MacKenzie and Dean (*3*) uses a sintered-glass disk filter stick on which are mounted a piece of filter paper and a glass tube. The filter paper is then transferred to a suitable sample holder. This method is somewhat complicated and requires a high degree of technical skill. The modified Büchner funnel technique of Armstrong and Schubert (*1*) is simpler to use, but the preparation of the sample holder is a rather involved process.

The use of the sintered-glass disk presented by a Pyrex Gooch crucible as a sample holder has many obvious advantages over such a filter paper technique, and has been adopted by many workers in the field. For use with either a thin-walled or end-window Geiger-Müller tube, the usual practice is to cut off the top two thirds of the upper portion of the stock 15-ml. capacity crucible with a 20-mm. diameter disk. This leaves almost 5-ml. capacity above the disk, and allows the sample to be placed within 15 mm. of the window of the counter tube.

When Gooch crucibles modified in this manner are used in the conventional way, by fitting them to filter tubes by means of Gooch tubing and filter tubes passing through rubber stoppers into suction flasks, the possibility of radioactive contamination of the rubber parts is always present. There is also considerable inconvenience in the frequent removal of the filter tube from the rubber stopper, which is required for the careful cleaning necessary for use with radioactive materials.

An all-glass apparatus has been devised which retains the advantages of the Gooch crucible technique and has the important added one that the parts may be readily separated and cleaned.

The essential unit consists of a filter tube equipped with a flat ground surface to receive the modified crucible, equipped with a standard-taper ground joint and side arm for attachment to a suction pump. The receiver is an Erlenmeyer flask fitted with a standard-taper ground joint neck. Size 24/40 ground joints are most convenient for this purpose. The lower edge of the crucible is ground to fit on the flat surface of the filter tube. The fit of the two ground surfaces is usually good enough so that no lubricant need be used. Occasionally a water seal has been found helpful. The filtration assembly is shown in section in Figure 1.

The dimensions of the modified crucible will be determined to a certain extent by the type of Geiger-Müller tube and lead shielding available. It will probably be necessary to make changes in the sample holder of any commercially available model so that it will accommodate the crucible. Those shown in the figure have an over-all height of 22 mm., and the distance from the top of the disk to the lower edge is 9.6 mm., with a tolerance of 0.05 mm. Such close tolerances are desirable for soft β-emitters, but for use with P^{32} a tolerance of 0.1 mm. is adequate. The crucibles used are selected for relative uniformity of disk diameter and also for exactness of the plane of the disk.

The distance of 15 mm. between the disk and the counter window is relatively unimportant in the case of high energy β-particles such as those from P^{32}. With soft β-emitters, such as C^{14} or S^{35}, the air absorption plus the reduction in solid angle resulting from this sample distance may reduce by about 50% the "geometry" of the counting system. For counting such isotopes, the adaptation of the methane flow proportional counter described by Bernstein and Ballentine (*2*) is very useful. This apparatus utilizes the full length of the Gooch crucible as the windowless counter chamber. The distance between the sample and the end of the center wire is approximately 3 mm.

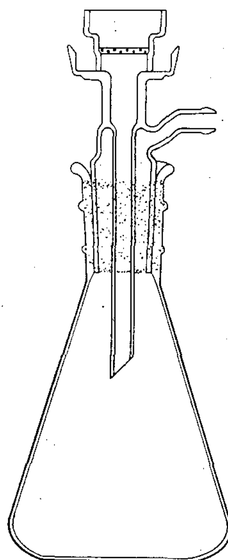


Figure 1. Sectional View of Filtration Apparatus

Although the filter tube described was designed primarily for use in radioactive tracer experiments, it is also useful for any ordinary gravimetric determination in which the Pyrex Gooch crucible can be used. For general analytical purposes, any stock crucible can be used, and needs only to have the lower end ground flat.

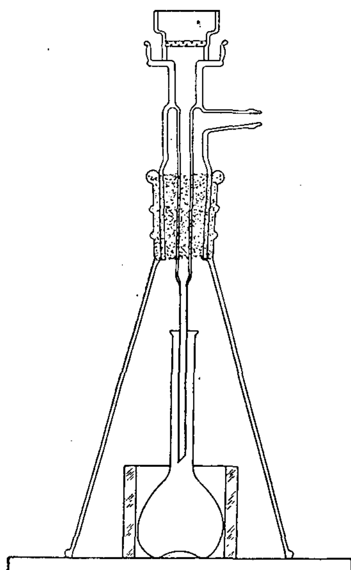


Figure 2. Sectional View of Assembly for Solution of Precipitate

The Gooch crucible technique is suitable for almost any radioactive isotope which is capable of yielding a precipitate in such physical form that it can be filtered off satisfactorily and form a uniform layer of material on the surface of the disk. In many cases slight modifications of standard gravimetric procedure are necessary to obtain such uniform distribution of the precipitate.

In the particular problem for which the apparatus was devised, phosphate containing P^{32} is precipitated as ammoniumphosphomolybdate. The well-known tendency of this precipitate to creep has been overcome by washing first with 5% ammonium nitrate to remove the nitric acid, and then with a 0.1% solution of Aerosol MA in 5% ammonium nitrate. Occasionally it is necessary to use a rubber policeman to facilitate washing the last traces of the precipitate down from the walls of the crucible onto the disk. The aerosol and ammonium nitrate are then washed out with ethanol, and the crucible and contents are dried in air. Other surface-active agents have been tried, but none was as satisfactory as Aerosol MA. Acetone has been used to wash out the salt and surface agent, but it tends to cause the precipitate to pile up unevenly over the surface of the disk.

The experiments in progress, which consist of a study of the relative turnover rates of the acid-soluble phosphorus compounds of liver, are such that it is more satisfactory to determine the radioactivity of the samples obtained before chemical determinations of their phosphorus content are made. The apparatus shown in Figure 2 has been devised to obtain quantitative solution of the phosphomolybdate precipitate.

The filter tube has been modified by making the terminal portion of tubing 4 mm. in outside diameter, to fit inside the neck of the 25-ml. volumetric flask used as receiver. The Lucite ring in which the flask sits serves to prevent the flask from tipping over when the filter tube is removed. The suction flask consists of a 500-ml. Erlenmeyer flask with standard-taper ground joint neck. The bottom is cut off and the edge ground flat to fit the ground-glass plate. A Pyrex bottle with ground joint neck could be used instead of the Erlenmeyer flask. The phosphomolybdate precipitate is dissolved by adding 1 ml. of phosphate-free 1 *N* sodium hydroxide, filtering by suction, and washing with successive small portions of water. The contents of the flask are then made up to the mark and suitable aliquots taken for the colorimetric determination of phosphorus.

As a test of the completeness of the solution process, duplicate aliquots of P^{32} phosphate solution containing about 10,000 counts per minute were taken, carrier phosphate was added, and the material was precipitated in the usual manner. After counting, the precipitates were dissolved by the usual technique, and the crucible was dried without any further washing and again counted. One crucible now gave 6, the other, 4 counts per minute above background.

The amounts of phosphorus encountered in the experiments range from 50 to 1500 micrograms. Known amounts of phosphorus as phosphate, within this range, were precipitated as phosphomolybdate and treated as described above. With 100 to 200 micrograms, the recoveries were between 98 and 100%.

LITERATURE CITED

(1) Armstrong, W. D., and Schubert, J., Anal. Chem., 20, 270 (1948).
(2) Bernstein, W., and Ballentine, R., *Rev. Sci. Instruments*, 20, 347 (1949).
(3) MacKenzie, A. J., and Dean, L. A., Anal. Chem., 20, 559 (1948).

Received September 13, 1948. Research carried out at Brookhaven National Laboratory under the auspices of the Atomic Energy Commission.

Modified Dumas Nitrogen Apparatus

WILLIAM K. NOYCE
University of Arkansas, Fayetteville, Ark.

THE volumetric determination of nitrogen in organic compounds as originally developed by Dumas has undergone many changes and refinements. The apparatus described here is not suggested as a substitute for the elegant equipment of the specialist, but rather as an inexpensive modification of conventional macroapparatus that may be easily assembled from common items usually found in the chemistry laboratory. It has given excellent results in the hands of inexperienced operators, and reduces the time required for the usual macroprocedure to approximately one half. The apparatus and procedure described by Fisher (*1*) served as the starting point around which the modifications were developed. The main features are a convenient carbon dioxide source, the use of a back-flush technique, and provision for cooling the combustion tube outside the furnace.

APPARATUS

The carbon dioxide source, which is shown diagrammatically in Figure 1, is assembled around a Kipp generator.

Air is prevented from coming in contact with the acid by connecting two 3.785-liter (1-gallon) bottles, *H*, to the upper bulb of the generator as indicated. This allows the acid level to rise and fall without drawing air into the Kipp generator. It is simpler than the use of a second generator as suggested by Niederl and Niederl (*5*), and it requires less attention than the system of mercury valves described by Hein (*3*) and by Trautz and Niederl (*7*). It is also less wasteful of carbon dioxide. The usual precautions are taken in setting up and charging the generator (*5*). (In using the procedure outlined by Niederl and Niederl, the Kipp generator should be evacuated with extreme care, for even the vacuum easily attained by a water-suction pump may be enough to collapse the generator. The broad, flat bottom of the lower section, obviously is not designed to withstand such pressures.)

The two bottles are filled with freshly boiled distilled water and then thoroughly flushed to displace the air with carbon dioxide. Every few days a small amount of carbon dioxide is allowed to pass into the upper bulb in order to ensure a sufficient volume in the trap. As there is always a positive pressure within the system, leakage of air into the apparatus is prevented.

In order to minimize the amount of hydrogen chloride and water in the combustion train, the carbon dioxide is bubbled through water and then through concentrated sulfuric acid. Because of fluctuations in the pressure in the Kipp generator at times the liquids in these traps tend to back up. To meet this situation the bottle of liquid is preceded in each case by an empty bottle with the outlet tube extending to the bottom, so that liquid which may have sucked back will be forced into the proper bottle again when the flow of gas is resumed. If the return tubes are of small diameter and in a vertical position, they tend to become partially filled with liquid, resulting in a very erratic flow of carbon dioxide. To prevent this, the return tubes are of large diameter (9 mm. in outside diameter), and they are bent to extend to the side of the bottom of the bottle. (The size and shape of these tubes are not indicated in the drawing.) Sometimes during a combustion that is not carefully controlled, the pressure in the combustion tube may temporarily exceed the pressure in the Kipp generator.

Under such circumstances a reversal of flow is prevented by the mercury check valve, *G*. The whole assembly is essentially foolproof and needs very little attention from the operator.

The arrangement of stopcocks shown in Figure 1 allows carbon dioxide to be passed into the combustion tube from either direction (*4*). *A*, *B*, *C*, *D*, and *E* are all three-way stopcocks of 2-mm. bore. By using the T type at *D* it is possible to flush out the by-pass tube between *A* and *D*, and to check the purity of the carbon dioxide by means of the azotometer, without involving the combustion tube. The by-pass is of glass tubing 6 mm. in outside diameter, connected to the stopcocks with short lengths of rubber tubing. This arrangement allows no "dead-end" pockets where unwanted gas could collect and later diffuse into other parts of the apparatus. The loops in the lines connecting the stopcocks indicate 250-mm. sections of rubber tubing which make it possible to remove the combustion tube from the furnace without disturbing any connections. The tubing is of the thick-walled type commonly used in combustion trains, and it is treated as usual to remove impurities and reduce porosity (*2*). Two buret clamps, attached to the front of the furnace, provide a place for the combustion tube while it is cooling and being reloaded.

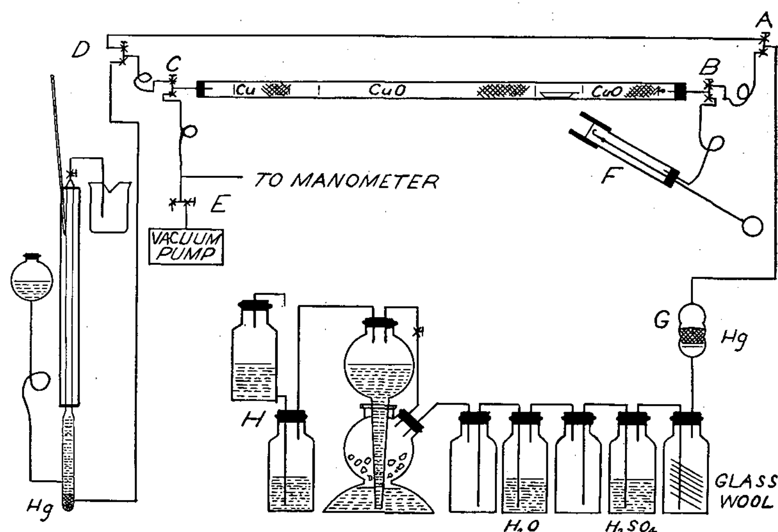


Figure 1. Modified Dumas Nitrogen Apparatus

The loading tube, *F*, is a 150-mm. section of an old combustion tube. A snug-fitting sleeve (made from a No. 8 rubber stopper) is slipped over the upper end, and the lower end is closed with a two-hole rubber stopper fitted with the inlet tube connected to stopcock *B*, and the wire hook. A small rubber plug is attached to the wire near the hook, so that the second hole may be closed when the hook is drawn back into the tube. A one-hole rubber stopper fitted with a short length of capillary tube is provided for the upper end. (This stopper is omitted in the diagram.) The use of the loading tube is explained below.

The usual azotometer arrangement has been altered only in detail. The azotometer used has a capacity of 33 ml. and is graduated in 0.1 ml., giving greater accuracy than the 100-ml. azotometers commonly available for the macroapparatus. A jacket is provided, and instead of a funnel at the top, an inverted U-tube is used with a beaker as shown in the figure. A vacuum pump and a manometer are attached as indicated. The furnace is like that described by Fisher (*1*), and the combustion tube is similar except that Pyrex brand glass No. 172 is used.

PROCEDURE

For the sake of brevity this discussion includes only those parts of the procedure that have been modified from that given by Fisher (*1*).

The copper oxide is placed in the tube and prepared for use by heating while the tube is alternately evacuated and flooded with carbon dioxide. For evacuation stopcock *B* is closed while *C* and *E* are turned to the appropriate positions for connecting the pump with the combustion tube. Before *B* is opened to admit carbon dioxide, *E* is closed. For re-evacuation these positions are again reversed; *B* is closed first. In this way a minimum of volume is involved and the pressure in the tube may be observed at all times. The copper gauze may be removed for reduction and reinserted in the usual manner; stopcocks *A* and *B* are turned to allow carbon dioxide to flow through the combustion tube while it is open.

After the apparatus has been prepared for the combustion, the sample is inserted. Stopcocks *A* and *D* are turned to allow carbon dioxide to flow through the by-pass and into the combustion tube from the left end by way of stopcock *C*. *B* is turned to allow the gas to escape through the loading tube, *F*. By keeping this tube in an approximately vertical position and closing the hole in the lower stopper where the wire passes through (using the plug on the wire), the air is displaced by the heavier carbon dioxide in 2 or 3 minutes. As soon as the stopper of the combustion tube is removed, the rubber sleeve of the loading tube is slipped over the end and the copper oxide spiral is withdrawn with the wire hook; the small rubber plug is used to close the hole in the stopper. The tube containing the spiral is then removed from the end of the combustion tube and the upper end is closed with a rubber stopper. Thus the spiral is left in a carbon dioxide environment while the sample is being placed in the combustion tube. (During all this time there is a back flow of carbon dioxide through the combustion tube.)

Then the loading tube is again connected to the end of the combustion tube and the copper oxide spiral is pushed into place. The carbon dioxide is allowed to sweep out the tube in the reverse direction for 2 or 3 minutes, after the stopper has been reinserted in the combustion tube, to prevent contamination of the rest of the filling. The combustion itself can proceed as soon as microbubbles are obtained.

Later tests have shown that the amount of time required to obtain microbubbles is not shortened appreciably by the use of the loading tube as described above. It would no doubt be more efficient if a continuous stream of carbon dioxide were passed into it during the change. Even then the saving in time is open to question. However, the use of the tube without any carbon dioxide is found to be advantageous, particularly for the inexperienced student. Ordinarily the copper oxide spiral is removed with a hook, often handled with tongs, and then it must be laid down while the sample is being inserted. The mechanical wear on the spiral, as well as the chances for contamination, is considerably less when the loading tube is used.

In starting the actual combustion the usual procedure (*1*) is to move one section of the furnace slowly over the sample. In many cases it was found more satisfactory not to move a section of the furnace during the first part of the combustion. Thus the copper oxide on each side of the boat remains properly heated. This leaves the part of the tube containing the boat exposed and heating is begun with a brush flame from a Bunsen burner. The combustion may be started more quickly without loss of control and a too rapid evolution of nitrogen is more easily averted. The large middle section of the furnace is moved over the boat for the final heating. The volume of nitrogen is observed while the gas is over the potassium hydroxide solution, and corresponding vapor pressure corrections are made. The apparatus may be calibrated for such errors as adhesion of the solution to the sides of the azotometer (*6*). A funnel is not needed at the top, as liquids do not have to be poured in from the top. By using the inverted U-tube and a beaker there is less danger of an overflow at the top and, if desired, any amount of solution may be removed from the top with ease. Approximately 1 ml. of potassium hydroxide solution (sufficient to prevent the entrance of air into the azotometer) is left above the stopcock during the entire time that nitrogen is being collected.

When two or more runs are to be made consecutively, a considerable saving in time is afforded by the fact that the combustion tube may be removed from the furnace as soon as the sweeping out is complete. Thus it can be cooling rapidly while the operator is waiting to take the reading of the azotometer. A small fan or a stream of air from a compressed air line may be used to hasten the cooling of that part of the tube containing the boat and the copper oxide spiral. No breakage of combustion tubes has resulted from this practice, and a determination of the cooling rate

Table I. Determination of Nitrogen

Substance	Nitrogen (Theory), %	1st Trial Nitrogen, %	1st Trial Error, 0/00	2nd Trial Nitrogen, %	2nd Trial Error, 0/00	Difference, 0/00
Anthranilic acid ($C_7H_7O_2N$)	10.22	10.18	4	10.21	1	3
Phenylhydrazine ($C_6H_8N_2$)	25.90	25.80	4	25.70	8	4
Aniline (C_6H_7N)	15.04	15.00	3	15.00	3	0
Benzamide (C_7H_7ON)	11.56	(A)11.49	6	11.56	0	6
		(B)11.50	5	11.41	13	8

with a Chromel-Alumel thermocouple placed in the center of the spiral showed a saving of from 6 to 8 minutes in the cooling period. The removal of the tube from the furnace also shortens the heating period, for all sections of the furnace may be kept at full heat while the boats are being changed. In this way the new sample may be inserted, the tube returned to the furnace, and the next run started within 15 minutes of the time that the sweeping is completed for the previous run. The reduced copper spiral lasts for several runs without any attention, and the copper oxide is sufficient for three or four runs before reoxidation is necessary.

Using the apparatus as described, and with the combustion tube previously prepared, four consecutive runs can be made in 4 hours or less. In some cases one determination has been completed in approximately 50 minutes. Samples smaller than those sometimes used for macroanalysis have been satisfactory—i.e., in the range of 0.10 gram or less. There is no apparent reason why the apparatus could not be adapted to the semimicro scale successfully.

The results shown in Table I indicate that the method is capable of sufficient accuracy. These data were obtained by students with no previous experience in the use of the Dumas apparatus. In each case only two determinations were made.

LITERATURE CITED

(1) Fisher, H. L., "Laboratory Manual of Organic Chemistry," 4th ed., pp. 341–70, New York, John Wiley & Sons, 1938.
(2) Gattermann, L., and Wieland, H., "Laboratory Methods of Organic Chemistry," 24th ed., pp. 56–7, New York, Macmillan Co., 1938.
(3) Hein, F., *Z. angew. Chem.*, 40, 864 (1927).
(4) Kirsten, W., Anal. Chem., 19, 925 (1947).
(5) Niederl, J. B., and Niederl, V., "Organic Quantitative Microanalysis," 2nd ed., pp. 79–82, New York, John Wiley & Sons, 1942.
(6) *Ibid.*, p. 95.
(7) Trautz, O. R., and Niederl, J. B., Ind. Eng. Chem., Anal. Ed., 3, 151 (1931).

Received March 22, 1948. Presented before the Division of Analytical and Micro Chemistry at the 113th Meeting of the American Chemical Society, Chicago, Ill.

Microdetermination of Total Carbon in Carbonates, Cyanides, and Alkali or Alkaline-Earth Organic Salts and Mixtures

J. R. LAFORCE, D. F. KETCHUM, AND A. E. BALLARD
Kodak Research Laboratories, Rochester, N. Y.

In the course of work on the microdetermination of carbon in alkali cyanides and carbonates containing C^{14}, it was found desirable to recover the carbon as barium carbonate for subsequent isotopic analysis in the mass spectrometer. It appeared that the use of the organic microcombustion apparatus and the collecting procedure of Dauben and co-workers (*1*) might offer a satisfactory method, provided that the cyanide or carbonate carbon could be liberated quantitatively and collected.

The use of sodium bisulfate to cover the sample in the platinum microcombustion boat proved to be a satisfactory solution to this problem, and some extensions of this procedure were made which showed that it is equally applicable to the estimation of carbon in organic salts of alkalies and for the estimation of total carbon in mixtures of organic and alkali or alkaline-earth carbonates and cyanides.

As the procedure is in effect a bisulfate fusion in an oxygen atmosphere, it should prove valuable with difficultly combustible organic substances.

Apparatus. A Hallett microcombustion apparatus (*3*) and tube filling with an automatically propelled pyrolysis furnace (*2*) at 750° ± 25° C. was used.

Procedure. A 5- to 20-mg. sample, or enough to give from 3 to 20 mg. of carbon dioxide, was weighed accurately into a platinum microcombustion boat and covered with approximately 60 mg. of powdered sodium bisulfate. The combustion was carried out in the normal manner, and the liberated carbon dioxide was absorbed in Ascarite. The Drierite tube must be placed between the combustion tube and the Ascarite absorption tube to absorb the water formed.

Discussion. The accuracy and precision of the method, as shown in Table I, were about as high as could be expected for the determination of organic carbon in this apparatus (*4*).

Table I. Determination of Carbon

Compound	Sample Taken, Mg.	CO_2 Found, Mg.	Carbon Found, %	Carbon Calcd., %	$NaHSO_4$ Added, Mg.
K_2CO_3	13.30	0.20	<1	8.7	None
	12.76	3.96	8.5		60
	15.73	5.07	8.8		
	14.34	4.51	8.6		
$CaCO_3$	13.24	5.89	12.1	12.0	None
	15.80	6.98	12.0		60
	12.52	5.53	12.1		
$BaCO_3$	15.20	0.380	<1	6.1	None
	15.78	3.60	6.2		60
KCN, 98.0%	14.01	2.60	5	18.4	None
	16.07	10.77	18.3		60
	14.03	9.41	18.3		
	13.40	8.95	18.2		
	14.16	9.54	18.4		
Na_2CO_3	16.20	0.10	<1	11.3	None
	16.22	[illegible].87	11.6		60
Potassium acid phthalate	9.04	15.10	45.6	47.1	None
	7.95	12.56	43.1		None
	7.59	13.16	47.3		60
	6.71	11.59	47.1		60
	8.42	14.61	47.4		60
Benzyl isothiourea hydrochloride	5.29				
Potassium carbonate	12.80	13.24	20.0	19.9	60

LITERATURE CITED

(1) Dauben, W. G., Reid, J. C., and Yankwich, P. E., Anal. Chem., 19, 830 (1947).
(2) Hallett, L. T., Ind. Eng. Chem., Anal. Ed., 10, 101–3 (1938).
(3) Hallett, L. T., in "Scott's Standard Methods of Chemical Analysis," 5th ed., Vol. II, pp. 2475–82, New York, D. Van Nostrand Co., 1939.
(4) Niederl, J. B., and Niederl, V., "Organic Quantitative Microanalysis," 2nd ed., p. 132, New York, John Wiley & Sons, 1942.

Received July 21, 1948. Communication 1208 from Kodak Research Laboratories.

Colorimetric Adaptation of Levvy Method for Arsenic

EVAN W. McCHESNEY

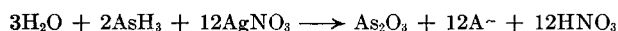
Sterling-Winthrop Research Institute, Rensselaer, N. Y.

THERE is no dearth of methods for the determination of arsenic in the minute quantities that are usually found in biological materials. Some of the most satisfactory methods are based on the distillation of arsenic as arsenic trichloride (*5, 9*) or arsenic pentabromide (*6*), or on carrying over the arsenic as arsenic trihydride in a stream of hydrogen (*1, 2, 4*). In spite of efforts at simplification, the procedures remain comparatively laborious, for they all involve the three distinct steps of digestion, distillation, and estimation (either titrimetric or colorimetric). Any changes that would lighten the work of the analyst would represent an improvement.

The method of Magnuson and Watson (*6*), as modified by Maren (*7*), leaves little to be desired from the point of view of precision and accuracy. Some analysts, however, prefer the method of Allcroft and Green (*1*) as modified by Levvy (*4*) because of its greater technical simplicity, even though it is not so precise. It does not claim to determine less than 5 micrograms of arsenic, whereas the Magnuson-Watson method can be applied if the quantity is as low as 1 microgram. An examination of the Levvy technique shows several points at which improvements are clearly desirable. Even if the quantity of arsenic present is fairly small (50 micrograms), the arsine formed from it cannot be quantitatively absorbed in one tube of silver nitrate solution of the specified strength. This necessitates routinely providing a second, or guard tube, and titrating it in case it appears to contain any appreciable amount of precipitated sliver. If the quantity of arsenic is fairly large (100 micrograms or more), a third tube may be needed. The presence of precipitated silver in the solution tends to render the delicate end point difficult to identify with confidence. The present work represents an attempt to eliminate these two difficulties.

An obvious means of increasing the arsine-absorbing capacity of a single tube of silver nitrate solution is to increase its concentration. Levvy used 1.5 ml. of 0.02 *N* solution in each receiving tube of the series. It has been found in this work that if 2 ml. of 0.1 *N* solution are placed in the receiving tubes, quantities of arsenic as high as 700 micrograms are absorbed in a single tube, and only a trace passes through. Furthermore, even 50 micrograms are not completely absorbed in a single tube unless this concentration is used. (In the procedure described, the working concentration of silver nitrate is actually only 0.05 *N*, or sometimes less, but the total amount used is always that given above.) Levvy apparently did not examine the possibilities of using a more concentrated solution on the ground that there was danger of oxidizing the arsenic to arsenate (*3*); indeed, indirect evidence (*1*) indicates that this occurs. However, in this work no evidence of such oxidation has been found.

In order to eliminate the final tedious titration, the metallic silver formed in the reaction



$$3H_2O + 2AsH_3 + 12AgNO_3 \longrightarrow As_2O_3 + 12A- + 12HNO_3$$

is oxidized as rapidly as it is formed by having present an excess of a standard solution of ceric sulfate. The amount of the excess is then determined colorimetrically along lines suggested by the work of Sendroy (*8*). The reaction consumes 6 equivalents per mole of arsenic, which is an advantage over the 2 equivalents consumed in the iodine titration of the original Levvy method.

SOLUTIONS AND EQUIPMENT

Solutions Required. Biological materials are first prepared by wet oxidation as described by Levvy (small scale process), and his reagents for this purpose are required, as well as the following:

Stannous chloride, 40% solution in 5% hydrochloric acid
Sodium hydroxide, 40% solution
Silver nitrate, 0.1 *N* (approximately 1.8%)
Sulfuric acid, approximately 1 *N* solution
Sulfuric acid, 20 volumes % solution, specific gravity, 1.17
Ceric sulfate, 0.1 *N*

[Approximately 11 grams of ceric sulfate [$Ce(HSO_4)_4$] are dissolved in 200 ml. of 1 *N* sulfuric acid, titrated against 0.1 *N* thiosulfate, and then diluted exactly to 0.100 *N* with 1 *N* sulfuric acid. Such a solution is known to be stable for as long as 40 weeks (*11*). From this stock solution 0.01 and 0.002 *N* working concentrations are prepared daily by dilution with 1 *N* sulfuric acid. A method for preparing these weaker solutions in a stable form has been described by Weybrew, Matrone, and Baxley (*10*).]

Standard Arsenic Solution. A convenient concentration is 500 micrograms per ml. Weigh accurately into a 1-liter volumetric flask 660 mg. of C.P. arsenious acid and dissolve it in 100 ml. of 1 *N* sodium hydroxide. Dilute to about 800 ml. with water, add 100 ml. of 1 *N* sulfuric acid, and dilute to the mark with water. From this stock solution prepare working concentrations of 10 and 100 micrograms per ml.

Equipment. Each unit consists of generating flask, wash tube, and receiving tube. The generating flasks are 125-ml. Erlenmeyer flasks with 24/40 ₮ necks. The adapters which fit into the neck of these flasks have outlet tubes bent at right angles, about 5 cm. (2 inches) long (see, for example, Ace Glass Co. catalog No. 5205). The gas is passed through a washing solution which consists of 1.5 ml. of 40% sodium hydroxide; this solution is renewed after about a dozen determinations. It may be placed in a 15-ml. centrifuge tube with attached side arm (see Figure 1). The gas is led in through a glass delivery tube which has an internal diameter of about 0.5 to 1 mm. at the tip. The delivery tube is inserted in the rubber stopper in such a way that the tip will come as nearly as possible to the bottom of the wash tube. The outlet from the wash tube is connected to the delivery tube of the receiver. The receiving tube has the same construction as the wash tube, but is accurately calibrated at the 10-ml. mark (Figure 1). Four units may be set up in one test tube rack. If duplicate generating flasks and receiving tubes are available, as many as 36 determinations may be completed in a working day, exclusive of the digestion step, with this equipment.

PROCEDURE

Charge the receiving tube with 2 ± 0.1 ml. of 0.1 *N* silver nitrate and exactly 2.00 ml. of ceric sulfate (either 0.01 *N* or 0.002 *N*, depending on the amount of arsenic estimated to be present—i.e., whether more or less than 100 micrograms). Measure into the generating flask the sample to be analyzed (usually in 20 volume % sulfuric acid, after wet oxidation), and enough 20 volume % sulfuric acid to bring the volume to 50 ml. (Small-scale digests, in 10 ml. of concentrated sulfuric acid, may be transferred to the generating flask with the aid of enough distilled water to bring the volume up to about 50 ml., or the digestion may be carried out directly in Kjeldahl flasks with ₮ necks.) Add 3 drops of stannous chloride solution, and about 8 grams of C.P. granular zinc, 30-mesh (low in arsenic, lead, and iron). Add the zinc through a wide-mouthed funnel, so that particles will not stick in the neck of the flask. Connect quickly to the adapter. Allow the generation of hydrogen to continue until it practically stops (about 35 minutes),

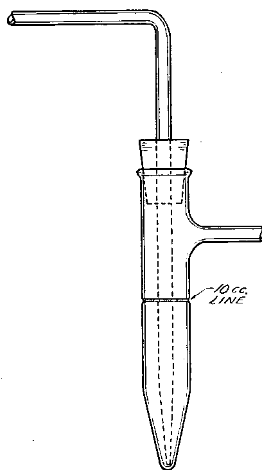


Figure 1. Design of Wash Tube and Receiving Tube

Only receiving tube need be calibrated at 10 ml.
One third actual size

then disconnect the generating flask and the receiver. (If the ceric sulfate becomes completely decolorized during the generation process and metallic silver begins to precipitate, add carefully, while keeping the delivery tube well below the surface of the solution, another 2-ml. portion of the ceric sulfate. It is not urgent that this addition be made as soon as the decolorization occurs, for there is always a large excess of silver nitrate, and the metallic silver will react quickly when more of the oxidizing agent is added. If the amount of arsenic is very large, the addition of even a third 2-ml. portion of ceric sulfate may be necessary, but more than this is not practicable, and it is then better to repeat the determination on a smaller aliquot.)

Remove the delivery tube from the receiver after making sure that all metallic silver both inside and outside the tube have reacted. Wash the delivery tube down with a little 1 N sulfuric acid, and dilute to the 10-ml. mark with more acid. (The delivery tubes which lead into the receivers should be cleaned occasionally by dipping in concentrated nitric acid, followed by washing in distilled water.) Centrifuge briefly to ensure absolute clarity, and read in the Evelyn colorimeter as described below.

Table I. Recovery of Arsenic Added as As_2O_3, Carried through Arsine Distillation Only

Arsenic Added, γ	No. of Trials	Ceric Sulfate Added, ml.	Ceric Sulfate Reduced, av., ml.	Arsenic Found, Av. ± Standard Error, γ
A. Using 0.002 N ceric sulfate in receiver				
0	4	2.0	0.07	1.8 ± 0.5
5.0	12	2.0	0.276	6.9 ± 1.8
12.5	8	2.0	0.584	14.6 ± 2.0
25.0	12	2.0	1.116	27.9 ± 2.0
50.0	8	3.0	2.076	51.9 ± 1.1
100.0[a]	11	5.0	3.96	99.0 ± 2.1
B. Using 0.01 N ceric sulfate in receiver				
100.0	10	2.0	0.83	103.8 ± 4.9
150.0	8	2.0	1.22	152.5 ± 5.5
200.0	22	2.0	1.58	197.5 ± 3.0
300.0[a]	4	4.0	2.39	298.8 ± 6.0
378.6	4	4.0	3.04	380.0 ± 4.9
500.0	7	5.0	3.94	492.5 ± 1.4
700.0	8	6.0	5.49	685.5 ± 6.3

[a] Quantities of arsenic that required more than 2 ml. of standard solution initially were run by putting 2 ml. of ceric sulfate in receiver, then adding further amounts when metallic silver began to precipitate.

Calibration of Colorimeter. The calibration of the instrument simply involves setting up dilution series for the two standard solutions. The reaction can always be arranged so that the excess of ceric sulfate is not more than 2 ml.; hence only this range need be covered in the calibration.

Measure into tubes (graduated accurately at 10 ml.) 2 ml. of 0.1 N silver nitrate and quantities of 0.01 N ceric sulfate ranging from 0 to 2 ml. in steps of 0.2 ml. Dilute each to the mark with 1 N sulfuric acid and read in the Evelyn colorimeter, setting the galvanometer at 100 with the solution containing no ceric sulfate, and using the 420 filter. Convert the readings so obtained to optical densities and plot them, on large graph paper, against milliliters of ceric sulfate solution present. The smooth curve which is obtained is not a straight line, but deviates from linearity at its mid-point by about 27%. The optical density for 2 ml. of ceric sulfate is about 0.77.

Table II. Recovery of Arsenic Added to Typical Biological Materials

Arsenic Added[a], γ	Arsenic Found, ±S.E., γ: A. Urine[b]	Arsenic Found, ±S.E., γ: B. Feces[c]
0	1.4 ± 0.8	1.5 ± 1.0
10	11.6 ± 0.9	12.3 ± 0.8
20	22.1 ± 1.3	23.9 ± 0.4
40	40.6 ± 3.2	41.8 ± 1.2
80	79.1 ± 1.7	78.6 ± 2.2
200	196.6 ± 2.7	194.0 ± 4.0

[a] As As_2O_3.
[b] 25-ml. samples digested with 20 ml. of concentrated sulfuric acid and nitric acid, excess nitric acid boiled off, and digest made up with water to 100 ml. 20-ml. aliquots taken for analysis in quadruplicate. Amounts of arsenic in digests were therefore five times those shown in table.
[c] 4 grams of dry rat feces digested with 20 ml. of concentrated sulfuric acid and nitric acid, finishing with nitric-perchloric acid mixture. Excess nitric acid boiled off, and digest made up with water to 100 ml. aliquots of 20-ml. were taken for analysis, with amounts of arsenic in whole digests again five times those shown in table.

Proceed in the same way to calibrate the instrument for the 0.002 N solution of ceric sulfate, but use the 375 filter. The curve of optical densities so obtained deviates from a straight line by about 31% at its mid-point, and the optical density for 2 ml. of ceric sulfate is about 0.94.

Calculation of Results. From the observed optical density of an unknown, determine the corresponding amount of unused ceric sulfate. Subtract this amount from the total which was put in the receiver (usually 2 ml., but occasionally more), and multiply by the factor 125 for 0.01 N ceric sulfate or by 25 for 0.002 N. This gives the result as micrograms of arsenic in the aliquot used. Subtract the value of a blank determination run on the reagents.

Results. Typical values obtained with this procedure are given in Table I. The weaker solution of ceric sulfate gives more precise results. Because arsenic is determined by difference, the absolute error remains the same regardless of the amount present. This means that the percentage error increases in inverse proportion to the amount of arsenic found. The percentage error is within the usual limits of colorimetric methods, however, except when the amount of arsenic is less than 50 micrograms. Below this amount the absolute error remains small, but becomes increasingly important on a percentage basis. Recoveries of arsenic from typical biological materials are given in Table II.

Working Precautions. Fallaciously high results are not to be expected from this procedure. Low results must be particularly guarded against, and may arise from two causes:

A poor-fitting ⊤ joint on the generating flask. A fragment of zinc lodged in the neck is the usual cause. To avoid this the neck of each flask should be cleaned routinely with a dry cloth before each use, and stopcock lubricant should be applied frequently to ensure an absolutely air-tight connection.

Incomplete oxidation of the precipitated silver because too small an excess of ceric sulfate is present. In this case another 1-ml. portion may be added and, after making sure that the oxidation reaction has been completed, the result read as usual. A situation of this sort might arise, for example, when 0.002 N ceric sulfate is being used and the amount of arsenic is between 40 and 50 micrograms.

DISCUSSION

In addition to the two improvements in the Levvy procedure which have been pointed out, a third improvement consists of using a different process for the generation of hydrogen. The generation is started at room temperature, rather than at 50° C., and the initial rate is low, when the concentration of arsine is high. The rate of evolution of hydrogen continues to rise steadily for 8 or 9 minutes (by which time the concentration of arsine has become low), then falls off gradually for about the next 30 minutes. Each generation, therefore, follows almost exactly the same pattern. These circumstances guarantee that the liberation and absorption of arsenic will be reproducible and practically quantitative, providing the apparatus is perfectly set up.

It may not, in all cases, be possible to decide in advance whether more or less than 100 micrograms of arsenic is present. In this case the 0.002 N solution of ceric sulfate should be used to charge the receiver. If it is decolorized very rapidly (within a minute) and silver begins to precipitate, the amount of arsenic is too large to be determined with this solution. One should now add 2 ml. of the 0.01 N solution and, if necessary, still another 2-ml. portion. When the calculation is made the amount of ceric sulfate added is calculated as 2.4 or 4.4 ml. of 0.01 N solution, and the subsequently determined excess of 0.01 N is subtracted from this. In this manner an amount of arsenic up to about 500 micrograms can be accurately determined, even though it was expected in advance that less than 100 micrograms would be found. Thus, only in the unusual circumstance that the amount of arsenic exceeds 500 micrograms is a repetition of the determination necessary.

The colorimetric readings may be reserved for a time when a dozen or more are available to be read at once. Some economy of reagents is effected, since the Levvy method requires about 1 gram of potassium iodide for each determination whereas the present method requires none.

The results tend to be lower than the theoretical when the amount of arsenic is 200 micrograms or more, particularly when the blank correction is subtracted. No method has been found which will correct this difficulty consistently. Allcroft and Green also found the results to be about 3% low with amounts of arsenic of this order.

SUMMARY

The Levvy method for arsenic determination has been simplified in two respects: A greater concentration of silver nitrate is used, so that as much as 700 micrograms of arsenic may be absorbed as arsine in a single receiver; and the quantity of liberated metallic silver is determined by oxidizing it with an excess of a standard solution of ceric sulfate, the excess of which is determined colorimetrically. Quantities of arsenic ranging from 0 to 100 micrograms may be determined with an average standard error of 1.8 micrograms. Quantities ranging from 100 to 700 micrograms may be determined with an average standard error of 4 micrograms.

LITERATURE CITED

(1) Allcroft, R., and Green, H. H., *Biochem. J.*, **29**, 824 (1935).
(2) Cassill, C. C., and Wichmann, H. J., *J. Assoc. Offic. Agr. Chemists*, **22**, 436 (1939).
(3) Kiese, M., *Arch. Exptl. Path. Pharm.*, **186**, 360 (1937).
(4) Levvy, G. A., *Biochem. J.*, **37**, 598 (1943).
(5) Maechling, E. H., and Flinn, F. G., *J. Lab. Clin Med.*, **15**, 779 (1930).
(6) Magnuson, H. J., and Watson, E., Ind. Eng. Chem., Anal. Ed., **16**, 339 (1944).
(7) Maren, T. H., *Ibid.*, **18**, 521 (1946).
(8) Sendroy, J., Jr., *J. Biol. Chem.*, **144**, 243 (1942).
(9) Sultzaberger, J. A., Ind. Eng. Chem., Anal. Ed., **15**, 408, (1943).
(10) Weybrew, J. A., Matrone, G., and Baxley, H. M., Anal. Chem., **20**, 759 (1948).
(11) Willard, H. H., and Young, P., *J. Am. Chem. Soc.*, **51**, 151 (1929).

Received August 25, 1948.

CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology

20. γ-Hexachlorocyclohexane (Gammexane, Benzene Hexachloride)

THE gamma isomer is one of the most important of the isomers of hexachlorocyclohexane because of its use as an insecticide. Crystals of this isomer may occur in any one of three polymorphic forms, although only rapid cooling of most solutions will give the unstable forms. Most normal recrystallizations if not carried out too rapidly will give the stable modification (I) described below. Slade (*3*) has published a useful table of solubility date for the isomers of hexachlorocyclohexane.

Good crystals of γ-hexachloride (I) are obtained from any of the common solvents.

Crystal Morphology (determined by W. C. McCrone).
Crystal System. Monoclinic.
Form and Habit. Plates and tablets on the basal pinacoid {001}; other forms are: prisms {110}; orthopinacoid {100}; and clinopinacoid {010}.
Axial Ratio. $a:b:c = 1.51:1:1.35$.
Interfacial Angles (Polar). $110 \wedge \bar{1}10 = 108° 20'$.
Beta Angle. 109°; 121 (*4*).
X-Ray Diffraction Data (determined by J. Whitney and I. Corvin).
The powder lines reported here agree with the unit cell and space group determined by van Vloten *et al.* (*4*). It is interesting to note that the forms observed for this crystal are isomorphous with a "unit cell" (a', b', c'; β equals 109 degrees), centered on the a'-c' face, and having twice the volume of the simplest primitive unit cell. The axes of this "morphological unit cell" are related to those of the primitive cell by the vector equations: a' equals $2a$ plus c; b equals b'; c' equals c. It is felt that, because this crystal habit occurs in crystallization from a great variety of solvents, it will better suit the needs of the analyst to describe the morphology and crystal optics in terms of the morphological unit cell.
Space Group. $P2_1/c$ (*4*).
Cell Dimensions. $a = 15.43$ Å.; $b = 10.24$ Å.; $c = 13.85$ Å. $a = 8.5$ Å.; $b = 10.3$ Å.; $c = 13.9$ Å. (*4*).
Formula Weights per Cell. 8; 4 (*4*).
Formula Weight. 290.85.
Density. 1.87 (flotation) 1.88 (x-ray).
Optical Properties (determined by W. C. McCrone and A. Underwood).

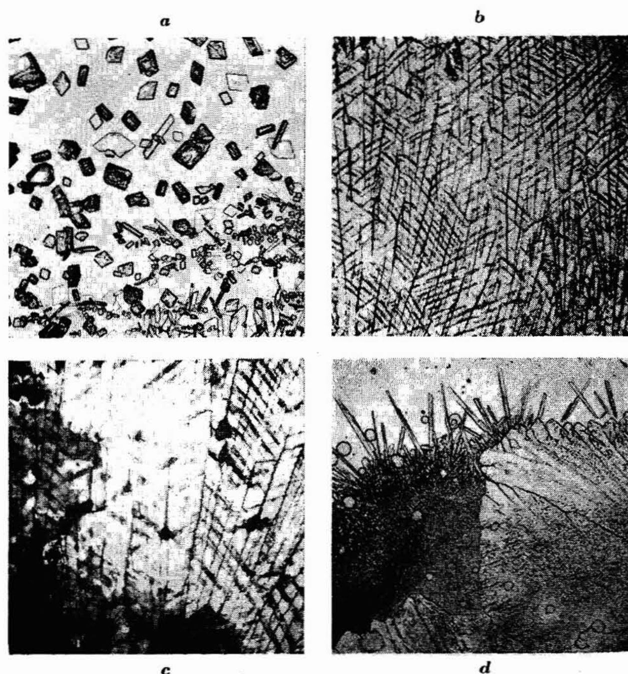


Figure 1. Hexachlorocyclohexane

a. Crystals of modification I from thymol
b. Modification of pseudomorphs of III after solid-solid transformation, showing characteristic herringbone pattern
c. Modification I (*lower left*) growing through II pseudomorphs of III at room temperature
d. Thymol mixed fusion of I (*right*) and II (*left*). The rods growing into the thymol are II; the larger crystals on the right are I. The transformation is progressing through the solid state in the lower left and through the solution phase in the upper right

Refractive Indexes (5893 Å.; 25° C.). $\alpha = 1.630 \pm 0.002$; $\beta = 1.633 \pm 0.004$ (calcd.); $\gamma = 1.644 \pm 0.002$.
Optic Axial Angles. (5893 Å.; 25° C.). $2V = 55°$; 65° (*1*) $2H = 60°$.
Dispersion. Very slight, $v > r$.
Optic Axial Plane. ⊥010.
Sign of Double Refraction. (+).

Acute Bisectrix. γ.
Extinction. $\alpha \wedge c = 10°$ in acute β.
Molecular Refraction (R) (5893 Å.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.636$. R (calcd.) = 56.9. R (obsd.) = 55.7.

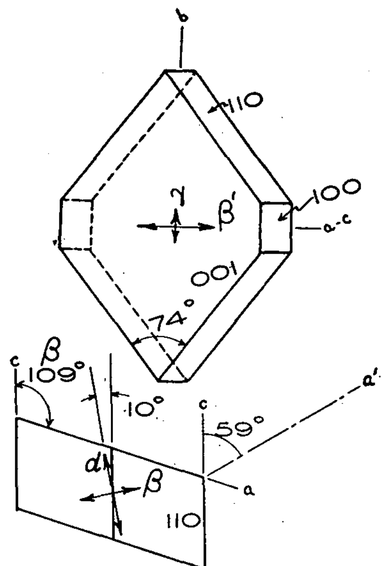


Figure 2. Typical Crystal of γ-Hexachlorocyclohexane (I)

Broken line labeled a is the a axis of van Vloten (4). The b and c axes are identical with the two different choices of axes

Fusion Data (determined by W. C. McCrone).

Hexachlorocyclohexane melts at 114° C. with a slight tendency for sublimation. This compound shows three polymorphic forms when crystallized from fusion. If fused completely and allowed to cool spontaneously either on a cool surface or in air, form III crystallizes very rapidly as low birefringent (usually first order white) rods. Within a few seconds a second modification (II) grows across the field by one of two mechanisms: at high temperatures (above 50° to 60° C.) the new modification nucleates spontaneously at many points throughout the field to give smoky patches; at lower temperatures form II grows more slowly and with a "herringbone pattern" (see Figure 1, b). On rewarming, this transformation reverses at about 90° C. Form II has very low birefringence (first order gray).

If the melt is seeded with room temperature-stable form I, higher birefringent plates and rods will grow rapidly, although often if the temperature is low enough, Form III will nucleate at the crystal front of I and two fronts will then grow simultaneously: melt → III; III → I. Occasionally if the slide temperature falls to about 30° before crystallization is complete the transformation of III → II will occur. Modification I will grow rapidly through III but much more slowly through II (Figure 1, c). The rate of II → I is nearly zero at room temperature. On reheating in a hot stage this transformation (II → I) increases in rate to about 90° C., when it increases discontinuously because II → III. The rate of III → I then decreases on further heating and reverses at 113.8° C. Form I then melts at 114.2° C. and Form III at 114.3° C.

Principal Lines

d	I/I_1	d	I/I_1
6.55	0.21	2.48	0.06
5.89	0.26	2.40	0.24
5.50	Very weak	2.35	0.29
5.08	0.21	2.29	0.13
4.68	Very weak	2.19	0.22
4.34	0.21	2.17	Very weak
4.19	0.12	2.12	0.16
4.01	0.12	2.10	Very weak
3.88	0.09	2.04	0.09
3.67	0.29	1.99	Very weak
3.50	0.24	1.97	Very weak
3.41	1.00	1.94	0.13
3.26	0.18	1.89	0.14
3.14	0.47	1.83	0.12
3.10	0.32	1.79	0.15
3.01	0.21	1.75	Very weak
2.93	0.15	1.724	Very weak
2.91	0.09	1.717	Very weak
2.78	0.50	1.69	Very weak
2.70	0.06	1.67	Very weak
2.61	0.32	1.64	0.12
2.55	0.24	1.60	0.15

Kauer (2) reports x-ray powder data in agreement with that given herewith.

LITERATURE CITED

(1) Daasch, Anal. Chem., **19**, 779 (1947). Crystallographic data by O. S. Tuttle.
(2) Kauer *et al.*, *Ind. Eng. Chem.*, **39**, 1335 (1947).
(3) Slade, *Chem. and Ind.*, **1945**, 315.
(4) van Vloten *et al.*, *Nature*, **162**, 771 (1948).

Symposium on Fine Particles and Resolution

F. A. HAMM, *General Aniline & Film Corporation, Easton, Pa.*

The second symposium sponsored by the Armour Research Foundation of the Illinois Institute of Technology and the Physics Department of the institute was held on June 9, 10, and 11 at the Stevens Hotel, Chicago, Ill. The meeting was known as a Symposium on Fine Particles and Resolution. Approximately 225 people attended.

The philosophy of the meeting was unique in that formality was held to a minimum. In general, experimental results, new instruments, new techniques, and theories were briefly presented by invited experts who formed a panel. This was followed by informal discussions between members of the panel, including active participation by the audience. The Armour Research Foundation and its Physics Group deserve much credit for successfully promoting this novel type of scientific meeting. The consensus of opinion suggests that the purpose of the symposium was achieved.

Although the term "resolution" may be defined and is interpreted in various and sundry ways, depending upon the instrument or principles utilized by the investigator, there is no real distinction between macromolecules and small particles. This is borne out when one examines the three major topics considered at the symposium: formation and characterization of fine particles, light scattering, and microscopy of fine particles. It is an obvious consequence that dimensions varying from a few Ångströms to several microns were under consideration. The success of the meeting was largely due to the efforts of the recognized authorities, who, acting as chairmen of their sessions, coordinated the question and discussion periods. Herman F. Mark of the Polytechnic Institute of Brooklyn served as chairman of the first session. The second session was conducted under the chairmanship of Peter J. W. Debye of Cornell University. Because of the corroborative nature of light and electron microscopy, it was perhaps only natural that C. W. Mason of Cornell University and R. C. Williams of the University of Michigan should serve as cochairmen of the third session. The discussions were well balanced because the invited members of the discussion panels represented both academic and industrial laboratories.

The first session on the formation and characterization of fine particles exemplified the fusion of theory and practice. Polymerization by means of addition, polycondensation, and vulcanization was treated from the standpoints of reaction kinetics and statistics. Several interesting points were made clear. The kinetics approach to polymerization becomes extremely cumbersome because of the tremendous number of different-size reactants (radicals). For this reason the statistical approach using probability functions now appears to be in better usage. Perhaps the

biggest obstacle encountered in the determination of macromolecule molecular weights is the ability to isolate clean, narrow product fractions. Much progress is yet to be made in overcoming this experimental difficulty. The speculation that polystyrene, presumably a linear polymer, might be cross-linked was also of interest. The relationships between molecular weight and the type of polymerization, number of functional groups, catalyst content, viscosity of medium (diffusion rate), etc., were all considered primarily from the theoretical point of view.

Data and theory for the techniques employing the ultracentrifuge and sedimentation rates were also presented. The particle shape and diffusion rate are apparently not important factors in the latter technique. Inhomogeneities, size, and concentration are, however, significant factors.

The technique used to make monodispersed sulfur sols having particles with a diameter of 1400 Å. ± 5% is finding useful applications in the preparation of other molecular compounds. The critical limit of supersaturation, in either liquid or vapor phase (aerosols) is the most important aspect in this problem. The primary particles (nuclei) must get closer than 2 or 3 Å. in order for molecular forces to overcome the electrostatic repulsive forces so that "aggregates" may form. The light-scattering technique (light intensity ratio for 4000 Å. light against time) is used to follow the reactions leading to these monodispersed systems. The monochromaticity of the scattered beam (Tyndall) is a measure of particle size uniformity—for example, the addition of 10% of particle A having a radius 2% larger than particle B is readily detectable, demonstrating the usefulness of the light-scattering technique.

The session on light scattering was virtually all-inclusive and left very little unsaid. The theory was reviewed, but the main theses consisted of new applications, instruments, and testing the theories by analyzing relatively large particles. It was a pleasant surprise to learn that the size of monodispersed polystyrene latex particles agreed very well with the value (ca. 2500 Å.) previously determined in the electron microscope.

Not unlike other physical methods of analysis, the investigator must take full cognizance of many details both instrumental and theoretical. In so far as light scattering is concerned, when differential refractometry or turbidity is utilized, the effect of wave length and concentration must be taken into account. In general, for particle size measurements, as the particle size increases, it becomes imperative to use longer wave-length radiation. The infrared, therefore, is best for particles in the 4000 Å. range. Furthermore, the weight average particle diameter is always calculated from light-scattering data.

This session was concluded by discussing low-angle x-ray scattering in solids.

The last session was devoted to the light and electron microscopy of fine particles. Discussions on resolution, magnification calibration, accuracy of size-frequency data, etc., were the natural consequence of the main subject. It would seem that more precise information including more specific details might have been in order. Presumably the discussions consisted mainly of generalizations rather than specific details because the audience contained both light and electron microscopists. Perhaps a few specific particle size problems which would demonstrate the effective overlapping of both instruments might have served a useful purpose.

The effects of lens aberrations, apertures, depth of field, conditions of illumination, stray magnetic fields, vibration, cleanliness, specimen preparation technique, etc., were discussed as related to the particular instrument. One fact stands out in bold relief—the monochromaticity of the electron is of tremendous significance in minimizing chromatic aberration, which is a constant thorn in the side of the light microscopist.

The vitally different phenomena which give rise to the images in the light and electron microscope were also discussed. A clear understanding of the mechanisms resulting in these imageries is fundamental to the intelligent use of both instruments. Thus, the roles of diffraction, reflection, refraction, and absorption in the formation of the light microscope image were stressed. Only the scattering of the electron by the specimen is the significant factor in the formation of electron microscope images.

In one respect the light microscopist still holds the ace card—namely, many electron microscopists prefer to base their magnification calibration on a calibrated light microscope image. However, experience also suggests that replicas of diffraction gratings (preferably 15,000 lines per inch) may be used to calibrate the electron microscope with a reproducibility of a few per cent.

Although it may at first appear paradoxical, it develops that electron microscope lenses are of such extreme high quality from the standpoint of spherical aberration that further improvement is perhaps undesirable, and at present a well focused image of a thin specimen reveals very little. More practical considerations concerning specimen drift, specimen contamination, power supply stability, etc., will aid the electron microscopist in realizing better resolution.

Perhaps a subject of vital interest to all microscopists is that of representative sampling, counting, and measuring from the statistical point of view, in either particle size or morphological studies. A more critical discussion of this subject might have been desirable.

The symposium was novel in its nature from the standpoints of subject matter and informality. It can perhaps be described as a successful experiment. It is hoped that a new precedent has been established.

BOOK REVIEWS

Methods of Quantitative Micro-Analysis. Collected and edited by *R. F. Milton* and *W. A. Waters.* viii + 599 pages. Longmans, Green & Co., Inc., 55 Fifth Ave., New York, N. Y., 1949. Price, $15.

The editors state that, as a consequence of their wartime experience, they have planned a fairly comprehensive survey of modern microanalytical techniques, and invited specialist contributions from practicing analysts well conversant with the inherent laboratory procedures, and difficulties, of each branch of the subject. They claim that they have checked each section from the standpoint of the practical worker at the bench. It seems permissible to conclude that actual testing of the recommended procedures by the contributors is not necessarily implied.

In the definition of microanalysis the editors take the catholic point of view, and one half of the book is consequently dedicated to colorimetry, nephelometry, fluorometry, polarography, amperometric titration, and conductometric titration. The theoretical foundations are briefly outlined in each section, followed by the description of a selection of apparatus and a choice of applications, some in table form and some supplied with working directions. A large fraction of the examples of application has been taken from the field of biochemical assay, and the same tendency is apparent in the discussion of the development of microanalysis.

Less than 10% of the book (pp. 11–54) is given to Part I dealing with gravimetric apparatus and general microchemical techniques and containing sections on dialysis, ultrafiltration, and organic reagents. The discussion of errors in weighing is unsatisfactory. The directions for observing the deflection of the microchemical balance are contrary to good practice. The use of lead shot in the preparation of tares has been abandoned by a number of microanalysts, and filter sticks are neither brushed before weighing (p. 17) nor used for stirring rods (p. 21). The relatively large amount of space given to description of work with micro Gooch crucibles could have been better used for copious references to the literature on filtration in quantitative microanalysis.

Part II, on ultimate analysis of carbon compounds and determination of molecular weight and functional groups (pp. 55–126), has been contributed by Ingram and Waters. For the determination of carbon and hydrogen, the authors seem to prefer Ingram's boat filling to Pregl's universal filling of the combustion tube. In general, they follow Continental rather than American trends, which should make this chapter interesting reading for the American specialist.

For Part III, on volumetric analysis (pp. 127–218), the editors had the cooperation of K. M. Wilson. The theory of redox titration has been made somewhat confusing by assuming that a "normal" hydrogen electrode is inserted into the titrated solution. It then seems to follow as a general rule that "the oxidation potential of a solution decreases as its acidity decreases." A reasonable selection of volumetric apparatus is described, and a number of applications are discussed.

R. F. Milton is the author of Part IV (pp. 219–403) dealing with colorimetry, nephelometry, and fluorometry. Of the photoelectric instruments only the Evelyn photometer, the Morris photometer, and the Hilger Spekker absorptiometer are described. Detailed procedures are given for the estimation of metals, acid radicals, a large number of organic compounds, and gases and vapors. Procedures are outlined for the analysis of steel, aluminum alloys, blood, and water, and for the determination of normal mineral constituents of foods as well as the estimation of heavy metals in foods and drugs.

J. T. Stock, author of Part V on electrochemical methods of microanalysis (pp. 405–503), treats in a concise manner potentiometry, polarography, electrodeposition, coulometric analysis, and conductometric analysis. Emphasis is placed on theory and special equipment; examples of application are for the larger part listed in table form with references to the literature.

Part VI on gasometric methods of microanalysis (pp. 505–578) by K. M. Wilson, presents a brief but reasonably adequate description of a cleverly selected choice of methods. The techniques of Blacet and Leighton, T. C. Sutton, and R. Spence, and the glycerol-entrained bubble method applied to the analysis of gas bubbles in glass are described for the purpose of gas analysis. The techniques of Van Slyke (26 pages), Warburg, and Barcroft are suggested for manometric methods of microanalysis. Five tables and two graphs for use with the Van Slyke apparatus are appended.

The book contains no author index, but there are indexes on scientific principles and general techniques, microchemical apparatus, reagents, inorganic analysis, and organic analysis.

The scope of the book would have defeated any attempt to present a complete and critical survey. The authors have wisely limited themselves to methods that appeared to them most practical. Even with this limitation, definite statements on accuracy, precision, and limitations are frequently lacking, and ambiguity may occasionally be found. Nevertheless, the editors and contributors must be congratulated for the enthusiasm which enabled them to complete a difficult and arduous task. The book should be valuable for quick reference in any analytical laboratory which has to deal with a great variety of materials, to analyze small samples, or to determine trace constituents.

A. A. Benedetti-Pichler

Quantitative Pharmaceutical Chemistry. *G. L. Jenkins, A. G. DuMez, J. E. Christian,* and *G. P. Hager.* 3rd edition. xii + 531 pages. McGraw-Hill Book Co., 330 West 42nd Street, New York, N. Y., 1949. Price, $4.75.

The four authors of this new edition of a well known book represent both personal reputation and institutional prestige in pharmaceutical chemistry. Such cooperative effort should provide the perspective needed to eliminate many of the minor deficiencies so often found in singly authored books. The objective in this edition was to bring the material of the second edition up to date with the United States Pharmacopoeia XIII and the National Formulary VIII. The two junior authors are new on this edition.

A total of 141 exercises is included for making specific determinations, either of the amount of a desired constituent or of some physical property, such as solubility, of a given system. In general, the examples are selected from the two standard pharmaceutical references mentioned. Each kind of method is accompanied by a table listing other pharmaceutical products to which it is applicable. The operating directions seem clear and adequate. It is doubtful, however, that the authors have completely achieved their stated objective of "imparting a thorough fundamental knowledge of the theory . . . of analytical procedures."

The exercises, together with certain general material, are arranged in the form of a fairly conventional approach to elementary quantitative chemical analysis. The general viewpoint underlying the classification of methods seems to the reviewer the weakest point in the presentation. To him all analytical methods, whether applied to pharmaceutical products or to other kinds of materials, consist of (1) the chemical preparative and/or separative operations necessary to get the sample ready for measurement, and (2) the physical operation of the measurement. A functional nomenclature and a consistent classification would then take these basic items into account. Viewed in this way, the writer can see nothing "special," for example, in the volatilization-gravimetric determination of ash and moisture (Chapter 20), or in the extraction-titrimetric determination of certain alkaloids (Chapter 26). Similarly, the procedures of Chapter 19 are gravimetric measurements, the electrodeposition involved being merely a separative operation. If one accepts gasometric as one kind of method (Chapter 10), consistency would seem to imply that the other two kinds are liquidometric and solidometric. The colorimetric measurements discussed on pages 288 and 327 are both comparimetric, and so would seem to belong together.

To assist the student each exercise is subdivided as follows: object; materials needed; procedure, including operating directions and explanatory comments on the chemistry and calculations involved; and questions and numerical problems.

This kind of book raises an old pedagogical question. Is it necessary, or most efficient, to teach a given subject under conditions that happen to be of most personal interest to each student? For example, can the chemistry student best learn German word order by using only texts containing chemical terms; or can the analytical student best learn to operate and understand a balance only by having samples of soda ash for engineers, baking powder for dietitians, aspirin for pharmaceutical chemistry majors, or spheroidal residues from the sheep barn for agricultural chemistry majors? The writer believes that weighing is a perfectly general unit operation of quantitative analysis, and that, as such, it has no specific connection with the nature of the object to be weighed. Admittedly, interest is psychologically important for motivation; but generality of viewpoint is important for broad education.

The critical reader will hardly be satisfied with certain statements of fact. The analytical balance is not essential in all quantitative methods of analysis (p. 32). In some gravimetric determinations the sample is not weighed nor is the precipitate a compound (p. 47). A titrant may be measured by mass as well

as by volume, and, obviously, a standard solution may be specified in terms of the mass of reagent per unit mass of solution (p. 69). The cubic centimeter may be officially the one-thousandth part of a liter for the American Pharmaceutical Association; but in the metric system it is the one-millionth part of the cubic meter, and, as such, it is not related to the liter (p. 70). The Bronsted definition of a base (p. 78) seems not to be used later (pp. 83, 104). Because normality is not always an unambiguous specification of titrant value, equal volumes of oxidizing and reducing solutions of equal normality are not necessarily equivalent (p. 181).

Analytical teachers in chemically self-contained schools of pharmacy should find this book very well adapted for work in quantitative pharmaceutical analysis. If the instructor believes in dispensing to students samples of known composition, some products, such as hydrogen peroxide or chlorinated lime, must present a serious problem. For teachers of general quantitative analysis the book is valuable as a reference to the wide variety of pharmaceutical applications, including the chemistry involved in the methods.

M. G. MELLON

Trace Elements in Food. *G. W. Monier-Williams.* viii + 511 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1949. Price, $6.

This book by the well known British authority on food analysis contains 28 chapters devoted to 38 elements found in the human body and in foods, to the extent of 0.005% as the upper limit. The last chapter is a catchall for ten elements not found very often, described in rather sketchy fashion.

The definition of trace elements embraces iron, a trace element in most foods, though the animal body is regarded as containing more than a trace. Some of the elements discussed are essential to animal life; others, only to plants. Some are important because they enter foods as the result of agricultural practices or industrial processes. Certain elements are definitely toxic; others, relatively harmless. The author treats these elements in an excellent and readable manner from the standpoint of their natural occurrence and advent into human foods, their necessity for animal or plant nutrition, their toxicology, and, finally, their determination in foods. The text is invaluable to one interested in the role of trace elements in soil-plant-animal relations, as well as to those concerned with food analyses in the interest of public health. Adequate references up to about 1947 are given at the end of each chapter.

Nutritionists, toxicologists, and chemists all can get a clear, concise, over-all background picture of the present knowledge of the trace elements. There is, inevitably, a gap between date of publication (1949) and the latest literature cited. This explains, perhaps, why some of the latest nutritional and pharmacological discoveries are not discussed more fully. For example, no mention is made of fluorine as a possible essential element in animal nutrition or of its possible role in normal tooth structure. It is unfortunate that the author was unable to include recent information on the presence of cobalt in the vitamin B_{12} complex and on the toxicology of lithium. Pharmacologists might wish a more extended discussion of the toxicology of those trace elements, tersely described or even omitted—for example, gold, which is more prevalent than has been suspected. Such extended discussion would have increased the size of the volume; but this is worth consideration in future editions.

The same gap between about 1947 and date of publication can be noticed in the analytical literature, particularly in relation to some of the newer dithizone methods.

The author is to be commended for connecting organic compounds, enzymes, catalyses, or vitamins with various trace elements contained therein, the combination of which affects nutrition or other biological processes so strongly as to make the element essential to life. This required no small amount of boldness and courage. The reviewer also commends the author's practice of giving the daily intake and excretion of toxic elements in terms of milligrams per kilogram of body weight. It is on such facts that storage, nonstorage, and incidence of toxic effects are determined.

The analytical sections of the various chapters are given in general outline rather than in detail; more than one method is described and compared simply but adequately. The book is intended as a companion to, not as a substitute for, pertinent chapters and sections of "Official and Tentative Methods of Analysis," of the Association of Official Agricultural Chemists or others like it. The author gives to the reader seeking analytical knowledge on trace elements, a background not found in other books devoted to food analysis.

Only one serious error was noted. In the dithizone method for lead the wave length used to read the lead dithizonate color should be 510 instead of 570 mμ.

This book has a decided and delightful English flavor, and it is only natural that references to the English literature are emphasized. This is well exemplified in the analytical section of the lead chapter. The colorimetric lead sulfide method is good, even if many analysts think newer pastures are greener; and the holding fast to the things that are good is a sterling ingredient of the English character.

H. J. WICHMANN

Techniques of Histo- and Cytochemistry. *David Glick.* xxii + 531 pp. Interscience Publishers, Inc., New York, N. Y., 1949. Price, $5.

Glick has supplied a comprehensive guidebook to a field that must before long engage a significant fraction of biological research. Histo- and cytochemistry (tissue and cell chemistry) have been at times defined too narrowly in terms of specific microscopic techniques. Because the validity of some of the earlier microscopic methods was questionable, the field has been slow to gain recognition. Glick's book helps materially to broaden the definition of histochemistry. With the presentation of a very wide variety of methodologies, it becomes obvious that none of them defines the field and that histochemistry is actually a concept rather than a specific approach to a problem.

The book is divided into three main sections. The first covers microscopic techniques, and is comparable to *Histochemie Animale,* but the material has been consolidated and extended. Two important trends are made evident. There has been a persistent and successful effort to increase the specificity of microscopic methods, and there is a new emphasis on the quantitation of measurements under the microscope. An amazingly ingenious array of techniques is described in rather full detail. The more dramatic include measurements of absorption spectra (visible and ultraviolet) in small areas of a single cell, measurement of the concentration of certain elements in tissue sections with x-ray absorption, radioautography, and, probably most potentially fruitful, localization of enzymes. Throughout the author is properly critical and warns the reader of the less satisfactory procedures.

The second and largest section of the book is devoted to microchemical procedures suitable for measurements on entire histological sections or other small biological objects. These methods do not have the exquisite sensitivity of reactions conducted under the microscope but are in general more specific and quantitative, and are actually amazingly sensitive. The various toylike tools are carefully described, and detailed instructions are given for more than 60 individual microchemical methods. This section should be of interest to anyone concerned with microchemistry.

The final section describes the isolation of cell components on a macro scale by differential centrifugation. As this approach is at present yielding our most definite information concerning cell nuclei, mitochondria, and other cell particulates, it is particularly timely.

There is a theme written between the lines of this book which may be more important than any of the discrete tools described. This is an affirmation that the living tissue functions not because it contains certain enzymes and salts, nor because it has a certain microscopic architecture, but because the structure is a chemical and enzymatic one, and because the active systems are segregated and organized on cellular and intracellular levels.

OLIVER H. LOWRY

Recent Advances in Analytical Chemistry. *R. E. Burk* and *O. Grummitt*, editors. Vol. VII. vi + 209 pp. 15 × 23 cm. Interscience Publishers, Inc., 215 4th Ave., New York 3, N. Y., 1949. Price, $4.50.

The present work is Volume VII of the annual series of lectures at Western Reserve University on the general subject of frontiers in chemistry. Certain aspects of modern analytical chemistry comprise this latest report. The following subjects are included: voltammetry and amperometric titrations (I. M. Kolthoff); inorganic analysis with organic reagents (J. H. Yoe); recent colorimetric and gravimetric organic reagents (J. H. Yoe); application of infrared spectroscopy in analysis (O. Beeck); electron microscopy and microanalysis—new methods in chemistry (J. Hillier); fractionation, analysis, and purification of hydrocarbons (F. D. Rossini); and applications of the mass spectrometer (J. A. Hipple).

These reports vary in length from 18 to 54 pages, the two shortest being those on organic reagents and the longest that on instruments utilizing a medium voltage electron beam. The material for each subject approximates that which one might expect to be presented as a lecture to a reasonably well informed local section audience of the AMERICAN CHEMICAL SOCIETY. Thus, Kolthoff discusses the general principles of voltammetry and polarography and gives typical examples of applications, together with a selected list of references. The other chapters dealing with instruments are treated similarly. The figures include illustrative schematic diagrams, general views of selected equipment, and tabular and graphical experimental data. The lectures on organic reagents represent essentially a brief summary of part of the book by Yoe and Sarver (organic analytical reagents), and a summary of published work of Yoe *et al.* on certain reagents for silver, palladium, iron, titanium, and tungsten.

These lectures are all by competent men. The reports seem to be critically evaluated, brief summaries of contemporary knowledge for the various subjects. As such, they should interest especially advanced undergraduate and graduate students and many teachers. Herein may be found that perspective of a field which one so often needs. The reviewer would welcome many others of similar nature.

M. G. MELLON

Semimicro Qualitative Analysis. A Non-Hydrogen Sulfide System. *Jacob Cornog. Herman T. Briscoe*, editor. xi + 259 pages. Houghton Mifflin Co., 2 Park St., Boston, Mass., 1948. Price, $3.

This book presents a semimicro scheme of qualitative inorganic analysis in which ammonium sulfide in buffered acetate solution is substituted for the usual hydrogen sulfide precipitations of the iron and tin groups. This edition should serve well as a laboratory work book for use in a college elementary course. According to one of the prefaces, the book has been tested and modified during several years of experience in many classes. Examination of the book indicates that it was written with an awareness of the problems of the beginning student in this field.

The text is concise but sufficiently detailed so that fundamental points of theory and practice are adequately covered. The analytical scheme is easy to follow and is interspersed with notes and problems. Except for the precipitation of the sulfide groups, the order and techniques of the group separations are not unusual.

Approximately the last third of the book is devoted to theory and includes a good review of the exponential arithmetic required for calculations of solubility products and ionization constants. The text is preceded by a comprehensive bibliography.

A modified decimal system of numbering paragraphs and figures is used. This is satisfactory except in a few instances, such as on page 134, where instructions referring the student to certain paragraphs may be confusing owing to insufficient punctuation of the reference numbers.

A work of this quality merits a better format; the cover is paper and the spiral wire binder is small for the number of pages.

W. C. JONES, JR.

Laboratory Outlines and Notebook for Organic Chemistry *C. E. Boord, W. R. Brode*, and *R. G. Bossert*. Second edition. xi + 282 pp. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1949. Price, $3.

This laboratory manual was designed for the usual 36-week course in organic chemistry with two laboratory periods per week (or three periods per week for 24 weeks under the "quarter" plan). It could, of course, be used for shorter courses by making proper omissions.

The authors have included a larger proportion of experiments dealing with the chemistry of aliphatic compounds than is found in most laboratory manuals. The order of the experiments is such that laboratory and lecture work will be closely parallel when the latter is presented in the traditional manner. The experiments are well chosen as to type and interest, and the directions and discussions are clear and concise. Special attention should be called to several experiments which utilize molecular models to evolve the idea of homology and isomerism.

The book is constructed on the notebook style—i.e., blank space has been left so that the questions concerning the experiments can be answered in the notebook. The book is bound by means of spiral wire; therefore, individual exercises can be removed for grading as soon as they are completed. Such a system does reduce the time required for correction of notebooks and should enable the instructor to handle a relatively large number of students and spend more time in laboratory supervision. However, this fill-in type notebook does not emphasize to students the importance of organizing their own experimental results and it frequently leads to a less conscientious attitude on the part of the poorer student.

The book is bound in stiff cardboard and is printed on a good grade of paper. The appendix is complete and gives an adequate description of the amount of chemicals each student will need per experiment.

W. E. PARHAM

The Analyst's Calendar

Fourth Instrument Conference and Exhibit. Municipal Auditorium, St. Louis, Mo., September 12 to 16

American Society for Testing Materials. Fairmont Hotel, San Francisco, Calif., October 10 to 14

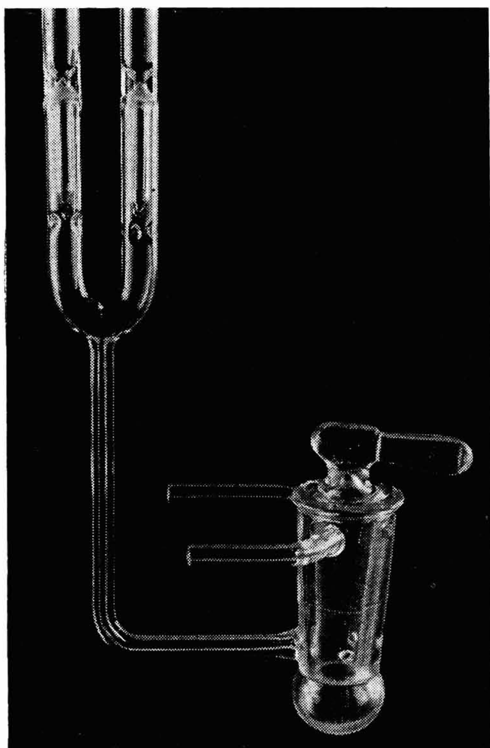
Optical Society of America. Hotel Statler, Buffalo, N. Y., October 27 to 29

American Council of Commercial Laboratories. Miami, Fla., December 5 to 7

Third Symposium on Analytical Chemistry. Louisiana State University, Baton Rouge, La., January 30 to February 2, 1950

Improved Mercury Float Valve. I. Shapiro, U. S. Naval Ordnance Test Station, Pasadena, Calif.

FREQUENTLY in high-vacuum work it is found necessary to keep vapors and gases from coming in contact with the grease used in stopcocks, and in these instances the replacement of stopcocks with mercury float valves has proved useful.



A float valve consists essentially of a pair of ground-glass plugs in a U-tube arrangement, a mercury reservoir, and a method of controlling the flow of mercury from the reservoir to and from the U-tube. As mercury enters the U-tube the plugs float up into position and thus seal off communication between the two arms of the U-tube; then as a vacuum is pulled on the mercury reservoir, the mercury is withdrawn from the U-tube and the plugs drop to an open position, thus permitting vapors and gases to pass between the two arms. In any arrangement it is necessary to supply both air and vacuum to the mercury reservoir. In some of the older arrangements an ordinary stopcock (or ground plug) is placed between the reservoir and the U-tube, and in operation a rubber tubing connected to a vacuum pump is placed over the open end of the reservoir in order to pull a vacuum on the valve, or the open end of the reservoir is left untouched in order to get positive air pressure. When one has a number of these mercury float valves in a system, operation of the valves by this method becomes very cumbersome.

Recently there has appeared on the market a float valve in which a five-way stopcock effectively replaces the ordinary stopcock and allows air or vacuum to be piped directly to each reservoir and thereby facilitate the manipulation of the float valves. However, it is possible for all the mercury to drain back into the reservoir, thus exposing the grease in the stopcock to the vapors or gases, and the short distance along the ground barrel of the stopcock between the entrance to the U-tube and the end of the stopcock increases the danger of air leaking (especially after long usage) into the high vacuum system.

The float valve described herein circumvents these difficulties and eliminates the use of a separate mercury reservoir in that it incorporates the reservoir (volume, 18 ml.) in the hollow stopcock barrel. This type of float valve has been in operation for a considerable period of time and its performance has been excellent.

The U-tube is 11 mm. in outside diameter, with hollow-ground plug with iron core, and is connected to the reservoir by 2-mm. capillary tubing. The stopcock barrel contains three holes, two at the bottom level and one at the top level, so arranged that each hole at the bottom level will be in line with the capillary tube connecting to the U-tube as the hole at the top level of the barrel coincides with either protruding arm. One arm can be connected directly to a vacuum pump and the other arm left exposed to the air. Then as the stopcock is turned from one position to the other, the mercury will either rise or fall in the U-tube. In the neutral position the mercury level will remain stationary. The mercury can never fall below the bend in the capillary tube and the length of the ground barrel eliminates any danger of air leakage into the high-vacuum system. The entire assembly can be supported by placing a clamp around the middle of the stopcock.

Assembling Multiple-Junction Thermocouples. E. H. Graham and Ralph Scruby, Graham Instrument Laboratory, Boulder, Colo.

THE following method produces thermocouple assemblies that are mechanically rugged and withstand flexure indefinitely without short circuits.

After the alternate strands of wire are joined at their ends in the usual manner, they are gathered together in a loose bundle and twisted into a gentle spiral throughout their entire length. The potentiometer leads are left free of the main bundle.

To avoid kinking, the bundle is held gently taut while it is passed full length through a latex solution three times, with a drying period of 2 to 5 minutes between each pass. The potentiometer leads are given a similar latex coating, and the assembly is hung vertically to dry.

A suitable length of varnished "spaghetti" tubing forms the outer protective layer of the assembly. A No. 22 copper wire is threaded through the spaghetti, looped to the thermal bundle, which is then drawn into this outer tube.

The potentiometer leads, which have been kept separate from the main bundle of wires, are then similarly encased in spaghetti tubes, which are seized or bound for a short distance with a wrapping of linen thread to the main bundle. The ends of the spaghetti, beyond which the junctions and leads extend, are seized with linen thread wrappings and coated with latex, Glyptal, or other suitable bonding.

Although not recommended for applications at much above room temperature, thermocouples of this construction have been used for low temperature measurement where they are subjected to continuous cyclic flexure at 2 cycles per second over a period of months without failure.