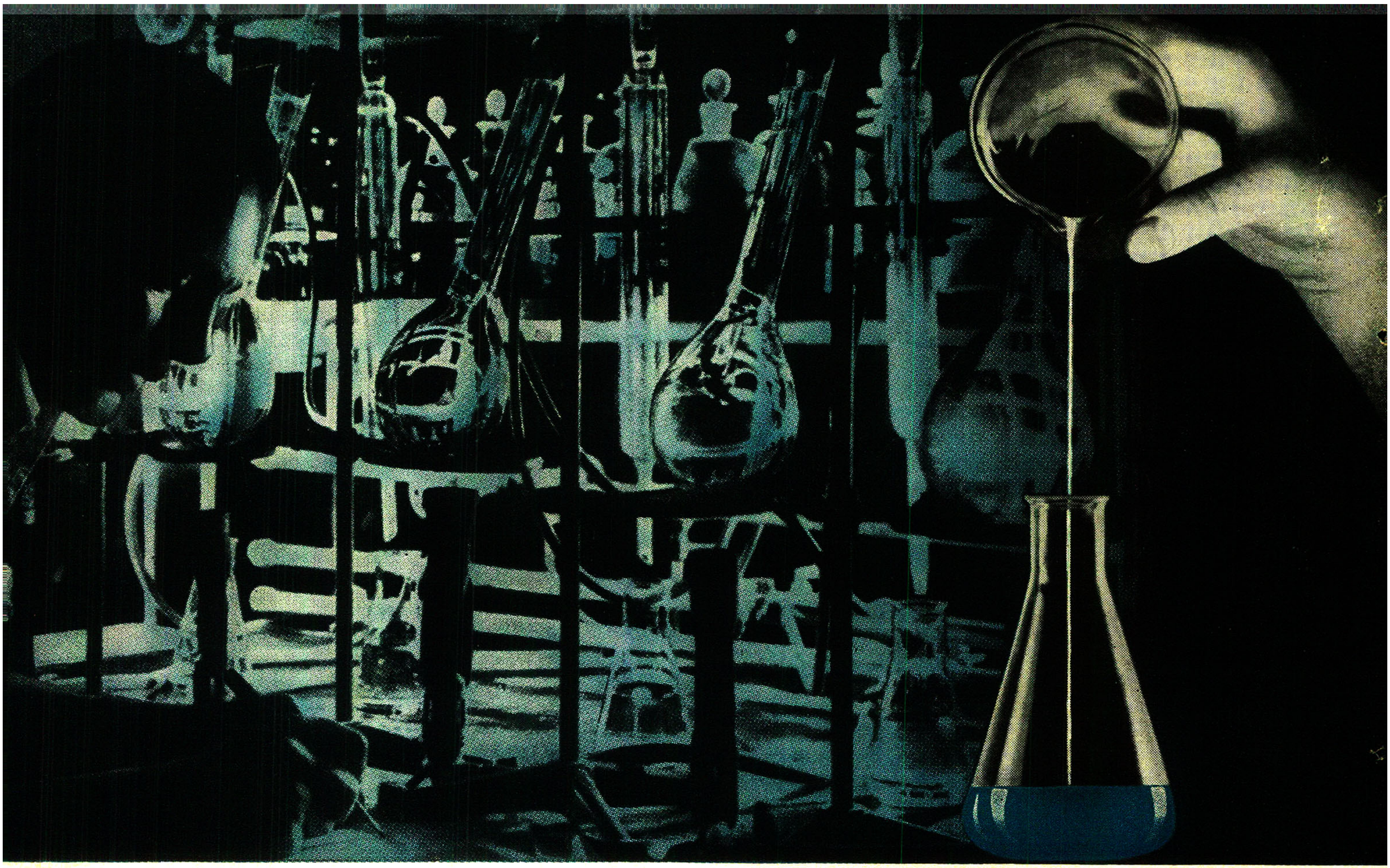
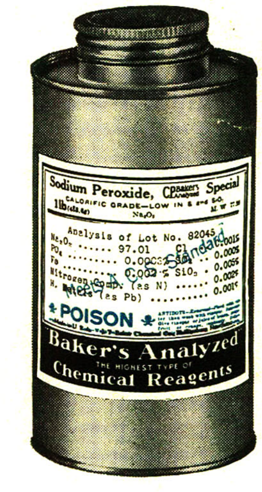
ANALYTICAL CHEMISTRY

MARCH 1947

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ANALYTICAL CHEMISTRY

Volume 19, Number 3
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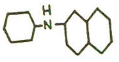

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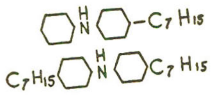

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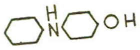

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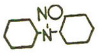

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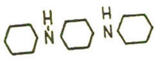

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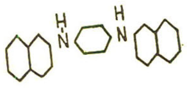

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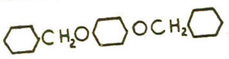

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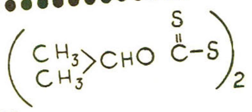

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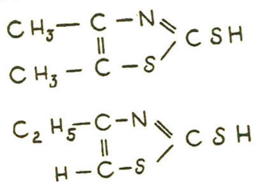

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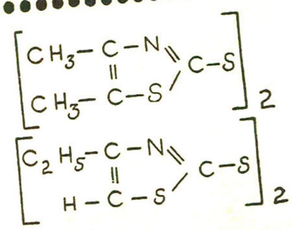

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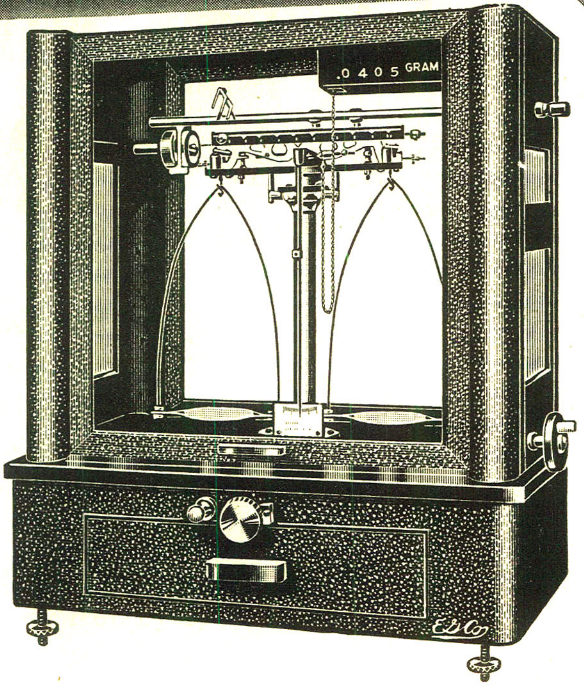
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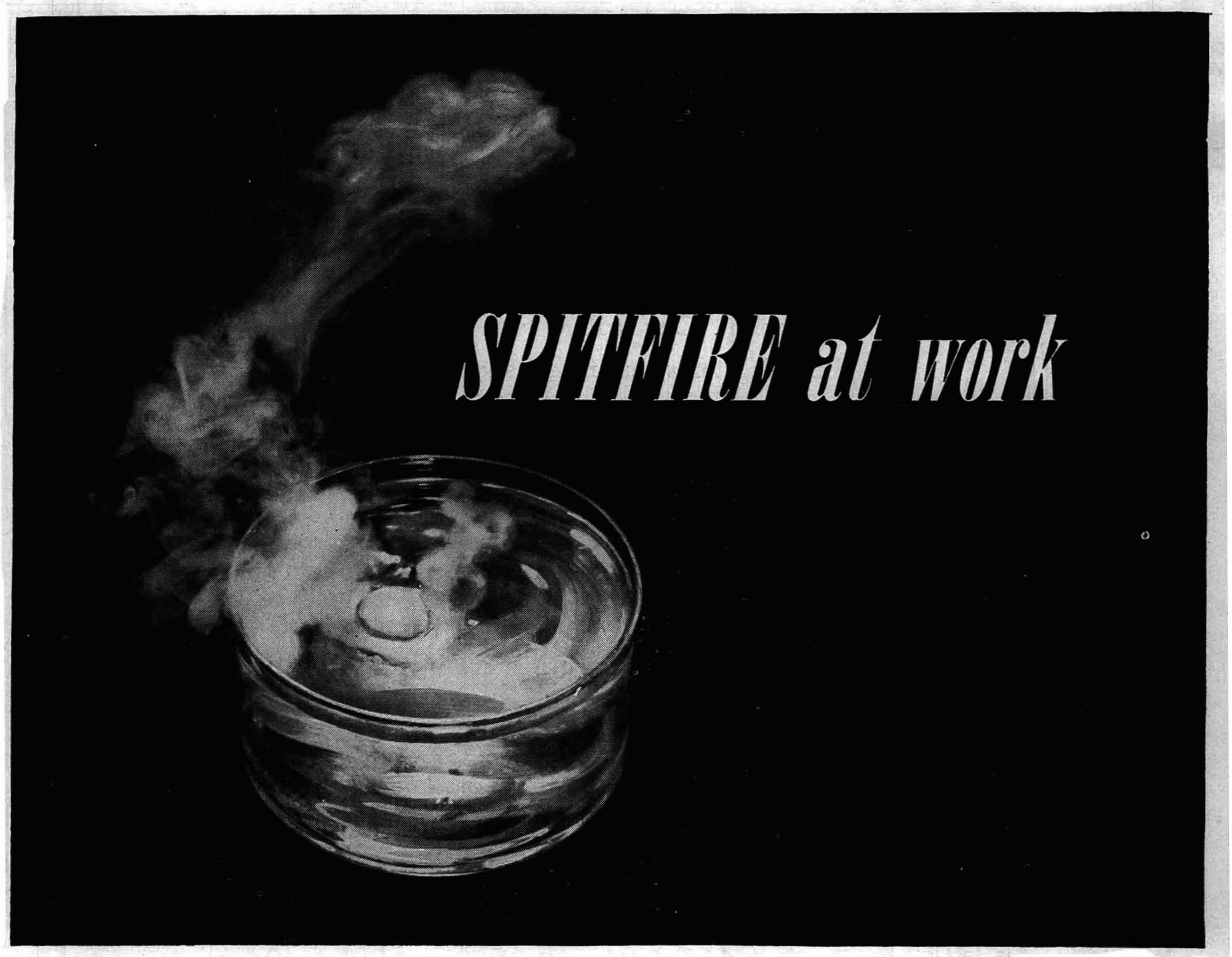
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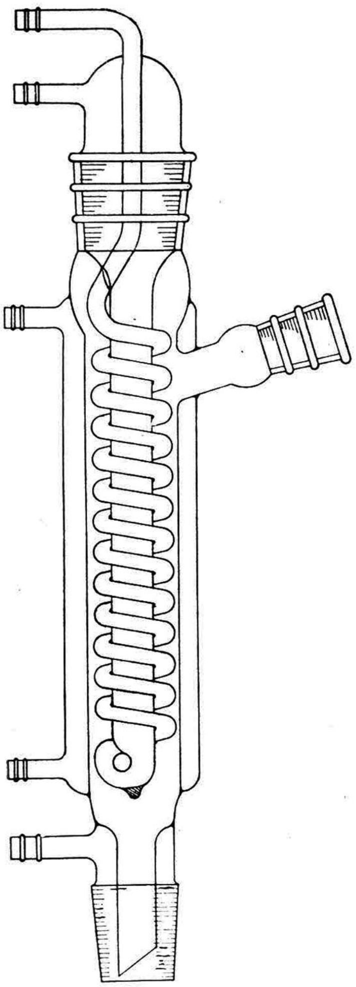

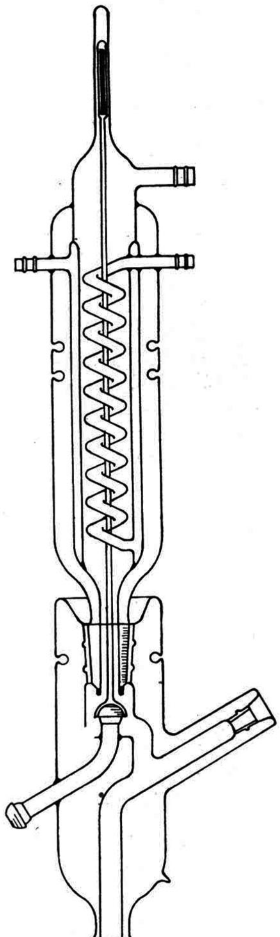

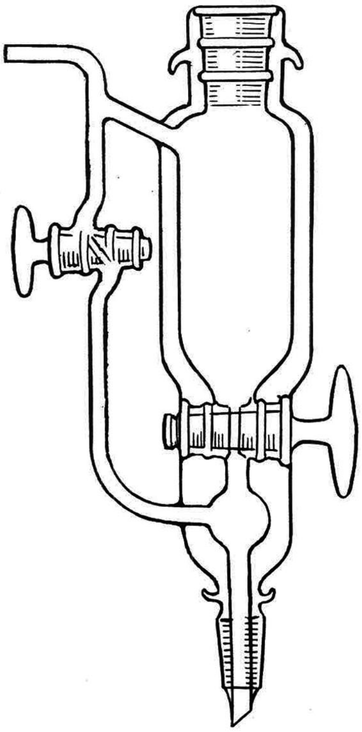

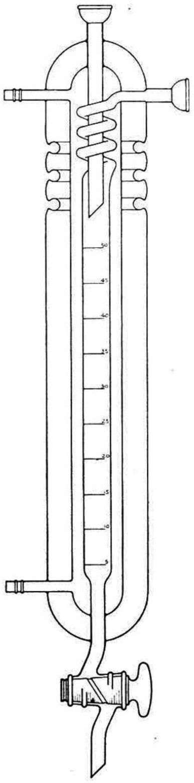

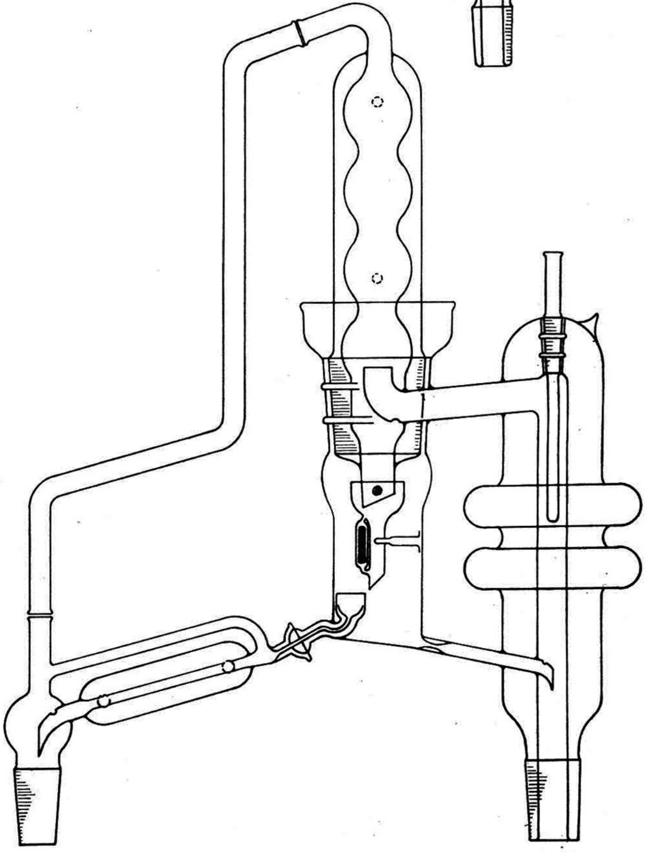


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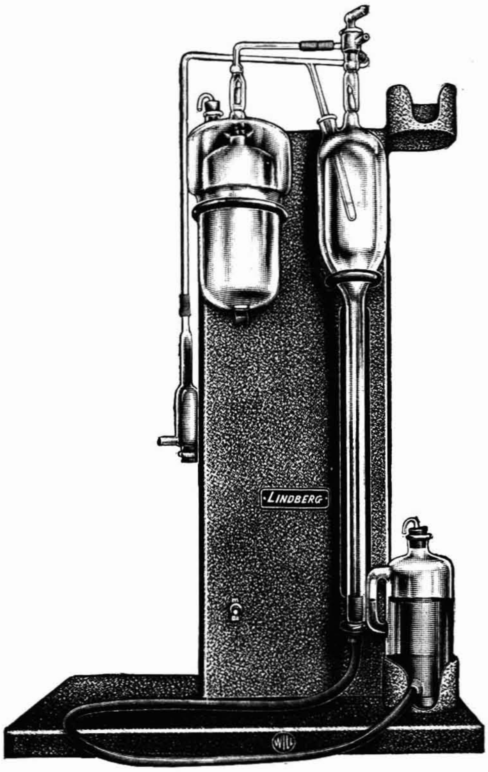
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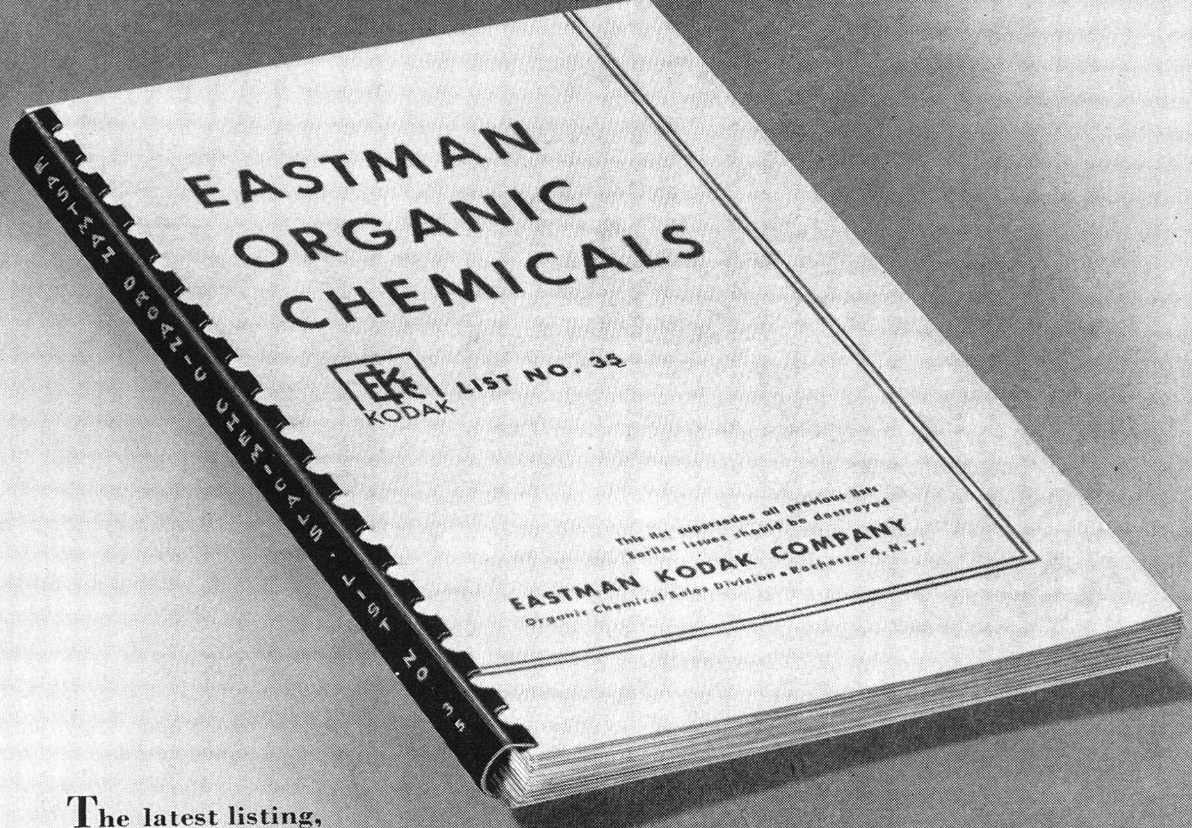
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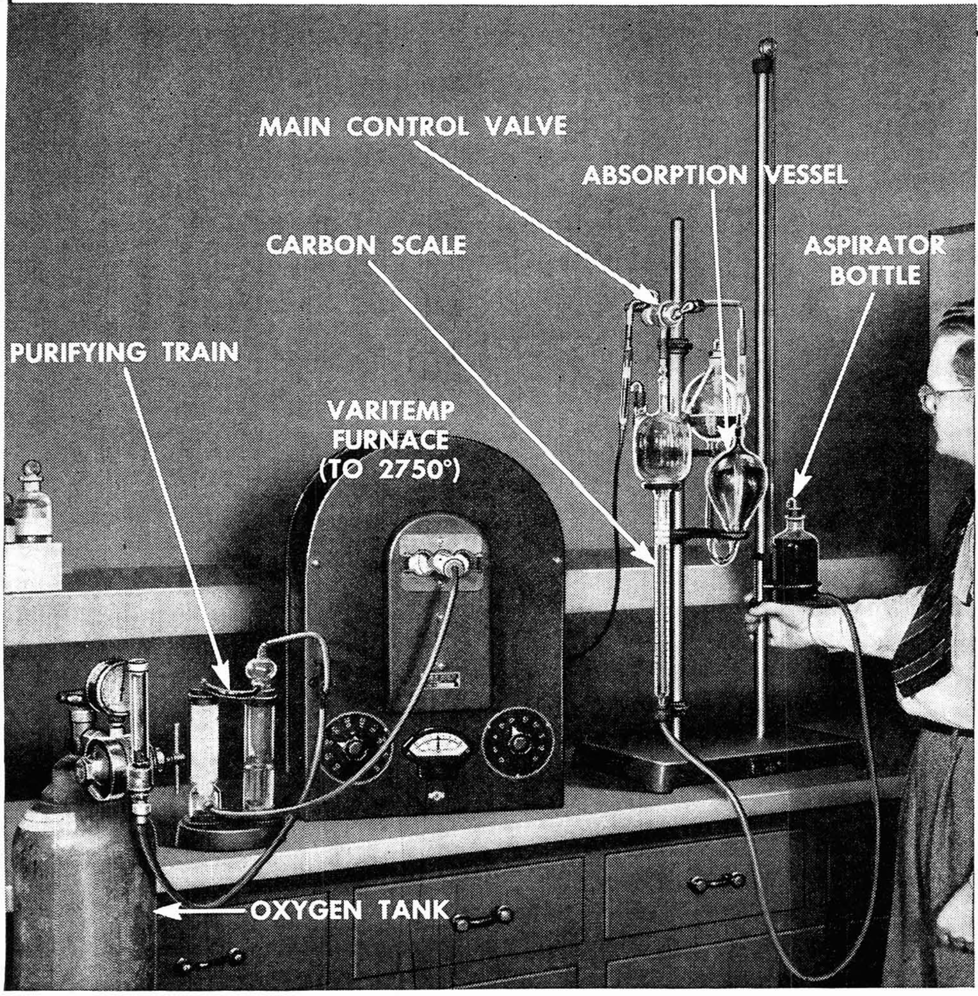

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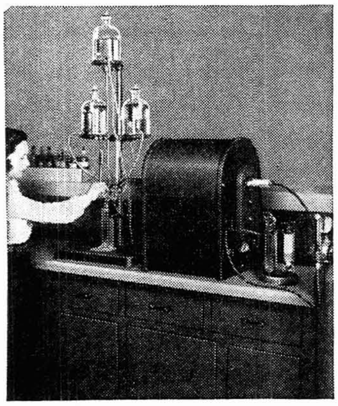

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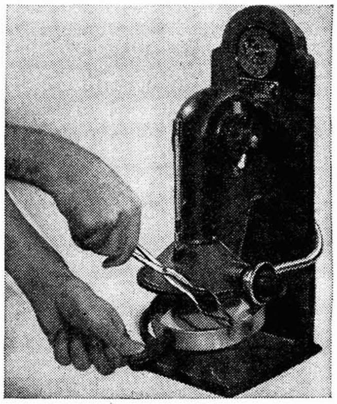

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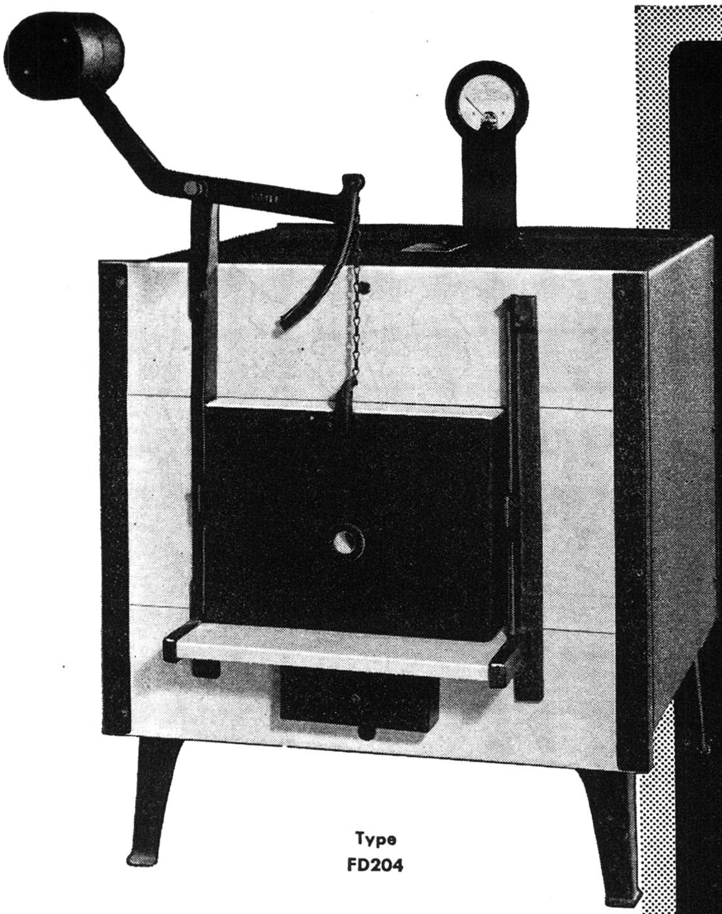

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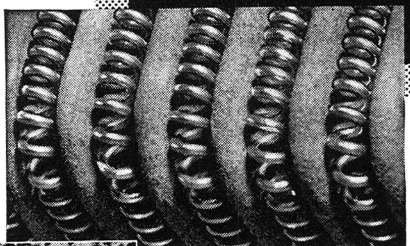

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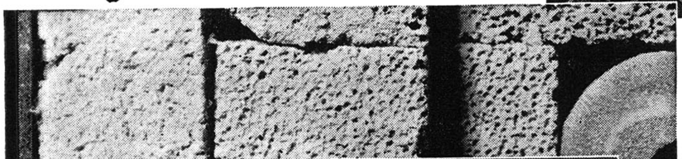

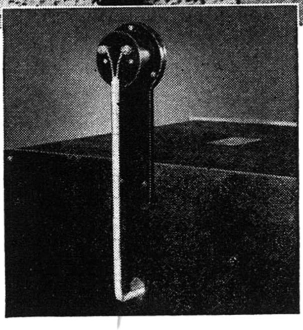

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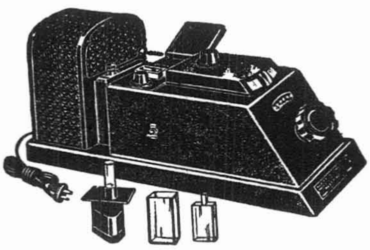

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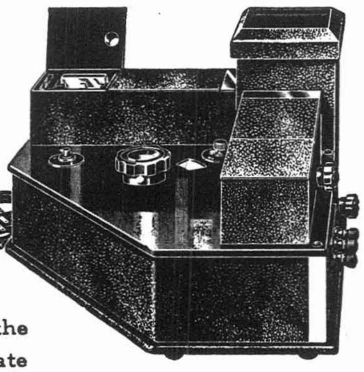

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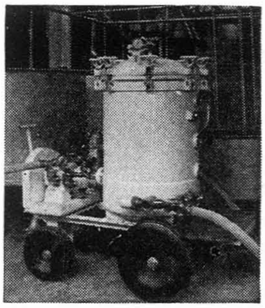

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the analyst's column

"STATISTICS in Analytical Chemistry" was the subject of an address given by William J. Youden (Boyce Thompson Institute for Plant Research, Inc.) at New Haven on Feb. 6 before a joint meeting of the New Haven sections of the AMERICAN CHEMICAL SOCIETY and the American Statistical Association. We asked Mr. Youden to prepare a short summary of this address, and we think you will be interested in the following thoughts which he presented:

Analytical chemists working out a new analytical procedure can satisfy themselves, as well as convince others, of the merits of the new method by making use of some very simple computations that statisticians have designed for that express purpose. . . . These applications must not be confused with the case of routine duplicate or triplicate analyses run by an established analytical procedure. In this latter case the chemist has *a priori* knowledge about the errors of the method which is much more reliable than that obtained by calculating an error based on only two or three analyses.

Most analytical methods involve a linear relation between the amount of material taken for analysis and the observed quantity, whether this be gravimetric or volumetric. Thus, if in developing a new method, samples of varying size $S_1, S_2, \ldots S_n$ be taken, and corresponding weights of precipitate $W_1, W_2, \ldots W_n$ be found, it is instructive to determine the constants in the following equation:

$$W = a + bS$$

Note that if there is no blank, a will be zero within the error of the work and is itself an estimate of the blank. Further b, the slope, is the change in W per unit change in S—that is, it is the amount of W corresponding to one unit of S. This is precisely the quantity sought in the analysis and customarily computed from the formula $\frac{1}{n}\left(\frac{W_1}{S_1} + \frac{W_2}{S_2} + \ldots + \frac{W_n}{S_n}\right)$. (Reasons can be advanced for preferring to use alternatively the formula $\frac{\Sigma W}{\Sigma S}$ since this gives more weight to the larger samples.) In either event, result should be compared with the slope by computing

$$b = \frac{n\Sigma WS - \Sigma W\Sigma S}{n\Sigma S^2 - (\Sigma S)^2}$$

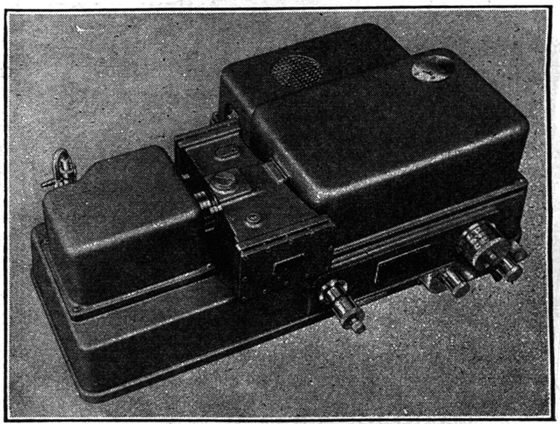
This quantity is not affected by any constant errors in the analysis, since the slope is not changed by raising or lowering all points the same amount. Agreement between b and $\Sigma W/\Sigma S$ is a good recommendation for the method. Disagreement, as judged by appropriate statistical tests, invites further work on the method in the laboratory.

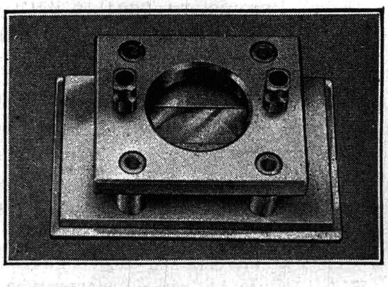
As most of us know, a great deal of work was done during the war period on the chemistry of fluorine, particularly as part of the organic molecule. Much of this work was on problems of a secret nature, but the results of some of the research are now being disclosed. Six papers on the analytical chemistry of fluorine are given in this issue. The first three papers are part of a fluorine symposium sponsored by the Division of Industrial and Engineering Chemistry at the fall 1946 meeting of the A.C.S. in Chicago. The paper by Kimball and Tufts is considered part of the symposium but was not read at the meeting. The paper by Teston and McKenna on "Semimicromethod for the Simultaneous Determination of Carbon, Fluorine, and Chlorine in Halogens" appears as the first paper in the Micro section. The entire March issue of *Industrial and Engineering Chemistry* is devoted to fluorine papers.

THE A.C.S. Committee on Analytical Reagents, headed by Edward Wichers, again presents its report, page 210, on recommended specifications for analytical reagent chemicals.

L. T. Hallett

Associate Editor





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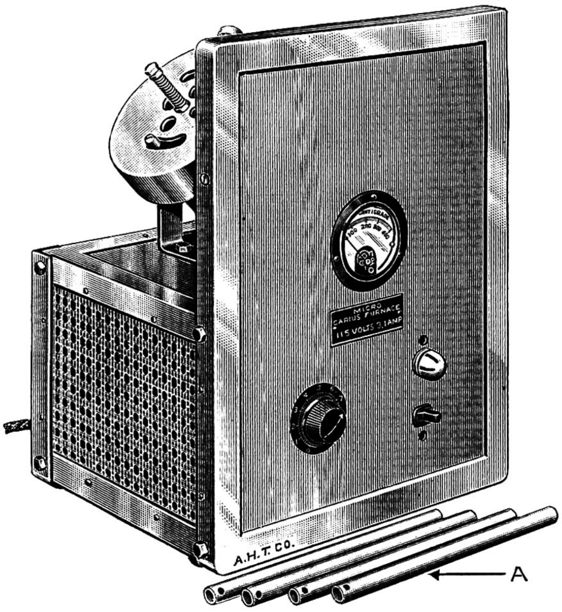
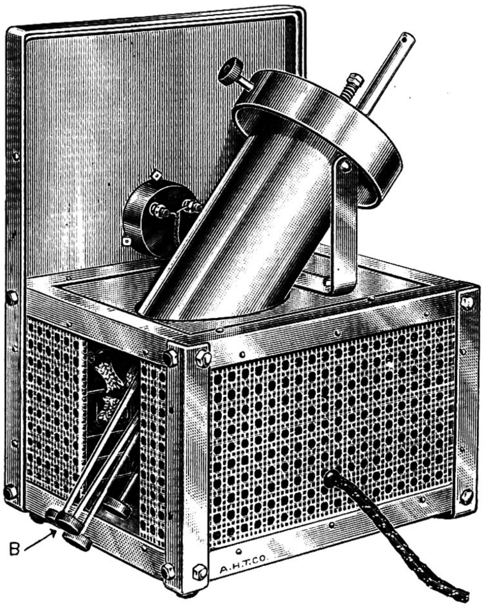


5713-F. Fig. 1.
Front View, showing control equipment mounted on front, and adapter tubes A



5713-F. Fig. 2.
Rear View, showing inclined furnace chamber with built-in push rods B.

CARIUS MICRO FURNACE, Electric, A. H. T. Co. Specification. New model with inclined chamber. For organic reactions requiring the high pressures which result from heating reactants in sealed glass tubes as in the determination of halogens or sulfur by the Carius method. Designed to provide the optimum combination of oxidation and precipitation conditions and to minimize danger of injury to the operator in the event of accidental explosion during heating. Suitable for semi-micro procedures by using the furnace without the cylindrical adapter tubes A of Fig. 1.

Consisting of an aluminum block with four openings, 240 mm long × 14.3 mm diameter, and cartridge-type heating unit enclosed in insulated cylindrical Monel metal jacket, with explosion-proof cover, and mounted at an angle of 45° in a partly enclosed angle iron frame with frontal shield of reinforced aluminum.

The control equipment, including pyrometer, rheostat for adjusting furnace temperature between 140° and 400°C, pilot lamp and on-off switch are mounted on the front shield. Pyrometer range 0 to 400°C in 10° divisions, with estimation possible to 5°C; rheostat dial graduated 0 to 10 in 0.1 divisions.

The furnace cover consists of a cast aluminum head with flange 25 mm deep and four circular openings which admit the combustion tubes; cover can be rotated within controlled limits to close the furnace in use. It is attached to the furnace chamber by means of a central post and spiral spring to permit safe escape of the high pressure, in the event of accidental explosion, by allowing the cover to lift approximately 10 mm. Under such conditions, the flange directs emitted glass particles downward behind the frontal shield.

Built-in metal push rods, B of Fig. 2, with fiber knobs are provided for each opening to facilitate removal of combustion tubes, but the weight of the complete outfit permits tipping, if necessary, for removal of debris from openings. Adapter tubes of Monel metal, with open ends, 235 mm long × 10.5 mm inside diameter, are supplied for use with Carius combustion tubes for micro determinations. They not only reduce the size of the openings but are an added protection in event of explosion.

All parts, excepting those of Monel metal, are finished with heat-resistant aluminum paint. Overall dimensions 13 inches wide × 10 5/8 inches deep × 17 inches high. Net weight 29 lbs. Power consumption 350 watts.

5713-F. **Micro Furnace, Electric, Carius,** as above described, complete with pyrometer with iron-constantan thermocouple, four adapter tubes A, 3-ft. cord and plug, and directions for use. For use on 115 volts, d. c. or 25 to 60 cycles, a. c. Without glassware........150.00
5713-H. Ditto, but without adapter tubes; for semi-micro work........145.00

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ANALYTICAL CHEMISTRY

Published by the American Chemical Society Walter J. Murphy, Editor

The Profession of Analytical Chemist

TWENTY-FIVE years ago when a chemist with a bachelor's degree started his professional career, nine times out of ten it was as an analytical chemist. Actually the more accurate description would have been control chemist or possibly a chemical intern, or chemist-in-training. A quarter of a century ago the general idea seemed to be that if the new arrival showed real promise, was intelligent and mentally resourceful, and indicated a high degree of manual dexterity in handling laboratory equipment, apparatus, and devices of one kind or another, he could expect transfer within a reasonable period of time to the research department. The analytical lab to all but a few was considered to be a proving ground, a place for separating the wheat from the chaff, a stepping stone to something much better, including more money.

There was some foundation in fact for such a plan 25 years ago. Analytical techniques then were almost wholly volumetric or gravimetric, methods in many instances were not too standardized, and usually a graduate chemist was required, for the work demanded more skill and a greater degree of independent judgment than could be expected of a laboratory technician. Indeed, the laboratory technician was almost unheard of in those days. The work, however, all too frequently was largely repetitive, usually long drawn out, tedious, dull, uninteresting, and therefore uninspiring to the truly professional. There was little to challenge the really inquiring type of mind that is so characteristic of the real researcher, unless he was assigned to research on new analytical procedures and techniques. Frequently such work was carried on by the more inquisitive and ambitious simultaneously with routine analysis.

Today the situation is much different, yet the legend persists in and out of the profession and particularly in top-flight management circles of many companies. The advances in the field of analytical chemistry in the past decade or so have been nothing short of phenomenal, but few outside the profession are at all aware of this progress. In that period the field of analytical chemistry has undergone profound changes, but these changes have had little publicity and are none too well understood.

The analytical chemist all too frequently still is thought of as a strictly routine worker, one who is several steps below the research chemist and members of the chemical profession generally. He frequently suffers in prestige and monetary rewards because of the continued belief in an outmoded tradition.

The widespread introduction of instrumentation has caused a sharp division in the analytical laboratory between those of professional and subprofessional training, experience, and ability. Today thousands of analytical procedures are carried on readily by laboratory technicians. The true professional is expected to direct, to administer, and to pioneer research in analytical chemistry. He is therefore required to be an organic chemist, an inorganic chemist, a physical chemist, and may, at times, be expected to be a biochemist, a metallurgist, a specialist, if you will, in a dozen or more highly specialized fields. He most certainly must be somewhat of an expert in electronics—he must be almost as much a physicist as physicists themselves. In addition, he is usually expected to be specially skilled in some field within the profession of analytical chemistry.

What practical steps can be taken to correct the existing erroneous impression of what the analytical chemist is and does? How can we best publicize the contributions made by the analytical chemist to the over-all advancement of the science of chemistry?

The editors offer the following program, with the understanding, of course, that it is not an overnight cure-all and is probably but a partial solution to the problem.

1. Insistence upon a sharp distinct line of demarcation in title between the professional chemist and the laboratory technician. This is not easy to achieve, for some individuals with professional degrees fail in the long run to develop the requisite originality and leadership required of the professional. Nevertheless, for the over-all good of the profession, the governing factor should be the work the individual is doing, not his array of degrees, or lack of them. Management must be taught to make these distinctions plainer than in the past, through the use of both proper descriptive work titles and salaries commensurate with the training, experience, and responsibilities demanded of analytical chemists.

2. A thorough study by competent analytical chemists representing industry, fundamental research, and the teaching profession, looking to the promulgation of an ideal curriculum, or ideal curricula. At present no college or university to our knowledge specifically trains analysts or grants the master's degree or doctorate in analytical chemistry. It is common knowledge that the field of instrumentation is frequently neglected and in some cases ignored almost entirely in undergraduate training.

3. The establishment of at least one award for outstanding original work in the field of analytical chemistry. In addition, several awards for postgraduate students are highly desirable. Such recognition would stimulate and sustain the interest of young men and women in the field of analytical chemistry.

4. Consideration of ways and means of educating industry and particularly top-flight management on the true importance of analytical chemistry and analytical chemists. To many nontechnically trained executives the analytical department is a necessary evil, a nuisance that cannot be eliminated, of course, but one that is just a dead-weight expense. The analytical chemist and his modern techniques in the industrial field make possible new industries and new processes, protect manufacturers' reputations by guarding the quality of both raw materials and finished products, frequently make possible the upgrading of old products, help to eliminate wastes. The analytical chemist is the guardian of the nation's health and helps to raise health standards. As a result of this and other contributions to society, the analytical chemist is a mighty important individual—he is entitled to greater professional recognition and monetary rewards than frequently has been his lot to date.

Six months ago we commented along lines somewhat similar to those stressed in this editorial and asked for the comments of our readers. Frankly, the response was more than disappointing —it was practically nonexistent.

Once more we invite our readers to discuss these and other problems in the pages of ANALYTICAL CHEMISTRY.

Determination of Hydrogen in Fluorine-Containing Halohydrocarbons

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A rapid and accurate method is described for the determination of hydrogen in halohydrocarbons containing fluorine. The sample is pyrolyzed at a temperature of 1300° C. in a platinum tube in an atmosphere of nitrogen. The pyrolysis products are swept from the platinum tube by a stream of nitrogen and absorbed in distilled water. The resulting solution is filtered to remove carbonaceous material. If fluorine is the only halogen present, the solution is boiled and titrated. If chlorine is present in the sample, aliquots are taken. Free chlorine is determined in one aliquot by reaction with potassium iodide, followed by titration of the liberated iodine with a thiosulfate solution. Hydrogen peroxide is added to the other aliquot, the solution is boiled for 5 minutes, and the total acidity is determined by titration with standard alkali. A correction is made for acidity due to free chlorine, and the hydrogen concentration is calculated from the net acidity.

AN INCREASING amount of research on the preparation and use of organic halo compounds has been conducted in recent years. As a result, there was a need for a procedure by which the percentage of hydrogen in these compounds could be determined. A standard combustion method for the determination of hydrogen is satisfactory for chlorohydrocarbons, but no reference could be found to a method for determining hydrogen in fluorine-containing halohydrocarbons. Fluorocarbons were of interest to the Manhattan District, and it was especially important to know the hydrogen content, if any, of such materials produced both in the laboratory and in the plant.

The present method involves thermal decomposition of fluorine-containing compounds and depends upon assumptions:

1. Dehydrohalogenation of the sample is complete at temperatures above 1300° C.
2. Free fluorine is not liberated as a result of the decomposition.
3. Free chlorine, which may be liberated, will react quantitatively with potassium iodide to give iodine.
4. Hydrogen fluoride is absorbed in water to form hydrofluoric acid, or reacts with glass to form silicon tetrafluoride which hydrolyzes to form hydrofluoric acid.
5. Dilute solutions of hydrochloric acid and hydrofluoric acid are unaffected by boiling for short intervals. The validity of this assumption was demonstrated experimentally.
6. Chlorine dissolved in slightly acidic solutions is reduced to hydrochloric acid by hydrogen peroxide according to the following equation:

$$H_2O_2 + Cl_2 = 2H^+ + 2Cl^- + O_2 \qquad (1)$$

REAGENTS

Potassium Iodide, reagent grade.

Sodium Hydroxide, 0.1 *N*.

Alkaline Pyrogallol. Prepared by mixing 7 volumes of a potassium hydroxide solution containing 600 grams of potassium hydroxide per liter with 2 volumes of a pyrogallol solution containing 300 grams of pyrogallol per liter.

Water. It is necessary to use either freshly boiled redistilled water or conductivity water, the acidity of which is determined daily. This acidity should be determined titrimetrically using phenolphthalein as the indicator. Water requiring more than 0.30 ml. of standard 0.1 *N* alkali per 250 ml. is unsuitable.

Nitrogen. The nitrogen must be oxygen-free to avoid combustion resulting in the conversion of hydrogen in the sample to water. Purification is accomplished by passing the nitrogen through a purification train comprising alkaline pyrogallol, sulfuric acid, copper heated to 600° C., and anhydrous calcium chloride.

Sodium Thiosulfate, about 0.1 *N*. This solution is standardized against iodine liberated from excess potassium iodide solution by weighed samples of standard potassium dichromate.

APPARATUS

A diagram of the assembled apparatus is shown in Figure 1.

Decomposition Tube, *K*. A platinum combustion tube 1.25 cm. (0.5 inch) in inside diameter, and 80 cm. (32 inches) in over-all length (J. Bishop and Co.), is used. A 12.5-cm. (1-inch) coil of platinum gauze, *M*, is placed inside the combustion tube, which is supported in the furnace, *T*, by a McDanel high-temperature combustion tube, *L*. The inlet of the supporting tube is equipped with a ground platinum joint, *I*.

Furnace, *T*. A Burell high-temperature master model CTA 2-9 furnace is used in the work. The furnace is equipped with a thermocouple, *N*, pyrometer, *O*, tap transformer, *S*, and safety switch, *R*.

Absorption Train, *P*, *Q*. A 500-ml. Erlenmeyer flask equipped with delivery tube made by sealing 16-mm. Pyrex tubing to 8-mm. Pyrex tubing is used for the first absorption vessel. The second absorption flask is a 250-ml. Erlenmeyer flask with an inlet of 8-mm. Pyrex tubing, which must extend below the surface of the water.

Purification Train, *C*, *D*, *E*, *H*. The purification train for removal of oxygen from the nitrogen (cylinder *A* to which is at-

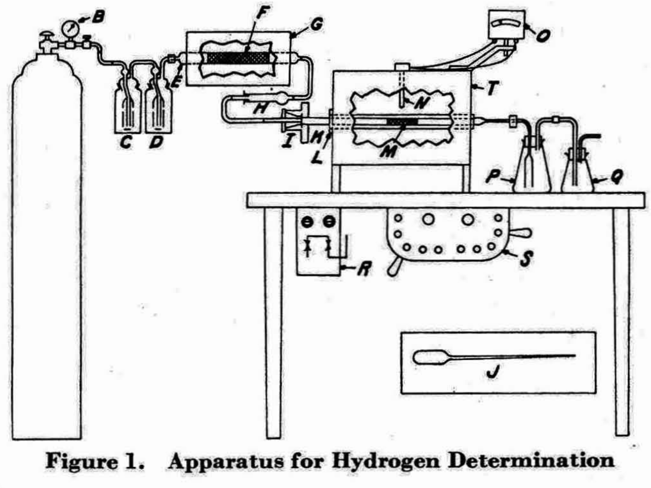

Figure 1. Apparatus for Hydrogen Determination

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Two papers presented in the Symposium on Fluorine Chemistry, Division of Industrial and Engineering Chemistry, at the 110th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill., are printed here (pages 146 to 149). Other papers in the symposium appear in the March issue of *Industrial and Engineering Chemistry*.

tached gage *B*), used to purge the apparatus and to carry vapors to be decomposed into the pyrolysis zone, comprises an alkaline pyrogallol scrubber, *C*, a sulfuric acid scrubber, *D*, a combustion tube, *E*, filled with copper gauze, *F*, and a drying tube, *H*, filled with calcium chloride. The combustion tube is heated to 600° C. by a high-temperature furnace, *G*.

Sample Vial, *J*. Sample vials are made from Pyrex tubing and have a shape similar to that shown in Figure 1.

PROCEDURE

Samples weighing from 0.20 to 0.35 gram are used. The method of weighing and introducing a particular sample into the system varies with physical properties. Liquids boiling below 200° C. are weighed in vials made by sealing one end of a 5-cm. length of 7-mm. Pyrex tubing and drawing out the other end into a fine capillary about 5 cm. long. The vial is weighed and the sample introduced by heating the vial, dipping the capillary tip into the sample, and allowing the sample to be drawn into the capillary as the vial cools. The vial containing the sample is weighed and the tare deducted to obtain the weight of the sample. Materials boiling above 200° C. are weighed in a platinum boat.

The combustion tube is moved into the furnace to a position such that about 15 cm. (6 inches) of the inlet end of the tube extends from the furnace. Gauze wicks, dipping into water, are wrapped around each end of the combustion tube about 2.5 cm. (1 inch) from the furnace. These wicks cool the exposed ends of the tube and thus permit the use of rubber connections for attaching the combustion tube to the rest of the assembly.

When the temperature of the furnace has reached 1300° C., the system is purged with a rapid stream of purified nitrogen for 5 minutes to expel all the air. The first absorption vessel, containing about 150 ml. of redistilled water, is attached to the combustion tube with rubber tubing; the rate of nitrogen flow is adjusted so that 30 to 40 bubbles per minute are formed in the end of the delivery tube. If the ratio of hydrogen to halogen in the sample is greater than 1, chlorine purified by passing over phosphorus (V) oxide is added along with the nitrogen.

The sample is introduced by opening the inlet end of the combustion tube, shoving the vial, capillary end first, or the boat containing the sample, into the tube to a point about 5 cm. (2 inches) from the open end, and then quickly closing the tube. The remainder of the absorption train is then attached. Low-boiling samples are almost completely volatilized by heat flowing back from the furnace. After no further reaction is noted, as evidenced by carbonaceous material issuing from the exit end of the tube, the cooling wick at the inlet end is removed and the combustion tube is moved into the furnace at a rate of about 1 cm. every 5 minutes. After each move, some time is allowed for complete reaction.

If the sample is introduced in a glass vial, care must be taken to avoid introducing any part of the vial into the furnace, to avoid sealing the sample tube before complete removal of the sample, and to prevent molten glass from adhering to the platinum. If the sample is introduced in a platinum boat, the tube is eventually shoved into the furnace as far as possible without burning the rubber connections. Complete decomposition is ensured by controlling the rate of evaporation to allow about 30 minutes for the decomposition of sample boiling below 200° C., and about 45 minutes for samples boiling above 200° C

When vaporization is complete, pyrolysis products are removed from the combustion tube by sweeping with nitrogen for an additional 15 minutes. Then the tube is pushed back into the furnace to remove condensation products. The absorption vessels may be removed, detaching the last vessel first and proceeding to the first vessel, which is detached at the combustion tube. All essential products of pyrolysis usually collect in the first absorption vessel and the remainder of the train serves only to absorb excess free chlorine or other volatile products. Carbonaceous material suspended in the solution in the first absorption vessel is removed by filtration through a Pyrex fritted-glass funnel.

While the solution of products is being filtered, preparations are made for a succeeding determination. The cooling wick at the end of the combustion tube is removed and the tube positioned in the furnace, so that the exit end is completely inside the heated zone. If the sample was introduced in a glass vial, the container is removed. Air is blown through the combustion tube to burn out any carbonaceous material. Then the position of the combustion tube is changed to place the inlet end as far inside the furnace as possible, and air is blown through as described previously. The tube is then moved into the position described for the determination.

The technique of handling the decomposition products varies with the composition of the compound. If fluorine is the only halogen present, the filtrate is boiled for 5 minutes and the hot solution titrated with standard alkali to a phenolphthalein end point. If chlorine is present, alone or with fluorine, the filtrate is diluted to 500 ml. in a volumetric flask and two 100-ml. aliquots are taken. To one aliquot is added 1 ml. of 30% hydrogen peroxide, after which the solution is boiled for 5 minutes and titrated while hot with standard sodium hydroxide to a phenolphthalein end point. The second 100-ml. aliquot is placed in an iodine flask, and 10 ml. of 6 *N* sulfuric acid and 10 ml. of 30% potassium iodide are added. The solution is shaken and allowed to stand in the closed container in the dark for 10 to 15 minutes. This solution is then titrated immediately with 0.1 *N* sodium thiosulfate to a starch end point. A blank correction should be made for distilled water and reagents used. This correction should be applied to all titrations.

Calculations are made by substituting appropriate values in the following equation:

$$\% \text{ H}_2 = \frac{100\{0.001[(\text{volume of NaOH} \times \text{N}_1) - (\text{volume of Na}_2\text{S}_2\text{O}_3 \times \text{N}_2)]\}}{(\text{weight of sample}) \dfrac{\text{ml. of aliquot}}{500}} \qquad (2)$$

DISCUSSION OF RESULTS

Only a few standard materials were available for analysis, but the results obtained for them show the high accuracy of the method. Research materials of high purity were also analyzed. Data obtained are shown in Table I. Since results obtained for hydrogen are in agreement with those expected, it appears that assumptions made at the outset are correct. While this procedure has been applied only to compounds containing less than 2% hydrogen, it should be applicable to compounds containing a greater hydrogen percentage.

Table I. Analysis of Halohydrocarbons

Sample	Purity	No. of Detns.	Per Cent Hydrogen	
			Theory	Found
Chloroform	C.P.	2	0.837	0.833, 0.841
Pentadecafluoroheptane	Infrared standard	2	0.270	0.271, 0.272
Polychloroheptanes	Research material, analyzed by microcombustion method	2	. . .	0.775, 0.755[a] 0.78 ± 0.02[b]
Dichloro-bis(trifluoromethyl)-benzene	Research material, b.p. 168–169° C.	5	0.707	0.719, 0.686, 0.750, 0.735, 0.757
Monochloro-bis-(trifluoromethyl)-benzene	Research material	3	1.205	1.17, 1.15, 1.19

[a] This procedure.
[b] Found by Huffman Microanalytical Laboratories, Denver 2, Colo.

Probable sources of error in this determination are incomplete decomposition of sample due to excessively rapid volatilization, inaccurate and infrequent determinations of blanks of water and reagents, incomplete removal of traces of oxygen from the nitrogen stream, and possible loss of hydrogen fluoride by etching of Pyrex apparatus used. The last item may be almost entirely eliminated by using a platinum delivery tube in the first absorption bottle.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of A. M. Ribley in making many of the routine analyses in connection with this paper. The investigation was conducted under a contract with the U. S. Army Corps of Engineers.

PRESENTED before the Division of Industrial and Engineering Chemistry, Symposium on Fluorine Chemistry at 110th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.

Decomposition and Analysis of Organic Compounds Containing Fluorine and Other Halogens

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A method was developed for the decomposition and subsequent analysis of organic compounds containing fluorine and other halogens. Decomposition is accomplished by reaction with sodium in liquid ammonia in a closed system at room temperature. The halogens following the decomposition are present as halide ions in a system permitting determination without further separation. Halogens, except fluorine, are determined by standard methods. The fluorine is determined as lead chlorofluoride using closely controlled conditions of temperature and chloride-ion concentration. The method is applicable to the routine analysis of solid, liquid, and gaseous substances.

EXTENSIVE investigations in the field of polyhalogenated organic compounds, especially those containing fluorine, led to a demand for a rapid routine method for the analysis of a large number of samples. The analysis of such materials may be divided into two distinct parts: decomposition of the sample, and determination of the halide ions.

DECOMPOSITION OF THE ORGANIC COMPOUND

The methods described in the literature for the decomposition of halogenated organic compounds either give incomplete decomposition of the very stable highly halogenated compounds or require an undesirable amount of time. Excellent reviews of the literature are given by Elving and Ligett (*1*) and by Nichols and Olsen (*4*).

The sodium and liquid-ammonia method of Vaughn and Nieuwland (*5*) is readily adaptable to routine analysis, but it does not completely decompose a high percentage of the polyhalo compounds. However, results obtained by this method indicated that it might be possible to obtain complete decomposition using a higher temperature and longer reaction time. In the method here proposed, the reaction is conducted at room temperature and reaction time may be varied according to the ease of decomposition of each particular sample. This is accomplished by the use of a sealed glass tube as a reaction container.

REAGENTS AND APPARATUS

Reagents. All chemicals employed are reagent grade or the highest purity obtainable. Reagents should be tested to ensure absence of halogens.

Reaction Tubes. A 50-cm. length of 13- to 14-mm. Pyrex tubing, standard wall thickness, closed at one end with a test-tube seal, constitutes the reaction container. Because of the high internal pressure generated during reaction, tubes should be free of flaws.

Agitation. The apparatus for holding and rotating the reaction tubes is shown in Figure 1. The machine consists of a steel rack made to hold 60 tubes and to rotate slowly (12 r.p.m.) on an axle in such a manner that the reaction tubes turn end-over-end. A 55-cm. (22-inch) length of $^1/_2$-inch I.P.S. iron pipe, closed at one end, is used as a safety shield for the glass tube. A hole, 0.3 cm. (0.125 inch) in diameter, is drilled about 2.5 cm. (1 inch) from the open end of the pipe to allow for escaping gases in case of failure of the glass tube. A cotton plug at the bottom and a short piece of 0.25-inch rubber tubing held in place by a spring clip at the top prevent the glass tube from moving and breaking due to mechanical shock. A metal plate is fitted over the open ends of the iron pipes and fastened to the frame with bolts and wing nuts.

Safety Equipment. Goggles, face mask, and rubber gloves are provided for general protection in handling the reaction tubes and liquid ammonia. An ammonia gas mask should be readily available.

DECOMPOSITION OF SAMPLE

The manner of weighing samples depends upon the physical state. Gases and low-boiling liquids (<50° C.) are weighed in sealed Pyrex vials, gases being condensed before weighing. The vials may be made by drawing out both ends of a short length of 7-mm. Pyrex tubing to a fine capillary and sealing one end. The sample is introduced into the tared vial by warming the main body of the vial, and then dipping the unsealed capillary into the liquid sample at the time the body of the vial is dipped into a dry ice and alcohol bath. When a sufficient quantity of sample has entered the tube, the open tip is removed from the main body of sample, all liquid in the capillary is allowed to flow into the vial, and the capillary is sealed. The vial is then removed from the cooling bath, wiped dry, and weighed. Glass-stoppered Victor Meyer weighing vials, open vials, or small porcelain microcombustion boats are utilized for weighing other than low-boiling liquids, depending upon volatility and viscosity. Solids are weighed in either open vials or porcelain boats.

The vial or boat containing 0.120 to 0.002 gram of sample is introduced into a reaction tube containing about 5 ml. of anhydrous ethyl ether. As all materials examined were at least slightly soluble in ethyl ether, this solvent was used in preference to others which become solid at the temperature of a dry ice and alcohol bath. Metallic sodium (0.5 to 1.0 gram), cut in slender strips or small cubes, is added and the tube is placed in a dry ice–alcohol bath. Then, liquid ammonia (10 to 15 ml.) is distilled into each tube, after which the charged tube is sealed in the same manner as a Carius tube and shaken for at least 5 hours at room temperature. After decomposition is complete, the tubes are removed from the shaker, cooled in a bath of dry ice and alcohol, and opened by applying a pin-point flame to a spot near the seal. This allows the slight internal pressure to blow out an opening and release the pressure. The sealed tip is first broken off and placed in a 500-ml. Erlenmeyer flask containing about 10 ml. of 95% ethanol, after which the reaction tube is removed from the bath, wiped dry with a clean cloth, and inverted into the Erlenmeyer flask. When vigorous reaction has ceased, the inside of the reaction tube is rinsed several times with small portions of ethanol and then with hot distilled water, all washings being transferred to the Erlenmeyer flask. The volume of the washings should not exceed 150 ml. If carbonization occurs during decomposition, the solution is filtered through a fine Pyrex fritted-glass filtering funnel, Büchner type. The samples at this point are ready for determination of halide ions.

DETERMINATION OF HALIDE IONS

The determination of halide ions, other than fluoride, is accomplished by a modification of the Volhard method, using nitro-

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benzene to coagulate, coat, and remove the silver halide from the reaction medium rather than filtering. If more than one halide other than fluoride is present, an indirect method is used for determination which combines the Volhard method with precipitation, filtration, and weighing of the silver halide.

For the determination of fluoride ion, the precipitation of lead chlorofluoride by the method of Hawley (*2*), followed by the titration of the redissolved precipitate as suggested by Hoffman and Lundell (*3*), offers a rapid procedure. However, early experience indicated that results of this sequence were not consistent. Variations in temperature of solution during precipitation appeared to exert some influence, and it was noted that low results were obtained for compounds containing less than 25% or more than 60% fluorine, while high results were obtained for compounds having between about 35 and 55% fluorine.

A study of the variables concerned led to a modified procedure for the precipitation of lead chlorofluoride. The accuracy of results is greatly influenced by small changes in chloride-ion concentration of the solution. By carefully controlling the amount of dilute hydrochloric acid added to the solution before precipitation and by maintaining the temperature at 5° ± 1° C., accurate results are obtained.

DETERMINATION OF FLUORIDE ION

After decomposition, the solution containing the decomposition products is transferred to a 250-ml. volumetric flask and diluted to the mark with distilled water. Two 100-ml. aliquots are transferred, one to a 500-ml. Erlenmeyer flask and the other to a 400-ml. beaker. The solution in the flask is acidified with nitric acid, and the halide, other than fluoride, determined by the modified Volhard method. If the composition of the sample is known within the limits of 5%, the volume of dilute hydrochloric acid (100 ml. of C.P. acid diluted to 1 liter) to be added to the aliquot for the fluoride ion determination is calculated by referring to Table I and correcting for the chloride ion furnished by the sample. If the composition of the sample is unknown, a preliminary determination is made assuming 50% fluorine and a more precise determination is made later from the initial results.

After addition of the required volume of dilute hydrochloric acid, the solution is neutralized to a methyl orange end point with dilute (1 to 3) nitric acid, and 3 drops excess acid are added. The solution is cooled to 5° ± 1° C., precipitated by addition of 15 ml. of a 10% lead acetate solution containing 80 ml. of glacial acetic acid per liter, and allowed to stand with frequent stirring in an ice-water bath at 5° ± 1° C. for 1 hour. The precipitate is filtered, washed three or four times with cold distilled water, and dissolved in warm dilute (1 to 3) nitric acid, and the chloride is titrated by the Volhard method. The percentage of fluorine in the sample is calculated from the ratio of one atom of fluorine to one atom of chlorine in lead chlorofluoride.

Table I. Volume of Hydrochloric Acid Solution for 0.12-Gram Samples Containing Different Percentages of Fluorine

Fluorine %	HCl *Ml.*	Fluorine %	HCl *Ml.*
5	3.80	45	1.96
10	3.23	50	2.02
15	2.68	55	2.09
20	2.18	60	2.16
25	1.95	65	2.27
30	1.77	70	2.43
31.5[a]	1.73	75	2.59
35	1.79	80	2.75
40	1.90	85	2.91

[a] At 31.5% F, the minimum quantity of chloride ion is required.

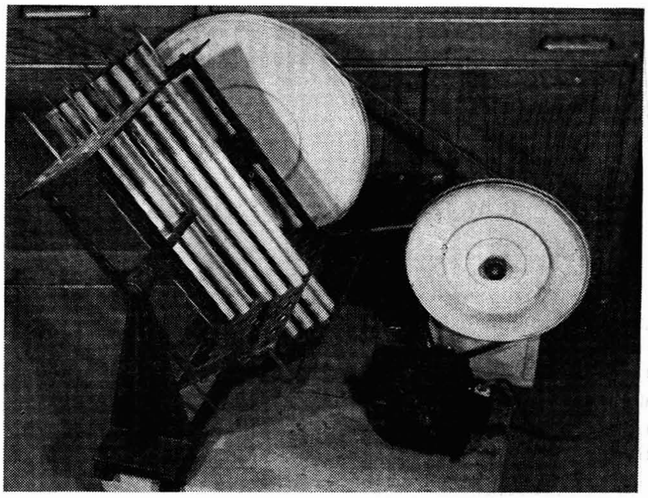

Figure 1. Shaking Machine

APPLICABILITY OF THE PROCEDURE

The procedure described for the decomposition and analysis of polyhalogenated organic compounds is adaptable to the routine analysis of fluorine-containing compounds, including perfluoro compounds. Complete decomposition was obtained with all materials investigated, and the fluoride ion determination is as accurate as other known procedures and far less time-consuming. The time required for a single determination is about 7 hours but, by simultaneously charging a plurality of tubes in late afternoon, allowing decomposition to occur overnight, and completing the analysis the next day, two analysts can make duplicate determinations of 10 to 15 samples per day.

Data showing the results obtained with representative samples containing fluorine and chlorine are presented in Table II. No materials containing bromine and iodine were available as standards, but several research materials were analyzed satisfactorily. The sample of perfluoroheptane was used as a standard for the regular checking of the accuracy of the fluorine determination.

ACKNOWLEDGMENTS

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Table II. Analysis of Organic Halogen Compounds

Compound	Purity B.P. ° *C.*	No. of Detns.	Theory F %	Theory Cl %	Found F %	Found Cl %
Perfluoroheptane	81.7	10	78.35	...	78.2 ± 0.6	...
Monochloroperfluoroheptane	...	2	70.6	8.8	69.5 ± 0.1	...
Dichloro-bis(trifluoromethyl)-benzene	168–169	4	40.3	25.1	40.2 ± 0.3	24.8 ± 0.3
Perfluorodimethylcyclohexane	...	2	76.1	...	76.1 ± 0.1	...
Perfluorocyclohexadiene	56.6	2	67.9	...	67.9 ± 0.1	...
Monochlorohexafluorobutenes	38.0–38.3	2	57.4	17.9	57.1 ± 0.3	18.0 ± 0.2
Tetrachlorotrifluoropropane	127.5–129	2	...	60.1	...	60.4 ± 0.2
Tetrachlorotetrafluoropropane	111.1	2	...	55.9	...	56.6 ± 0.1

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Determination of Fluorine and Chlorine in Organic Compounds

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In the analysis of organic compounds containing fluorine, or both fluorine and chlorine, the sample is weighed in a gelatin capsule or glass ampoule, and heated with metallic potassium in a nickel bomb at 500° to 550° C. for 2 hours. The bomb is washed out and the resulting solution is made up to volume. Half of this solution is titrated for chloride by the Volhard method. The other half (or less) is analyzed for fluoride by distillation and titration with thorium nitrate. The method is particularly suitable where high accuracy is desired. The bomb method of decomposition is very convenient and certain, and the determination of chloride is short and simple. The distillation and titration of fluoride are rather laborious, and correct interpretation of the end point requires some practice. The lead chlorofluoride method as recently improved by Donovan (*3*) might be used in the determination of fluoride, with some saving in the time required of the analyst.

IT IS recognized that many of the methods commonly employed for the decomposition of organic compounds, while adequate to bring chlorine, bromine, or iodine completely into ionic form, do not succeed in transforming organically bound fluorine quantitatively to fluoride ion. An excellent summary and bibliography of the various decomposition methods which have been attempted have been given by Elving and Ligett (*5*). They employ heating with metallic potassium in a sealed Pyrex tube at 400° C. for 30 minutes. Various shortcomings of this procedure are mentioned, and the suggestion is made that better results might be achieved by increasing the time and temperature of the decomposition period.

DISCUSSION

It is pointed out by Elving and Ligett (*5*) that compounds containing two or three fluorine atoms on a single carbon atom are particularly resistant to attack. This was corroborated by the present investigation. Pure benzotrifluoride was not completely decomposed by heating with potassium at 400° C., even when the heating period was extended to 1.5 hours; the value obtained for fluorine varied from 37.4 to 38.7%, compared to a theoretical fluorine content of 39.01%. The use of higher temperatures and longer heating periods did not improve results, and led to extensive attack upon the glass tubes, sufficient in some cases to use up all the excess of potassium.

Tubes made of Corning alkali-resistant glass proved to be more resistant to attack, allowing the decomposition to be carried out at 450° C. for 2.5 hours. The attack on the glass was reduced, and some excess potassium was still present at the end. However, several results were obtained as high as 1% fluorine above theory, and it seemed possible that fluorine was being extracted from the glass.

To overcome these disadvantages, a small nickel bomb was designed and constructed. This has proved to be a convenient and satisfactory means of carrying out the decomposition under sufficiently drastic conditions. The most resistant fluorine compounds are quantitatively decomposed by heating in the bomb with metallic potassium at 500° to 550° C. for 2 hours in a muffle furnace. After suitable chemical treatment, a clear solution is obtained in which chloride and fluoride ion can be determined by standard methods.

Titration of chloride is carried out by the Volhard method. The determination of fluoride is based on the familiar distillation method of Willard and Winter, which has been widely used in the estimation of micro amounts of fluorine (*1*, *11*). The successful analysis of macro amounts is, however, a much more exacting problem. The recovery of 90% of the fluorine can be considered satisfactory when dealing with a few parts per million, but when a compound containing 20 to 80% of fluorine is being analyzed no such losses can be tolerated.

The method of titration with thorium nitrate was adapted from that of Rowley and Churchill (*10*). Since the completion of this work, a comparable degree of accuracy has been reported by Matuszak and Brown (*9*), who include an excellent bibliography. The use of silver perchlorate follows Eberz, Lamb, and Lachele (*4*)

ANALYTICAL PROCEDURE

The sample for analysis is weighed in a gelatin capsule or glass ampoule, and decomposed by heating with metallic potassium in a nickel bomb. An aliquot of the resulting solution is titrated for chloride by the Volhard method. A second aliquot is analyzed for fluoride by distillation and titration with thorium nitrate.

For convenience, the procedure is divided into three sections: decomposition of the sample, determination of fluoride, and determination of chloride.

DECOMPOSITION OF THE SAMPLE

Apparatus and Reagents. DECOMPOSITION BOMB. Details of construction are shown in Figure 1.

Before use, the steel parts, *C* and *D*, of a new bomb should be heated up slowly in the muffle, until they take on a blue oxide coating. This prevents freezing. The threads and bearing surfaces between steel and nickel are kept lubricated with grease and graphite. A high-temperature grease such as Merco-Nordstrom No. 665-S is suitable.

The gasket employed between the polished nickel faces of cover *A* and cup *B*, is a single 3.44-cm. (1.375-inch) circle of heavy waterproof cellophane. As the closed bomb is heated, the differential expansion of nickel and steel increases the pressure between the nickel faces as the gasket carbonizes, and ensures a perfect seal, with no tendency for the faces to stick or seize.

After the bomb is charged and assembled to finger tightness, the steel socket nut, *D*, is held in a vice or suitable bench jig, and the inner nut, *C*, is tightened down well with a 16-inch wrench. To open, *C* is loosened a part turn, and *A* and *B* are tapped gently to break the seal, before *C* and *D* are removed. This safely releases any small pressure which may be present, without danger of loss.

REFLUX APPARATUS for decomposition with methanol consists of a strong Pyrex cylinder resembling a large test tube 5 × 17 cm., large enough to hold the nickel bomb cup, *B*. The cylinder is closed with a large rubber stopper, bearing a straight 40-cm. reflux condenser. The cylinder is heated in the steam bath.

ELECTRIC MUFFLE FURNACE, with heat control and temperature indication. The standard laboratory size with inside dimensions 7.5 × 10.6 × 25 cm. (3 × 4.25 × 10 inches) will serve.

REAGENTS. Metallic potassium (Baker's).

Methanol. Four liters of C.P. grade are redistilled, after the addition of 10 grams of solid caustic, discarding the first and last 500 ml. It should give no test for chloride.

Ammonium bicarbonate, c.p.

Cylinder of carbon dioxide.

A volumetric flask calibrated to contain 203 ml. (to allow removal of two 100-ml. aliquots).

No. 3 gelatin capsules (Parke, Davis or Eli Lilly are satisfactory, in original package under a single manufacturer's lot number).

Light petroleum ether.

Procedure for Decomposition. Ordinary solid or liquid samples are weighed in a No. 3 gelatin capsule, with a tight cover. Very volatile liquids can be weighed in a glass ampoule, which should be thin, so as to reduce the amount of glass present to react with the metallic potassium. For gases, the ampoule bulb is blown in the center of a capillary, and is cooled with dry ice while the gas is slowly drawn through it until sufficient has condensed in the bulb. The sample size depends only on the fluorine content and disregards the chlorine content. It should vary from 0.10 gram for high to 0.35 gram for low fluorine content.

Clean and dry the bomb. Under light petroleum ether, cut clean pieces of potassium totaling about 1.0 gram. Quickly dry them by evaporation and drop them into *B*. Close the cup with a cork stopper. Weigh the sample in a covered gelatin capsule, and drop the capsule into the bomb cup. Immediately insert the circle of cellophane, close, and tighten the bomb.

The muffle furnace has meanwhile been brought up to temperature. Place the bomb in it, supported in a moderately slanting position to keep the molten potassium away from the gasket. Heat it for 2 hours at 500° to 550° C.

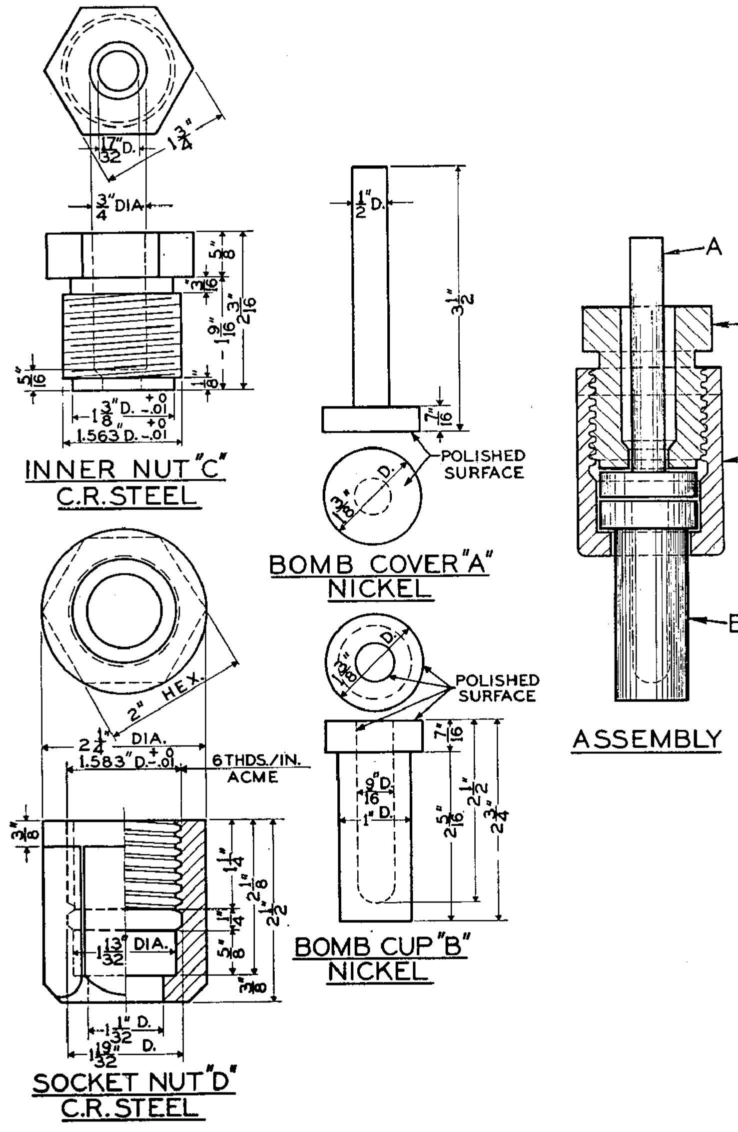

Figure 1. Decomposition Bomb

Remove and cool the bomb, preferably under an air blast. Open it as described, which releases any slight pressure which may be present, but keep cover *A* on cup *B*. Place 10 ml. of purified methanol in the bottom of the reflux apparatus, assemble it, and replace the air with carbon dioxide through a tube leading down through the reflux condenser and extending about 2.5 cm. (1 inch) below it. Remove the condenser, and by means of suitable tongs (made by slight bending of ordinary crucible tongs) carefully lower *B* with *A* still in place into the reflux cylinder, and finally lift out *A*. Attach the reflux condenser and purge again briefly with carbon dioxide, then lift out the carbon dioxide inlet tube.

Heat the apparatus in the steam bath until the methanol refluxes vigorously. As it condenses and runs down inside the bomb cup, it decomposes the excess potassium safely and quietly. After about 10 minutes, reach down inside the bomb cup with a long glass rod through the reflux condenser, and break up any lumps, which usually enclose potassium and prevent its decomposition. Leaving the glass rod in place, continue the reflux for 10 minutes longer. Then add 20 ml. of water, using it to rinse the rod as it is lifted out. Continue the reflux for 15 minutes to complete the decomposition.

With warm water, rinse *A*, *B*, and the reflux apparatus into a 500-ml. Erlenmeyer flask, using a rubber policeman to loosen any carbonaceous material sticking to the bomb. About 200 to 250 ml. of liquid should be collected. To this add about 1.5 grams of solid ammonium bicarbonate and a few boiling beads, and boil it down to 75 to 100 ml. This removes the methanol and most of the hydrocyanic acid (formed from the gelatin capsule); it converts potassium hydroxide to carbonate; and it extracts any remaining chloride or fluoride from the carbonaceous residue. Filter this solution into a volumetric flask calibrated to hold 203 ml., wash the residue on the filter thoroughly, make up the volume to 203 ml., and shake well. This solution (Solution X) should be clear and colorless.

DETERMINATION OF FLUORIDE

Reagents. Soft glass boiling beads.

Powdered soft glass, made by grinding in an agate mortar.

A 33% solution of silver perchlorate (GFS hydrated) in water.

Vacuum-distilled 72% reagent perchloric acid.

Thorium nitrate solution containing 2.0 grams of thorium nitrate tetrahydrate per liter, in 0.01 *N* nitric acid.

Nitric acid, 0 5 *N*.

Solid ferrous sulfate heptahydrate.

Potassium permanganate solution, 5%.

Sodium bicarbonate solution, 5%.

Indicator solution containing 0.100 gram of alizarin red (sodium alizarin sulfonate) in 1 liter of water.

Buffer Solution. Dissolve 9.4 grams of monochloroacetic acid in 30 ml. of water, and dilute it to 60 ml. Neutralize 38 ml. with 20% sodium hydroxide and mix with the remainder. Dilute to 100 ml. This solution does not keep well and should be made up fresh every two weeks.

Apparatus. The distillation equipment is shown in Figure 2. Steam is generated in a 3-liter round flask two-thirds full of water, containing 1 to 2 grams of potassium permanganate and a few boiling beads. The flask is provided with a safety tube 4 or 5 feet long, to allow for moderate steam pressure. The steam-distillation flask, *A*, made by Scientific Glass Apparatus Company, Bloomfield, N. J., Catalog No. J-1699, is a 250-ml. Pyrex round flask with thermometer well and ₮ 24/40 ground joint. A little mercury in the thermometer well ensures good contact. An ordinary 3-bulb condenser is used, with the inner tube lengthened to reach to the bottom of a 500-ml. volumetric flask serving as the receiver *A* is heated by a burner through a 5.6-cm. (2.25-inch) opening in a 20-cm. (8-inch) square of Transite board (*2*). This feature, together with the design of the special distilling head, *B*, contributes materially to the success of the determination by reducing the amount of acid carried over into the distillate.

Standardization of Thorium Nitrate Solution. An ideal standard would be an inorganic fluoride of high and exactly known purity. The preparation of such a sample is, however, a difficult and laborious process (*7, 8*). The authors have therefore used two different standards, and concluded from the close agreement obtained that the results are sufficiently accurate for all practical purposes.

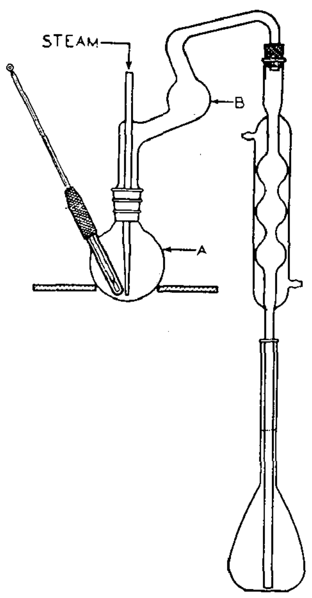

Figure 2. Distillation of Fluoride

Standardization by Sodium Fluoride. The material used was Baker's C.P. analyzed sodium fluoride. Correction was made for the stated impurities of insoluble sulfate, sulfite, chloride, and hydrogen fluoride. These totaled 0.07%, some of which was compensated for by the presence of hydrogen fluoride, so that the fluoride content was calculated to be that of a sodium fluoride 99.99% pure. The material was dried in the oven at 140° to 150° to constant weight, and a determinate solution made up by weight to contain exactly 1.0000 gram of fluoride per liter or 1 mg. of fluoride ion per ml.

A 50-ml. portion containing 50 mg. of fluoride is distilled by exactly the same procedure to be used later in the determination. The thorium nitrate solution is standardized and the titration blank is determined by titration of this distillate.

Pipet 50 ml. of the standard sodium fluoride solution into the evolution flask, *A*, and dilute it to 100 ml. with water. Add 8 to 10 boiling beads and about 0.5 gram of ground glass. This acts as an abundant source of the necessary silica and greatly reduces the etching of the flask. Add 5 ml. of 5% sodium bicarbonate solution to the 500-ml. volumetric flask which serves as the receiver. Add 1 ml. of 33% silver perchlorate to 25 ml. of 72% perchloric acid, and pour into *A*. Set the distilling head in place.

Meanwhile, the steam generator should have been heated to boiling. Connect the distilling head to the condenser, and attach the steam generator. While a very slow current of steam passes through *A*, evaporate the sample solution over a strong flame, until the thermometer in the well reads 128° to 132° C. Then hold this temperature in the evolution flask, increase the flow of steam, and continue the distillation until 440 to 470 ml. of distillate have been collected, which requires about 0.75 hour.

Shut off the burners, and disconnect the steam delivery tube. (A T-tube with pinchclamp can be inserted into this line if desired.) Detach the condenser and rinse it down into the volumetric flask. Make the distillate up to the mark with distilled water and shake thoroughly.

The thorium nitrate solution is now standardized, and the titration blank is determined by titrating a 50- and a 10-ml. aliquot of this distillate, containing 5 and 1 mg. of fluoride ion.

Pipet 50 ml. of the distillate into a 125-ml. Erlenmeyer flask. Pipet in 1 ml. of indicator, and add 0.5 *N* nitric acid drop by drop until the yellow acid color of the indicator is barely reached. Pipet in 1 ml. of buffer solution.

The solution is now titrated with the standard thorium nitrate solution. It is essential to avoid any local excess of thorium nitrate during the titration, which would cause the precipitated thorium fluoride to acquire a pink color before the true end point is reached. To prevent this, the thorium solution is added dropwise no faster than 5 ml. per minute, with continuous swirling. The end point is the first permanent tinge of pink. This is best seen by comparison with a blank titration.

The blank is conveniently prepared by diluting a portion of the standard fluoride solution fivefold. Place 20 ml. (containing 4 mg. of fluoride) in a 125-ml. Erlenmeyer flask, add 30 ml. of water, and 1 ml. each of indicator and buffer solution. Run in slowly 12.5 ml. of the standard thorium nitrate solution, which is 1.5 ml. below the equivalent amount. One blank will serve for several hours before replacement.

The titration and the blank are best compared by placing the two flasks side by side on a white paper in front of a daylight titration lamp and looking down through the solutions from above. As the end point is approached, the two flasks are compared after the addition of each drop of thorium nitrate. They will match exactly until the end point is reached, when the faint pink color produced by the first excess of thorium nitrate will throw the colors out of balance. The total time for each titration should be held uniform at 10 to 15 minutes. The flocculent thorium fluoride that settles out after the titration is finished should have a faint pink color that persists after several hours' standing.

In exactly the same way, titrate a 10-ml. aliquot of the same distillate, made up to 50 ml. with water and containing 1 mg. of fluoride ion. Let *A* equal the milliliters of thorium nitrate required to titrate 5 mg. of fluoride ion, and *B* the milliliters required for 1 mg. Then:

$$\begin{aligned}
A &= \text{ml. equivalent to 5 mg. of } F^- + \text{titration blank}\\
B &= \text{ml. equivalent to 1 mg. of } F^- + \text{titration blank}\\
A - B &= \text{ml. equivalent to 4 mg. of } F^-\\
(A - B)/4 &= \text{ml. equivalent to 1 mg. of } F^- = C\\
B - C &= \text{ml. equivalent to titration blank}\\
5/(A - \text{titration blank}) &= \text{mg. of } F^- \text{ per ml. of thorium nitrate}
\end{aligned}$$

If the thorium nitrate solution is standardized directly against sodium fluoride without going through the distillation, an appreciable error results, which seems to be caused by a small constant fraction of 0.8% of the fluoride which escapes distillation. This error is avoided by standardizing with the same distillation procedure as used in the determination. It is often convenient to determine the exact relationship between the titration of the sodium fluoride solution with and without distillation, and thereafter to use the solution directly for standardization, making the necessary correction. An actual comparison is shown in Table I.

In practice it is also frequently necessary, when dealing with smaller quantities of fluorine, to evaporate a larger aliquot of the distillate to dryness, and to rinse the residue into the small Erlenmeyer flask and dilute to 50 ml. for titration. Table I, in which the samples starred were subjected to such an evaporation, shows that no error is thereby introduced. Distillation 1 was used to standardize the thorium nitrate, giving 0.2890 mg. of fluoride ion per ml., and a titration blank of 0.14 ml. to be subtracted. By the use of these figures, it was then possible to distill and titrate from 5 to 100 mg. of fluoride ion with high precision, as shown by Table I.

Standardization by Lead Chlorofluoride. This method depends on the precipitation of lead chlorofluoride under conditions where the precipitate should have the correct composition. The procedure is that usually employed for the preparation of a lead chlorofluoride wash solution (*6*).

Table I. Distillation and Recovery of Sodium Fluoride

Distillation No.	F^- Distilled	Thorium Nitrate	F^- Titrated	F^- Found	Recovery
	Mg.	*Ml.*	*Mg.*	*Mg.*	%
1	50	17.44	5	...	...
		17.45	5	...	...
		17.44	5	...	...
		3.60	1	...	...
2	25	17.49	5*	5.010	100.2
		17.44	5*	4.996	99.9
		8.78	2.5	2.495	99.8
		8.79	2.5	2.498	99.9
3	25	17.45	5*	5.004	100.1
		8.77	2.5	2.494	99.8
4	10	7.04	2*	1.993	99.7
5	5	3.58	1*	0.994	99.4
6	100	17.48	5	5.012	100.2
Without distillation		3.65	1	...	...
		17.60	5	...	...
		17.60	5	...	...

Ten grams of lead nitrate were dissolved in 200 ml. of water, and the solution was poured into 100 ml. of water containing 1.0 gram of sodium fluoride and 2 ml. of hydrochloric acid. The precipitate was washed thoroughly by decantation with 200-ml. portions of water, until the wash gave only a small constant trace of chloride. Enough 20% sodium hydroxide solution was added to dissolve the precipitate easily at room temperature, and the solution was diluted to 1 liter. The concentration of chloride in this solution was carefully determined by the Volhard titration, and from this value the concentration of fluoride was calculated.

Distillation of 100- and 20-ml. portions of this solution and titration with standard thorium nitrate solution were carried out as described. The value obtained for the thorium nitrate was 0.2886 mg. of fluoride per ml. This is close enough to the 0.2890 mg. of fluoride per ml. obtained from sodium fluoride to justify the choice of the latter as sufficiently accurate for all practical purposes.

The authors also attempted to use Bureau of Standards' fluorspar sample No. 79 as a standard. The results were far from those above and seemed to indicate a higher fluorine content than given in the Bureau of Standards analysis.

Procedure for Determination of Fluoride. Pipet 100 ml. of solution *X* into the evolution flask *A*. If this aliquot contains more than 70 mg. of fluoride, use a 50-ml. aliquot instead and dilute it to 100 ml. with water. Add to the flask 10 drops of 5% potassium permanganate solution, and heat on the steam bath for one hour. Hold the purple color by adding a few more drops of permanganate solution, if necessary.

Add about 0.5 gram of solid ferrous sulfate. This serves to reduce the permanganate, which is harmless when fluoride alone is present; but when the solution also contains chloride, the acid permanganate evolves a little free chlorine which distills over and bleaches the indicator during the titration of fluoride.

While the flask is still hot, add 8 to 10 boiling beads and about 0.5 gram of ground glass. Add 2 ml. of 33% silver perchlorate, which must be in excess of the chloride present; this quantity will take care of chloride up to 100 mg. Add 5 ml. of 5% sodium bicarbonate solution to the receiver, and connect up the evolution apparatus. Finally, just before connecting the steam, add 25 ml. of 72% perchloric acid through the steam inlet tube, by means of a slender funnel. This avoids possible loss of silicon tetrafluoride through the evolution of carbon dioxide from the potassium carbonate present. Connect the steam inlet tube and start the distillation without delay.

Conduct the distillation exactly as described for the sodium fluoride solution. Titrate the distillate in a volume of 50 ml., containing from 2 to 6 mg. of fluoride ion. With the higher ranges of fluorine content, this can be obtained by pipetting an aliquot of the distillate directly into the 125-ml. titration flask and diluting to 50 ml. of necessary. With lower concentrations of fluoride, it is necessary to evaporate a larger aliquot to dryness on the steam bath. Rinse the residue into the Erlenmeyer flask with hot water and dilute to 50 ml. for titration. It is advisable to use the blank titration to aid in obtaining the end point. The presence of a little nitric acid increases the stability of the thorium nitrate reagent, but the authors find it advisable to restandardize at least once a month.

The gelatin capsules and reagents used have always been free from fluorine. A blank should be run as described for chloride.

DETERMINATION OF CHLORIDE

Reagent. Silver nitrate and ammonium thiocyanate solutions, 0.1 *N*.

Nitric acid, chloride-free.

Hydrogen peroxide, 3%, chloride-free.

Potassium permanganate solution, 5%.

Nitrobenzene, chloride-free.

Ferric Alum Indicator. Dissolve 2.27 kg. (5 pounds) of ferric ammonium alum in 2 liters of water containing 30 ml. of concentrated sulfuric acid, and add 3 liters more water.

Procedure for Determination of Chloride. Pipet 100 ml. of solution X into a 500-ml. glass-stoppered Erlenmeyer flask. Add 10 drops of 5% permanganate solution and heat on the steam bath, adding more permanganate if necessary to hold the purple color. After one hour, add dilute hydrogen peroxide drop by drop to reduce the excess of permanganate. Acidify with nitric acid, and add more peroxide if necessary to dissolve any manganese dioxide. Cool the solution, and titrate for chloride by the Volhard method.

Run a blank on the gelatin capsule and the reagents, by carrying a complete determination through the bomb and subsequent treatments, using a single capsule without the sample. It is best to titrate this blank in the same volume of approximately 150 ml. as used in titration of the determination, so that the indicator blank will be the same. The chlorine content of gelatin capsules is sufficiently constant within the same manufacturer's lot number, but a new blank should always be run on capsules bearing a different lot number.

Table II. Analytical Results on Substances of Known Composition

Sample	F Theory %	F Found %	Cl Theory %	Cl Found %
Benzotrifluoride, $C_7H_5F_3$	39.01	39.2, 39.1 38.7, 38.9 38.9	... ...	....
Freon-113, $C_2Cl_3F_3$	30.4	30.5	56.8	56.5
Dichlorohexafluorobutene, $C_4Cl_2F_6$	48.7	48.6	30.75	30.9
Perfluoroheptane, C_7F_{16}	78.34	78.5, 78.3 78.6, 78.5 78.7, 78.6 78.4	...	....
Dichloro-bis (trifluoromethyl)-benzene, $C_8H_2Cl_2F_6$	40.3	40.3, 40.6	25.05	25.2, 25.2 25.1, 25.0 25.3, 25.1
Dichloro(trifluoromethyl)-perfluorocyclohexane, $C_7Cl_2F_{12}$	59.5	59.0, 59.5	18.5	19.1, 19.2
Trichloro(trifluoromethyl)-perfluorocyclohexane, $C_7Cl_3F_{11}$	52.4	52.4, 52.6	26.6	26.7, 26.8 26.8
Tetrachloro(trifluoromethyl)-perfluorocyclohexane, $C_7Cl_4F_{10}$	45.7	46.1, 45.7 45.7	34.1	33.7, 33.8 33.6

As an illustration of the magnitudes involved, the actual titration of a blank determination on one capsule, in 150-ml. volume, was 0.04 ml. of silver nitrate. This, of course, represents the combined reagent, capsule, and indicator blank. Considered as milliliters of silver nitrate, it is the resultant of a positive indicator blank and a negative reagent and capsule blank. In the present case the 0.04 ml. of silver nitrate is a negative blank, and should be subtracted from the milliliters of silver nitrate used in the determination.

The capsules used have never contained any detectable fluorine. It is a curious fact that a blank titration, or a determination in which fluoride is completely absent does not show any indicator blank for the thorium titration—that is, the first drop of thorium nitrate gives the pink end point. When fluoride is present, however, there is a definite titration blank which is determined and used as described.

Results on a number of substances of known composition are given in Table II. The last five samples were obtained through the courtesy of E. T. McBee of Purdue University.

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Constant-Temperature Steam-Distillation Apparatus for Isolation of Fluorine

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An improved apparatus made entirely of glass for the isolation of fluorine is described, with details of design and a procedure for its use. The process is shorter and more convenient than processes previously described. Data are presented to show the accuracy and the effect of possible interfering agents.

FLUORINE has been separated and isolated by evolution of silicon tetrafluoride in the absence of water in a glass system by Armstrong (*1*) and Kolthoff and Stansby (*10*). The isolation of fluorine from an aqueous solution was accomplished by Willard and Winter (*16*) by distilling the sample in the presence of sulfuric or perchloric acid at a temperature of 135° C., maintained constant by addition of water during the distillation. Essentially the same method has been used by others (*4, 5, 6, 8, 9*). The original apparatus of Willard and Winter was modified by Scott and Henne (*15*) by placing an inverted U-shaped side arm on the distillation flask to prevent contamination of the distillate due to bumping. Steam was added to the distillation flask by Rempel (*14*) to maintain a temperature of 135° C. A distillation apparatus described by McClendon and Foster (*11*) had a spray trap included in the neck of the flask which reduced contamination of the distillate and improved the efficiency of the distillation. Armstrong (*2*) used silver perchlorate to remove chloride ion in the distillation of fluorine from a perchloric acid solution, and McClure (*12*) used silver sulfate with sulfuric acid for the same purpose.

Gilkey, Rohs, and Hansen (*7*) describe a distillation apparatus in which steam is introduced into a distillation flask mounted in a metal container in which tetrachloroethane is refluxed. This equipment provides an almost automatic arrangement for the regulation of temperature to 145° C. However, when distillation equipment was constructed by the authors to the exact specifications stated in the above-mentioned paper, low and erratic yields of fluorine were obtained. It was found that slight air currents in the laboratory atmosphere would cause enough fluctuation of temperature inside the metal container to cause incomplete volatilization of fluorine or on the other hand contamination of the distillate by the volatilization of traces of sulfuric acid. The heat furnished to the metal reflux container was varied over a wide range, but satisfactory results were not obtained. Moreover, the use of rubber stoppers in the apparatus was unsatisfactory because of the solvent action of hot tetrachloroethane. Gilkey, Rohs, and Hansen (*7*) do not show analytical data, but it appears that possibly some compensating error is present in their work such as entrainment of traces of sulfuric acid into the distillate and/or incomplete removal of fluorine to the distillate.

Design of an improved apparatus embodying the essential principles as described by Gilkey, Rohs, and Hansen (*7*) should entail the following:

1. The reflux chamber for the tetrachloroethane should be made of a material having low enough thermal conductivity so that drafts in the laboratory will not appreciably influence the temperature in the distillation chamber.
2. The reflux liquid should not come into contact with any soluble material.
3. The operation of the apparatus should be as nearly automatic as possible, and the time for each distillation should be held to a minimum.

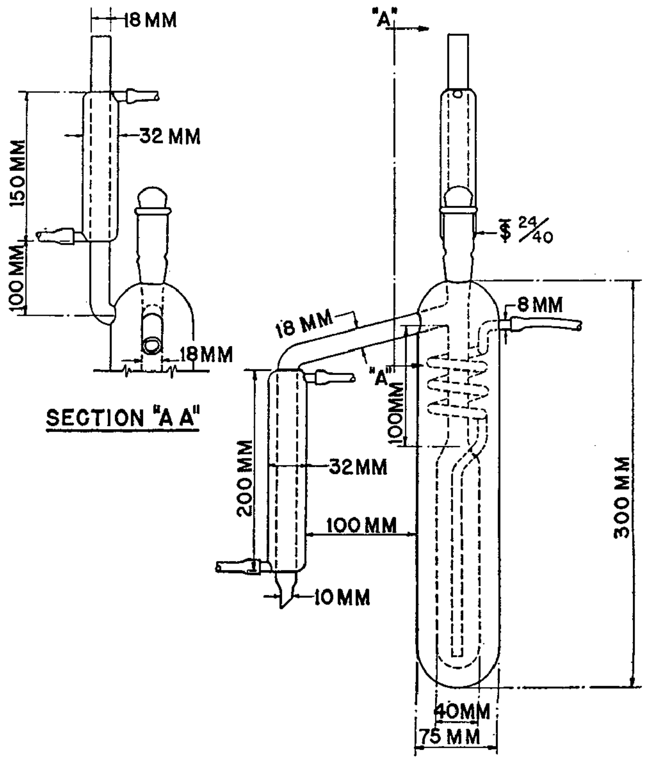

Figure 1. Diagram of Apparatus

The apparatus shown in Figure 1 has been found to fulfill the requirements listed above.

The apparatus is made entirely of Pyrex and is of one-piece construction. Redistilled *sym*-tetrachloroethane is added to the reflux condenser until approximately three quarters of the distillation bulb is covered. Sulfuric acid and sample are introduced through the ground joint by means of a long-stemmed funnel. Steam enters from a generator through the 8-mm. inlet, is preheated in the glass coil, and bubbles through the liquid in the bottom of the distillation chamber. The distillate vapor passes through the 18-mm. side arm to the condenser. Liquid is collected at the bottom of the condenser in a 100-ml. volumetric flask. The apparatus is heated with a 750-watt shallow-cone electric heater. Steam is most conveniently generated from a 2-liter flask containing distilled water made just alkaline to phenolphthalein. The steam generator is heated by a 250-watt coil of Nichrome wire immersed in the flask and the voltage applied to the coil is controlled by a variable autotransformer. This electric heating arrangement gives an almost instantaneous control of the volume of steam generated.

Even when the equipment was mounted 2 feet from an open window, the temperature in the reflux jacket did not vary over 0.5° C. A single charge of tetrachloroethane has lasted for

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[1] Deceased.

over one year of almost continuous operation without changing its boiling characteristics. Each distillation requires only 0.5 hour and samples which contain only small concentrations of salts may be distilled one after another without changing the sulfuric acid or cleaning the equipment.

When it is necessary to clean the distilling chamber, the heater is turned off and the apparatus is allowed to cool to room temperature. A 350-mm. length of glass tubing is inserted through the ground joint to the bottom of the distilling chamber. A length of rubber tubing is used to connect this glass tube to a suction flask to which suction is applied with a water jet aspirator. As water is added through the ground joint the solution and rinsings are carried to the suction flask. Steam is also allowed to pass through the flask, thereby washing the inner tube.

In Figure 2 a dual apparatus is shown as used in this laboratory. A single generator furnishes steam to both units.

PROCEDURE

Add 20 ml. of c.p. sulfuric acid (98%) to the distilling chamber through a long-stemmed funnel which extends well below the 18-mm. side arm. Add not more than 50 ml. of sample through the funnel, wash with a small amount of water, remove funnel, and insert glass plug. Turn on heater and start a slow flow of steam (approximately one bubble per second) to mix the solution. After the reflux condenser has begun to return tetrachloroethane (boiling point 146° C.) to the boiling chamber, increase the rate of steam until approximately 5 ml. per minute of distillate are collected. Collect distillate until it fills a 100-ml. volumetric flask. Turn off the heater; when the apparatus cools to approximately 50° C., another sample may be entered.

When sulfate is an interfering substance in the titration of fluoride ion, as in the thorium nitrate titration (*13*, *16*), a blank determination must be made on the apparatus after the operating conditions have been established. This blank probably is caused by a trace of sulfuric acid carried over to the distillate. Table I shows that there was a constant amount of fluorine calculated from the titers of thorium nitrate in successive 50-ml. portions of distillate collected after the second fraction. The value of this blank may be subtracted from the amount of fluorine obtained in the first two 50-ml. portions of distillate collected to obtain the corrected fluorine recovered. In practice a blank determination is made on the second 100-ml. portion of distillate. The amount of fluorine calculated from the thorium nitrate titration of the blank solution is subtracted from the amount of apparent fluorine contained in the first 100-ml. portion of distillate to obtain the true amount of fluorine in the sample. As long as the operating conditions of the apparatus remain constant, a blank value will be the same. To determine the blank value more than once per month is unnecessary.

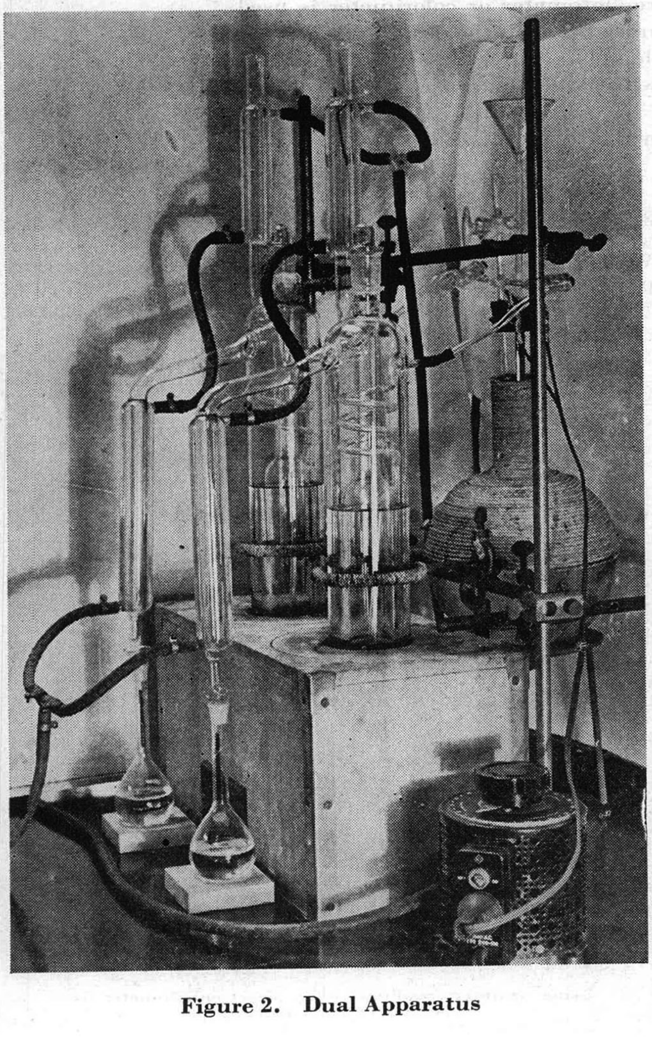

Figure 2. Dual Apparatus

Table I. Effect of Continued Distillation

(0.909 mg. of fluorine added as NaF)

Successive 50-Ml. Portions Collected	Apparatus 1		Apparatus 2	
	Fluorine found	Fluorine (found − blank)	Fluorine found	Fluorine (found − blank)
	Mg.	*Mg.*	*Mg.*	*Mg.*
1	0.913	0.909	0.892	0.888
2	0.009	0.005	0.021	0.017
3	0.004	0.000	0.004	0.000
4	0.004	0.000	0.004	0.000
5	0.004	0.000	0.004	0.000
6	0.004	0.000	0.004	0.000
7	0.004	0.000	0.004	0.000
8	0.004	0.000	0.004	0.000
		0.914		0.905

Table II. Analysis of Samples of Known Fluorine Content

Sample No.	Fluorine Added	Fluorine Found	
		Apparatus 1	Apparatus 2
	Mg.	*Mg.*	*Mg.*
1	0.0027	0.0027	0.0027
2	0.0462	0.0462	0.0461[a]
3	0.0462	0.0462	0.0459[b]
4	0.0462	0.0464	0.0462[c]
5	0.0545	0.0545	0.0545
6	0.0818	0.0810	0.0808
7	0.231	0.234	0.230[a]
8	0.231	0.229	0.226[b]
9	0.231	0.231	0.228[c]
10	0.363	0.365	0.359
11	0.462	0.461	0.460[a]
12	0.462	0.464	0.462[b]
13	0.462	0.462	0.461[c]
14	0.636	0.645	0.634
15	0.681	0.689	0.684
16	0.909	0.914	0.905

[a] Fluorine distilled from suspension containing 2 grams of freshly precipitated silica.

[b] Solution contained 2 grams of dissolved alumina.

[c] Fluorine distilled from suspension containing 2 grams of freshly precipitated barium sulfate.

Some samples of c.p. sulfuric acid have been found to contain traces of fluorine. To eliminate error from this source it is advisable, when a new supply of acid is used, to add 50 ml. of water in place of the sample and collect 100 ml. of distillate before using the apparatus for analysis.

Results shown in Tables I and II were obtained by titrating distillates from samples of a sodium fluoride solution. Thorium nitrate was used to titrate the fluorine in the distillate according to the method of Willard and Winter (*16*), using the sodium alizarin sulfonate indicator of Armstrong (*3*) and the half-neutralized monochloroacetic acid buffer of Hoskins and Ferris (*8*). A stock solution of sodium fluoride was prepared from c.p. sodium fluoride dried at 110° C. and double-distilled water. To ensure elimination of titration errors, an identical volume of stock solution was withdrawn for standardization of the thorium nitrate solution and for distillation. Results are shown in Tables I and II for similar distillations in two different units.

Data are also included in Table II to show that there is no appreciable tendency toward low results for fluorine when silica or barium sulfate has been precipitated in the presence of the fluoride or when large amounts of dissolved alumina are present. Appreciable amounts of chloride ion should be removed by precipitation with silver solution (*12*). (In the case of samples 4, 9, and 13 shown in Table II, silver sulfate was used to precipitate the chloride ion which had been added as barium chloride.)

The effect of the presence of boric acid was not checked, since the data of Willard and Winter (*16*) showed it to be similar in behavior to silicic acid.

The efficiency of the volatilization for a particular sample type may be checked readily by the collection of a third 100-ml. portion of distillate, or by collection of 50-ml. samples in three or four portions.

In Table II the amount of fluorine found is within ±1% of the amount added, except in three cases. This is equal to the accuracy of the titration of fluorine by the thorium nitrate method, and the results of the distillation process may be better than Table II indicates. Values for recovery of fluorine in the distillate, shown by Eberz, Lamb, and Lachele (*6*) for the lengthy and troublesome distillation of Willard and Winter, are no better than those shown in Table II.

ACKNOWLEDGMENT

The authors are indebted to S. E. Knisely for suggestions and help furnished in fabrication of the apparatus described.

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Spectrophotometric Determination of Fluorine in Glass

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Precision in the determination of fluorine in glass can be attained with the peroxidized titanium method when a spectrophotometer or colorimeter is used, the temperature is controlled, and the volume of the solution is accurately measured. This procedure is directly applicable to boron-free glasses containing up to 2% fluorine, and can be used for those with higher fluorine content by mixing them with boron- and fluorine-free glass. If more than 2.5% boron and 0.5% fluorine occur together in a glass, the method gives low fluorine values.

FLUORINE occurs in many glasses in amounts ranging from 0.1 to 12%. Its determination by the Berzelius gravimetric method as described by Hillebrand (*3*) and modified by Groves (*2*) is a lengthy procedure and the accuracy of the results is questionable unless extreme care is taken because the final precipitate, calcium fluoride, is partly soluble in water. Of the colorimetric methods outlined by Snell (*5*), only Steiger's peroxidized titanium procedure is practical when fluorine is present in greater amounts than a few parts per million. Fahey (*1*) has successfully applied his ferron method to rocks and minerals containing up to 10% fluorine by using an aliquot portion of the solution of the sample. Steiger's procedure (*6*) as refined by Merwin (*4*) utilized the powerful bleaching action of fluorine on yellow peroxidized titanium solutions. Beer's law does not hold, but the fluorine content can be determined from the amount of bleaching by reference to a calibration curve. Since, in most cases, the amount of bleaching is slight as determined by visual comparison, a General Electric recording spectrophotometer was used in the present work to increase the precision of the colorimetric measurements.

Reagents (all C.P.). Sodium carbonate, solid, anhydrous.

Zinc nitrate solution. Ten grams of zinc oxide are dissolved in a solution of 180 ml. of water and 20 ml. of concentrated nitric acid.

Hydrogen peroxide, 6%.

Titanium solution containing 0.001 gram of titanium dioxide per ml. Titanium potassium fluoride (3.00 grams) is evaporated with 100 ml. of 1 *N* sulfuric acid until fumes of sulfur trioxide appear. The fuming condition is maintained for 0.5 hour. Water is added to restore the original volume and the evaporation is repeated twice. After cooling, 10 ml. of 1 *N* sulfuric acid are added and the solution is diluted to 1 liter.

Sulfuric acid, concentrated.

Procedure. A 1.0000-gram sample of glass is fused with 3.5 ± 0.1 grams of sodium carbonate. The fused cake is leached with hot water, filtered with suction, and washed with hot water. With the exception of fluorine, boron, and the alkalies, the greater part of the remaining glass constituents are thus separated as water-insoluble carbonates. To precipitate any remaining

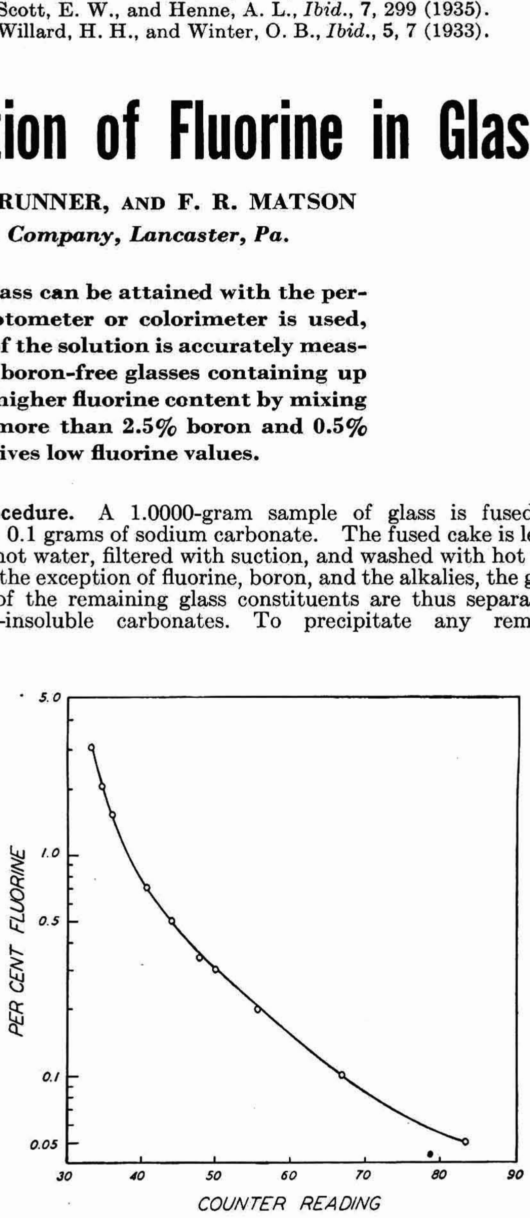

Figure 1. Calibration Curve for Fluorine at 440 Millimicrons

Using counter readings when spectrophotometer is operated on log density cam

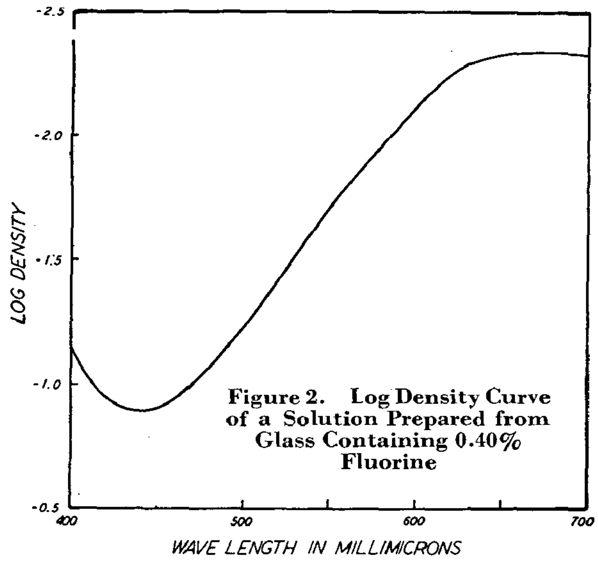

Figure 2. Log Density Curve of a Solution Prepared from Glass Containing 0.40% Fluorine

silica, alumina, and ferric oxide, 20 ml. of zinc nitrate reagent are added to the filtrate, and the solution is filtered with suction and washed with hot water. Then 4 ml. of hydrogen peroxide and 10 ml. of titanium solution are added to the filtrate from pipets and 3 ml. of sulfuric acid are introduced slowly from a buret. The volume is adjusted to 100 ml. and the temperature to 30° C. The sample is placed in a 1-cm. cell and compared spectrophotometrically with a blank prepared from fluorine-free glass.

The spectrophotometer is operated on the log density cam $\left(\text{log density} = \text{log log} \frac{1}{\text{transmission}}\right)$. This setting is used because a greater difference is thus obtained at most wave lengths between two fluorine solutions than when either the transmission or density cam is employed. The cell containing the blank is put in the sample chamber and the test solution (which is the lighter of the two in color if it contains fluorine) is placed in the reference position. The wave-length scale is set at 440 millimicrons and the counter reading is recorded. The fluorine content is then determined from the calibration curve (Figure 1). The sample must be measured within 1.5 hours after it is prepared. The counter reading is proportional to the log density and may be converted to log density by means of the formula

$$\text{Log density} = 0.5 - 0.03\, R$$

where R = counter reading.

DISCUSSION

Calibration Curve. The end members used to establish the curve were National Bureau of Standards glasses 80 and 91. Spectrographic analysis confirmed the statement that No. 80 contained no fluorine. No. 91 is reported as having 5.72% fluorine. The log densities of ten samples ranging in fluorine content from 0.05 to 3% were measured to prepare the calibration curve. The slope of the curve becomes steeper with increasing fluorine content. This makes the direct determination of more than 2% fluorine in a glass inaccurate.

Table I. Effect of Temperature on Apparent Fluorine Content of Glass Solutions

(Calibration curve prepared at 30° C.)

Temperature ° C.	Fluorine %	Temperature ° C.	Fluorine %
25	0.16	35	0.23
30	0.16	20	0.20
35	0.15	30	0.20
25	0.26	40	0.18
30	0.25		

Table II. Effect of B_2O_3 on Analysis of Fluorine

Compounded		Analyzed	
B_2O_3 %	F_2 %	F_2 %	Deviation in F %
1.0	0.5	0.51	2
2.5	0.5	0.49	2
5.0	0.5	0.44	12
10.0	0.5	0.44	12
1.0	1.0	0.92	8
2.5	1.0	0.84	16
5.0	1.0	0.78	22
1.0	2.0	1.65	17.5
2.5	2.0	1.32	34
5.0	2.0	1.33	33.5

The minimum point of the log density curve for a glass solution containing fluorine (Figure 2) is at approximately 440 millimicrons. This wave length was therefore chosen for the determinant position. Many other types of spectrophotometers or colorimeters could be used for this determination, provided the transmission is measured at approximately 440 millimicrons.

Reproducibility. In the preparation of the calibration curve several points when rechecked with freshly made samples and blanks agreed within 0.003% fluorine. The determination of fluorine in amounts less than 2% by the method outlined is precise to within 0.01%. The accuracy is, of course, dependent upon the reported value of 5.72% for the base glass, No. 91.

An opal glass with a high fluorine content was analyzed twice by taking portions of the glass equivalent to one fourth and one tenth, respectively, of the total test sample and mixing them in the correct proportion with glass 80. The results from the calibration curve when multiplied by 4 and 10 agreed well—11.40 and 11.50%. By this method, glasses with fluorine contents greater than 2% can be analyzed.

Time. The stability of the color of the peroxidized titanium solutions was tested at 0.5-hour intervals. There was no change in the log density at 440 millimicrons 1.5 hours after the solutions were prepared, but at that time a slight decrease was observed for the wave lengths above 510 millimicrons. Therefore, it would be inadvisable to delay measuring a solution longer than 90 minutes after it is made up or to use a blank older than that.

Temperature. The solutions were adjusted to 30° C. before their colors were measured. With the three samples reported in Table I, the temperature was intentionally varied 5° and 10°. A drop in temperature of 10° has no effect on the determinations. In glasses containing less than 0.2% fluorine, a rise in temperature of 5° is unimportant, but with greater concentrations increasing the temperature decreases the apparent amount of fluorine present. Therefore the calibration curve should be established for the maximum temperature likely to be encountered in the laboratory.

Dilution. Hillebrand (*3*, p. 229) in discussing Merwin's method (*4*) says, "the total color of the solutions is not significantly affected by 10% change of water content". To test this statement, water was added in 1-ml. increments to two solutions of 100-ml. volume after they had been measured spectrophotometrically. It was found that there was a straight-line relationship between dilution and fluorine content. Additions of even 1% water in excess of the amount specified appreciably affected the results. An increase of 10% in the water content resulted in fluorine values that were double their true amounts.

Boron. Boron in glasses interferes with the determination of fluorine by the peroxidized titanium method when more than 0.5% fluorine and 2.5% boron are present, as is shown in Table II. The effect was most pronounced in the glasses containing the largest amounts of fluorine. Bureau of Standards glasses 91 (5.72% fluorine) and 93 (12.72% boron) were used to prepare the test samples.

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Determination of Allyl Groups in Polyallyl Ethers and Esters

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Allyl ether and allyl ester groups undergo a quantitative reaction with various reagents for the addition of halogen. In this study it has been found that allyl acetate, allyl phthalate, and triallyl glycerol can be accurately analyzed for allyl groups by numerous methods—for example, by the Wijs, rapid Wijs, Rosenmund and Kuhnhenn, and bromine methods. The Kaufmann method gave results which were approximately 10% low. The number of allyl groups—the degree of substitution—in polyallyl derivatives can be determined by the same methods. The most rapid and simplest is the rapid Wijs method.

IN ETHERIFICATION and esterification of polyhydric alcohols, the degree of reaction or the degree of substitution may be ascertained by a Zeisel determination for the ether groups or a saponification equivalent for the esters. With the increasing interest in polyallyl ethers and polyallyl esters, a more convenient method of analysis for degree of substitution is highly desirable.

The purpose of this work was to determine the applicability of various known methods for the determination of unsaturation to the analysis of allyl ethers and allyl esters, and to establish a reliable method for the determination of the degree of substitution of polyallyl derivatives.

CHEMICALS

Allyl acetate was prepared and purified according to known methods; boiling point 105°, $n_D^{25°} = 1.4015$.

Allyl phthalate was prepared and purified according to known methods; boiling point 126° at 0.7 mm., $n_D^{25°} = 1.5169$.

Allyl sucrose was prepared according to the procedure of Nichols and Yanovsky (*7*), with slight modifications.

Allyl starch was prepared by the procedure of Nichols and coworkers (*6*), with a few modifications.

Triallyl glycerol was prepared according to the method of Nichols and Yanovsky (*7*); $n_D^{20°} = 1.4501$.

REAGENTS AND GENERAL PROCEDURE

In all cases approximately 0.1-gram samples were used, and with the relatively volatile allyl acetate it was necessary to have the reaction flasks containing 10 ml. of chloroform cooled in a refrigerator in order to eliminate loss of sample.

Rapid Wijs. The usual Wijs reagents were prepared while the mercuric acetate catalyst was prepared and the analyses were carried out according to the procedure of Hoffman and Green (*3*).

One-Hour Wijs. The reagents were prepared and the analyses were carried out as outlined in "Official and Tentative Methods of Analysis" (*1*).

Kaufmann. An approximately 0.1 *N* bromine solution in methanol which had been saturated with sodium bromide was prepared and the analyses were made according to the directions of Kaufmann and Hartwig (*4*).

Rosenmund and Kuhnhenn. The pyridine sulfate dibromide solution was prepared and the analyses were made according to the procedure of Rosenmund and Kuhnhenn (*8*).

Bromine Method. A 0.5 *N* solution of bromine in chloroform (10 ml.) was added to a cold flask containing a 0.1-gram sample dissolved in 10 ml. of chloroform. The flasks were placed in a refrigerator at approximately 4° and after approximately 10 minutes the stoppers were sealed with a few milliliters of potassium iodide solution and the flasks were allowed to stand at 4° for the desired time. If the sealing is carried out before the flasks and contents have completely cooled, the potassium iodide solution will be drawn into the reaction flask.

EXPERIMENTAL RESULTS

In order to determine the validity of the various analytical procedures for determination of unsaturated groups, the analyses were first carried out on known compounds. For this study highly purified samples of allyl acetate, allyl phthalate (the diester), and triallyl glycerol were prepared. The results of a study of five different analytical methods on these three compounds are tabulated in Table I.

The analyses of the allyl derivatives should be performed as soon as the substances have been prepared, although inhibitors such as hydroquinone can be added in order to decrease polymerization. Storing in the cold under an inert atmosphere such as nitrogen or carbon dioxide likewise decreases polymerization. Samples of triallyl glycerol showed a decrease of 2 to 4 units in iodine values (three different analytical methods) upon standing for 2 days at room temperature in the absence of inhibitors.

Skell and Radlove (*9*) observed that methyl ricinoleate and methyl ricinelaidate gave theoretical iodine values by the Wijs method but gave high values by the rapid Wijs method, whereas methyl *o*-propionylricinoleate behaved normally. They concluded that this anomalous effect is due to the presence of the free hydroxyl group. Consequently it was of considerable interest to note that a sample of α,α^1-diallyl glycerol, prepared from glycerol dichlorohydrin and allyl alcohol, gave iodine values of 291.3 and 292.0 by the rapid Wijs method as compared to a theoretical value of 295.1. Likewise it can be observed from the results in Table II that the presence of free hydroxyl groups in partially allylated allyl sucrose and allyl starch offers no difficulties in analysis.

DISCUSSION

From the iodine values obtained on pure known compounds it is apparent that numerous methods can be used for determining the number of allyl groups in a polyallyl ether or ester. Of these, the simplest and most rapid (4 minutes) is the rapid Wijs method, which in all instances gave iodine values less than 1% lower than the theoretical value. The ordinary Wijs method gave slightly lower values, but this is not surprising since McCutcheon (*5*) found that the iodine values of ethyl linoleate and methyl linolenate, obtained by the Wijs method, were 162.4 and 257.3 as compared to the theoretical values of 164.7 and 260.5.

Table I. Comparison of Iodine Values Obtained on Known Compounds

Method	Allyl Phthalate	Allyl Acetate	Triallyl Glycerol
1-hour bromine method	207.5, 209.6	252.1, 251.2	.....
2-hour bromine method	207.8, 208.4	251.7, 251.8	352.0, 352.6
3-hour bromine method	204.0, 205.0	249.7, 251.0	.....
Rapid Wijs	205.5, 204.0	252.3, 252.0	355.4, 355.7
1-hour Wijs	204.0, 203.0	249.2, 248.3	.....
Rosenmund and Kuhnhenn	208.0, 207.0	251.0, 249.0	354.1, 354.0
Kaufmann	181.1, 182.8	225.3, 227.4	319.6, 326.9
Theoretical iodine number	206.1	253.8	358.3

Table II. Analysis of Allyl Sucrose and Allyl Starch

Method	Allyl Sucrose Iodine No.	Allyl Sucrose D.S.	Allyl Starch Iodine No.	Allyl Starch D.S.
1-hour bromine method	268.3, 268.1	6.25	183.8, 181.7	1.62
2-hour bromine method	270.6, 269.6	6.32	180.6, 181.0	1.60
3-hour bromine method	271.0, 272.2	6.42	180.4, 180.5	1.59
Rapid Wijs	273.0, 274.0	6.45	176.7, 177.4	1.55
1-hour Wijs	272.1, 271.3	6.42	175.8, 176.6	1.54
Rosenmund and Kuhnhenn	269.1, 264.3	6.30 6.10	174.6, 175.6	1.53
Kaufmann	231.3, 233.8	4.95	143.5, 152.5	1.23

It is of interest that the Rosenmund and Kuhnhenn method gave results which differed from the theoretical values by approximately 1%, since Earle and Milner (*2*) found that this method gave results appreciably low for all vegetable oils having iodine numbers greater than 100. In all instances the Kaufmann method gave results approximately 10% lower than theoretical or the average of the other methods. The degree of substitution for triallyl glycerol as calculated from the iodine values varied between 2.90 and 2.96, with the rapid Wijs method giving the degree of substitution of 2.96.

In applying these methods to the determination of the degree of substitution of allyl starch and allyl sucrose the iodine values were in good agreement, as were the degree of substitution values.

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Polarographic Determination of Vanadium in Steel and Other Ferroalloys

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A method is described for the polarographic determination of vanadium in steel and other ferroalloys, based on the removal of interfering elements by electrolysis with a mercury cathode from a dilute sulfuric-phosphoric acid solution, and subsequent measurement of the anodic diffusion current produced by the oxidation of +4 to +5 vanadium in a supporting electrolyte containing 0.5 to 3 *N* sodium hydroxide and 0.1 *M* sodium sulfite. Results obtained in the analysis of ten Bureau of Standards samples of ferroalloys, containing from 0.01 to 2% vanadium and large amounts of manganese, molybdenum, tungsten, chromium, nickel, copper, and other common alloying elements, were in excellent agreement with the bureau's values.

THE polarographic determination of vanadium in steel and other ferroalloys described in this paper is based on the measurement of the anodic wave produced by the oxidation of +4 to +5 vanadium in a strongly alkaline supporting electrolyte. The general characteristics of this wave have been described in a previous paper (*6*). Iron and other interfering elements are removed by electrolyzing a solution of the sample in a phosphoric-sulfuric acid solution with a mercury cathode. Of the elements likely to be present in ferroalloys this procedure leaves in the solution, in addition to vanadium in the +3 state, only molybdenum, tungsten, titanium, uranium, columbium, tantalum, aluminum, and a trace of manganese. None of these elements interferes in the determination of the vanadium. The residual solution is treated with hydrogen peroxide and then with sulfite (sulfurous acid) in excess to convert the vanadium to the +4 state, and is made up to a known volume. An aliquot portion of this solution is added to a known volume of air-free 1 *N* sodium hydroxide in a polarographic cell and the polarogram is recorded.

A complete determination requires only about 90 minutes' elapsed time. Results obtained with a variety of Bureau of Standards samples demonstrate that the method is as accurate as the classical methods for steels containing a few per cent of vanadium, and with very small amounts of vanadium the polarographic method is probably more reliable.

The only previously reported method for the polarographic determination of vanadium in steel is that of Stackelberg *et al.* (*11*). These authors used the classical sodium hydroxide precipitation method for separating iron and various other elements from +5 vanadium, and the latter was finally determined in an ammoniacal supporting electrolyte. This method is rapid, but it involves the danger of coprecipitation of some of the vanadium, particularly when much manganese is present, and the results quoted by Stackelberg *et al.* are less accurate than those obtained by the present method.

In preliminary work the electrolytic separation with the mercury cathode was carried out by the usual technique from a dilute sulfuric acid solution (*1*, *9*), but difficulties arose when much manganese and molybdenum were present. Manganese was partially oxidized to manganese dioxide and permanganate ion at the anode, and molybdenum tended to precipitate (probably hydrous MoO_2) during the electrolysis. By adding phosphoric acid as recommended by Chlopin (*2*) these difficulties were avoided.

EXPERIMENTAL TECHNIQUE

The cell used for the electrolytic separation was of the Melaven type (*1*, *9*, *10*); it had a capacity of about 200 cc. and the area of the cathode mercury was about 25 sq. cm. A coil of platinum wire served as anode. Stirring was accomplished by a glass propeller stirrer whose blades were partly immersed in the mercury, so that the mercury-solution interface was well stirred. A current of 3 to 5 amperes was used, at a total applied e.m.f. of about

10 volts. Electrolysis for 3 ampere-hours per gram of sample was usually adequate.

Most of the polarographic measurements were made with a manual apparatus (*3*), but some polarograms were recorded with a Sargent-Heyrovský Model XI polarograph. The galvanometer of the polarograph was calibrated at frequent intervals by the usual technique (*3*).

An H-type polarographic cell, with a saturated calomel anode (*3*), was used, and all measurements were made with the cell in a water thermostat at 25.00° ± 0.05° C. The dropping mercury electrode assembly, which included a stop-clock device for automatically measuring the rate of flow of mercury, was of the type previously described (*5*), except that the rubber pinchcock between the stand tube and the mercury reservoir was replaced by a very lightly lubricated glass stopcock. Purified hydrogen was used to remove dissolved air from the solutions.

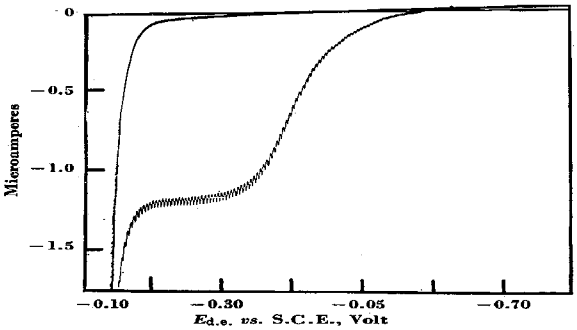

Figure 1. Typical Polarogram of +4 Vanadium in 1 *N* Sodium Hydroxide–0.1 *M* Sodium Sulfite Obtained with Mo-W-Cr-V Steel 134

Concentrations were computed from the relation $C = i_d/Im^{2/3}t^{1/6}$ millimoles per liter, where i_d is the observed diffusion current (microamperes), m is the rate of mercury flow from the dropping electrode (mg. per second), t is the drop time (seconds) at the potential at which the diffusion current is measure, and I is the diffusion current constant (*4*). The use of this relation is much more convenient than the repeated calibration of each dropping electrode with known concentrations of the substance being determined, but it must not be applied with capillaries whose drop time is smaller than about 1 second (*7, 8*). In 0.5 to 3 *N* sodium hydroxide containing 0.1 *M* sodium sulfite the I-value for the anodic wave of +4 vanadium was found to be 1.466 ± 0.002 at 25° C., which agrees well with a previous measurement (*6*). The half-wave potential is −0.432 volt *vs.* the saturated calomel electrode (see Figure 1).

Alkaline solutions of +4 vanadium are very easily oxidized by atmospheric oxygen (*6*), and hence care must be taken to compose the final solution out of contact with air. A known volume of the +4 vanadium solution should be added to a known volume of the supporting electrolyte previously freed from dissolved air with hydrogen or nitrogen in a polarographic cell. To ensure the complete absence of oxygen, the supporting electrolyte should also contain about 0.1 *M* sulfite ion. Solutions prepared with these precautions were found to be stable for at least 12 hours.

The residual current of the supporting electrolyte alone should be determined before adding the vanadyl solution, and subtracted from the total current to obtain the corrected diffusion current. It is not necessary to record the entire wave, and it is sufficient to make single measurements of the residual current and the diffusion current at −0.25 volt (compare Figure 1).

PROCEDURE

Transfer a 0.5- to 2.5-gram sample to a small Kjeldahl flask, and add 20 cc. of 6 *N* (1 to 1) hydrochloric acid, 5 grams of disodium phosphate dodecahydrate, and 3 cc. of concentrated nitric acid in small portions. When the action moderates, add 3 cc. of concentrated sulfuric acid and evaporate to fumes of sulfur trioxide to remove oxides of nitrogen and chloride. Disregarding any graphitic and/or siliceous residue, transfer the solution to a Melaven cell (*10*) with water, and dilute to about 100 cc. This solution will be about 0.3 *M* in respect to sulfuric acid and about 0.14 *M* in phosphoric acid.

Electrolyze with a current of 3 to 5 amperes for a length of time corresponding to at least 3 ampere-hours per gram of sample—i.e., for 45 minutes if a 1-gram sample was used and the current is 4 amperes. If the amount of molybdenum in the sample is more than about 100 times greater than the amount of vanadium (a most unusual circumstance), the electrolysis should be prolonged for a time corresponding to 30 ampere-hours per gram of molybdenum present. (Molybdenum is only partially deposited in this procedure. As long as the amount remaining in solution is not more than about 100 times the amount of vanadium present it does not interfere, but larger amounts produce erratic results in the polarographic determination of the vanadium.)

Transfer the residual solution to a Kjeldahl flask, add 2 to 5 cc. of 30% hydrogen peroxide to oxidize any +3 vanadium, and boil gently for a minute or two. Then add 2 grams of sodium sulfite to reduce the vanadium to the +4 state, evaporate the solution to about 75 cc., cool, transfer to a 100-cc. volumetric flask, add 1 gram of sodium sulfite, and dilute to volume. Add a suitable aliquot portion of this solution—e.g., 10 cc.—to a suitable volume—e.g., 50 cc.—of air-free 1 *N* sodium hydroxide–0.1 *M* sodium sulfite supporting electrolyte in a polarographic cell, and measure the diffusion current at 25° C. at −0.25 volt *vs.* the saturated calomel electrode—i.e., at the middle of the plateau. Subtract the previously measured residual current from the observed diffusion current. Measure the drop time at −0.25 volt, and the m-value of the capillary, and compute the concentration of vanadium from the relation $C = i_d/1.466\ m^{2/3}t^{1/6}$.

RESULTS AND DISCUSSION

Results obtained in the analysis of ten Bureau of Standards steels and ferroalloys, with percentages of vanadium between 0.01 and 2, are shown in Table I. In every case the polarographic values agree with the bureau's values to well within the probable uncertainty of the latter.

In order to attain maximal precision in these analyses the measurements were made with the manual apparatus (*3*), rather than with the recording polarograph. To further increase the

Table I. Polarographic Determination of Vanadium in Bureau of Standards Steels and Ferroalloys

Sample and Bureau of Standards Certificate Values	Vanadium Found, %
Co-Mo-W steel 153 V 2.03, C 0.86, Mn 0.22, P 0.026, S 0.009, Si 0.19, Cu 0.10, Ni 0.12, Cr 4.14, Mo 8.36, W 1.58, Co 8.43 (provisional)	2.00
Mo-W-Cr-V steel 132 V 1.64, C 0.803, Mn 0.252, P 0.027, S 0.004, Si 0.239, Cu 0.149, Ni 0.094, Cr 4.11, Mo 7.07, W 6.29	1.635
Mo-W-Cr-V steel 134 V 1.13, C 0.810, Mn 0.155, P 0.016, S 0.006, Si 0.323, Cu 0.114, Ni 0.077, Cr 3.37, Mo 8.68, W 1.82	1.133
Cr-W-V steel 50b V 1.02, C 0.73, Mn 0.32, P 0.029, S 0.008, Si 0.30, Cu 0.11, Ni 0.09, Cr 4.09, Mo 0.40, W 18.06, Sn 0.025 (provisional)	1.009
Cr-V steel 30D V 0.190, C 0.363, Mn 0.786, P 0.031, S 0.031, Si 0.286, Cu 0.092, Ni 0.150, Cr 1.15, Mo 0.034	0.190
18 Cr-8Ni steel 101B V 0.049, C 0.069, Mn 0.597, P 0.017, S 0.025, Si 0.483, Cu 0.168, Ni 8.99, Cr 18.49, Mo 0.078, Co 0.78, Cb 0.062, Sn 0.012, N 0.021	0.0500
Ferromanganese 68A V 0.045, C 6.83, Mn 80.07, P 0.294, S 0.014, Si 0.81, Cr 0.025, Co 0.02, As 0.035	0.0432
Spiegeleisen 66 V 0.012, C 4.05, Mn 19.93, P 0.070, S 0.016, Si 2.22, Fe 73.45, Cu 0.019, Ni 0.015, Cr 0.009, Mo 0.005, Ti 0.20, Co 0.01	0.0108
Mn rail steel 100 V 0.011, C 0.617, Mn [illegible], P 0.023, S 0.021, Si 0.191, Cu 0.124, Ni 0.151, Cr 0.180, Mo 0.005	0.0111
Cu-Ni-Cr cast iron 115 V 0.009, C 2.42, Mn 1.01, P 0.113, S 0.032, Si 1.60, Cu 6.44, Ni 15.89, Cr, 2.17, Mo 0.002, Ti 0.021, As 0.007, Co 0.08	0.0092

Table II. Typical Data Obtained in Analysis of Mo-W-Cr-V Steel 134

0.967-gram sample, electrolyzed 1.5 hours with 3 amperes, and residual solution finally diluted to 100 cc. Initial volume of supporting electrolyte = 49.86 cc. Diffusion current measured at −0.25 volt *vs.* the saturated calomel electrode, and corrected for the residual current (0.037 microampere). Temperature = 25.00° C. $m^{2/3}t^{1/6}$ = 2.490 mg.$^{2/3}$ sec.$^{-1/2}$

Sample Solution Added *Cc.*	i_d (Corrected) *Microamperes*	Vanadium %
1.00	0.152	1.133
2.00	0.306	1.142
3.00	0.451	1.148
4.00	0.580	1.133
5.00	0.716	1.129
6.00	0.845	1.133
7.00	0.972	1.135
8.00	1.070	1.117
9.00	1.205	1.132
10.00	1.310	1.127
	Av.	1.133
	Av. deviation	±0.005

precision ten successive 1-cc. portions of the vanadyl solution were added from a calibrated microburet to 50 cc. of the supporting electrolyte, the diffusion current was measured after each addition, and the measurements were averaged to compute the result. The precision attainable is illustrated by the typical data in Table II, which were obtained in the analysis of the Mo-W-Cr-V steel 134.

The data in Table II demonstrate that a precision of about 0.5% (in terms of the average deviation from the mean) can be obtained under optimum conditions when special care is exercised in measuring the diffusion current and residual current. When measurements are made from recorded polarograms, as in routine analytical practice, results as precise as those in Table II cannot be expected. The precision also decreases, of course, when the concentration of vanadium—i.e., the diffusion current—is very small, and the correction for the residual current is correspondingly large.

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Polarographic Analysis of Mixtures of Maleic and Fumaric Acids

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A polarographic study has been made of fumaric and maleic acids, and a method is described for the simultaneous polarographic determination of the two acids or their salts. Mixtures of the maleate and fumarate ions are analyzed by comparing the current readings at three applied potentials to those of a standard solution of the two ions at the same potentials, using an ammonium hydroxide-ammonium chloride buffer solution of pH 8.2 as the supporting electrolyte. In the presence of interfering substances maleate and fumarate can be separated by precipitation of their barium salts in alcoholic solution; the precipitate is soluble in the base solution used.

AS PART of a general program of examination of available and possible methods for the determination of 1,3-butadiene the reaction of butadiene with maleic anhydride was extensively investigated. It is possible to remove butadiene from gaseous mixtures containing appreciable amounts of it by absorption in molten maleic anhydride and determination of the decrease in volume. However, for a number of reasons, this method cannot be advantageously applied to the determination of traces of butadiene in gaseous mixtures or in the presence of substances of appreciable physical solubility in molten maleic anhydride except by the use of rather elaborate apparatus and technique. A possible method for butadiene in gaseous mixtures would consist of passing a measured volume of gas through a known weight of molten maleic anhydride and then determining either the tetrahydrophthalic anhydride formed by the reaction of the maleic anhydride with the butadiene or the maleic anhydride which had not reacted. The unreacted maleic anhydride could be determined by dissolving the final reaction mixture in water, converting the anhydrides to acids, and determining the maleic acid polarographically. The original sample of maleic anhydride could have been assayed for maleic acid content in the same manner.

In connection with this method it was decided to investigate the polarographic behavior of maleic acid. Since fumaric acid might possibly be present and there are no satisfactory chemical procedures for differentiating between these two isomeric cis-trans unsaturated dicarboxylic acids, it was also decided to study the polarographic behavior of fumaric acid. Of additional interest was the fact that the polarographic method for the simultaneous determination of maleic and fumaric acids in mixtures was found to be deficient (*1*).

Previously suggested methods for the analysis of mixtures of maleic and fumaric acids include, in addition to the use of polarography, differential neutralimetric titration based on the difference in magnitude of the primary ionization process for the two acids, the slight solubility in water of fumaric acid compared to maleic, and the formation of different esters.

Various methods for the polarographic determination of maleic and fumaric acids in mixtures have been described in the literature. Vopička (*13*) reported obtaining two distinct polarographic waves for maleic and fumaric acids in mixtures by polarographing the sodium salts of the acids in solutions which were 0.1 *N* in potassium chloride and 0.5 to 1 *N* in sodium acetate. When this procedure was attempted with a solution containing approximately 10^{-4} gram per ml. of maleic and fumaric acids, no separation of the polarographic waves was obtained. Sèmerano and Rao (*12*) found that in exactly neutral or, at most, slightly alkaline solution the waves due to maleic and fumaric acids can be resolved. They suggest using the calcium salts in an unbuffered medium of 0.5 *N* ammonium chloride for the determination of maleic acid in the presence of fumaric. Since maleic and fumaric acids show similar polarographic behavior in acid solutions (*3*), this medium is also unsatisfactory in that the resulting pH of the solution is approximately that of ammonium chloride (ca. 5.7), and consequently no separation of the polarographic waves is achieved at this pH. If the pH is increased to approximately 8 by the addition of calcium hydroxide, as was tried by the present authors, fumarate and maleate ions do give separate waves, but the separation is not sufficient for the quantitative analysis of mixtures of the two. For the detection and determination of small amounts of fumaric acid in the presence of maleic acid, Semerano and Rao (*9, 12*) recommend the use of the lithium salts in 0.1 *N* lithium chloride as the supporting electrolyte. The results claimed by these authors could not be duplicated when this latter method was tried by the present authors—i.e., the polarographic waves of the two acids could not be differentiated. Clark and Knopf (*1*) also were unable to duplicate the results of Semerano and Rao on the determination of maleic and fumaric acids.

The solution to the problem was eventually found in the use of an ammonium hydroxide–ammonium chloride buffer at a pH of approximately 8 as the supporting electrolyte for the barium salts of the acids. The barium salts were selected because of the consideration that maleic and fumaric acids can be quantitatively precipitated and separated from interfering substances by reacting them with barium hydroxide in alcoholic solution. These salts can then be redissolved and polarographed in the ammonium hydroxide–ammonium chloride base solution. Under the experimental conditions used maleic and fumaric acids give separate and distinct waves which are suitable for the quantitative analysis of mixtures of the two acids.

The mechanism of the polarographic reduction of unsaturated acids such as maleic and fumaric acids has been discussed in a series of papers by Herasymenko (*2, 3*), Schwaer (*7, 8*), Semerano (*10, 11*), Vopička (*13*), and their co-workers. Most of this work was done in acidic solution at pH values less than 7.0; some of the work in neutral and alkaline solution is of doubtful validity because of the use of unbuffered solutions. The mechanism of reduction of maleate and fumarate ions in alkaline solution is now under investigation by the authors; it is hoped to publish an account of this material in the future.

APPARATUS AND MATERIALS

Apparatus. The polarographs used in the studies described were the Fisher Elecdropode and the Leeds & Northrup Electro-Chemograph. In order to determine the limiting current, the galvanometer deflection of the Elecdropode was calibrated so that the scale readings could be readily converted to microamperes. This was accomplished by substituting for the polarographic cell a 200,000-ohm Akra-ohm resistance. At a sensitivity of 10×, each scale division corresponds to 0.225 microampere throughout the potential range of applied voltages of 0.0 to −2.5 volts. A linear relationship was found between the sensitivity of the Elecdropode and the microamperes per scale division when the galvanometer sensitivity was changed to 2×, 5×, and 20×.

The polarographic cell used was a water-jacketed cell of about 35-ml. capacity, whose jacket was connected in series through a small circulating pump to a constant-temperature bath, thermostatically controlled at ±0.2° C.

Maleic and Fumaric Acids. Recrystallized Pfanstiehl C.P. toxilic acid and recrystallized Eastman Kodak technical grade fumaric acid were used. Standard solutions of the salts of these acids were prepared by dissolving the purified acids in distilled water and neutralizing with a saturated solution of barium hydroxide, using phenolphthalein as an indicator. The concentration of the maleic acid stock standard was 1.507×10^{-3} gram per ml. (1.30×10^{-2} *M*) and the concentration of the fumaric acid stock standard was 1.555×10^{-3} gram per ml. (1.34×10^{-2} *M*)

Base Solutions. Ammonium hydroxide–ammonium chloride buffer solutions of different pH values were prepared by adjusting the pH of a 1.0 *M* ammonium chloride solution, prepared from the C.P. Baker's analyzed salt, to the desired value by the addition of concentrated ammonium hydroxide solution.

PROCEDURE

For the polarographic measurements, aliquots of the stock standard maleate and fumarate solutions were pipetted into a 100-ml. volumetric flask, 70 ml. of the ammonium hydroxide–ammonium chloride base solution were added, and the solution was diluted to volume with distilled water. The resulting solution had essentially the same pH as the buffer which was used.

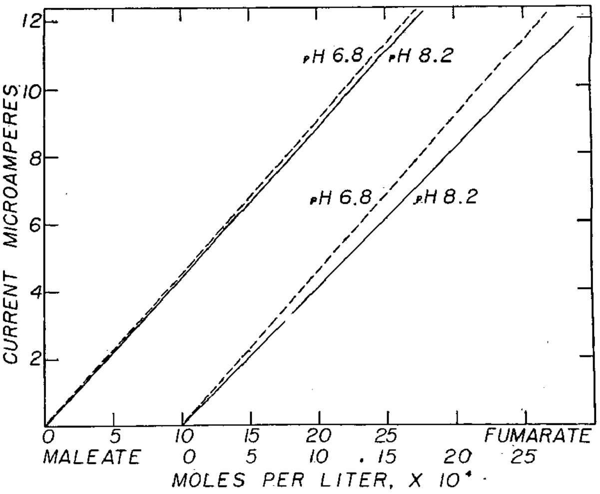

Figure 1. Effect of Concentration and pH on Diffusion Currents of Fumarate and Maleate Ions at 25° C.

The concentration range investigated was approximately 7.5×10^{-5} to 3.0×10^{-4} gram per ml. (6.5×10^{-4} to 2.6×10^{-3} *M*) for the acids alone and in mixtures of each other. These solutions were then electrolyzed in the polarographic cell, using a quiet mercury pool as the anode and a constant height of the mercury column for the dropping mercury cathode.

The potentials of the dropping mercury electrode *vs.* the quiet mercury pool were converted to potentials of the dropping mercury electrode *vs.* the saturated calomel electrode by correcting for the potential between the saturated calomel electrode and the pool.

STUDY OF pH, TEMPERATURE, AND CONCENTRATION EFFECTS

Since the analytical procedure finally adopted was based on a study of the effects of pH, temperature, and concentration on the polarographic behavior of maleic and fumaric acids, the pertinent facts found in these studies are summarized in the following paragraphs.

Capillary Constants. The capillary constants were obtained in a buffer base solution, 0.7 *N* in ammonium chloride and 0.04 *N* in ammonium hydroxide, at pH of 8.2 and a temperature of 25° C. The values for the electrocapillary curve are given in Table I. The mass of mercury dropped per second, m, was obtained at an applied potential of 0.00 volt and was found to be 1.084 mg. per second. The value of $m^{2/3} t^{1/6}$ for the capillary used in these studies is 1.40 mg. $^{2/3}$ sec. $^{-1/2}$

Effect of pH. The separation of the polarographic waves of the salts of maleic and fumaric acids depends, to a large extent, on the pH of the base solution. Polarographic curves over a range of concentration were obtained at pH values of 6.8, 8.2, and 8.9, using the ammonium hydroxide–ammonium chloride buffer solutions described as the supporting electrolyte solutions. It was found that the diffusion currents of the barium salts of the acids showed a linear relation with concentration in the range investigated at the three pH values selected. This relationship was also found with mixtures of the two substances.

At a pH of 8.9 the readings on the galvanometer were very unsteady and difficult to obtain accurately. This was due probably to the relatively large amount of ammonia required to obtain a buffer of the desired pH which, through volatilization, resulted in an agitational action of the solution. The buffer solution of pH 6.8 is not so suitable as that of pH 8.2 for the quantitative analysis of mixtures, since there is less of a separation of the polarographic waves at the lower pH. Moreover, the buffer capacity of an ammonium hydroxide–ammonium chloride buffer at pH 6.8 is extremely small. This consideration is important, since it was also found that the diffusion coefficient of the maleic acid decreases with increasing pH, which fact necessitates the use of a good buffer to maintain a constant pH.

The decrease in the diffusion current of barium maleate

Table I. Electrocapillary Curve in Ammonium Hydroxide–Ammonium Chloride Base Solution of pH 8.2

Applied potential, volts	−0.0	−0.20	−0.40	−0.55	−0.60	−0.80	−1.00	−1.15	−1.30	−1.43	−1.60	−1.75	−1.90
Drop time, seconds	5.47	6.10	6.30	6.41	6.30	6.22	5.70	5.42	5.02	4.66	4.12	3.53	1.90

amounted to approximately 10% when the pH was raised from 6.8 to 8.2. The wave height of barium fumarate was only slightly affected by the same change in pH. The polarographic behavior of maleic and fumaric acid at pH 6.8 and 8.2 under the conditions used is shown in Figure 1; the data given for the individual acids in the upper half of Table II fall on the straight-line curves of Figure 1.

In view of these and other experimental facts, the optimum pH for the analysis of mixtures of maleic and fumaric acids, using an ammonium hydroxide–ammonium chloride buffer solution as the base solution, was considered to be approximately 8.2.

Effect of Concentration. The diffusion current was found to be proportional to the concentration of the acids up to about 2.6×10^{-3} *M* (3.0×10^{-4} gram per ml.). When the concentration exceeds the latter value at pH 8.2, the readings become unsteady and erratic. Moreover, at this upper concentration level, with mixtures of the acids, there is an overlapping of the polarographic waves. It is therefore, advisable to work with total concentrations no greater than 1.5×10^{-3} *M*. Figure 2 represents the actual curves obtained with mixtures containing varying amounts of maleic and fumaric acids. In curve 7 where the concentration of each acid is 2×10^{-3} *M*, it can be seen that the plateau between the two waves tends to disappear. The potentials shown in Figure 2 are the applied voltages used on the Electro-Chemograph and should be increased in the positive direction by approximately 0.08 volt to obtain the potentials relative to the saturated calomel electrode.

Failure to work at a low enough concentration range may have been the cause of the difficulties encountered by others who have investigated the polarographic analysis of mixtures of maleic and fumaric acids.

When the concentration of the concentration–diffusion current relationship, typical data for which are given in Table II, is extrapolated to 0 gram per ml., as shown in Figure 1, the straight line obtained passes through the origin, indicating that the diffusion current is directly proportional to the concentration of the maleic and fumaric acids at pH values of 6.8 and 8.2. The linearity of each curve is shown by the agreement of the ratios of diffusion current to concentration at the same pH.

Effect of Temperature. The effect of temperature was studied at pH 8.2 for the temperature range of 20° to 30° C.

The temperature coefficient for the maleate ion was found to be 2.0 to 2.7% per degree Centigrade, and the temperature coefficient of the fumarate ion was approximately 1% per degree. These values are in agreement with normal behavior, since most ions and molecules have a temperature coefficient of this magnitude. For quantitative measurements, the temperature of the solution being examined should be maintained constant for the measurement of both standard and sample solutions.

Half-Wave Potentials. In addition to experiments of the types mentioned, the effect of temperature, pH, and concentration on the half-wave potentials was also observed. All half-wave potentials refer to the dropping mercury electrode *vs.* the saturated calomel electrode.

It was found that at a pH of 8.2 the half-wave potentials were constant over a temperature range of 20° to 30° C. and a concentration range of 0.65×10^{-3} to 2.60×10^{-3} *M* at −1.36 volts for the maleate ion and −1.60 volts for the fumarate ion. At a pH of 6.8 the half-wave potentials were shifted to slightly less negative values of −1.31 for the maleate and −1.55 volts for the fumarate.

ANALYTICAL PROCEDURE

Mixtures of maleic and fumaric acids or their salts can be analyzed by noting the current readings at applied voltages of −1.175, −1.460, and −1.775 volts (dropping mercury electrode *vs.* saturated calomel electrode), and comparing the true wave heights obtained to the true wave heights of a standard solution of a mixture of barium maleate and barium fumarate. The three potentials represent points before and after the increases in current due to the reduction of the maleate and fumarate, respectively. Contrary to the report of Riches (6) that the hydro-

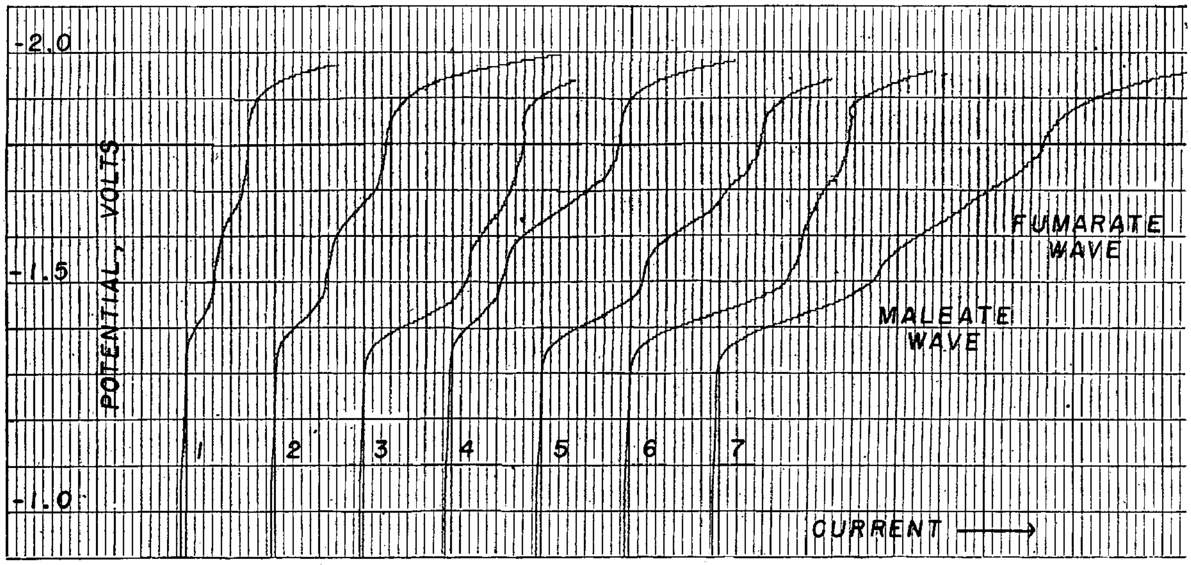

Figure 2. Current-Potential Curves (Electro-Chemograph) for Mixtures of Fumarate and Maleate Ions

Temperature, 25° C. pH, 8.2. Sensitivity, 1/100
Supporting electrolyte, 0.7 *N* NH_4Cl in 0.04 *N* NH_4OH

Curve No.	1	2	3	4	5	6	7
Fumarate ion, *M* × 10^4	4.02	6.70	6.70	13.4	13.4	6.70	20.1
Maleate ion, M × 10^4	3.90	6.49	13.0	6.49	13.0	19.5	19.5

Table II. Effect of pH and Concentration on Diffusion Current at 25° C.

pH	Maleic Acid				Fumaric Acid			
	Concentration		Diffusion current	Diffusion current / concentration	Concentration		Diffusion current	Diffusion current / concentration
	G./ml. × *10*^{5}	*Moles* × *10*^{4}	*Microamperes*	*Microamperes/ mole* × *10*^{3}	*G./ml.* × *10*^{5}	*Moles* × *10*^{4}	*Microamperes*	*Microamperes/ mole* × *10*^{3}
	Individual Acids							
6.8	7.53	6.49	2.98	4.59	7.78	6.70	3.01	4.50
	30.1	26.0	11.88	4.57	31.2	26.8	12.01	4.48
8.2	7.53	6.49	2.60	4.01	.78	6.70	2.96	4.42
	30.1	26.0	10.8	4.11	.2	26.8	11.99	4.47
	Mixtures of Maleic and Fumaric Acids							
8.2	7.53	6.49	2.50	3.85	7.78	6.70	2.96 (2.88)	4.41 (4.30)
	7.53	6.49	2.65	4.09	15.6	13.4	5.80 (5.71)	4.34 (4.26)
	15.1	13.0	5.13	3.95	7.78	6.70	3.07 (2.91)	4.56 (4.34)

gen wave appears in ammonium hydroxide–ammonium chloride solutions at about −1.7 volts with respect to the saturated calomel electrode, it was found in the present work that the hydrogen wave appears in the ammonium hydroxide–ammonium chloride buffer solution of pH 8.2 at −1.80 volts. If the concentrations of the two acids differ considerably, it is advisable to plot the complete curve, since the potential specified for the spot reading on the plateau between the maleate and fumarate current steps may be slightly displaced from the value given.

The current increment obtained for the fumarate current-step must, for precise work, be increased by an amount 0.033 times the maleate current increment. This correction is based on the electrocapillary curve (Table I) which indicates a drop time of 4.57 seconds at −1.460 volts and 3.42 seconds at −1.775 volts; the nature of the correction is discussed by Kolthoff (*4*). The correction factor is the ratio of the one-sixth roots of the drop times at the two potentials measured. The magnitude of this correction can be seen in Table II where the values in parentheses are the uncorrected diffusion currents. However, in actual analytical work, the corrections need not be applied if the standard solution used is of the same order of concentration as the unknown.

In the presence of substances which are polarographically reducible in the same potential range as the maleate or fumarate ions, the following procedure, which is adapted from that described by Milas and Walsh (*5*), should be used to separate the maleate and fumarate ions from interfering substances.

A sample containing a total of approximately 0.10 to 0.15 gram of the maleic and fumaric acids is neutralized with an approximately 0.35 *N* barium hydroxide solution using phenolphthalein as an indicator, and then an equivalent amount of barium chloride solution is added. The barium salts of the acids are quantitatively precipitated by the addition of 4 volumes of 95% ethanol to the mixture. After standing one hour the precipitate is filtered under suction onto a coarse sintered-glass crucible, and washed several times with small portions of 80% ethanol. The precipitate is dissolved directly in the crucible by adding approximately 0.2 *N* hydrochloric acid and stirring until solution is complete. The solution is collected in the filtering flask by applying gentle suction and the crucible is washed several times with the dilute hydrochloric acid solution. The combined solution and washings are neutralized to phenolphthalein with concentrated ammonium hydroxide, quantitatively transferred to a 100-ml. volumetric flask, and diluted to the mark with distilled water. A 10-ml. aliquot of this solution is transferred to another 100-ml. volumetric flask and diluted to volume with the ammonium hydroxide-ammonium chloride base solution of pH 8.2. The resulting solution is then examined polarographically in the manner described at a constant temperature—e.g., 25° C

The maleate and fumarate ion concentrations can be determined by calculating the observed wave heights which are obtained by noting the current or galvanometer scale readings at applied potentials of −1.175, −1.460, and −1.775 volts. The difference between the readings of the first and second points gives the observed wave height due to maleate ion; the difference between the readings of the second and third points is due to the presence of fumarate ion. The true wave heights are obtained by subtracting the corresponding differences of the scale readings of the base solution, at the same applied potentials, from the observed wave heights of the maleate and fumarate ions. These are compared to the true wave heights of a standard solution of a mixture of barium maleate and barium fumarate. For best results, the concentration of the standard should approximate that of the sample under observation, which should be of the order of 10^{-4} *M*.

The presence of anions other than maleate or fumarate in the barium precipitate such as oxalate or sulfate is immaterial, provided that they are not polarographically reducible in the range of −1.1 to −1.8 volts.

From the agreement of the ratios of diffusion current to concentration for the two acids alone and in mixtures, an accuracy of 2 to 3 relative % is apparently obtainable. Typical results for mixtures of the two acids, based on samples given to two different analysts as unknown solutions of the acids, are shown in Table II.

CALCULATIONS

$$\%\text{ by weight of maleic or fumaric acid } = \frac{W_s \times H_m \times 100}{H_s \times S}$$

where W_s = weight of maleic or fumaric acid in mg. in the standard
H_s = true wave height of maleic or fumaric acid in the standard
H_m = true wave height of maleic or fumaric acid in the sample
S = weight of sample polarographed in mg.

ACKNOWLEDGMENT

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Molecular Weight of GR-S Fractions

Simple Glass Osmometer for Use in Hydrocarbon Solvents

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Osmotic molecular weight measurements have been made on a sample of unfractionated GR-S and on eight fractions of this material. The molecular weights ranged from 10,000 to approximately 1,000,000, with a number average at 92,000. The relationship between molecular weight and viscosity for GR-S was determined. A simple all-glass osmometer for use in hydrocarbon solvents is described, and information on its use and the membranes employed is given.

MEASUREMENTS of molecular weights of high polymers by the osmotic pressure method are most commonly made with metal osmometers such as those described by Fuoss and Mead (*4*), Flory (*3*), and others (*18*). These instruments are expensive and somewhat difficult to construct and operate. This report describes a small, inexpensive, all-glass osmometer (*2*) which may be made and used in large numbers; it is somewhat different from simple glass osmometers described elsewhere (*18*, *19*). The instrument, shown in Figure 1, consists of a capillary tube connected to a mercury-sealed ground-glass joint, on the lower end of which is a short tube 15 mm. in diameter. The joint is held together with steel springs and the bottom of the osmometer is fastened to a membrane by means of a polyvinyl alcohol cement as described below.

The osmometer has certain advantages. Its volume is only about 5 cc.; it is inexpensive and easily constructed; it may be quickly and easily filled; and it seldom develops leaks. On the other hand the membrane area is small, necessitating a wait of several days for equilibrium to be established, and because of the method used for fastening on the membrane it is recommended only for hydrocarbon solvents.

Using this osmometer, osmotic pressures were measured on a sample of GR-S and on eight fractions of this material. This sample of GR-S was prepared by the Naugatuck Chemical Co., Naugatuck, Conn., in the autumn of 1941 and may have a somewhat different average molecular weight from the standard GR-S made in 1946. The fractionations and viscosity measurements were carried out by H. C. Tingey of these laboratories. The results are shown in Table I and Figure 2, where the reduced osmotic pressure is plotted against concentration. The slope of the curves, b, as recorded in Table I is observed to decrease with increasing molecular weight. This is believed to be due to increasing branching of the polymer chain as the molecules grow larger during polymerization and is observed in other systems (*1*, *4*, *12*, *13*, *16*).

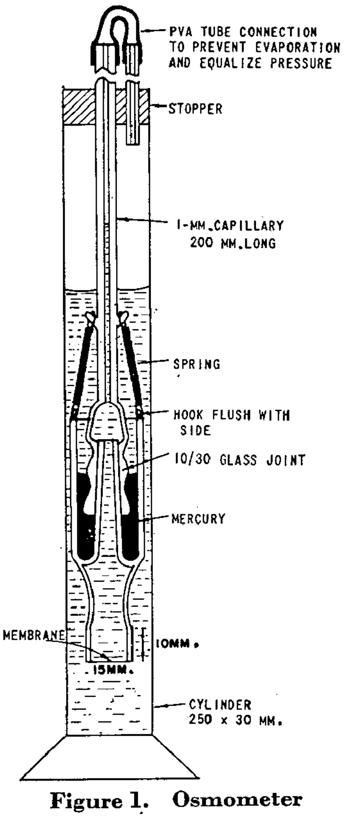

Figure 1. Osmometer

The units used in Table I are explained below in the section on calculation. $(h/C_w)_0$ is the value of the ordinate in Figure 2 at zero concentration. The values of b are proportional to the slopes of the curves (cf. Figure 2), from which they are obtained by means of Equation 5.

The molecular weight values in Table I for GR-S fractions and other values found later correlate with intrinsic viscosity in toluene at 30° C. in a manner shown in the following equation:

$$[\eta] = 5.4 \times 10^{-4} M^{0.66}$$

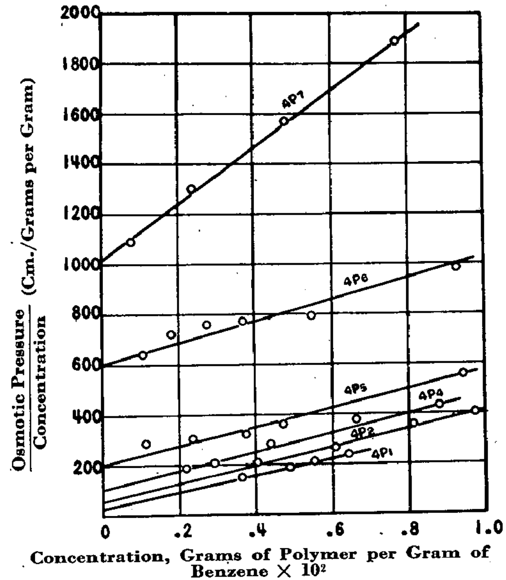

Figure 2. Variation of Reduced Osmotic Pressure with Concentration, GR-S in Benzene at 30° C.

Table I. Results from Osmotic Pressure Measurements of GR-S Solutions in Benzene at 30° C.

Designation	$(h/C_w)_0$	Molecular Weight (Number Average)	$[\eta]$	b	μ_1
Unfractionated polymer	280	92,000	2.37	1.7×10^{-3}	0.36
Fraction 4P1	28	920,000	4.74	1.5	0.38
Fraction 4P2	55	470,000	3.28	1.6	0.37
Fraction 4P3	80	320,000	2.37	...	...
Fraction 4P4	105	220,000	1.92	1.6	0.37
Fraction 4P5	200	130,000	1.22	1.7	0.36
Fraction 4P6	600	43,000	0.68	1.9	0.35
Fraction 4P7	1010	25,400	0.42	5.1	0.09
Fraction 4P8	(2580)?	(10,000)	0.30	(5.6)?	(0.05)?

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where M is the number average molecular weight of the fractions and $[\eta]$ is the intrinsic viscosity as determined with the concentration of solute in grams per 100 cc of solution.

This relationship has been confirmed by R. H. Ewart, H. C. Tingey, and M. Wales of these laboratories, who obtained $[\eta] = 4.9 \times 10^{-4} M^{0.67}$, and also by Scott and Magat (*14*), who obtained $[\eta] = 5.5 \times 10^{-4} M^{0.67}$. The form of this expression is not unexpected in view of much previous work (*1, 5, 7, 9, 10, 13, 17*).

EXPERIMENTAL

Membranes. Perhaps the most important and difficult factor in the measurement of osmotic pressure is the nature and use of the membrane. Membranes used with high molecular substances should have the following characteristics:

Their permeability should be such that impurities of low molecular weight will easily diffuse through them, yet no part of the solute being measured should pass.

The membrane should be inert and insoluble in the solvent being used.

The membrane should not be extensible and should not change its shape, wrinkle, or buckle during the measurements.

In practice four types of membranes have been most satisfactory for nonaqueous solvents: cellophane regenerated but undried (*18*), cellophane swollen with sodium hydroxide or zinc chloride solutions (*8, 15*), collodion reduced by denitration to cellulose (*11*), and Zsigmondy Ultracella "fine" and "finest". The latter is made of cellulose and gelatin and was formerly distributed through Pfaltz and Bauer, Inc., Empire State Bldg., New York, N. Y.

In these experiments nonwaterproofed cellophane 1 mil thick swollen with 57 to 64% solutions of zinc chloride was used. After swelling, the membranes are washed in a mixture of 0.5 volume triethylene glycol and 0.5 volume of water. The membranes may then be placed in air without becoming dry and impermeable.

The membranes are graded according to thickness as follows:

Grade	Thickness, Mils	Average "Permeability Constant" for Benzene, $P \times 10^5$
1	2.5–3	16
2	3–4	29
3	4–5.5	65

where $P = \dfrac{a \ln S_0/S_t}{At}$

a is the cross-sectional area of the glass capillary
A is the area of the membrane
t is the time in hours
S_0/S_t are the positions of the meniscus of benzene at time zero and time t

These values of the "permeability constant" compare with 100 to 300 for some reduced collodion films and with 70 to 250 for Zsigmondy Ultracella fine. Drying the membranes reduces their permeability to about a tenth of the above. Depending on the grade of membranes used, polymers of from 10,000 to 100,000 average molecular weight show erratic osmotic pressures because of diffusion of low molecular weight material through the membrane. In general, grade 3 films were too permeable for any except the highest molecular weight, while films less than 2.5 mils thick were used on one occasion down to 10,000 molecular weight.

Sodium hydroxide is now preferred as a swelling agent, since regulation of concentration is less critical than with zinc chloride. The present method of membrane preparation is to staple No. 300 Sylvania Corp. cellophane to a wire frame and soak overnight in a 40% sodium hydroxide solution. The membranes are then washed for 2 hours under running water and finally soaked for 3 hours in 50% by volume triethylene glycol solution. They are then smoothed out on a glass plate, covered with filter paper, and allowed to stand overnight. This swelling procedure increases the thickness from 0.0008 to about 0.003 inch (0.002 to 0.0075 cm.)

Sealing on the Membranes. The membranes are sealed to the open bottom of the osmometers with a polyvinyl alcohol cement made from 30 grams of PVA and 100 cc. of cold water, heated and strained. The brand of polyvinyl alcohol preferred is Solvar 5/7, made by the Shawinigan Products Corp., Empire State Bldg., New York, N. Y. PVA is allowed to come in contact with both the inside and outside of the end of the tube. A piece of the membrane moist with triethyleneglycol is laid flat on a piece of paper and the wet tube pressed on it. The tube is then inverted and held in place for about an hour. More PVA is then put around the joint with the end of a length of wire and the osmometer is clamped right-side up and the cement is allowed to dry for at least 16 hours and finally baked 15 minutes at 100° C. just before filling. Failure to bake the membranes and cement may cause them to shrink and change shape during the measurements.

Water will be removed during the baking, but the triethyleneglycol remains and enables the membranes to stay permeable. The triethyleneglycol is subsequently washed out in the solvent. Membranes sealed on in this way may be used several times in succession, provided they are not allowed to become dry.

Because of the nature of the cement, polar solvents are not recommended. However, some measurements have been made in methyl ethyl ketone. No osmotic effects have ever been observed with Solvar 5/7 polyvinyl alcohol in benzene.

Filling the Osmometers. About 35 cc. of a 1% solution of the polymer whose molecular weight is to be measured are made up and diluted so as to obtain four or five 10-cc. solutions at various concentrations between 0 and 1%. The solution is poured into the osmometer bottom and allowed to overflow into the cup of the mercury seal. By means of a rubber tube connected to the top of the capillary, solution from the cup of the mercury seal is sucked up through the partially opened ground-glass point to the desired place and the osmometer halves are connected. After the cup is rinsed, mercury is poured into the mercury seal and the osmometer is inserted in a glass cylinder containing solvent.

The cylinder is placed in a 30° C constant-temperature bath and allowed to come to temperature equilibrium. The level of the meniscus in the capillary is then adjusted to whatever position is required. Pressure readings are made by a cathetometer and are corrected for the capillary rise of the solution in each osmometer.

Calculations. The relationship between the osmotic pressure, π(dynes per sq. cm.), and the concentration, C (grams per cc.), may be conveniently expressed without any significant inaccuracy by the relation:

$$\frac{1}{RT} \times \frac{\pi}{C} = \frac{1}{M} + bC \tag{1}$$

provided the polymer concentration is, in general, of the order of 0.010 gram per cm.$^{-3}$ or less. Huggins (*6*) in a more general treatment gives constant b the value:

$$b = \frac{1}{V_1 d_2^2}\left(\frac{1}{2} - \mu_1\right) \tag{2}$$

(V_1 is molal volume of solvent; d_1 and d_2 are densities of solvent and polymer, respectively; g is acceleration of gravity; and R, the gas constant, is 8.31×10^7 dyne cm. per mole degree). The calculated values of Huggins' constant, μ_1, are given in Table I.

The measured quantities are the osmotic height, h (cm.) and the weight concentration, C_w (grams of solute per gram of solvent). In terms of these:

$$\frac{h}{C_w} = \frac{RT}{g} \times \frac{1}{M} + b'C_w \tag{3}$$

Values of the reduced osmotic height, (h/C_w), are plotted against the weight concentration and the plot is extrapolated linearly to zero concentration to obtain $(h/C_w)_0$ and the slope, b'.

The number average molecular weight of the polymer, M, and the constant, b, are then calculated from:

$$M = \frac{RT/g}{(h/C_w)_0} = \frac{8.477 \times 10^4\ T}{(h/C_w)_0} \tag{4}$$

$$b = \frac{b'}{d_1(RT/g)} \tag{5}$$

Reproducibility of Results. For one fraction of GR-S the osmotic pressure was taken three times with different membranes of the same permeability, the solutions being made up each time from the stock solution. Values of 31.0, 30.8, and 31.4 mm. were obtained.

For a sample of whole GR-S measurements were made with membranes of different permeability.

Concentration, %	% Solution of $ZnCl_2$ Used on Membranes	Osmotic Pressure, Mm. of Solution
0.927	55	55
	57	59
	60	57
	63	56
0.309	55	13.9
	57	12
	60	12.3
	63	12.3

ACKNOWLEDGMENT

The authors are greatly indebted to H. C. Tingey, who carried out the fractionation of the GR-S and determined the intrinsic viscosities.

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Derivatives of Diphenylamine as Oxidation-Reduction Indicators in Alkaline Solution

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The properties of various diphenylamine derivatives as indicators for the titration of ferricyanide with vanadyl sulfate in alkaline medium were investigated and about fifteen were found useful. Diphenylamine sulfonic acid and 2-aminodiphenylamine sulfonic acid-4 were found satisfactory for the titration of arsenite with hypobromite in alkaline solution. Trivalent arsenic, antimony, and chromium, and hydrazine sulfate were oxidized with excess of ferricyanide and the excess was titrated back with vanadyl sulfate. The end point was determined with various diphenylamine derivatives, the most desirable of which are diphenylamine sulfonic acid, 2-carboxy-2′-methoxydiphenylamine, 2-carboxy-2′-methyldiphenylamine, 2-carboxydiphenylamine, 2,2′-dicarboxydiphenylamine, 2-carboxy-2′-bromodiphenylamine, and 2-carboxy-3′-ethoxydiphenylamine. Direct titration of solutions of thiosulfate, thiocyanate, and trivalent antimony were performed with hypobromite in alkaline medium; using diphenylamine sulfonic acid and 2-aminodiphenylamine sulfonic acid-4 as indicators. The first five of the above diphenylamine derivatives are especially recommended in alkaline solution.

IN MANY oxidation-reduction reactions the strength and therefore the utility of an oxidizing or reducing agent depend on the concentration of the hydrogen ion in the solution. Although most of these reactions take place in acid medium, the number of those possible in alkaline medium is considerable.

Potassium ferricyanide is a relatively powerful oxidizing agent in alkaline medium and this oxidant has been employed in the oxidation of sugars, salts of metals like arsenic, antimony, tin, chromium, cobalt, manganese, cerium, and thallium; vanadyl sulfate; and sulfur-containing compounds (*2, 4, 5, 9, 21, 24*). In these reactions and other succeeding experiments with ferricyanide, the ferrocyanide thus formed was measured by titration with permanganate (*2, 4, 5, 23*), or ceric sulfate (*1*) in acid medium or iodometrically (*10*). Where direct titrations were made the end point was determined potentiometrically (*20, 26, 28, 29, 30*)

The hypohalites are strong oxidants in alkaline solution. Hypochlorite is a powerful oxidizing agent, is of special advantage in oxidations carried out in neutral or slightly alkaline solution, and is fairly stable. Hypobromite reacts faster than the hypochlorite, although it is very unstable. A solution with its properties can be produced by adding bromide to a hypochlorite solution. Hypohalites were first used by Fenton (*11, 12*) and Foster (*13, 14*) in the oxidation of urea, ammonium salts, guanidine, oxamide, and other nitrogen-containing compounds. Willard and Cake (*31*) determined sulfur in steel and in sulfides by absorbing hydrogen sulfide in alkaline solutions (2.5 N sodium hydroxide with hypobromite or 4 N alkali with hypochlorite). The excess of oxidant was determined iodometrically.

Among the miscellaneous oxidants are alkaline copper tartrate and ammoniacal copper sulfate, which were employed by Britton and Königstein (*3*) in the estimation of hydroxylamine and hydrazine. For organic compounds, Conant and co-workers (*8*) effected oxidation with tungsticyanide and molybdicyanide. Titrations made between potassium iodate and vanadyl sulfate (*25*) in alkaline medium have been reported. Phosphate was found to catalyze the reaction. Fresno and Mairlot reported several experiments using vanadyl sulfate as a reducing agent in strongly alkaline solutions. They reduced solutions of chromate (*15*), gold (*17*), permanganate, ferricyanide (*19*), copper, and silver (*18*) at temperatures of 50° to 70° C. In all experiments the end point was determined potentiometrically. In a 13 to 18% sodium hydroxide solution a mixture of ferricyanide and chromate can be titrated with vanadyl sulfate and two breaks in the curve were observed (*16*).

The indicators which have been used in alkaline medium are relatively few compared with those in acid medium. In the titration of hydrosulfite with ferricyanide (*7*) in alkaline solution, a 10% solution of ferrous sulfate was used and the end point taken when the dark blue color of the ferrous ferricyanide changed to yellow. Ionescu and Vargolici (*22*) in their titration of ferricyanide with sugar solutions added picric acid as indicator. Methylene blue was also suggested for this titration. In the oxidation of sulfides and hydrosulfites in solutions of about pH 9.4 with ferricyanide, Charlot (*6*) tried ferrous dimethylglyoxime indicator.

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Table I. Properties of Diphenylamine Derivatives as Indicators in Alkaline Solution

(Ferricyanide titrated with vanadyl sulfate)

Indicator	Color of Oxidized Form[a]	Drops of 0.02 *M* Indicator in 50 Ml. of Solution	Blank Correction, Ml. of 0.06 *N* Ferricyanide
2-Carboxy-2′-methoxydiphenylamine	Red	1	0.01
Diphenylamine sulfonic acid[b]	Red	1	0.04, 0.10[c]
2,2′-Dicarboxydiphenylamine	Blood red	2	0.01
2-Carboxy-2′-methyldiphenylamine	Red	2	0.04
2-Carboxydiphenylamine	Red	2	0.12
2-Carboxy-3′-ethoxydiphenylamine	Blood red	2	..
2-Carboxy-2′-bromodiphenylamine	Red	2	..
4-Aminodiphenylamine sulfonic acid-2	Red	4	..
2-Carboxy-4′-methyldiphenylamine	Orange pink	3	..
2,3′-Dicarboxydiphenylamine	Red	2	..
2-Carboxy-3′-methyldiphenylamine	Orange pink	2	..
2-Carboxy-4′-methoxydiphenylamine	Orange red	3	..
2-Carboxy-3′-bromodiphenylamine	Orange red	3	..
2-Carboxy-4′-bromodiphenylamine	Orange pink	3	..
2-Carboxy-4′-chlorodiphenylamine	Orange red	3	..
2-Aminodiphenylamine	Orange pink	4	0.12, 0.02[c]

[a] Reduced form of indicators is colorless.

[b] Indicator first oxidized in acid solution.

[c] Blank correction when arsenite is titrated with 0.10 *N* hypobromite solution.

In the present investgation the various derivatives of diphenylamine prepared by Thielke (*27*) according to methods outlined by him, were studied and their possibilities as oxidation-reduction indicators in alkaline medium were determined. Most of the compounds tried were carboxy derivatives plus another substituent in the other phenyl ring.

The oxidation-reduction systems employed were ferricyanide–vanadyl sulfate and hypobromite-arsenite. Those derivatives which possess desirable properties were used as indicators in the titration of arsenite, chromic sulfate, antimonite, thiosulfate, thiocyanate, hydrazine sulfate, and hydrogen peroxide in alkaline solutions.

EXPERIMENTAL

In a previous research (*27*) five compounds were suggested as indicators in alkaline solution. Four of these—diphenylamine sulfonic acid, 2-carboxydiphenylamine, 2,2′-dicarboxydiphenylamine, and 2-carboxy-2′-methyldiphenylamine—are oxidized by potassium ferricyanide in alkaline solution from colorless reduced form to red. Diphenylamine sulfonic acid must first be oxidized in acid medium to the green reversible stage before it acts as an indicator in alkaline solution. In the case of methylene blue the color change is from colorless to vivid blue. It has a lower potential and requires a considerable blank correction.

Potassium ferricyanide is a primary standard and has a high equivalent weight. For use in the titration the salt was dried overnight at 100° C. and the exact amount for about 0.05 *N* solution was weighed accurately and dissolved in distilled water. This solution is stable for at least a month.

Vanadyl sulfate is stable in acid solution but very easily oxidized in alkaline solution and thus requires an inert atmosphere to prevent its oxidation by the oxygen of the air. It is a very strong reducing agent in alkaline medium. Potassium ferricyanide is best titrated directly with this reagent. An acid solution of vanadyl sulfate was prepared by reducing ammonium vanadate in sulfuric acid solution with sulfur dioxide at the boiling temperature and removing the excess reducing agent by bubbling in carbon dioxide.

Titrations were made by adding a measured volume of ferricyanide and enough 10 *N* sodium hydroxide to make the final solution about 3 *N* and then saturating the solution with oxygen-free nitrogen gas. The indicator was added and with the bubbling of gas continued, the solution was titrated with vanadyl sulfate.

Hypobromite in alkaline solution is as strong an oxidizing agent as ferricyanide but requires standardization of the solution every time it is used. Direct titration with it is preferred. For determining the concentration of the hypobromite solution hydrazine sulfate, arsenic trioxide (both primary standards), and vanadyl sulfate were tried and the end point was detected with diphenylamine sulfonic acid indicator. The reaction with hydrazine sulfate was very slow in direct titration, while vanadyl sulfate did not react quantitatively Only arsenic trioxide was satisfactory. This was employed as the standard in all experiments for determining the normality of hypobromite.

The summary of the results is given in Table I, in which the diphenylamine derivatives are arranged in the order of decreasing usefulness. The derivatives like the chloro- or bromodiphenylamines, aminodiphenylamines, nitrodiphenylamines, hydroxydiphenylamine, and similar compounds which did not give satisfactory results in the qualitative test for indicator properties are not included in the table.

The indicators exhibit a reversible color change and are reasonably stable over the period required for the titration. The carboxydiphenylamine derivatives were very satisfactory in alkaline solution. Of these the 2-carboxy-2 -methoxydiphenylamine is especially recommended for use with the ferricyanide–vanadyl sulfate system. Where two or more isomers were tested, the ortho-substituted derivative exhibited the best qualities for this particular type of compound. Only two compounds, diphenylamine sulfonic acid and 2-aminodiphenylamine sulfonic acid-4, proved useful with the hypobromite-arsenite system. The hypobromite seemed to have either a retarding or destructive effect on the other indicators. 2-Aminodiphenylamine sulfonic acid-4 is very unstable in the presence of excess hypobromite and exhibits an irreversible color change, but diphenylamine sulfonic acid is reversible.

APPLICATIONS TO VOLUMETRIC REACTIONS IN ALKALINE SOLUTIONS

A great variety of organic and inorganic substances were oxidized with ferricyanide and hypobromite in sodium hydroxide solution for a general survey of substances which would react quantitatively and to ascertain which diphenylamine derivatives are suitable as indicators for these reactions. Those tested were selenite, tellurite, phosphite, hypophosphite, sulfide, arsenite, salts of cobalt, nickel, antimony, and chromium, hydrazine, hydrogen peroxide, thiocyanate, cyanide, thiosulfate, sulfite, and organic compounds. Neither reagent oxidized selenite, tellurite, phosphite, and hypophosphite quantitatively. Cobalt, nickel, and thallium salts were oxidized satisfactorily, but the method is not very practical. These compounds form insoluble oxidation products which must be filtered off before the excess oxidant can be titrated in the presence of the indicator.

Charlot (*6*) and Scagliarini (*26*) oxidized sulfides to sulfur in weakly alkaline solutions with ferricyanide. However, repeated experiments using a large excess of ferricyanide in about 3 to 5 *N* sodium hydroxide and boiling the mixture for 10 minutes effected oxidation to the state corresponding to a valence change of 6. This indicates that the sulfide was changed to sulfite. Further experiments revealed that sulfites are oxidized by ferricyanide to sulfate, which does not agree with the above results of oxidizing sulfide to sulfite.

Arsenite, salts of antimony and chromium, hydrazine sulfate, and hydrogen peroxide were oxidized with ferricyanide in alkaline solution, using various indicators for determining the end point of the reactions. Thiocyanate, cyanide, sulfide, antimony (trivalent), and thiosulfate containing a few drops of the indicator (oxidized diphenylamine sulfonic acid) were titrated potentiometrically with hypobromite in alkaline solution. In all cases the

Table II. Diphenylamine Derivatives as Indicators in Titration of Substances in Alkaline Solution

(Excess ferricyanide added and back-titrated with vanadyl salt)

Indicator	Substances Determined														
	Antimonite[a]			Arsenite[b]			Chromic Sulfate[b]			Hydrazine Sulfate[b]			Hydrogen Peroxide[c]		
	Obtained[d] Mg.	Deviation[e] Mg.		Obtained[d] Mg.	Deviation[e] Mg.		Obtained[d] Mg.	Deviation[e] Mg.		Obtained[d] Mg.	Deviation[e] Mg.		Obtained[d] Mg.	Deviation[e] Mg.	[f]
Diphenylamine sulfonic acid[g]	147.4	−0.1	+++	75.9	−0.7	+++	157.4	+0.7	++++	57.6	−0.2	+++	22.0	0	+++
2-Carboxy-2′-methoxydiphenylamine	124.0	−0.1	+++	112.2	−0.1	++++	208.7	−0.6	+++	50.4	0	++++	33.2	0	+++
2,2′-Dicarboxydiphenylamine	124.9	+0.7	++	112.4	+0.2	++	226.4	−0.2	++	50.5	+0.1	+++	27.5	0	++
2-Carboxydiphenylamine	...	...	....	104.3	+0.5	++	171.1	0	+++	43.2	0	++	32.7	0	++++
2-Carboxy-2′-methyldiphenylamine	...	...	....	103.8	0	++++	186.7	0	++++	50.9	0	+	21.8	+0.05	++
2-Carboxy-3′-ethoxydiphenylamine	...	...	....	121.1	0	++++	155.9	+0.4	++	40.0	−0.1	+	..	....	−
4-Aminodiphenylamine sulfonic acid-2	...	...	....	104.6	+0.7	+	....	...	−	43.3	+0.1	+++	..	....	−
2-Carboxy-4′-chlorodiphenylamine	..	...	....	104.6	+0.8	+	201.5	−0.7	+	55.7	+0.1	+	..	....	−
2-Carboxy-3′-bromodiphenylamine	...	...	....	121.9	+0.8	+	....	...	......	..	....	......	..	....	......
2-Carboxy-2′-bromodiphenylamine	...	...	....	...	...	......	202.41	+0.2	+++	43.2	0	+++	..	....	−

[a] Standard obtained by titration with $KMnO_4$ in acid solution.
[b] Standard, actual weight of substance taken for analysis.
[c] Standard obtained by potentiometric titration under the same conditions.
[d] Substance obtained from experiment. Value is average of replicate determinations.
[e] Deviation from standard: − experimental value lower, + higher than standard.
[f] Number of plus signs indicates increasing desirability of each indicator in titrations concerned, minus sign indicates that indicator is not recommended.
[g] Indicator oxidized to green form in acid solution before using.

indicator end point coincided with the potentiometric. The thiocyanate was completely oxidized to cyanate and sulfate in one step, sulfide to sulfate, and thiosulfate to sulfate. Smooth curves were obtained. Further investigation, however, eliminated cyanide and sulfide which did not give reasonable precision in the results. When titrated directly with hypobromite in the presence of the indicator, both exhibited a sluggish reaction and apparently atmospheric oxygen affects them, especially the sulfide.

Table III. Direct Titrations with Hypobromite

Indicator	Substances Titrated								
	Antimonite[a]			Thiocyanate[a]			Thiosulfate[a]		
	Obtained[b] Mg.	Deviation[c] Mg.	[d]	Obtained[b] Mg.	Deviation[c] Mg.	[d]	Obtained[b] Mg.	Deviation[c] Mg.	[d]
Diphenylamine sulfonic acid[e]	224.2	+0.2	++++	23.4	−0.2	++	49.2	−0.1	+++
2-Aminodiphenylamine sulfonic acid-4	...	...	......	..	...	..	67.4	+0.3	+++

[a] Standard obtained by potentiometric titration under the same conditions.
[b] Substance obtained from experiment. Value is average of replicate determinations.
[c] Deviation from standard: − experimental value lower, + higher than standard.
[d] Number of plus signs indicates increasing desirability of each indicator in titrations concerned. Minus sign indicates that indicator is not recommended.
[e] Indicator oxidized to green form in acid solution before using.

Formaldehyde, acetone, methyl alcohol, glycol, glycerol, dextrose, etc., were oxidized with ferricyanide, hypobromite, and hypochlorite in about 3 N sodium hydroxide. The reaction of these organic compounds is purely empirical. Parallel experiments using the three oxidants showed that while ferricyanide was good for a certain compound, hypobromite was better for another and hypochlorite acted on still another. The relative susceptibility of each material to the oxidants was rather difficult to predict. In the direct titration of ferricyanide in dilute sodium carbonate medium with dextrose solutions the end point was determined with diphenylamine sulfonic acid and methylene blue indicators. The preliminary trials indicated that the optimum conditions were a temperature of about 90° C. and just a slight alkalinity.

METHOD OF TITRATION

Solutions of arsenic, antimony, and chromium in their lower state of oxidation and hydrazine sulfate were treated with excess of ferricyanide in the presence of about 3 N sodium hydroxide. The mixture was heated to about 85° to 90° C., then cooled, and saturated with oxygen-free nitrogen gas, and the excess of the oxidant was titrated back with vanadyl sulfate. The end point was detected with the indicator. Blanks were carried out to eliminate variations in the reaction due to slight differences in alkali concentrations and the indicator correction. For comparison, the actual weights of arsenite, hydrazine, sulfate, and chromic sulfate (obtained by reducing potassium dichromate in acid solution) taken for analysis were used as standards. Antimony was determined also by oxidation with permanganate in hydrochloric and sulfuric acid solutions and this value taken as standard. Potassium ferricyanide was titrated directly at 70° to 80° C. in the presence of 3 N sodium hydroxide with hydrogen peroxide and the end point was determined with the indicator. For a check a potentiometric titration under the same conditions was carried out and the values obtained were taken as standard.

The use of an excess of hypobromite is not reliable unless the measurement of the excess includes the decomposition products of the hypobromite. Hence, experiments with hypobromite were limited to direct titration of the substances to be determined. For standards of comparison the potentiometric values obtained under the same conditions were used.

Results are shown in Tables II and III. The maximum deviation of the results of replicate determinations from the average value was ±3 parts per thousand.

It was observed in the experiments using 2,2′-dicarboxydiphenylamine that when there was only a slight excess of the oxidant present, the red oxidized form of the indicator was not vivid enough to show a distinct end point. Detection of the color transition was difficult, especially with chromium, in which the yellow color of the chromate interfered seriously. Cooling of the chromate solution diminished the intensity of the yellow color. Precipitation of chromate as barium chromate was not advantageous.

In the determination of hydrogen peroxide where the ferricyanide was titrated directly with the peroxide, the correction blanks of the indicators were taken into consideration. The end point in these titrations was not so sharp as in the reaction between ferricyanide and vanadyl sulfate. Some indicators which were satisfactory with the other substances analyzed failed to give a detectable end point. The results given in the table are the corrected values.

A comparison of the diphenylamine derivatives studied is given in the fourth column of Tables II and III. The usefulness of each compound was determined by taking into consideration precision, accuracy, sharpness of the end point, and feasibility, and the number of plus signs indicates the increasing desirability of each indicator in the titrations. The minus sign means that the indicator was tried but the results were not worth considering. In most cases the end point recorded by the indicator in these experiments is for the reaction between ferricyanide and vanadyl sulfate. Slight deviations from the standards may be due to differences in the readiness with which ferricyanide oxidizes the different substances.

Although 2,2′-dicarboxydiphenylamine exhibits a vivid, sharp end point, except with chromium, it did not give reasonable precision. The halogen-substituted carboxydiphenylamines were not so useful as the methoxy and methyl carboxydiphenylamines. Introduction of the amino group in the diphenylamine sulfonic acid molecule does not improve the indicator for the ferricyanide–vanadyl sulfate titration. However, with the hypobromite-arsenite system aminodiphenylamine sulfonic acid is slightly better than diphenylamine sulfonic acid. The indicator blank of the former derivative is much smaller with hypobromite than with ferricyanide. The reverse is true for diphenylamine sulfonic acid indicator.

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Determination of Carotene in Alfalfa

Studies on Methods for Meals and Fresh Leaves

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Methods are presented for the rapid, simple, and precise extraction and determination of carotene in fresh alfalfa leaves and in dried alfalfa meals. Numerous tests were made to clarify details of procedure. The carotene fractions of fresh and dried alfalfa were studied chromatographically and spectroscopically. Neo-β-carotene B was found in fresh alfalfa in addition to all-trans β-carotene. In dehydrated alfalfa members of the neo-β-carotene U, V, W group are also present. Blanched leaves may be refrigerated for future analysis after collecting trips. The method is precise to ±0.5 to 1%.

A RAPID and simple method for routine determination of the carotene fraction in fresh alfalfa and in alfalfa products was required in this laboratory. In this study the advantages and disadvantages of many detailed parts of different procedures have been considered carefully. The methods described below have proved satisfactory and a critical discussion of various points may be helpful, since the analysis of alfalfa products is recognized as difficult. No attempt is made here to review the literature extensively or to discuss all existing methods. In recent years numerous modifications have been described which are different combinations of well-known principles.

The carotene fraction contains the pigments of alfalfa which may possess vitamin A potency, in contrast to the xanthophylls, oxidation products of carotenoids, chlorophyll, and its decomposition products. For all practical purposes, the carotene fraction of alfalfa may be considered primarily a mixture of all-trans β-carotene and its cis-isomers.

EXTRACTION

Fresh Alfalfa Leaves. Five grams of fresh hand-picked leaves are wrapped in a cheesecloth package, tied with string or wire, and blanched by immersion in boiling water for 5 to 10 minutes. Excess water is removed by application of moderate pressure. Analysis may follow soon, or the sample may be frozen with dry ice for future analysis.

Carotene is extracted by blending 5 minutes in a Waring Blendor with 100 ml. of 40% (by volume) acetone in Skellysolve B in the presence of approximately 0.1 gram of magnesium carbonate. After 3 minutes of blending, the blender is stopped and the sides are cleaned by wiping downward with a piece of filter paper, which is then shredded and added to the mixture. Blending is continued 2 minutes more.

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The mixture is filtered under suction and the residue is washed successively with two 10-ml. portions of acetone, followed by Skellysolve B until the filtrate is colorless. The filtrate is transferred to a separatory funnel, the aqueous layer removed, and the hyperphase made to 200-ml. volume with Skellysolve B. No drying is necessary.

A 15-ml. aliquot of this solution is diluted with 15 ml. of Skellysolve B, and 10 to 20 ml. of the resultant solution are chromatographed as described below.

Dehydrated or Dried Alfalfa Meal. Two grams of dry meal (ground to 40-mesh) are used. The sample is placed between layers of cotton in a Coors porcelain extraction crucible, size 3, suspended in an A.S.T.M. extraction apparatus. Sixty milliliters of 30% acetone-Skellysolve B are put in the 400-ml. flask of the extraction apparatus and the sample is extracted hot for 3 hours on a steam-heated bath (with glycerol, or mineral oil for rapid heat transfer), with a drip rate of 100 to 150 drops per minute. This is a modification of the method of Wall and Kelley (*6*)

The extract is made to 100 ml. with Skellysolve B, resulting in a final acetone concentration of about 18%; no filtering or drying is required, although the solution is usually turbid with precipitated material. An aliquot of this solution, usually 15 ml. (from 5 to 20 ml. may be used), is chromatographed as described below.

CHROMATOGRAPHY

A short (about 6-cm.) column, 19 mm. in diameter, composed of a 1 to 1 mixture of activated magnesia (Micron brand No. 2642, Westvaco Chlorine Products Company, Newark, Calif.) and Hyflo Super-cel is packed dry with a wooden tamper, and then covered with 1 cm. of anhydrous granular sodium sulfate. Under these conditions the carotenes pass rapidly through the column and the chlorophylls, xanthophylls, and carotenoid oxidation products are held firmly in the upper 10 mm. of the column. The eluate from the column is caught in a 25-ml. volumetric flask, using a Fisher Filtrator, and the column is washed with 10% acetone-Skellysolve B to make the volume of the eluate to almost 25 ml. The upper zones expand to a depth of about 2 cm. during this washing.

Table I. Effect of Cold Storage (below −18° C.) on Carotene Content of Fresh Alfalfa Leaves

Storage Time	Carotene Content (Fresh Weight Basis)
Days	*P.p.m.*
1	163
21	162
30	166
66	164

PHOTOMETRY

The density of the 25-ml. solution is determined at 436 mμ with a Coleman Universal spectrophotometer, Model 11, or a Klett photometer with a No. 44 filter, and converted into carotene concentration by a calibration chart. Density values are between 0.15 and 0.95 and between 0.08 and 0.60 for the Coleman and Klett photometers, respectively, for samples having between 50 and 400 p.p.m. of carotene (15 ml. chromatographed). These instruments were calibrated by use of a carotene fraction (from alfalfa meal chromatographed on magnesia) which had a characteristic absorption curve like that reported by Beadle and Zscheile (*1*) for the carotene fraction of spinach leaves. This curve is intermediate between those for all-trans β-carotene and neo-β-carotene B (*1*, *7*). The concentration of carotene is measured with a Beckman spectrophotometer at 4360 Å. using the specific absorption coefficient 196 (*1*).

DISCUSSION OF CRITICAL FACTORS

Different plants, plant parts, or products made from plants require individual treatment and study, as extraction methods, identity of pigments, and interpretation of both chromatographic columns (or other fractionation procedures) and characteristic absorption curves cannot be carried over arbitrarily from one material to another. All must be checked for accuracy in the application at hand. The combined use of chromatography and spectrophotometry is important, because both can act as checks on the limitations of the analysis. The results of various tests of the above procedures are discussed herewith. Most of the tests were made with commercial "hexane" (b.p. 65–67°) instead of Skellysolve B.

Fresh Material. Carotene is extracted much more simply from fresh leaves than from dry meals, fresh stems, or whole fresh plant material. Leaves contain about 90% of the carotene in alfalfa at the 1/10 bloom stage. The ratio of stem to leaf is variable, and for practical applications, stems may be properly ignored. Relatively small samples are required to keep the amounts of solvents and labor of reasonable magnitude.

Since the carotene content of individual alfalfa leaves from the same stem, and of individual leaves from different stems and plants, may be expected to vary, the most practical sample for field use must contain enough leaves to minimize the effect of these variations; 5 grams of healthy leaves, picked by hand (not stripped) provide an adequate single sample. In field practice an analyst can procure three or four such samples in duplicate per hour. Since the moisture content of fresh leaves will vary appreciably, a 10-gram sample for dry matter determination should accompany each duplicate set. From many points of view the comparison of results on the dry weight basis is the better.

Extraction with 30% acetone was incomplete; 7 to 12% of the carotene could be re-extracted from the first residue of unblanched alfalfa, while the residue from blanched leaves contained 6% re-extractable carotene. When 40% acetone is used re-extraction increases the carotene content by 2% or less. Blanching softens the tissues and facilitates extraction, but it is not necessary from the enzymatic viewpoint if extraction is to follow very soon after picking. Fresh leaves may be held at room temperature 30 minutes or more without loss of carotene. The addition of calcium cyanide or mercuric chloride during blending to inactivate enzymes does not increase the yield of carotene. Magnesium carbonate is added to neutralize plant acids; this is not a vital point but rather a simple precaution which would be helpful if leaves with very acid sap were encountered.

The twofold dilution of the extract before chromatography is not necessary if the column is made sufficiently long and if zones are watched very carefully. However, time is saved and great certainty of adequate separation is achieved by this dilution.

In recovery experiments, measured quantities of a carotene eluate from other analyses were added to blanched samples immediately before blending. The amounts added were 10 and 100% of the carotene found in the leaves (138 p.p.m.). In both cases the loss was 8 p.p.m.; thus the losses were equal in absolute quantity, regardless of the amount added, and amount to about 5% for average material.

To illustrate the precision of the method and sampling, the following typical replicate analyses were obtained on successive 5-gram samples drawn from five lots of mixed fresh leaves from numerous plants: lot 1: 145, 147; lot 2: 158, 158; lot 3: 151, 153; lot 4: 153, 153; lot 5: 146, 150 p.p.m.

Fresh samples, blanched and frozen, may be kept for considerable periods at low temperature (0° F.) without loss of carotene. In Table I are analyses on replicate samples kept for different periods, partly in dry ice and partly in a deep-freezer. The results are essentially identical. Absorption curves of the carotene fraction remained unchanged during storage. Field collection and storage of samples are feasible if refrigeration is available. Blanched samples have been kept at 25° C. for 3 hours before freezing with dry ice without loss of carotene.

Since field samples are best frozen in dry ice before analysis, it was necessary to determine the effect of carbon dioxide on the carotene content. Zechmeister and Polgár (*8*) reported poor recovery of carotene from columns of calcium hydroxide when the solution was saturated with carbon dioxide. In the authors' experience with chromatography of a carotene extract, saturated by bubbling carbon dioxide through the solution for one hour and compared with the untreated extract, a 3.2% loss occurred when calcium hydroxide was used; identical results were obtained with magnesia 2642 (2.55, 2.55 micrograms per ml. of eluate).

Neo-β-carotene B was isolated from the carotene fraction of fresh leaves on calcium hydroxide columns and identified spectroscopically. No evidence of the neo-U, V, W group (*7*) could be detected.

Dried Alfalfa. The principal problem in dealing with dried alfalfa is to secure complete extraction of carotene. Numerous methods given in the literature were tried but none was found reliable on all samples studied. The following observations were made during the development of the method described above.

Chromatographic methods were used to study various extraction procedures. Tempering the 2-gram sample of meal with 6 grams of water for 30 minutes, followed by use of 40% acetone–hexane in a Waring Blendor gave results 14 to 20% lower than the procedure of Kemmerer (*2*) who soaked the meal overnight in 5% acetone–hexane at room temperature. Standing in 40% acetone–hexane gave higher results than with 5% acetone. The blender thus accomplished little more than stirring. Addition of 300% water before soaking in acetone-hexane always resulted in poor extraction.

Small amounts of water (2.5% of the acetone concentration) added with the acetone-hexane (10 to 20% acetone) had negligible effects upon the carotene extraction during overnight soaking. Refluxing the residues 2.5 hours with 30% acetone–hexane extracted only 2% additional carotene (6 micrograms). Hot extraction in a Soxhlet extractor 2.5 hours with 30% acetone–hexane was equivalent to overnight cold (room temperature) extraction with 10% acetone–hexane in the case of some samples. In other cases the soaking procedure gave results 10% low. Losses of carotene in these extracts, in the absence of meal, were approximately 3% (6 micrograms) during 22 hours' standing at room temperature in the dark or during a 3-hour reflux period in 10% acetone–hexane.

Extraction in a Waring Blendor for 5 minutes with 12% alcoholic potassium hydroxide (*4*) gave very poor extraction. A 0.5-hour reflux period with 30% acetone–hexane (*6*) gave results 8% lower than overnight soaking.

Variations of the acetone concentration and time of hot extraction in the A.S.T.M. extractor made it clear that (1) 20% acetone extracted 4% more carotene in 3 hours than 10% acetone and (2) 1 hour was too short and 4.5 hours too long. At times longer than 3 hours the decomposition rate of carotene exceeds the rate of additional extraction. It was desirable to keep the acetone concentration low enough to avoid the necessity of reducing volume, washing out the acetone, or making excessive dilutions with hexane for subsequent chromatography. The use of pure acetone or hexane or 50% acetone gave no better extraction than 20 to 30% acetone. Since acetone–hexane mixtures have a minimum boiling point (ca. 50° C.) at a composition of approximately 30% acetone (by volume), the use of this mixture was adopted as one that would give the most easily reproducible temperature conditions of extraction. The boiling point will not change appreciably, even though small accidental losses of vapor occur.

The substitution of Skellysolve B for hexane causes no numerical difference in the carotene content as determined on a Klett or Coleman instrument. Slight differences in wave length of maxima due to change of solvent are detectable with a Beckman spectrophotometer.

The above studies were made on commercial dehydrated alfalfa meal, ground to pass a 26-mesh screen. The following values were found on a meal ground to pass screen sizes of 20-, 40-, 60-, and 80-mesh, respectively: 190, 197, 196, and 193 p.p.m.; 40-mesh is a convenient laboratory size. Additional grinding does not alter the carotene content.

No carotene losses occur in meals during as much as 18 hours' heating at 75° C. in a vacuum oven. This is over twice as long as necessary for good grinding to 40-mesh size. In routine work on dry samples such drying makes the moisture contents more uniform and the results more comparable. Meals kept in bottles at −18° C. or lower lose no appreciable carotene during the first 4 months.

The over-all loss of carotene in this method is considered to be from 3 to 5% (about 1.5% is not extracted and 1 to 3% is lost through heat decomposition or oxidation during extraction) on samples containing 200 to 300 p.p.m. These losses are undoubtedly higher on the percentage basis for samples very low in carotene. Replicate samples of meal agree with ±0.5 to 1%.

Characteristic curves for the carotene fraction by hot extraction indicate the anticipated amount of isomerization of all-trans β-carotene (*1*) in comparison with a similar fraction from cold extraction. Chromatographic analysis on calcium hydroxide of the carotene fraction from magnesia demonstrated the presence of neo-β-carotene B (*5*, *7*) below all-trans β-carotene and evidence of the presence of isomers of the neo-U, V, W β-carotene group (*5*, *7*) was found in the column above all-trans β-carotene. This latter group was probably formed by heat during dehydration or isomerization during storage.

Chromatographic practices must be scrutinized continually for sources of error. No. 2641 magnesia will not effect this separation of carotenoids under these solvent conditions. When No. 2642 becomes old and has adsorbed sufficient moisture from the atmosphere its adsorptive power decreases and longer columns are required. With very fresh adsorbent, higher concentrations of acetone must be used for elution. It is probable that certain other adsorbent and solvent combinations would give equally good results. Magnesia is readily available.

Chromatography, accompanied by suitable absorption data as a check, provides the simplest and most direct expedient for separation of the carotene fraction from other plant pigments of the fat-soluble group. In general, properly tested adsorption methods may be expected to purify the carotene fraction more effectively than partition between immiscible solvents. Kemmerer (*3*) has stressed the need for more vigorous testing of adsorbents. In a comparative study of methods, Kemmerer and Fraps (*4*) found the lowest contents of crude carotene in dehydrated alfalfa by adsorption on magnesia. Better purification produces lower results.

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New Standard Samples for Metals

The National Bureau of Standards has added two new metals to its list of analyzed standard samples.

Standard nickel silver No. 157 has the following percentage composition: copper 72.14, nickel 17.91, zinc 9.70, cobalt 0.14, and iron 0.053. The price is $3 per 125-gram unit.

Standard chromium-molybdenum-silver steel No. 159 is certified for percentages of the following constituents: carbon 0.52, chromium 1.00, molybdenum 0.42, and silver 0.090. The price is $3 per 150-gram unit.

The bureau now issues more than 375 different kinds of standard samples—steels, irons, ferroalloys, nonferrous alloys, ores, ceramic materials, high-purity chemicals for standardizations, hydrocarbons, paint pigments for color, oils for viscometer calibrations, certain reference standards, and melting-point standards. A complete list of the standards, fees, and other information is given in the Supplement to Circular C398 which can be obtained free of charge upon application to the bureau, Washington 25, D. C.

Determination of Bismuth, Copper, and Lead in Aluminum Alloys

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An accurate method is presented for the determination of bismuth, copper, and lead in aluminum alloys, which is much shorter than the method of the Aluminum Company of America, since it eliminates a double hydrogen sulfide separation and two ignitions. The proposed procedure depends upon the insolubility of the bismuth in hydrochloric acid. Bismuth is determined colorimetrically as the iodide after precipitation as the oxychloride and the copper and lead are determined electrolytically from a nitric acid solution.

IN RECENT years aluminum alloys containing copper, bismuth, and lead have become increasingly important, especially in the manufacture of screw products (*1*). The method commonly used for the determination of copper, bismuth, and lead in these alloys is that of the Aluminum Company of America (*3*). This procedure, although accurate, is long and complicated, involving two hydrogen sulfide precipitations and two ignitions. An investigation was conducted for the purpose of developing a shorter method for the analysis of copper, bismuth, and lead in aluminum alloys.

Among the methods tried was the separation of bismuth from copper and lead by means of pyrogallol (*16*). The authors found it unsatisfactory because complete quantitative precipitation of bismuth was not obtained. The separation of lead as lead sulfate followed by a manganese dioxide precipitation, using potassium permanganate and manganous sulfate, to separate the bismuth from the copper (*14*) was also tried and found inaccurate, probably because of incomplete separation of the bismuth sulfate from the lead sulfate (*18*). Using the same separations as outlined in the proposed method the thiourea colorimetric procedure (*8, 9*) was tried instead of the bismuth iodide (*7*). It offered no special advantage and was consequently abandoned.

The method described in this paper was finally adopted as the most practical and workable procedure. It was found to be as accurate as the method of the Aluminum Company of America and it requires only one half the amount of work. Advantage is taken of the fact that the bismuth is insoluble in (1 to 1) hydrochloric acid (*4, 10, 17*). The bismuth is determined colorimetrically as the iodide after precipitation as the oxychloride, and the copper and lead are plated out simultaneously in a nitric acid solution.

This proposed method has been primarily designed for commercial aluminum alloys of copper, lead, and bismuth. These alloys usually contain 3.5 to 6% copper, 0.2 to 0.6% lead, and 0.2 to 0.6% bismuth. The procedure, however, might be adapted for the analysis of other percentages of these elements in aluminum alloys.

PROCEDURE

Dissolve a 2-gram sample in a 400-ml. beaker with 50 ml. of hydrochloric acid (1 to 1) without applying heat. Immediately after the reaction ceases add 50 ml. of distilled water and filter through a No. 40 Whatman filter paper, collecting the filtrate in a 600-ml. beaker. Wash with hot water. Dissolve the precipitate back into the original 400-ml. beaker with 40 ml. of hot nitric acid (1 to 1) and wash with hot water. Add 1 ml. of ferric nitrate solution (1%) and then ammonium hydroxide until the solution is just turbid. If the end point is overstepped make the solution acid again with nitric acid and again add ammonium hydroxide. Add 1 ml. of hydrochloric acid (1 to 1), dilute to 250 to 300 ml. with hot water, and let stand on a steam bath for 45 minutes. While the bismuth oxychloride is coagulating add 40 ml. of concentrated nitric acid and several glass beads to the first filtrate and boil down to a volume of about 5 ml. Filter the oxychloride precipitate through a No. 44 Whatman filter paper into the boiled down filtrate. Swab the beaker and wash precipitate with hot water. Dissolve the precipitate with 40 ml. of hot nitric acid (1 to 1) into a 1-liter volumetric flask. Dilute to about 500 ml. with cold water and add 4 ml. of sulfurous acid (1 part of saturated sulfurous acid solution to 3 parts of water) and 10 ml. of potassium iodide solution (20%). (For very accurate work fresh potassium iodide solution and fresh sulfurous acid should be used, since slightly inaccurate results were obtained when these solutions were more than 2 days old.) Dilute to the 1000-ml. mark and read the bismuth colorimetrically. The authors used a Klett-Summerson colorimeter (test tube model), filter No. 42.

To the combined filtrates containing the copper and lead add 30 ml. of concentrated nitric acid and boil down to a volume of about 10 ml. Add 15 ml. more of nitric acid and repeat the operation. Immediately add 10 ml. of concentrated nitric acid and dilute to about 50 ml. with hot water. Transfer the solution into a 200-ml. tall-form electrolytic beaker and electrolyze for 30 minutes at 2 amperes, using a platinum gauze anode and cathode. Add 2 ml. of sulfuric acid (1 to 1) and electrolyze for 30 minutes longer. Remove the electrodes and wash them first with water and then with alcohol. Dry the cathode in an oven at 100° to 105° C. for about 5 minutes and weigh as metallic copper as soon as cool. Dry the anode for 30 minutes at 210° C. and weigh as lead dioxide, which has a calculated factor of 0.866.

A working curve for bismuth can be drawn up by using a standard bismuth solution. This solution is best obtained by dissolving 0.4000 gram of metallic bismuth in 20 ml. of nitric acid (1 to 1), transferring to a 2-liter volumetric flask, and diluting to the 2-liter mark. Appropriate amounts of this standard solution are measured out into 1-liter flasks and then 40 ml. of nitric acid (1 to 1) and 5 ml. hydrochloric acid (1 to 100) are added. (Since the method calls for a 2-gram sample, 10 ml. of this solution are equivalent to 0.10% of bismuth.) The solution is diluted to about 500 ml., sulfurous acid and potassium iodide solution are added, and the bismuth is read as usual.

DISCUSSION

Analysis of many filtrates from the hydrochloric acid–insoluble material showed that bismuth is insoluble in hydrochloric acid (1 to 1), but that copper and lead are partially soluble. In the case of the 11S standard (5.11% copper and 0.48% lead) 0.2 to 0.3% copper and 0.2 to 0.3% lead were found to have gone into solution. This solubility of copper and lead obviously eliminated the possibility of discarding the hydrochloric acid filtrate.

In order to check the colorimetric method for bismuth three curves were made. The first curve was drawn up by using aluminum samples of known bismuth content; the second, by using high-copper aluminum alloys to which had been added weighed amounts of metallic bismuth. In order to maintain similar conditions known amounts of lead nitrate were added to the solution obtained by dissolving the insoluble hydrochloric acid residue in nitric acid. It was found impracticable to add metallic lead at the very outset, since the undissolved metallic lead in the residue

Table I. Reproducibility of Results for Type 142X Alloy

Sample No.	Copper %	Lead %	Bismuth %
1	4.16	0.37	0.42
2	4.18	0.39	0.43
3	4.19	0.39	0.42
4	4.17	0.39	0.43
5	4.19	0.37	0.42
6	4.19	0.40	0.42
7	4.19	0.40	0.41
8	4.20	0.39	0.42
9	4.23	0.39	0.42
10	4.17	0.38	0.42
Av.	4.19	0.39	0.42
Av. deviation	±0.01	±0.01	±0.00

could not readily be dissolved off the filter paper with nitric acid. The third and most rapid working curve, described under Procedure, was drawn up by the use of standard bismuth nitrate solution. The three curves followed Beer's law and were practically identical, proving conclusively the validity of the method.

In working with synthetic solutions it was found that a trace of hydrochloric acid is essential to stabilize the color, especially when the sample contains more than 0.40% bismuth. However, if too much hydrochloric acid is present (more than 1 ml. per liter), the colorimetric readings are lower than they should be. This is borne out by the literature, which cites interference when too much chloride ion is present (*12*). All metals (*8, 11*) that interfere with the colorimetric determination of bismuth, such as copper, lead, silver, tin, and antimony, are either not present in aluminum alloys or are removed by the hydrochloric acid–oxychloride separation. The sulfurous acid added reduces any oxidizing agents, such as ferric iron, that might interfere with the determination. No interference whatsoever is encountered in the colorimetric procedure of bismuth due to the presence of nickel. However, in the Aluminum Company of America method the bismuth results will tend to be high, if a large amount of nickel is present, unless considerable care is taken.

The yellow color of the bismuth complex ($BiI_3.3KI$ or $BiI_3.2KI.4H_2O$) (*15*), as developed in this method, is very stable. The color develops immediately and does not change upon standing for 24 hours.

Wiegand, Lann, and Kalich (*19*) have shown that the light absorption of the yellow iodobismuthite solution is at its maximum at 460 millimicrons wave length. However, the No. 42 filter used for the method outlined in this paper, although having a maximum transmission of 425 millimicrons, has proved entirely satisfactory.

In neutralizing the solution with ammonia before the precipitation of the bismuth as the oxychloride, an opalescence would appear even if no ferric ion were present. However, the authors recommend the addition of the ferric nitrate before the neutralization, because they found that the turbidity produced by the ferric hydroxide was much sharper than the turbidity that would be produced otherwise.

If so desired, bismuth can be determined gravimetrically by slightly modifying the regular procedure. The solution obtained by dissolving the hydrochloric acid–insoluble material into the original 400-ml. beaker is filtered into another 400-ml. beaker and washed with hot 10% nitric acid. The oxychloride is precipitated as usual, then filtered through a tared Gooch crucible and dried for one hour at 105° to 110° C. No exhaustive study was made of this modification, since the colorimetric method is faster and just as accurate. Using the gravimetric modification, the following bismuth results were obtained on sample 142X which contains 2% nickel and 1.5% silicon: 0.43, 0.42, and 0.44%. As can be seen from Table III, the average value for this sample by the Aluminum Company of America procedure is 0.42%.

The Aluminum Company of America states (*2*) that it is best not to plate out copper in the presence of large amounts of iron, nickel, and aluminum. However, for several years, this laboratory, using the method of Sloviter (*13*), has been plating out copper in aluminum alloys without any preliminary separations and has obtained excellent results. This method is not applicable to copper, lead, and bismuth alloys because bismuth partially plates on the cathode and partially on the anode (*5*)

Although manganese is not present in commercial copper, lead, and bismuth alloys, a study was made, using synthetic samples, of the possible interference of this element. It was found that some manganese plated on the anode, if the manganese content of the sample were above 0.05%. Therefore, if a high percentage manganese alloy were encountered, after electrolysis, the anode would have to be stripped with nitric acid (1 to 1) and the lead determined as lead sulfate. An alternate procedure would be to weigh the deposit and determine and correct for manganese.

Table II. Comparison of Results for Type 11S Alloy

Sample No.	Aluminum Company of America Procedure Copper %	 Lead %	 Bismuth %	Suggested Procedure Copper %	 Lead %	 Bismuth %
1	5.18	0.49	0.54	5.19	0.49	0.55
2	5.15	0.49	0.53	5.13	0.49	0.53
3	5.10	0.48	0.49	5.15	0.48	0.51
4	5.05	0.44	0.52	5.07	0.49	0.52
5	5.13	0.49	0.50	5.17	0.44	0.55
6	5.08	0.48	0.53	5.18	0.47	0.52
Av.	5.11	0.48	0.52	5.15	0.48	0.53
Av. deviation	±0.04	±0.01	±0.02	±0.03	±0.01	±0.01

Average Difference between Two Methods

Copper	Lead	Bismuth
0.04	0.00	0.01

Table III. Comparison of Results for Type 142X (2% Nickel) Alloy

Sample No.	Aluminum Company of America Procedure Copper %	 Lead %	 Bismuth %	Suggested Procedure Copper %	 Lead %	 Bismuth %
1	4.13	0.37	0.43	4.15	0.38	0.42
2	4.17	0.38	0.43	4.16	0.37	0.42
3	4.18	0.38	0.42	4.20	0.38	0.43
4	4.18	0.37	0.42	4.19	0.37	0.43
5	4.20	0.37	0.40	4.16	0.38	0.42
6	4.19	0.38	0.41	4.17	0.38	0.42
Av.	4.18	0.38	0.42	4.17	0.38	0.42
Av. deviation	±0.02	±0.01	±0.01	±0.02	±0.00	±0.00

Average Difference between Two Methods

Copper	Lead	Bismuth
0.01	0.00	0.00

An attempt was made to take the combined filtrates, containing the copper and lead, down to fumes of perchloric acid, thus eliminating the hydrochloric acid, which would interfere with the plating of the copper (*6*). As erratic results were obtained following this procedure, the nitric acid treatment was adopted. Three additions of nitric are recommended, although very good results for copper were obtained after only two additions. The boiled down solution, after the second addition of nitric acid, was found to give a slight positive test for chloride with silver nitrate, while no chloride was found after the third addition. After the removal of the hydrochloric acid, 10 ml. of nitric acid are added to ensure proper acidity for the electrodeposition of the copper and lead. The authors have found that this amount of nitric acid gives the best plating of the copper and lead, although theoretically it would seem to be too much to ensure proper electrolysis.

Table IV. Accuracy of Method

Sample No.	Per Cent Copper			Per Cent Lead			Per Cent Bismuth		
	Present	Obtained	Difference	Added	Obtained	Difference	Added	Obtained	Difference
1	3.88	3.90	+0.02	0.20	0.20	0.00	0.20	0.21	+0.01
2	3.88	3.88	0.00	0.25	0.25	0.00	0.23	0.23	0.00
3	3.88	3.95	+0.07	0.25	0.26	+0.01	0.25	0.24	−0.01
4	3.88	3.86	—0.02	0.29	0.29	0.00	0.28	0.28	0.00
5	3.88	3.92	+0.04	0.30	0.31	+0.01	0.34	0.34	0.00
6	3.88	3.94	+0.06	0.35	0.35	0.00	0.36	0.36	0.00
7	3.88	3.90	+0.02	0.40	0.41	+0.01	0.39	0.39	0.00
8	3.88	3.90	+0.02	0.44	0.43	−0.01	0.43	0.44	+0.01
9	7.87	7.91	+0.04	0.48	0.48	0.00	0.48	0.49	+0.01
10	7.87	7.91	+0.04	0.56	0.57	+0.01	0.52	0.52	0.00
11	4.18	4.13	−0.05	0.63	0.62	−0.01	0.54	0.55	+0.01
12	4.18	4.17	−0.01	0.63	0.63	0.00	0.58	0.59	+0.01

REPRODUCIBILITY

To test the precision of this method an aluminum alloy (No. 142X) containing copper, lead, and bismuth was run ten times and the results (Table I) show good agreement.

ACCURACY

Since there were no suitable Bureau of Standards samples available for aluminum alloys of the types discussed, the results of the proposed method were compared (Tables II and III) with the results obtained on laboratory standards using the Aluminum Company of America method. The accuracy of the method was further checked by adding known amounts of lead nitrate solution and metallic bismuth to an aluminum alloy, the copper content of which was known. The known amounts of copper present and the amounts of the lead and bismuth added agreed closely with the results obtained by the proposed method as shown by Table IV.

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Opinions expressed are those of the authors and should not necessarily be construed to represent the views of the Navy Department.

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Determination of Olefins, Aromatics, Paraffins, and Naphthenes in Gasoline

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A method of analysis is described which is suitable for the determination of olefins, aromatics, paraffins, and naphthenes in gasolines. The method is more reliable than previously published methods, especially for use with high-olefin samples, in that it contains several improvements in analytical procedures as well as several internal cross checks.

OF THE many papers in the literature dealing with the determination of olefins, aromatics, naphthenes, and paraffins in gasoline, the following have particularly influenced this work (*4, 5, 7-13, 15, 18, 23, 25, 26, 28, 29*). The present paper presents a method which has been developed in these laboratories over a period of years, and which is suitable for the analysis of straight-run, polymer, catalytically cracked, and thermally cracked gasolines, including those which are rich in olefins and aromatics.

The advantage of the method now presented over the methods previously available in the literature is that it is more reliable, particularly for samples very rich in olefins and aromatics. This reliability results from improved procedures and from a system of internal cross checks which ensure the accuracy of the analytical data obtained.

It is difficult to develop a satisfactory method of analysis for determining hydrocarbon types in a mixture such as gasoline because the various isomers within any one type often differ considerably both in chemical reactivity and in physical properties. There was therefore much uncertainty in the early work on hydrocarbon analysis.

The papers of Faragher, Morrell, and Levine (*7*), of Garner (*10*), and of Howes (*15*) give a good picture of the state of the art of hydrocarbon analysis in 1930 and earlier; therefore discussion of work prior to 1930 is omitted from this paper.

In the work of Faragher, Morrell, and Levine, olefins and aromatics were removed by a procedure which involved treating with 91% sulfuric acid, redistilling to remove polymers, and finally treating with 98% acid to remove any remaining olefins or aromatics. This gave total olefin plus aromatic. Aromatics were determined by nitration after removal of olefins by treating with sulfur monochloride and redistilling. Olefins were then determined by difference between the per cent total olefin plus aromatic and the per cent aromatic. The sulfur monochloride reaction for the separation of olefins did not prove to be too satisfactory in practice because of the variation in reactivity of the olefins, and because sulfur monochloride also has a tendency to react with nonolefinic constituents.

Kurtz and Headington (*18*) used a modification of the Faragher, Morrell, and Levine acid-treating procedure for the determination of total olefins plus aromatics, but depended entirely upon physical properties for determining the composition of the olefin-aromatic mixture and of the paraffin-naphthene mixture. The analysis of the olefin-aromatic fraction was based upon density and refractivity intercept ($n - d/2$) of the unsaturates calculated from the difference in physical properties of the respective cuts before and after removal of the unsaturates. ("Unsaturates" in this paper means those hydrocarbons which are not saturated—i.e., olefins and aromatics.) The method is not suitable in the presence of conjugated diolefins and a procedure for their removal with maleic anhydride was provided. The samples examined at that time seldom contained more than 3 to 4% of such conjugated diolefin. The method is not suitable for aromatics in higher boiling ranges (above 175° C.) where dicyclic aromatics often begin to appear, nor for naphthenes in the higher boiling fractions (above 175° C.) where dicyclic naphthenes are often present. In spite of these deficiencies the method proved very useful in routine use, but was very time-consuming and required highly trained laboratory personnel.

Thomas, Bloch, and Hoekstra (*25*) presented a procedure for gasoline analysis which depended for the olefin determination on bromide-bromate type of bromine titration. In spite of the variable reactivity of olefins with halogen, the bromide-bromate titration as used by them was shown to be reasonably accurate, and additional work by various laboratories has improved this type of titration (*2, 9, 17*).

Bates, Rose, Kurtz, and Mills (*5*) reported composition data on a number of cracked gasolines by a procedure, publication of which was held up because of the war, and which has been superseded by the method presented in this paper. The analytical method used by Bates, Rose, Kurtz, and Mills involved acid treating to determine total olefin plus aromatic, and bromide-bromate titration to determine olefins. The details of the procedures then used differ from those now recommended, but the authors feel that the application of present methods to the samples studied by Bates *et al.* would lead to the same general conclusions concerning composition of these samples.

PRINCIPLE OF PRESENT METHOD

This paper is restricted to a specific procedure recommended for the analysis of full-range gasoline samples having end points not over 225° C. (437° F.). Although this procedure can be modified in special cases, no attempt is made in this paper to discuss such modifications.

The first step in the analysis of the gasoline is the fractionation of the sample into cuts. It is necessary to divide the gasoline into cuts, since the distribution of various types of hydrocarbons throughout the boiling range is, in general, not uniform. For example, in the case of olefins, it is necessary to estimate a molecular weight for the olefin present in order to convert bromine number to per cent olefin (*3*). This can be done with a reasonable degree of accuracy for a cut of 25° C. boiling range; whereas such an estimate for a full boiling range gasoline would be relatively inaccurate. Similarly, in estimating specific dispersion of aromatics a much better estimate can be made for a 25° C. cut than on the whole gasoline. The cuts recommended in Table I are of approximately 25° C. boiling range, and the cut points are so chosen that the aromatics of specific molecular weights fall into separate cuts. It is important in analyzing the saturate fractions by means of physical properties to remember that the use of average properties is justified only where the boiling range of the cut is sufficiently broad, so that a considerable number of isomers in each class of hydrocarbons will probably be present. This is true with cuts of the breadth recommended in this paper.

Table I. Fractions Used for Gasoline Analysis

Cut No.	Cut Points ° F.	Cut Points ° C.
1	Initial- 50	Initial-10
2	50-115	10-46.1
3	115-150	46.1-65.6
4	150-205	65.6-96.1
5	205-251	96.1-121.7
6	251-302	121.7-150
7	302-347	150-175
8	347-392	175-200
Bottoms	392-end	200-end

1. The volume per cent of unsaturated hydrocarbons is determined by acid-treating with a mixture of 30% by weight of phosphorus pentoxide and 70% by weight of 95 to 96% (1.84 specific gravity) sulfuric acid. The acid treatment is carried out at ice temperature under controlled conditions. The method has been shown to give correct volumetric absorption over a wide range of olefin and aromatic concentrations (Table II). It has also been established that this procedure does not leave an olefinic polymer residue or affect paraffins or naphthenes, as has been the case with previous methods using sulfuric acid alone (*16*, *28*).
2. Olefinic unsaturates are determined by an improved bromide-bromate titration. The method used is satisfactory for most olefins, although it is known to give high results on highly branched olefins, such as those found in polymer gasoline. In the case of conjugated diolefins, approximately 15% of the second double bond reacts with bromine, so that conjugated diolefins react essentially as mono-olefins. The authors believe that no halogen titration method will be satisfactory for all classes of olefins, but that the procedure used is a good compromise.
3. The aromatic content of each cut is calculated from spe-

Table II. Determination of Olefinic Plus Aromatic Hydrocarbons by Sulfuric Acid–Phosphorus Pentoxide Absorption on Known Blends

Blend	Vol. % Saturate[a]	Vol. % Olefin[b]	Vol. % Aromatic[c]	Vol. % Unsaturate by Acid Absorption	Deviation
			10-Ml. Sample		
Q	100	0	0	0	0
21	92	4	4	9	+1
13	80.5	19.5	0	20.5	+1
14	80	0	20	20	0
R	79	0	21	20	−1
S	62	0	38	38	0
11	60	40	0	41	+1
10	60	20	20	41.5	+1.5
12	60	0	40	40	0
W	50	25	25	49	−1
7	40.5	40	19.5	60	+0.5
6	40.5	20	39.5	60	+0.5
9	40	0	60	60.5	+0.5
T	37	0	63	63.5	+0.5
2	20	40	40	79	−1
1	20	20	60	80	0
5	20	0	80	80	0
U	20	0	80	81	+1
20	4	4	92	98	+2
			5-Ml. Sample		
8	40	60	0	61	+1
4	20	80	0	81.5	+1.5
3	20	60	20	80.5	+0.5
X	15	85	0	83	−2
19	4	92	4	95	−1

[a] Saturated hydrocarbon fractions from straight-run gasoline or alkylate.
[b] Olefin blends of cyclohexene, diisobutylene, and caprylene.
[c] Aromatic blends of toluene and xylene or benzene and ethylbenzene.

cific dispersion and bromine number, using essentially the procedure described by Grosse and Wackher (*13*).

4. A cross check of the data obtained in paragraphs 1, 2, and 3 is obtained by adding the olefins as determined in paragraph 2 to the aromatics as determined in paragraph 3, and comparing with the sum of the olefins plus aromatics as determined in paragraph 1 If the hydrocarbon analysis is correct, these two values will agree within 2 to 3%.

5. If the values obtained in paragraph 4 do not agree within 3%, the olefins are determined by the nitrogen tetroxide method of Bond (*6*). The olefins determined in this manner are then subtracted from the olefins plus aromatics as determined by acid treatment, and the difference is taken as per cent aromatics.

This procedure classifies indene, styrene, and other molecules containing both olefinic double bonds and aromatic rings, as olefins. Furthermore, this type of olefin removal is equally satisfactory for mono-olefins, nonconjugated diolefins, and conjugated diolefins.

6. The saturate fraction remaining after removal of olefin and aromatic by acid treating is analyzed for paraffin and naphthene by means of physical properties. Specifically a graph of refractivity intercept *vs.* density (Figure 1) is used. This graph is based on the properties of average paraffins and average monocyclic naphthenes up to a density which corresponds to a boiling point of about 180° C. At this point an empirical adjustment is made to allow for increasing amounts of dicyclic naphthene.

A check on complete removal of the aromatics and olefins is obtained by comparing average boiling point estimated from Figure 1 with mid-boiling point of the cut. If the estimated boiling point is more than 10° higher than the mid-boiling point, the analysis should be checked.

7. The time and manpower requirements for this type of analysis on a routine basis are as follows:

Total elapsed time for stabilization and distillation, 24 hours.

Man-hours per sample, exclusive of distillation, if N_2O_4 treatment is not required, 10 hours.

Additional man-hours required for each cut which is examined by N_2O_4 treatment, assuming that two cuts are handled simultaneously by one operator, are 1 to 2 hours.

DETAILS OF ANALYTICAL METHOD

Distillation of Sample into Cuts. The samples analyzed in this work were first stabilized and subsequently fractionated.

STABILIZATION. The stabilizer used in this work has a 2-gallon still pot and is equipped with a fractionating column of 25-mm. inside diameter glass tubing packed to a height of 50 cm. (20 inches) with $^3/_{32}$-inch stainless steel helices. The column is insulated with glass wool and is maintained in an adiabatic condition by a liquid-cooled metal jacket. Heat is supplied to the pot by means of an immersion heater controlled by a variable transformer adjusted to give the proper boiling rate. A conventional dephlegmator is used to remove product. The reflux ratio is controlled by a solenoid-operated pivotal funnel actuated by a timing device.

A measured volume of sample, 1200 to 1500 cc., was charged to the stabilizer. Reflux ratio was 10 to 1 and take-off rate was 4 cc. per minute. Cut 1 indicated in Table I was collected at dry ice temperature, and its volume was measured and corrected to the temperature of the charge. The loss, 2% or less, was calculated as part of cut 1

DISTILLATION. The still used in this work is rated at 40 theoretical plates at total reflux. It has a still pot which will take a maximum charge of approximately 1 liter, and is equipped with an adiabatically wound stainless steel column 48 inches long and 0.5 inch in internal diameter which is packed with $^3/_{32}$ inch stainless steel helices. Heat is supplied to the pot by an immersion heater controlled by a variable transformer. The still head is equipped with a pivotal funnel reflux control actuated by a timing device.

A measured volume of stabilizer bottoms, approximately 1 liter, was charged to the still. This still was operated at 10 to 1 reflux ratio with a take-off rate of 1 cc. per minute. Cut points were as indicated in Table I. Volumes of cuts were measured and corrected to the temperature of the charge. Distillation loss, 2% or less, was calculated and the volumes of the cuts were corrected to a no-loss basis.

In general, the authors recommend that this type of analysis be carried out with a still having at least 25 theoretical plates at total reflux and that a reflux ratio of at least 10 to 1 be used. They furthermore recommend that, if the loss is greater than 3% of the charge, another distillation should be made.

Analytical Data and Methods. The data necessary for analysis of the fraction for olefins, aromatics, naphthenes, and paraffins are described in this section. More than one method is described for determination of per cent aromatics and per cent olefins. The combination of these methods into a cross check procedure is described below.

ORSAT ANALYSIS. The olefins in cut 1 are determined by absorption by the standard method used in the gas laboratory (*23*). The remainder of the sample consists of paraffinic hydrocarbons. No other analytical tests are performed upon this cut.

BROMINE NUMBER. The bromine number is determined on each cut by the bromide-bromate procedure described in A.S.T.M. emergency method ES-45a (*2*, *17*), except that the amount of sample is chosen according to the approximate bromine number:

Bromine No.	Size of Sample, Grams
0–20	3.0–5.0
20–100	2.0–3.0
More than 100	1.0–2.0

For cut 2, the sample should be weighed into the flask to avoid volatility loss. For the other cuts, the sample may be measured out by pipet and the corresponding weight calculated from the density of the cut.

The equation used to calculate olefins from bromine number is as follows:

$$\% \text{ olefins} = \frac{B \times M}{160} \qquad (1)$$

where B represents bromine number, and M is the molecular weight of the olefins in the cut under consideration. The average molecular weight for the olefins in each cut is obtained from the following table:

Cut No.	Molecular Weight of Olefins
2	70
3	80
4	91
5	104
6	118
7	133
8	149
Bottoms	166

The recommended equation actually calculates weight per cent olefins. Since the density of the olefins is usually close to the average density of the cut, for fractions of 20° to 30° C. boiling range it is possible to use volume per cent and weight per cent interchangeably, with an accuracy sufficient for this type of analysis.

SPECIFIC DISPERSION. Specific dispersions at 20° C. are obtained on cuts 3 to 8, providing the olefin content is less than 40% as determined by bromine number. Specific dispersion as used in this laboratory is the difference between the H_F and H_C refractive indices divided by the density.

Although the Pulfrich and Bausch & Lomb precision refractometers are the preferred instruments for measurement of dispersion, the Abbe-type refractometer was used in this work because it is at present more generally available. It has proved satisfactory when used carefully. With the latter instrument, the dispersion is calculated from the refractive index and the drum reading at the position where the prisms are set for compensation. This drum reading should be the average of eight readings, four for each of the two positions of complete color elimination. On each side of the drum, two settings are made by approaching from the red and two settings from the blue. Each operator should check himself on pure compounds of known dispersion.

If no instrument is available, specific dispersion may be calculated by the method of Lipkin and Martin (*21*) from density, refractive index for D line of sodium, and mid-boiling point of the cut. Such a calculated dispersion also serves as a cross check on the measured dispersion. Table III shows a comparison of the calculated and experimental specific dispersion of the fractions of gasoline G. The agreement is within experimental error of the dispersion measurement.

Aromatics are calculated from specific dispersion, δ, and bromine number, B, by Grosse and Wackher's (*13*) method as follows:

Table III. Comparison of Calculated (*21*) and Experimental Specific Dispersions on Original Cuts for Blend G

Cut	Mid-Boiling Point, ° C.	d_4^{20}	n_D^{20}	Experimental Specific Dispersion × 10^4	Calculated Specific Dispersion × 10^4	Difference
3	56	0.6657	1.3788	107	106	−1
4	81	0.7147	1.4022	108	110	+2
5	109	0.7421	1.4211	121	122	+1
6	136	0.7839	1.4434	133	132	−1
7	162	0.8051	1.4554	135	135	0
8	188	0.8084	1.4570	130	131	+1

$$\text{Volume \% aromatics} = \frac{(\delta\,\text{cut} \times 10^4) - 99 - 0.16B}{(\delta\,\text{aromatics} \times 10^4) - 99} \times \frac{\text{d}}{0.868} \quad (2)$$

where d is the density of the cut. In this equation 99 is taken as the specific dispersion × 10^4 of saturated hydrocarbons, and 0.868 is taken as the average density for monocyclic aromatics.

The specific dispersions for the aromatics present in each cut are given in the following table:

Cut No.	$\delta \times 10^4$	Cut No.	$\delta \times 10^4$
3	189	6	181
4	189	7	172
5	185	8	167

No value for the specific dispersion of aromatics present in the bottoms fraction is given because naphthalene derivatives may be present in this boiling range. Naphthalene derivatives have specific dispersions widely different from those of alkylbenzenes, making it inadvisable to use specific dispersion as a means of calculating aromatic content for such samples.

Recently Groennings (*12*) has suggested that the 0.16 factor recommended by Grosse and Wackher for correcting the specific dispersion for olefinic unsaturation should be replaced by a value read from a curve of correction factor *vs.* boiling point. Groennings in deriving his correction assumed that there was a 50–50 distribution between cyclic and noncyclic olefins throughout the boiling range.

On the basis of a limited amount of evidence it is the authors' belief that the olefins in the lower boiling cuts of cracked gasolines are almost exclusively noncyclic and that the olefins in the higher boiling cuts are almost exclusively cyclic. Therefore over the gasoline range, the 0.16 factor recommended by Grosse and Wackher is a reasonably good approximation, and has been used in this work.

SULFURIC ACID–PHOSPHORUS PENTOXIDE ABSORPTION. Per cent olefins plus aromatics are obtained on cuts 2 and higher by volumetric absorption of these hydrocarbons in a mixture of 30% by weight of phosphorus pentoxide and 70% by weight of 95 to 96% sulfuric acid (1.84 specific gravity). Table II shows data obtained by use of this procedure. It is anticipated that a paper on this procedure will be published. This method is described in detail in Appendix 2 of the 1945 report of A.S.T.M. Committee D-2 (*1*).

If the fraction contains less than 40% olefin (determined by bromine number method), 10 ml. of sample are treated; otherwise 5 ml. are treated. Sulfuric acid–phosphorus pentoxide mixture (25 ml.) is introduced into the sulfonation flask, which is then placed in the mechanical shaker and cooled to 0° C. The sample is shaken at 0° C. as follows: one shake per minute for the first 5 minutes, then continuously 250 ± 25 cycles (a forward and return stroke) per minute for the next 20 minutes. The length of each shaking stroke is 3 ± 0.5 inches. At the end of the shaking period, the sample is centrifuged, sufficient 1.84 specific gravity sulfuric acid is added to bring the unreacted hydrocarbon into the calibrated neck, and the sample is centrifuged again. The volume of unreacted hydrocarbon is read and the percentage of paraffins plus naphthenes is calculated as:

$$\%\,\text{P} + \text{N} = \frac{\text{volume of unreacted hydrocarbon} + 0.1\ \text{ml. solubility correction}}{\text{volume of original sample}} \quad (3)$$

$$\text{Then,} \quad \%\ \text{olefin} + \text{aromatic} = 100\% - \%\ (\text{P} + \text{N}) \quad (4)$$

The unreacted hydrocarbon is pipetted from the bottle into a small vial containing 1 to 2 cc. of 10% sodium hydroxide solution. The vial is stoppered and shaken vigorously, and the layers are allowed to separate. The hydrocarbon layer is used for density and refractive index determinations.

NITROGEN TETROXIDE TREATMENT. The nitrogen tetroxide method developed by Bond (*6*) for the determination of olefins is used as the referee procedure for olefin determination. The method is based on the fact that nitrogen tetroxide reacts quantitatively with the olefins to produce a high-boiling addition product from which the paraffins, naphthenes, and aromatics can be separated by steam-distillation. The volume of nonolefinic constituents is measured directly in this procedure and the per cent olefin is determined by difference. The difference between olefins by this method and the total per cent unsaturates by acid treatment gives the per cent aromatics. Acid treatment of the steam distillate produces a saturate fraction satisfactory for subsequent determination of paraffin-naphthene content.

For samples containing more than 40% olefin, Bond's procedure was modified. Such samples are diluted with an equal volume of toluene before nitrogen tetroxide treatments. This modification has been found to give more satisfactory results on certain highly olefinic samples, particularly on polymer gasoline.

DENSITY. API gravities are obtained on cuts 3 and higher using small API hydrometers. These values are corrected to 60° F. using the National Standard Petroleum Manual (*22*), and then to density at 20° C. using Figure 12 of Ward and Kurtz (*29*). If there is any doubt about the accuracy of these values, densities are checked using the pycnometer described by Lipkin, Davison, Harvey, and Kurtz (*19*).

Densities are also obtained on the aromatic olefin-free portions of these same cuts, using the pycnometer method.

REFRACTIVE INDEX. Refractive indices at 20° C. are obtained accurately within ±0.0002 for the *D* line of sodium on cuts 3 and higher and on the aromatic-olefin-free portions of these cuts. Precautions which should be observed in obtaining refractive indices on the Abbe-type refractometer may be found in (*2*) and

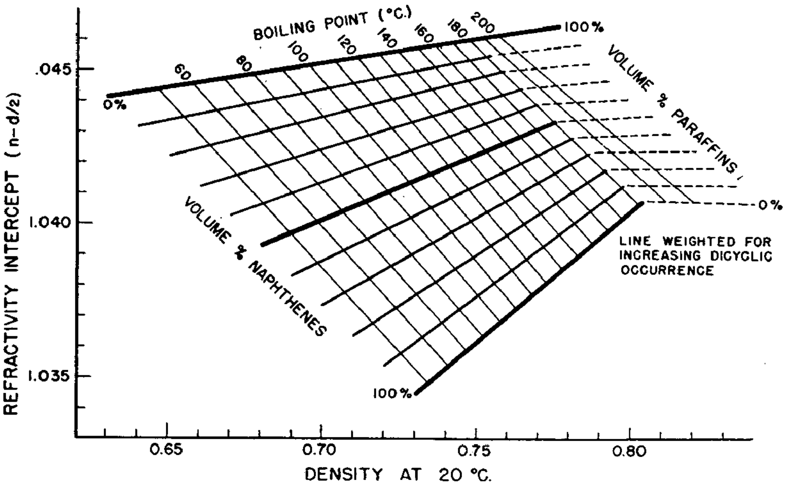

Figure 1. Graph for Determination of Per Cent Paraffins and Naphthenes in Mixtures of Saturated Hydrocarbons

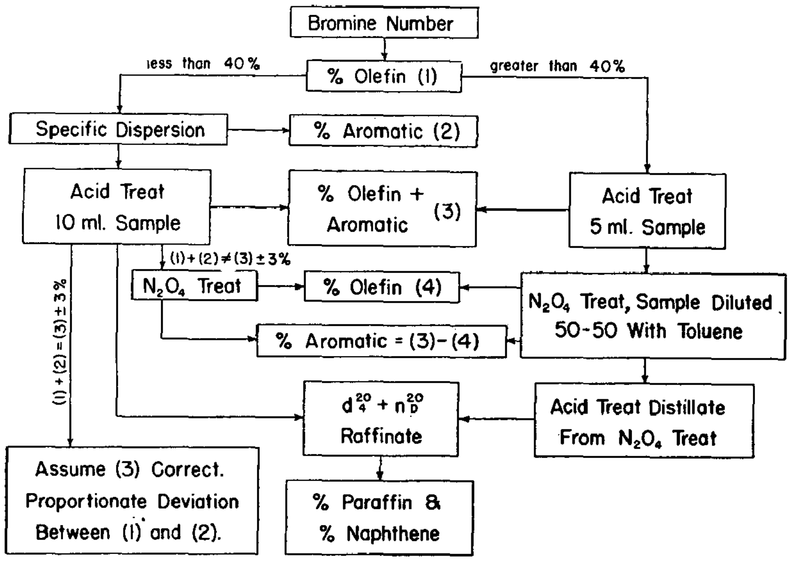

Figure 2. Scheme of Analysis for Cuts 2 and Higher

Per cent naphthenes and per cent paraffins are obtained from the refractivity intercept (n − d/2) and density (Figure 1) on the saturated hydrocarbon portion remaining after acid treatment of each cut. n is refractive index at 20° C. for the D line of sodium and d is density at 20° C. Table IV gives the data necessary for the construction of Figure 1.

The refractivity intercept method gives satisfactory results in the gasoline boiling range on cuts which are of sufficiently wide boiling range to contain several isomers of the naphthenic and paraffinic constituents.

The lower part of the naphthene line in the vicinity of 0.75 density has been adjusted to agree with the average properties for methylcyclopentane and the isomers of dimethylcyclopentane. Cyclopentane itself has not, up to the present time, been found to be an important constituent of natural or cracked gasolines. Cyclohexane has properties which are out of line in regard to both density and refractive index (as can be seen for density on Figure 2, page 1173 of Ward, Kurtz, and Fulweiler, *30*). Properties of methylcyclohexane are in reasonable agreement with the naphthene line of Figure 1. For cuts rich in cyclohexane, Figure 1 will give slightly high values for per cent naphthene. For such cuts, a more accurate value for per cent naphthene can be obtained from per cent carbon and hydrogen, determined, for example, by the method of Hinden and Grosse (*14*).

Table IV. Coordinates for Construction of Figure 1

Volume % Naphthene	Coordinates[a] for Construction of % Naphthene Lines: Solid Lines, d	Solid Lines, $n - \frac{d}{2}$	Solid Lines, d	Solid Lines, $n - \frac{d}{2}$	Dotted Line, d	Dotted Line, $n - \frac{d}{2}$
0	0.63	1.04410	0.749	1.04600	0.773	1.04640
10	0.64	1.04315	0.755	1.04548	0.780	1.04580
20	0.65	1.04217	0.760	1.04500	0.786	1.04526
30	0.66	1.04120	0.766	1.04442	0.792	1.04464
40	0.67	1.04024	0.771	1.04390	0.799	1.04412
50	0.68	1.03929	0.776	1.04336	0.805	1.04358
60	0.69	1.03830	0.782	1.04284	0.811	1.04290
70	0.70	1.03737	0.787	1.04234	0.818	1.04240
80	0.71	1.03638	0.793	1.04180	0.824	1.04188
90	0.72	1.03540	0.798	1.04130	0.830	1.04130
100	0.73	1.03450	0.804	1.04080	0.837	1.04072

Boiling Point, ° C.	Coordinates[a] for Construction of Boiling Point Lines: d	$n - \frac{d}{2}$	d	$n - \frac{d}{2}$
50	0.65	1.04396	0.73	1.03536
60	0.66	1.04428	0.74	1.03552
70	0.67	1.04444	0.74	1.03668
80	0.68	1.04456	0.75	1.03662
90	0.69	1.04462	0.75	1.03776
100	0.70	1.04462	0.76	1.03764
110	0.71	1.04452	0.76	1.03868
120	0.72	1.04432	0.77	1.03846
130	0.72	1.04528	0.77	1.03948
140	0.73	1.04494	0.78	1.03932
150	0.74	1.04466	0.78	1.04022
160	0.74	1.04538	0.79	1.04010
170	0.75	1.04502	0.79	1.04096
180	0.75	1.04570	0.80	1.04090
190	0.76	1.04532	0.81	1.04092
200	0.76	1.04582	0.82	1.04080

[a] d = density at 20° C. and n = refractive index for D line of sodium at 20° C.

Dicyclic naphthenes have been shown by A.P.I. Project 6 (*24*) to occur in straight-run fractions at boiling points as low as 146.7° C. The authors' experience indicates that negligible quantities of dicyclic naphthenes occur below 175° C. The naphthene line in Figure 1 has been adjusted to permit an approximate analysis of the cuts boiling above 175° C., assuming that some dicyclic naphthenes are present.

The per cent naphthenes and per cent paraffins are corrected to the original cut by multiplying by the percentage of saturated hydrocarbons in the original cut as determined by acid absorption.

The average boiling point of each saturated fraction is estimated from refractivity intercept and density using Figure 1. If this estimated boiling point is more than 10° C. higher than the mid-boiling point of the original cut, incomplete removal of aromatics or olefins is indicated and the density and refractive index are checked. If necessary, an additional acid treatment is run and the properties are redetermined on this raffinate.

Table V. Comparison o Calculated (*20*) and Experimental Refractive Indices on Paraffin-Naphthene Portions of Cuts from Blend G

Cut	Mid-Boiling Point, ° C.	d_4^{20}	Experimental n_D^{20}	Calculated n_D^{20}	Difference
3	56	0.6602	1.3748	1.3744	−0.0004
4	81	0.7072	1.3946	1.3956	0.0010
5	109	0.7285	1.4074	1.4070	−0.0004
6	136	0.7512	1.4179	1.4182	0.0003
7	162	0.7649	1.4248	1.4254	0.0006
8	188	0.7827	1.4328	1.4343	0.0015
Bottoms	210 (estimated)	0.7992	1.4413	1.4422	0.0009

Another method which indicates complete or incomplete removal of aromatics and olefins, from the data already obtained on the raffinate fraction, is the calculation of refractive index by the method of Lipkin and Martin (*20*). If the calculated refractive index is more than 0.0015 lower than the experimental refractive index, there is probably some aromatic or olefin remaining in the fraction. Table V shows agreement of the calculated and experimental refractive indices on the acid-treated fractions of gasoline G.

Method of Analysis. The gasoline to be analyzed is distilled into fractions as described above. An outline of the procedure used in the analysis of the fractions is shown in Figure 2.

Cut 1, which consists of C_4 and lighter hydrocarbons, contains only paraffins and olefins. The cut is analyzed for olefin content by Orsat analysis.

Cut 2 also contains only olefins and paraffins and is analyzed for olefin content by acid absorption and bromine number. If olefin by bromine number does not agree with the acid-treat value within 3%, the acid treatment should be checked. In case the two values still disagree, the acid-treat value is considered to be correct. The procedures should be followed carefully to avoid undue volatility losses.

The remaining cuts are analyzed by the procedure shown in Figure 2. Olefin content is determined from bromine number. If olefin content is less than 40%, aromatics are determined by

Table VI. Analysis of Gasoline G

A. Analytical Data

	Original Cuts								Acid-Treated Cuts			
Cut No.	Volume % cut	Boiling range, °C.	d_4^{20}[a]	n_D^{20}	Specific dispersion × 10^4	Bromine No.	% acid absorption	% olefin by N_2O_4	d_4^{20}	n_D^{20}	$n - \frac{d}{2}$	Estimated boiling point, °C.
1	7.1	Int.–10	....	....	...	...	..	..	....	....	....	...
2	12.3	10–46.1	....	....	...	50.6	22	..	....	....	....	...
3	5.8	46.1–65.6	0.6657	1.3788	107	39.5	24	..	0.6602	1.3748	1.0447	63
4	9.3	65.6–96.1	0.7147	1.4022	108	46.7	30	..	0.7072	1.3946	1.0410	86
5	18.9	96.1–121.7	0.7421	1.4211	121	114.2	68	58	0.7285	1.4074	1.0432	118
6	11.5	121.7–150	0.7839	1.4434	133	40.1	56	..	0.7512	1.4179	1.0423	137
7	11.9	150–175	0.8051	1.4554	135	27.8	58	18	0.7649	1.4248	1.0424	156
8	12.1	175–200	0.8084	1.4570	130	36.5	64	26	0.7827	1.4328	1.0414	166
Bottoms	11.1	200–End	0.8415	1.4738	...	...	53	26	0.7992	1.4413	1.0417	188

B. Olefin and Aromatic Analysis

	Olefins from Bromine No.			Aromatic from Specific Dispersion				Final % Olefin and % Aromatic					
Cut No.	Mol. wt. of olefin	Bromine No.	% olefin, *A*	Specific dispersion × 10^4	d_4^{20}	Specific dispersion × 10^4 aromatic	% aromatic, *B*	% olefin plus aromatic, acid absorption, *C*	Olefin + aromatic *A* + *B*, *D*	% olefin, *E*	% aromatic, *F*	% olefin by N_2O_4, *G*	% aromatic, *H*
1	...	...	..	..	...	...	..	..	..	33[b]	..	..	..
2	70	50.6	22	...	...	...	..	22	22	22	0	..	..
3	80	39.5	20	107	0.666	189	0	24	21	24	0	..	..
4	91	46.7	27	108	0.715	189	1	30	28	29	1	..	..
5	104	114.2	74	121	0.742	185	4	68	78	..	..	58	10
6	118	40.1	25	133	0.784	181	30	56	55	25	31	..	..
7	133	27.8	23	135	0.805	172	40	58	63	..	..	18	40
8	149	36.5	34	130	0.808	167	35	64	69	..	..	26	38
Bottoms	166	24.9	26	...	...	...	..	53	..	..	..	26	27

A. $\% \text{ olefin} = \frac{\text{bromine No.} \times \text{mol. wt.}}{160}$

B. $\% \text{ aromatic} = \frac{\text{specific dispersion} \times 10^4 - 99 - 0.16 \times \text{bromine No.}}{\text{specific dispersion aromatic} \times 10^4 - 99} \times \frac{\text{d cut}}{0.868}$

E. $\% \text{ olefin} = A \times \frac{C}{D}$

F. $\% \text{ aromatic} = B \times \frac{C}{D}$

H. $\% \text{ aromatic} = C - G$

C. Composition in Volume %

	Original Cuts								Whole Gasoline						
	Acid-Treated Cuts														
Cut No.	% paraffin	% naphthene	Paraffin and naphthene	Paraffin	Naphthene	Olefin and aromatic	Olefin	Aromatic	Volume % cut	Paraffin and naphthene	Paraffin	Naphthene	Olefin and aromatic	Olefin	Aromatic
1	100	0	67	67	0	33	33	0	7.1	4.8	4.8	0	2.3	2.3	0
2	100	0	78	78	0	22	22	0	12.3	9.6	9.6	0	2.7	2.7	0
3	100	0	76	76	0	24	24	0	5.8	4.4	4.4	0	1.4	1.4	0
4	55	45	70	39	31	30	29	1	9.3	6.5	3.6	2.9	2.8	2.7	0.1
5	48	52	32	15	17	68	58	10	18.9	6.0	2.8	3.2	12.9	11.0	1.9
6	50	50	44	22	22	56	25	31	11.5	5.1	2.5	2.6	6.4	2.9	3.5
7	43	57	42	18	24	58	18	40	11.9	5.0	2.1	2.9	6.9	2.1	4.8
8	23	77	36	8	28	64	26	38	12.1	4.4	1.0	3.4	7.7	3.1	4.6
Bottoms	18	82	47	8	39	53	26	27	11.1	5.2	0.9	4.3	5.9	2.9	3.0
									100.0	51.0	31.7	19.3	49.0	31.1	17.9

[a] Obtained with small A.P.I. hydrometer and converted to d_4^{20} by using Figure 12 (*29*). [b] Determined in gas laboratory.

Table VII. Calculations for Cuts 6 and 7 of Sample G

	Cut 6	Cut 7
% olefins by bromine No.	$\frac{40.1 \times 118}{160} = 25\%$	$\frac{27.8 \times 133}{160} = 23\%$
% aromatics by specific dispersion	$\frac{133\text{-}99\text{-}0.16 \times 40.1}{181\text{-}99} \times \frac{0.784}{0.868} = 30\%$	$\frac{135\text{-}99\text{-}0.16 \times 27.8}{172\text{-}99} \times \frac{0.805}{0.868} = 40\%$
Sum of 1 and 2	25 + 30 = 55%	23 + 40 = 63%
Total by acid absorption	56%	58%
Difference between 3 and 4	1%	5%
% olefin by N_2O_4	....	18%
Adjusted % olefin	$25 \times \frac{56}{55} = 25\%$	....
Adjusted % aromatic	$30 \times \frac{56}{55} = 31\%$	58 − 18 = 40%
% naphthenes in acid treated cut (Figure 2)	50%	57%
% paraffins in acid-treated cut	100 − 50 = 50%	100 − 57 = 43%
% naphthenes in original cut	50% × 0.44 = 22%	57% × 0.42 = 24%
% paraffins in original cut	50% × 0.44 = 22%	43% × 0.42 = 18%

specific dispersion, and total olefins plus aromatics are determined by acid-treating a 10-ml. sample. If the sum of olefins plus aromatics as determined by bromine number and specific dispersion agrees within 3% of the value determined by acid treatment, the latter value is assumed to be correct, and the small difference is apportioned between the olefins and aromatics. If the difference is greater than 3%, olefins are determined by nitrogen tetroxide treatment, and the aromatics determined as the difference between nitrogen tetroxide treatment and acid absorption. The raffinate from the acid absorption is used for the determination of paraffin and naphthene content.

If olefin content is greater than 40%, a 5-ml. sample is acid-treated to determine total olefins plus aromatics. Olefin content is determined by nitrogen tetroxide treatment of the sample diluted with an equal volume of toluene, and aromatic content is obtained by difference from the total obtained by acid treatment.

As a cross check, 10 ml. of the distillate from the nitrogen tetroxide treatment may be acid-treated, and the per cent aromatics thus determined is corrected for the dilution of the original sample with toluene. This value should check the per cent aromatics determined on the original cut.

The raffinate from the acid treated nitrogen tetroxide distillate is used to determine paraffin-naphthene content.

On the bottoms cut, the cross-check system using bromine number, specific dispersion, and acid absorption is not expected to give satisfactory results since the specific dispersion method is unreliable in this range. If the bromine number is less than 5, the per cent olefin is calculated from bromine number and per cent aromatic is the difference between this value and the total unsaturates by acid absorption. If the bromine number is greater than 5, the nitrogen tetroxide method must be used for olefin determination.

Specification of a change of procedure above a particular olefin content, such as 40%, is of course somewhat arbitrary. This particular point was chosen for several reasons:

Uncertainty in bromine titration method for the determination of per cent olefin becomes more serious with high concentrations. With certain types of olefins (such as occur in polymer gasoline), it is believed that results 10 to 20% too high may be obtained; and if 40% of such olefin were present in the cut, this would correspond to an error of 4 to 8% on the cut.

The uncertainty in the olefin correction which has to be applied to the specific dispersion method for the determination of aromatics is of the order of ±1 dispersion unit at 40% olefin concentration.

At concentrations above 40% olefin, some difficulty has occasionally been encountered in obtaining good physical properties on the saturated fraction remaining after acid treatment when nitrogen tetroxide is not used.

The authors believe that specification of 40% olefin as the concentration above which the nitrogen tetroxide should always be used is conservative, and that future experience may prove many types of samples containing more than 40% olefin can

Table VIII. Analyses of Samples E, F, and G (G = 50% E + 50% F)

Inspection tests	E	F	G
A.P.I. Gravity	54.6	60.0	56.7
Engler distillation	° F.	° F.	° F.
Initial	86	88	88
5	110	115	116
10	126	136	132
20	152	175	167
30	186	216	206
40	219	236	238
50	256	255	262
60	290	279	287
70	318	310	316
80	348	346	340
90	378	378	379
95	396	406	400
End point	412	434	426
Recovery, %	98	98	98
Color (Saybolt)	20	10	15
Cu gums, mg.	6	94	43
A.S.T.M. gums, mg.	0.6	4.0	2.2
R.v.p., 100° F., pounds per square inch	9.2	9.5	8.7
Sulfur weight %	0.032	0.041	0.035

Table IX. Cross Check of Olefins and Aromatics with Total Unsaturates

Gasoline E

Cut No.	% Olefin from Bromine No.	% Aromatic from Specific Dispersion	Sum of Olefin and Aromatic	Acid Absorption	Difference
3	9	0	9	10	−1
4	14	3	17	18	−1
5	10	23	33	33	0
6	8	38	46	49	−3
7	4	54	58	58	0
8	3	(59)[a]	(62)[a]	53	(+9)[a]

Gasoline F

		% Aromatic from Specific Dispersion	Sum of Olefin and Aromatic	Acid Absorption	% Olefin by N_2O_4	% Aromatic by Difference
3	61	0	61	54	54	0
4	63	0	63	52	51	1
5	91	0	91	88	84	4
6	74	6	80	60	50	10
7	44	18	62	58	33	25
8	66	16	82	74	40	34

Gasoline G

		% Aromatic from Specific Dispersion	Sum of Olefin and Aromatic	Acid Absorption	Difference	% Olefin by N_2O_4
3	20	0	21	24	− 3	...
4	27	1	28	30	− 2	...
5	74	4	78	67	+10	58
6	25	30	55	56	− 1	...
7	24	40	64	58	+ 6	18
8	34	35	69	64	+ 5	26

[a] High probably because of dicylic aromatics.

Table X. Analyses of Samples E, F, and G (G = 50% E + 50% F)

A. Per Cent Composition of Cuts

	Olefins					Aromatics				
			G					G		
Gasoline Cut	E	F	Calcd.	Determined	Difference	E	F	Calcd.	Determined	Difference
1	32	39	37	33	−4	0	0	0	0	...
2	15	31	21	22	+1	0	0	0	0	...
3	10	54[a]	19	24	+5	0	0	0	0	...
4	15 } 12[b]	51[a] } 78[b]	26 } 48[b]	29 } 44[b]	+3 } −4	3	1	2	1	−1
5	10	84[a]	65	58[a]	−7	23	4	9	10	+1
6	9	50[a]	27	25	−2	40	10	27	31	+4
7	4	33[a]	16	18[a]	+2	54	25	42	40	−2
8	3	40[a]	23	26[a]	+3	50	34	41	38	−3
Bottoms	2	47[a]	23	26[a]	+3	41	18	30	27	−3

	Paraffins					Naphthenes				
1	68	61	63	67	+4	0	0	0	0	...
2	85	69	79	78	−1	0	0	0	0	...
3	90	46	81	76	−5	0	0	0	0	...
4	45	29	40	39	−1	37	19	32	31	−1
5	27	7	12	15	+3	40	5	14	17	+3
6	21	25	23	22	−1	30	15	23	22	−1
7	14	20	17	18	+1	28	22	25	24	−1
8	8	10	9	8	−1	39	16	27	28	+1
Bottoms	7	10	8	8	0	51	25	39	39	0

B. Total Cut Yield

			G		
	E %	F %	Calcd. %	Determined %	Difference %
1	5.3	11.7	8.5	7.1	−1.4
2	12.8	7.0	9.9	12.3	+2.4
3	8.8	2.2	5.5	5.8	+ .3
4	12.6	5.2	8.9	9.3	+ .4
5	10.8	30.4	20.6	18.9	−1.7
6	12.8	9.5	11.2	11.5	+ .3
7	11.8	8.6	10.2	11.9	+1.7
8	13.9	15.6	14.8	12.1	−2.7
Bottoms	11.2	9.8	10.5	11.1	+ .6

[a] Olefins determined by N_2O_4 treatment. [b] Average for cuts 3 to 5, weighted according to volumes of cuts.

Table XI. Analyses of Samples E, F, and G (G = 50% E + 50% F)

Per Cent Composition of Whole Samples

			G		
	E	F	Calcd.	Determined	Difference
Olefins	9.9	54.5	32.1	31.1	−1.0
Aromatics	25.9	11.5	18.6	17.9	−0.7
Olefins + aromatics	35.8	66.0	50.7	49.0	−1.7
Paraffins	37.2	23.3	30.3	31.7	+1.4
Naphthenes	27.0	10.7	19.0	19.3	+0.3

be satisfactorily analyzed without nitrogen tetroxide treatment. The percentage of olefins, aromatics, naphthenes, and paraffins in each cut is multiplied by the ratio of the cut volume to the total volume, and the values for each hydrocarbon type are summed to obtain the analysis on the whole gasoline.

Example of Calculation. Table VI gives the detailed analysis of gasoline G and the tabulation sheets used in analysis of this cut. The physical property and analytical data are shown in Table VI,A, the calculation of olefins and aromatics are shown in Table VI,B, and the calculation of paraffins and naphthenes and the total analysis in Table VI,C.

As examples of the calculations involved in this analytical method, cuts 6 and 7 are followed in detail in Table VII.

RESULTS

In this work three samples were analyzed as follows:

E. Catalytically cracked gasoline.
F. A blend of thermally cracked and polymer gasoline.
G. A 50–50 mixture of samples E and F.

The catalytically cracked sample was selected as a sample rather low in olefin content which could be analyzed satisfactorily without the use of the nitrogen tetroxide treatment. Blend F was chosen as a sample rich in olefin which would require nitrogen tetroxide treatment. This sample consisted of a polymer gasoline blended with thermally cracked gasoline because it was known that it is difficult to obtain an accurate bromine titration on the olefins in polymer gasoline. It was thought that by including 50% polymer gasoline in the high olefin blend a very severe test of the proposed method would be provided.

Samples E, F, and G were all analyzed for per cent olefin, per cent aromatic, per cent paraffin, and per cent naphthene. The composition of sample G, which is a 50–50 mixture of samples E and F, was then calculated from the analysis of the two components, and this calculated analysis compared with the experimentally determined analysis of the blend, sample G.

Table VIII gives inspection tests on the three samples. Table IX shows the cross check between olefins plus aromatics and total unsaturates for gasolines E, F, and G, respectively. These tables show the value of the nitrogen tetroxide treatment when a satisfactory cross check has not been obtained.

Table X,A shows the composition of each cut of gasolines E, F, and G and compares determined composition of G with the calculated values, using the yield figures shown in Table X,B.

Table XI presents a similar comparison for the over-all composition of each gasoline. The agreement between calculated and determined composition is within 2% for each component.

The agreement of the above analyses is particularly significant since every cut in sample F (except cuts 1 and 2) required the use of the nitrogen tetroxide treatment, none of the cuts in sample E required nitrogen treatment, and only part of the cuts in sample G required nitrogen tetroxide treatment. The agreement of the analytical results, in spite of the use of nonidentical methods in the case of the three samples, indicates that all the procedures involved are reasonably accurate.

With regard to analysis of individual cuts, it will be seen that out 5, sample F, contained 84% of olefin, which is mainly isooctenes. The olefin content of cut 5 of blend G is 7% different from what might be anticipated from the composition of the two components. The authors attribute this to the difficulty of obtaining identical cuts in several distillations and also probably to azeotropic effects. If the composition of a blend of cuts 3, 4, and 5 is calculated, the percentage of olefin in this cut of blend G agrees within 4% with what is predicted from the composition of the components. In general, the agreement between the composition of the blend as found by direct analysis, and the composition as predicted by calculation from the composition of the components, is within 2% of being correct. A considerable number of samples have been run by the procedure shown in this paper and it has been found satisfactory for routine use. In the majority of cases, it has not been necessary to use the nitrogen tetroxide treatment. The nitrogen tetroxide treatment, however, is extremely important as a means of getting out of trouble when there is apparent discrepancy in the analysis as carried out by the bromine number and specific dispersion.

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The laboratory work on samples E, F, and G was mainly done by Miss I. E. Wolfe. Miss D. J. Bellar carried out much of the laboratory work in connection with revision of the acid-treating technique.

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Calculation of Weight Per Cent Ring and Number of Rings per Molecule for Aromatics

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Per cent ring and average number of rings per molecule for mixtures of alkyl aromatic hydrocarbons are determined from density and density coefficient, which may be derived from mid-boiling point and density. The methods have been found accurate, on pure compound data, within 3% ring and 0.1 ring per molecule. Aromatics with naphthenic or olefinic side chains cause some interference but are usually not present in sufficient concentration to affect significantly the accuracy of the methods for petroleum fractions boiling below 400° C.

THIS paper continues the general investigation in this laboratory of the temperature coefficient of density for hydrocarbons, and the relation of this physical property to other physical properties and to hydrocarbon structure. A series of papers on the temperature coefficient of density has now been presented. This particular paper is concerned with methods for the analysis of aromatics for number of rings per molecule and for proportion of ring and side chain.

The first paper in the density coefficient series related this property to molecular weight—a single curve was found applicable to nearly all hydrocarbons. Recently Griswold and Chew (*6*) have developed separate relationships for the different classes of hydrocarbons. For practical purposes, there is little difference between the relationships except for benzene and toluene. Since toluene and especially benzene are usually present in small concentrations in petroleum products, the general correlation (*11*) is satisfactory for most purposes. The small differences in density coefficient between hydrocarbon classes do not affect the later correlations in this series because the temperature coefficient of density is not determined experimentally, but is derived from approximate molecular weight in both the derivation and application of these correlations.

By plotting density coefficient against density, there was developed a hydrocarbon class "map" which showed linear relationships for paraffins and for naphthene rings without side chains. A similar hydrocarbon class "map" was developed by plotting the temperature coefficient of density against refractive index. Using these maps, it was possible to develop methods for determining the proportion of ring and chain in mixtures of paraffins and naphthenes (*14*), and an equation relating density, refractive index for the *D* line of sodium, and the temperature coefficient of density (*12*). This equation permits the calculation of the refractive index of paraffin-naphthene mixtures with an accuracy nearly that of the Abbe-type refractometer. When aromatics or olefins are present, the calculated refractive index is lower than the experimental value, and the specific dispersion is a linear function of the difference (*13*).

The hydrocarbon class map obtained on plotting density against the temperature coefficient of density is the basis for the two methods of analysis developed in this paper: analysis of aromatics for proportion of ring and chain and for number of rings per molecule.

RING-CHAIN ANALYSIS

Derivation. The first method, analysis of aromatics for proportion of ring and chain, is similar to the method of ring-chain analysis developed for naphthenes. Per cent ring is defined as 100 times the number of ring carbon atoms divided by the total number of carbon atoms. The method was developed from the hydrocarbon class map shown in Figure 1. In this figure, aromatics with no side chain are shown in addition to the paraffin and naphthene ring lines shown in a previous paper (*14*). A noncondensed aromatic ring line is drawn through the points for benzene and diphenyl, and a condensed aromatic ring line branching from this line is drawn through the points for naphthalene and phenanthrene. The addition of side chain to an aromatic ring causes the properties to approach those of a paraffin of infinite molecular weight, and the distance of approach is approximately proportional to the percentage of chain.

There are few aromatics without side chain on which reliable densities are reported in the liquid state, because the melting points of these compounds are so far above room temperature. (Anthracene and the terphenyls are among those aromatics on which no liquid densities are available.) The densities of the high-melting aromatics used in Figure 1 were corrected to 20°, using the correlation of Lipkin and Kurtz (*11*).

As shown in Figure 1, there is a difference between the 100% ring lines for the condensed and noncondensed aromatics. Since the polycyclic aromatics in petroleum may be of either type, naphthalene or diphenyl, three graphs have been derived: Figure 2 for the condensed type aromatics, Figure 3 for the noncondensed type, and Figure 4 for the average mixture assuming an equal distribution of the condensed and noncondensed types. (Noncondensed polycyclic aromatics include all aromatics containing two or more phenyl groups joined together by a

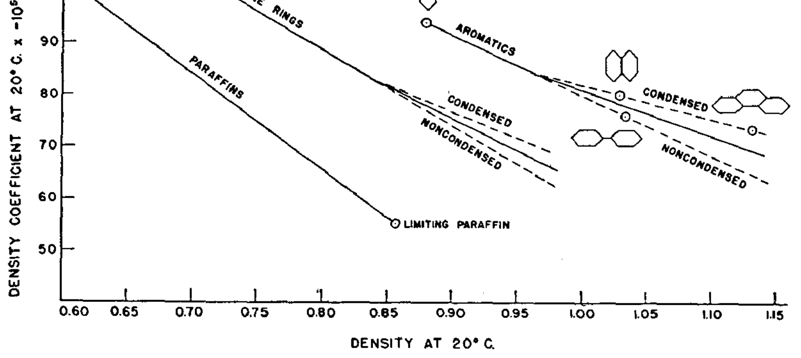

Figure 1. Relation of Density and Density Coefficient to Structure

Table I. Coordinates for Construction of Figure 2

(For condensed ring aromatics. 0% ring point: d = 0.856; *A* = 55.2)

Radial Lines Drawn from 0% Ring to Following Points:

No. of rings	d	*A*	No. of rings	d	*A*
0.9	0.857	95.0	1.8	1.089	95.0
1.0	0.883	95.0	1.9	1.114	95.0
1.1	0.909	95.0	2.0	1.140	95.0
1.2	0.934	95.0	2.2	1.140	87.7
1.3	0.960	95.0	2.4	1.140	82.7
1.4	0.986	95.0	2.6	1.140	79.1
1.5	1.012	95.0	2.8	1.140	76.2
1.6	1.037	95.0	3.0	1.140	74.0
1.7	1.063	95.0			

Intersections of Per Cent Ring Lines with Radial Lines

% ring	With 1.0 ring line *A*	With 1.5 ring line *A*	With 3.0 ring line *A*
100	94.5	84.9	73.8
90	90.8	82.0	72.0
80	87.0	79.0	70.1
70	83.3	76.0	68.2
60	79.3	73.0	66.4
50	75.4	70.1	64.5
40	71.4	67.1	62.6
30	67.4	64.2	60.7
20	63.4	61.3	58.8
10	59.4	58.3	57.0

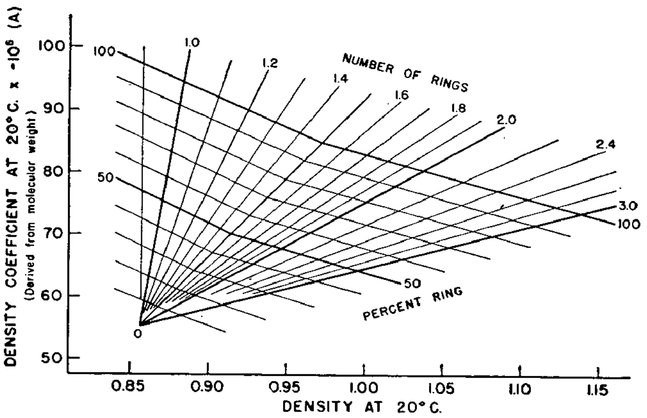

Figure 2. Rings per Molecule and Weight Per Cent Ring for Condensed Ring Aromatics

single carbon-to-carbon bond or separated by one or more carbon atoms.) The data necessary for the construction of Figures 2, 3, and 4 are given in Tables I, II, and III, respectively.

In the derivation of these figures, the 100% ring lines are slightly different from those shown in Figure 1, because adjustment was necessary to fit the data for the aromatics containing paraffinic side chains. The density of the limiting paraffin point used in this paper is slightly different from the value used previously (*14*). The density of the limiting paraffin point is derived by dividing the molecular weight by the molecular volume of a CH_2 increment in a paraffin. The values of the limiting paraffin density derived from the molecular volume correlations of Huggins (*8*), Calingaert (*2*), and Kurtz and Lipkin (*9*) vary between 0.851 and 0.861. The value 0.856 used in the present paper fits the data for aromatics better than the value 0.861 used previously.

The data used in this paper were collected from Doss (*4*), Eaton (*5*), Thorpe and Larsen (*21*), and Ward and Kurtz (*23*), and densities were corrected to 20° C. where necessary using (*11*).

Procedure. In order to obtain an analysis by this method, it is necessary to obtain density and temperature coefficient of density of the aromatics. The temperature coefficient of density is always calculated from the approximate molecular weight (Table I, *14*), which in turn may be obtained from density and

Table II. Coordinates for Construction of Figure 3

(For noncondensed ring aromatics. 0% ring point: d = 0.856; *A* = 55.2)

Radial Lines Drawn from 0% Ring to Following Points:

No. of rings	d	*A*	No. of rings	d	*A*
0.9	0.854	95.0	1.8	1.114	95.0
1.0	0.883	95.0	1.9	1.143	95.0
1.1	0.912	95.0	2.0	1.140	91.0
1.2	0.941	95.0	2.2	1.140	85.5
1.3	0.970	95.0	2.4	1.140	81.5
1.4	0.999	95.0	2.6	1.140	78.4
1.5	1.028	95.0	2.8	1.140	76.0
1.6	1.056	95.0	3.0	1.140	74.0
1.7	1.085	95.0			

Intersections of Per Cent Ring Lines with Radial Lines

% ring	With 1.0 ring line *A*	With 1.5 ring line *A*	With 3.0 ring line *A*
100	94.5	83.0	70.0
90	90.8	80.2	68.4
80	87.0	77.5	67.0
70	83.3	74.8	65.5
60	79.3	72.0	64.0
50	75.4	69.2	62.5
40	71.4	66.4	61.0
30	67.4	63.6	59.6
20	63.4	60.8	58.1
10	59.4	58.0	56.6

Table III. Coordinates for Construction of Figure 4

(Average for condensed and noncondensed ring aromatics. 0% ring point: d = 0.856; *A* = 55.2)

Radial Lines Drawn from 0% Ring to Following Points:

No. of rings	d	*A*	No. of rings	d	*A*
0.9	0.856	95.0	1.8	1.102	95.0
1.0	0.883	95.0	1.9	1.130	95.0
1.1	0.910	95.0	2.0	1.140	92.8
1.2	0.938	95.0	2.2	1.140	86.5
1.3	0.965	95.0	2.4	1.140	81.9
1.4	0.993	95.0	2.6	1.140	78.6
1.5	1.020	95.0	2.8	1.140	75.9
1.6	1.047	95.0	3.0	1.140	74.0
1.7	1.075	95.0			

Intersections of Per Cent Ring Lines with Radial Lines

% ring	With 1.0 ring line *A*	With 1.5 ring line *A*	With 3.0 ring line *A*
100	94.5	83.6	71.9
90	90.8	80.8	70.2
80	87.0	78.0	68.5
70	83.3	75.3	66.9
60	79.3	72.4	65.2
50	75.4	69.5	63.5
40	71.4	66.7	61.8
30	67.4	63.8	60.1
20	63.4	60.9	58.4
10	59.4	58.1	56.8

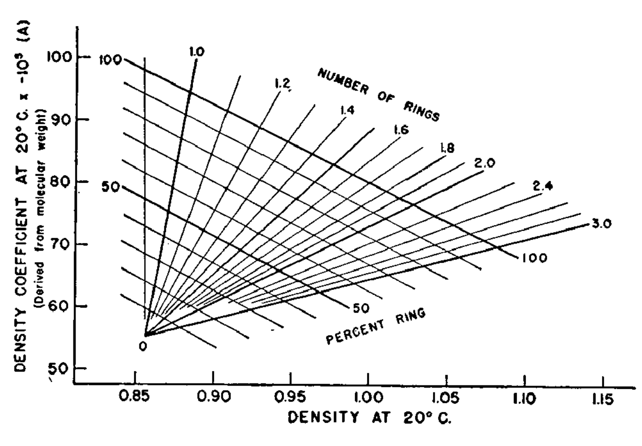

Figure 3. Rings per Molecule and Weight Per Cent Ring for Noncondensed Ring Aromatics

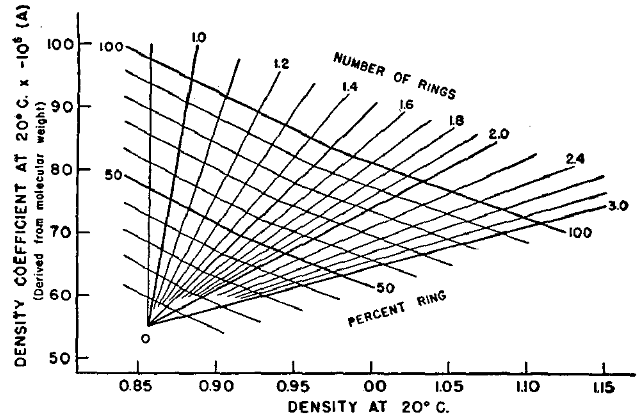

Figure 4. Rings per Molecule and Weight Per Cent Ring for Mixtures of Condensed and Noncondensed Ring Aromatics

mid-boiling point (Mills, Hirschler, and Kurtz, *19*). This means that only two physical properties are necessary, density and boiling point.

The aromatic material usually occurs mixed with other hydrocarbon types, such as paraffins, naphthenes, and olefins. There are two methods of obtaining physical properties on the aromatic material: (1) by determination on aromatics which have been separated from other hydrocarbon types; (2) by calculation from the properties of the sample before and after removal of the aromatics, in which case the aromatics are not recovered.

Where olefins are absent, as in straight-run petroleum products, the aromatics can be separated from the other hydrocarbon types by the silica gel methods of Mair and Forziati (*15, 16*)[1]. Solvent extraction is a less satisfactory method for obtaining a quantitative separation of the aromatics.

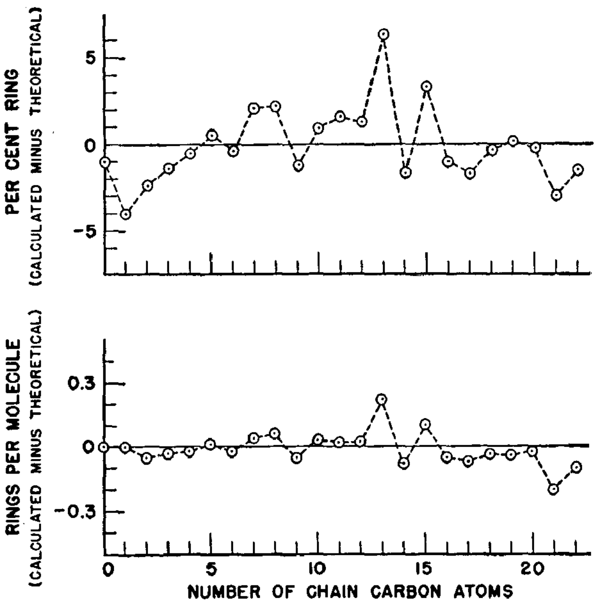

Figure 5. Agreement of Aromatic Analysis for Alkyl Benzenes

In the gasoline boiling range, again where olefins are absent, it is possible to remove aromatics quantitatively and determine them volumetrically by acid treatment (*1*), and to calculate the properties of the aromatics from the volume per cent aromatics, the density and mid-boiling point of the original material, and the density of the raffinate remaining after acid treatment.

For the analysis of petroleum products, it is desirable to have some knowledge of the type of aromatic present, since this method is dependent on the degree of condensation of the aromatic. The selection of the proper graph to be used is made on the following basis:

1. Where only monocyclic aromatics are present, either Figure 2, 3, or 4 may be used, because they are identical for monocyclics.
2. For cracked petroleum products, where polycyclic aromatics are present, Figure 2 is recommended because meager information on hand indicates that the condensed type of aromatic predominates.

Table IV. Agreement of Data for Aromatic Hydrocarbons with Paraffinic Side Chains

Aromatic Type	No. of Compounds	Weight % Ring: Av. deviation	Weight % Ring: Deviation of av.	Weight % Ring: Max. deviation	Number of Rings Per Molecule: Av. deviation	Number of Rings Per Molecule: Deviation of av.	Number of Rings Per Molecule: Max. deviation
	A.	Using Recommended Graphs					
Monocyclic	221	3	0	+24	0.1	0	+0.6
Condensed dicyclic	41	2	−1	− 5	0.1	−0.1	−0.5
Noncondensed dicyclic	30	3	−1	+ 7	0.1	0	+0.5
Condensed tricyclic	6	2	0	− 4	0.1	0	−0.2
Noncondensed tricyclic	1		+2			0	
Average by class		3	0		0.1	0	
	B.	Using Average Graph (Figure 4)[a]					
Condensed dicyclic	41	4	+4	+ 9	Deviations do not differ from those shown above		
Noncondensed dicyclic	30	5	−5	− 8			
Condensed tricyclic	6	9	+9	+11			
Noncondensed tricyclic	1		−9				

[a] For monocyclics all graphs give the same results.

Table V. Agreement of Analyses of Aromatic Extracts from Petroleum with Analyses after Hydrogenation

Fractions	Approximate Boiling Range, ° C.	50% B.P., ° C.	d_4^{20}	n_D^{20}	Weight % Ring[a]	Difference, %	No. of Rings per Molecule[b]	Difference
East Texas straight-run A	90–180	146	0.8625	1.4943	69	8	0.9	0.0
Hydrogenated A		128	0.7754	1.4272	77		0.9	
East Texas straight-run B	180–260	232	0.9231	1.5330	67	2	1.4	0.1
Hydrogenated B		210	0.8394	1.4576	69		1.5	
East Texas straight-run C	260–390	329	0.9744	1.5601	66	6	2.1	0.3
Hydrogenated C		307	0.8943	1.4841	72		2.4	
Catalytic cracked D	310–400	[c]	1.0856		80	3	3.1	0.2
Hydrogenated D		[c]	0.9330	1.5008	83		3.3	

[a] Weight per cent ring of hydrogenated fractions calculated with estimated accuracy of 8% ring by method of Lipkin, Martin, and Kurtz (*14*).

[b] Rings per molecule of hydrogenated fractions calculated with estimated accuracy of 0.2 ring by method of Vlugter, Waterman, and Van Westen (*22*).

[c] 50% boiling point could not be obtained by Engler distillation and molecular weights were estimated from viscosities at 100° and 210° F., using method of Hirschler (*7*). Fraction D: $\text{vis}_{100} = 109.2$ and $\text{vis}_{210} = 5.37$ cs. Hydrogenated fraction D: $\text{vis}_{100} = 14.0$ and $\text{vis}_{210} = 2.74$ cs.

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[1] After this manuscript was submitted, a paper entitled "Separation and Determination of Aromatics from High-Boiling Petroleum Fractions by Adsorption", by M. R. Lipkin, W. A. Hoffecker, C. C. Martin, and R. E. Ledley was prepared for presentation before the Division of Petroleum Chemistry at the Atlantic City A.C.S. Meeting, April 1947. This paper describes the complete separation of aromatic concentrate s from cracked as well as straight-run petroleum products using silica gel.

Table VI. Agreement of Analysis with Theory[a] for Aromatics in Straight-Run Fractions of Petroleum

Boiling Range, °C.	d_4^{20}	n_D^{20}	Volume % Aromatic[b]	Dearomatized Fractions		Weight % Ring			Rings per Molecule		
				d_4^{20}	n_D^{20}	Theory[a]	Calcd.[c]	Difference	Theory[a]	Calcd.[c]	Difference
				Mixed Straight-Run Crudes							
96–121	0.7561	1.4186	9	0.7453	1.4135	86	81	−5	1	1.0	0
121–150	0.7721	1.4305	16	0.7528	1.4192	75	75	0	1	1.0	0
150–175	0.7914	1.4411	16	0.7765	1.4296	67	64	−3	1	1.0	0
175–200	0.8037	1.4469	14	0.7923	1.4377	60	58	−2	1	1.0	0
200–218	0.8232	1.4571	15	0.8086	1.4453	54–100	65	...	1–2	1.2	...
218–225	0.8165	1.4520	.9	0.8084	1.4458	50–100	59	...	1–2	1.2	...
				University Crude							
125–150	0.7687	1.4259	6	0.7631	1.4230	75	68	−7	1	0.9	−0.1
150–175	0.7905	1.4410	15	0.7759	1.4298	67	65	−2	1	1.0	0
175–200	0.8050	1.4483	14	0.7924	1.4391	60	62	2	1	1.1	0.1
200–225	0.8129	1.4515	6	0.8048	1.4457	54–100	78	...	1–2	1.4	...

[a] Determined from molecular weight of aromatics which can be present in boiling range of each fraction.

[b] A.S.T.M. Method D875–46T (*1*).

[c] From calculated properties of material removed by acid treat. Molecular weight is calculated by method of Mills, Hirschler, and Kurtz (*19*) from mid-boiling point of cut and density of aromatic. Density of aromatic is calculated from density before and after acid treatment and volume removed by acid treatment, assuming volume per cent additivity.

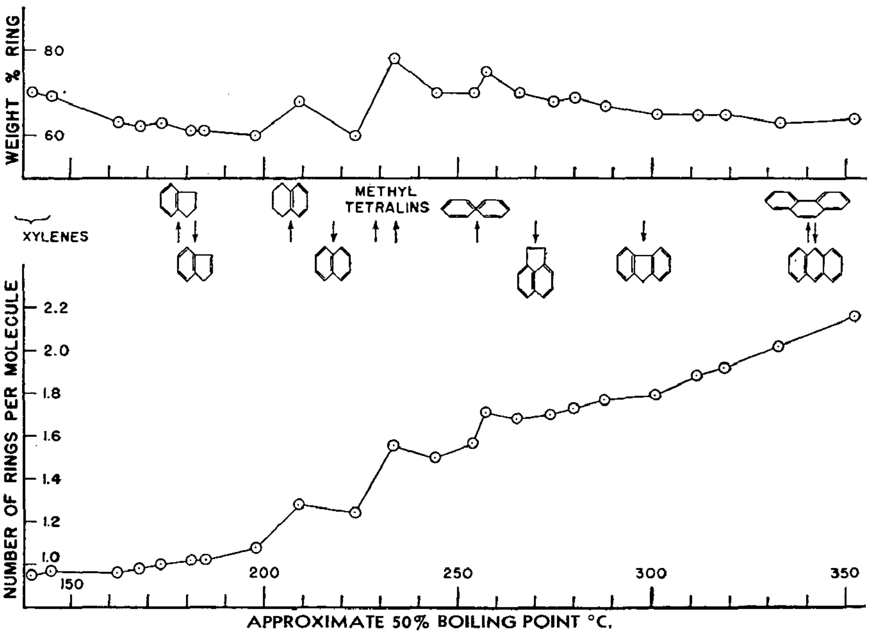


Figure 6. Analysis of Aromatics Separated from East Texas Crude

3. For straight-run petroleum products, where polycyclic aromatics are present, Figure 4 is recommended for the present because it is believed that both condensed and noncondensed aromatics may be present.

4. Where only monocyclic and noncondensed polycyclic aromatics are present, Figure 3 should be used. Present information does not indicate that any petroleum product normally found in the refinery contains a predominance of noncondensed polycyclic aromatics.

Results. Pure compound data on 299 unsubstituted aromatics and alkyl aromatics ranging from one to three rings per molecule show an average deviation of 3% ring as shown in Table IV,A. The recommended graphs were used for the condensed and noncondensed polycyclics.

Table IV, B, shows the results which are obtained by the use of the average graph (Figure 4) instead of the recommended graphs. Using the average graph, the calculated percentage of ring is too high for the condensed type of aromatic and too low for the noncondensed type by about 5% for dicyclics and 10% for tricyclics. The increasing error, as number of rings increases, is due to the fact that the noncondensed and condensed aromatic ring lines (Figure 1) become more widely separated.

Figure 5 shows that there is little systematic deviation throughout the molecular weight range. The difference between calculated and theoretical per cent ring, averaged for each group of isomers, is plotted against number of chain carbon atoms for monocyclic aromatics.

Table V shows an example of the accuracy of this method of analysis for three fractions of aromatics boiling from 90° to 390° C. separated from East Texas straight-run, and a 310° to 400° C. aromatic fraction from catalytically cracked stock. A comparison is made of the per cent ring determined on the aromatic extracts and the per cent naphthene ring determined by the method of Lipkin, Martin, and Kurtz (*14*) on the aromatic extracts after hydrogenation. The average difference is 5%.

Table VI demonstrates an analysis obtained on the aromatics in several gasoline fractions without recovery of these aromatics. The density of the aromatic is calculated from the density before and after acid treatment and the volume per cent aromatics, assuming volume per cent additivity of density. In the boiling range where only monocyclic aromatics can exist, the per cent ring from aromatic analysis and per cent ring calculated from molecular weight agree very closely.

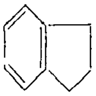
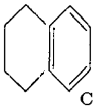
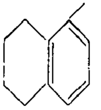
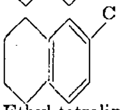
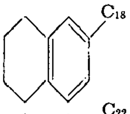
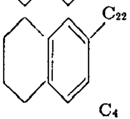
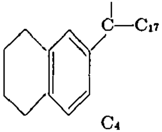
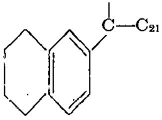
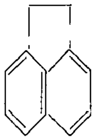
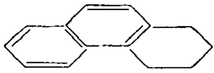
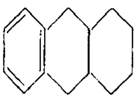
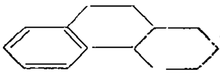
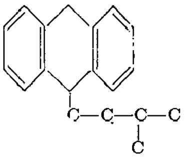
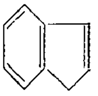
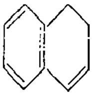
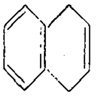
Figure 6 demonstrates an application of this method of analysis to narrow-boiling aromatic fractions from East Texas crude boiling below 350° C. The graph shows the percentage of ring decreasing through the monocyclic and dicyclic boiling ranges, and increasing in the boiling range where dicyclic aromatics begin to appear. There are sharp increases in the amount of ring at certain boiling points, but in this particular example the boiling points were corrected from about 9-mm. pressure and are not sufficiently accurate to warrant drawing conclusions as to the individual aromatics present.

Limitation of Method. This method has been developed for aromatics with paraffin side chains. In petroleum, aromatics containing a naphthene ring or olefin double bond in the same molecule interfere with this method of analysis.

Tables VII to X show the deviations in per cent ring for the available data on these mixed-type aromatics. In general, a naphthene ring in the aromatic molecule causes low results, and an olefin double bond causes high results for per cent ring. The theoretical per cent ring as used in this paper includes both aromatic and naphthenic carbon atoms by definition.

The following is an attempt to evaluate a few of the trends shown by mixed-type aromatic molecules. Table VII shows that

Table VII. Deviations of Pure Compound Data

	Formula	Weight % Ring Calcd.	Weight % Ring Calcd. − theoretical	No. of Rings Calcd.	No. of Rings Calcd. − theoretical
Aromatics Condensed with Naphthene Rings, Dicyclics					
	C_9H_{10}	92	− 8	1.5	−0.5
	$C_{10}H_{12}$	86	−14	1.6	−0.4
	$C_{11}H_{14}$	81	−10	1.7	−0.3
	$C_{11}H_{14}$	78	−13	1.6	−0.4
Ethyl tetralin	$C_{12}H_{16}$	72	−11	1.6	−0.4
Propyl tetralin	$C_{13}H_{18}$	67	−10	1.6	−0.4
Butyl tetralin	$C_{14}H_{20}$	61	−10	1.6	−0.4
ert-Butyl tetralin	$C_{14}H_{20}$	62	− 9	1.6	−0.4
	$C_{28}H_{48}$	30	− 6	1.4	−0.6
	$C_{32}H_{56}$	24	− 7	1.4	−0.6
	$C_{32}H_{56}$	26	− 5	1.5	−0.5
	$C_{36}H_{64}$	22	− 6	1.4	−0.6
Aromatics Condensed with Naphthene Rings, Tricyclics					
	$C_{12}H_{10}$	99	− 1	2.5	−0.5
	$C_{14}H_{14}$	90	−10	2.6	−0.4
	$C_{14}H_{18}$	77	−23	2.2	−0.8
	$C_{14}H_{18}$	79	−21	2.3	−0.7
	$C_{19}H_{22}$	67	− 7	2.6	−0.4
Aromatics Condensed with Cyclo-olefins					
	C_9H_8	99	− 1	1.7	−0.3
	$C_{10}H_{10}$	92	− 8	1.8	−0.2
	$C_{10}H_{10}$	93	− 7	1.8	−0.2

a naphthene ring or a cyclo-olefin condensed with the aromatic nucleus causes results roughly 10 and 5% too low, respectively. Table VIII shows that the deviations of the noncondensed aromatic naphthenes and aromatic-cyclo-olefins are about twice as large as for the corresponding condensed compounds. Table IX shows that the effect of a double bond in a two-carbon chain attached to a benzene nucleus is +10% ring, and that the deviation decreases with increasing molecular weight. Table X shows that the effect of two double bonds in the side chain is about twice as great as one double bond.

The deviation of these mixed-type molecules is usually about 10 to 15%, and the maximum deviation shown in these tables is about 25%. Assuming 12% to be the average deviation, it would be necessary for these compounds to be present in more than 25% concentration to cause as much as 3% deviation, which is the average deviation for aromatics with paraffinic side chains.

There are practically no aromatic-olefins or aromatic-naphthenes which are likely to be present in petroleum fractions boiling below 175° C. In the kerosene boiling range, Mair and Streiff (*17*) and Rossini (*20*) have shown the presence of mixed aromatics such as tetralins and phenyl cyclopentane. In the lube oil range, Mair, Willingham, and Streiff (*18*) have shown that most of the aromatic molecules contain naphthene rings. Therefore, this method of analysis is limited to petroleum fractions boiling below 400° C.

Table VIII. Deviation of Pure Compound Data

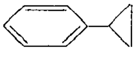
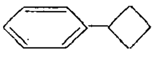
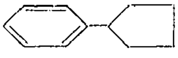
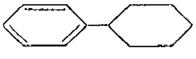
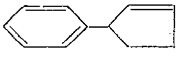
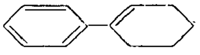
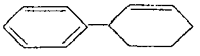
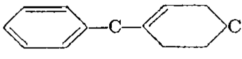
	Formula	Weight % Ring Calcd.	Weight % Ring Calcd. − theoretical	No. of Rings Calcd.	No. of Rings Calcd. − theoretical
Noncondensed Aromatic Naphthenes					
	C_9H_{10}	87	−13	1.3	−0.7
	$C_{10}H_{12}$	82	−18	1.4	−0.6
	$C_{11}H_{14}$	73	−27	1.3	−0.7
	$C_{12}H_{16}$	74	−26	1.5	−0.5
Noncondensed Aromatic Cyclo-olefins					
	$C_{11}H_{12}$	93	− 7	1.7	−0.3
	$C_{12}H_{14}$	90	−10	1.8	−0.2
	$C_{12}H_{14}$	85	−15	1.7	−0.3
	$C_{13}H_{16}$	77	−15	1.7	−0.3

Table IX. Deviation of Aromatics Containing One Olefinic Double Bond in Side Chains

Nucleus	No. of Carbons in Side Chains	No. of Isomers	Formula	Weight % Ring		No. of Rings	
				Calcd.	Calcd. − theoretical	Calcd.	Calcd. − theoretical
Phenyl	2	1	C_8H_8	86	11	1.1	+0.1
	3	5	C_9H_{10}	77^a	10	1.2^a	+0.2
	4	12	$C_{10}H_{12}$	69^a	9	1.2^a	+0.2
	5	13	$C_{11}H_{14}$	62^a	8	1.2^a	+0.2
	6	6	$C_{12}H_{16}$	56^a	6	1.1^a	+0.1
	7	1	$C_{13}H_{18}$	53	7	1.1	+0.1
	8	1	$C_{14}H_{20}$	47	4	1.1	+0.1
	9	1	$C_{15}H_{22}$	47	7	1.2	+0.2
	13	1	$C_{19}H_{30}$	36	4	1.1	+0.1
	21	1	$C_{27}H_{46}$	23	1	1.1	+0.1
	22	1	$C_{28}H_{48}$	24	2	1.1	+0.1
	26	1	$C_{32}H_{56}$	18	−1	1.0	0
	44	1	$C_{50}H_{92}$	10	−2	0.9	−0.1
2 phenyls	2	2	$C_{14}H_{12}$	92^a	6	2.2^a	+0.2
	3	2	$C_{15}H_{14}$	88^a	8	2.2^a	+0.2
	4	1	$C_{16}H_{16}$	81	6	2.1	+0.1
	14	1	$C_{26}H_{36}$	44	−2	1.9	−0.1
	16	1	$C_{28}H_{40}$	40	−3	1.8	−0.1
	18	2	$C_{30}H_{44}$	39^a	−1	1.9^a	−0.1
	22	1	$C_{34}H_{52}$	34	−1	2.0	0
	26	1	$C_{38}H_{60}$	31	−1	2.0	0
3 phenyls	2	1	$C_{20}H_{16}$	96	6	3.1	+0.1
	3	1	$C_{21}H_{18}$	87	1	3.0	0
Naphthyl	22	1	$C_{32}H_{50}$	31	0	2.0	0
	26	2	$C_{36}H_{58}$	24^a	−4	1.6^a	−0.4
	28	1	$C_{38}H_{62}$	24	−2	1.8	−0.2

^{a} Averages.

Table X. Deviation of Aromatics Containing Two Olefinic Double Bonds in Side Chains

Nucleus	No. of Carbons in Side Chains	No. of Isomers	Formula	Weight % Ring		No. of Rings	
				Calcd.	Calcd. − theoretical	Calcd.	Calcd. − theoretical
Phenyl	3	1	C_9H_8	75	8	1.1	0.1
	4	7	$C_{10}H_{10}$	79^a	19	1.3^a	0.3
	5	4	$C_{11}H_{12}$	70^a	16	1.3^a	0.3
	6	2	$C_{12}H_{14}$	66^a	16	1.3^a	0.3
	7	2	$C_{13}H_{16}$	66^a	20	1.4^a	0.4
	8	1	$C_{14}H_{18}$	59	16	1.7	0.7
2 phenyls	18	1	$C_{30}H_{42}$	43	3	2.2	0.2

^{a} Averages.

If there is a predominance of aromatic-naphthene or aromatic-olefin in a petroleum fraction, the per cent ring analysis may be checked by a method independent of the presence of the naphthenic ring or the olefinic double bond. This method consists of completely hydrogenating the aromatic concentrate and determining per cent naphthene ring by the method of Lipkin, Martin, and Kurtz (*14*).

The per cent ring analysis of aromatic extracts from straight-run and catalytic products has been checked by the procedure described above as shown in Table V. These fractions boil between 90° and 400° C., and the analyses by the two methods are in good agreement. This agreement indicates that the per cent ring method will give satisfactory results on petroleum fractions boiling below 400° C.

ANALYSIS OF NUMBER OF RINGS PER MOLECULE

Derivation. The second method, analysis of aromatics for number of rings per molecule, is also based on the hydrocarbon map shown in Figure 1, and uses the same physical properties as required in the analysis for per cent ring.

In deriving Figure 2 for analysis of condensed ring aromatics and Figure 3 for analysis of noncondensed ring aromatics, three lines were drawn from the limiting paraffin point through the data for mono-, di-, and tricyclics. By interpolating between these radial lines, it is possible to determine the average number of rings per molecule. In Figures 2 and 3, the monocyclic lines are of course identical; the condensed dicyclic line differs by 0.1 ring from the noncondensed dicyclic line; and the tricyclic lines are identical because there were insufficient data to warrant drawing separate lines for condensed and noncondensed aromatics.

The average graph, Figure 4, was derived assuming an equal distribution of condensed and noncondensed types. Results obtained from the average graph cannot differ by more than 0.05 ring from those obtained on Figures 2 and 3.

The method of interpolation between mono-, di-, and tricyclic lines is based on equal increments along a constant density coefficient (*A*) line. This system was developed by calculating properties of hypothetical mixtures of benzene and naphthalene, and benzene and diphenyl assuming volume per cent additivity of densities.

Results. Pure compound data for the 299 unsubstituted aromatics and alkyl aromatics in Table IV show an average deviation of 0.1 ring per molecule.

Figure 5 shows that there is little systematic deviation throughout the molecular weight range. The difference between the calculated and theoretical values for number of rings per molecule, averaged for each group of isomers, is plotted against number of chain carbon atoms for the monocyclic aromatics.

Table V demonstrates the accuracy of this method for several aromatic fractions separated from petroleum. Number of rings per molecule obtained on the aromatic extract is compared with number of rings per molecule obtained on the completely hydrogenated sample by the method of Vlugter, Waterman, and Van Westen (*22*). The analyses by both methods agree within 0.1 ring per molecule on the lower boiling fractions. The analyses of the two fractions boiling above 260° C. show slightly larger deviations which are probably due to the presence of some naphthene ring in the aromatic molecules.

The method of Vlugter, Waterman, and Van Westen, which depends on Lorentz-Lorenz specific refraction and molecular weight is reported to be accurate within 0.2 naphthene ring per molecule (*10*). This reported accuracy has been confirmed on pure hydrocarbon data in this laboratory. Deanesly and Carleton (*3*) have reported a correlation of specific refraction against carbon-hydrogen ratio which is somewhat different from the correlation of Vlugter *et al.* (*22*), and which will give slightly different results for number of rings per molecule.

Table VI demonstrates the accuracy of this method using the calculated properties for the aromatics in straight-run gasoline fractions. In the boiling range where only monocyclic aromatics can be present, the values obtained by this method do not deviate more than 0.1 ring per molecule from the theoretical value. In the boiling range where dicyclics may be present, the number of rings per molecule obtained by this method is considerably higher than one ring.

Figure 6 shows the application of this method to narrow-boiling fractions of aromatics extracted from East Texas crude boiling up to 350° C. Through the monocyclic range, the method shows 1.0 ring per molecule, and from there, the number of rings increases steadily through the boiling range. As in the per cent ring analysis, there are marked increases in number of rings per molecule at certain points in the dicyclic range. At the boiling points of phenanthrene and anthracene, the analysis shows more than 2.0 rings per molecule, which may indicate the presence of these compounds.

Limitations of Method. This method is subject to the same limitations as the per cent ring analysis method. Mixed-type aromatics cause low results for number of rings per molecule where naphthene ring is present, and high results where olefin double bond is present. Table VII shows that an aromatic nucleus condensed with a naphthene ring or with a cyclo-olefin causes deviations of about −0.4 and −0.2 ring, respectively Table VIII shows that the corresponding noncondensed aromatic-naphthenes and aromatic-olefins give deviations of about −0.6 and −0.3 ring, respectively. Table IX shows that the effect of a double bond in a side chain is +0.1 or 0.2 ring, and Table X shows that the effect of two double bonds in a side chain is about +0.3 ring. Again it is apparent that the interfering-type compounds would have to be present in considerable concentration in a petroleum fraction to cause a deviation as large as 0.1 ring, the average deviation for the alkyl aromatics.

The method may be checked, as shown in Table V, by determining number of rings per molecule on the completely hydrogenated sample by method of Vlugter, Waterman, and Van Westen (*22*). The check method is independent of the presence of naphthene ring or olefin double bond in the original aromatic extract.

ACKNOWLEDGMENT

The authors are indebted to I. W. Mills for data used in Table VI.

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Standardization of Chromatographic Adsorbents

Rate of Flow of Developing Solvent

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The usefulness of permeability in characterizing an adsorbent is pointed out and a convenient grouping of terms ($kA/760\alpha$), for this purpose is suggested; with standard packing it is possible to calculate the rate of flow for different values of the pressure, column length, and solvent viscosity.

THE author has introduced several terms for the characterization of chromatographic adsorbents (*3*). Among these is V_c, which is defined as the rate of flow of the solvent through the column after a steady state is reached. In order to use this term to compare the permeability of adsorbents, the solvent, column length, and applied pressure must be specified. Generally benzene, a full water-pump vacuum, and a 75-mm. column furnish sufficiently good data; however, it is often necessary to estimate the usefulness of an adsorbent in columns of different dimensions with a variety of solvents and pressures; for this purpose a more general term is needed to describe an adsorbent.

Ideally, a knowledge of the particle size of a substance and the use of a standard degree of packing should permit the direct calculation of V_c for any set of conditions. In most adsorbents, however, there is generally a wide range of particle sizes and shapes, so that this procedure is not practical.

The "permeability" of a porous solid is derived from Darcy's law (*5*) and expressed by the equation:

$$k = \eta Q/A(P_1 - P_2)/L$$

where k is the permeability in darcys, η is the viscosity in centipoises, Q is the flux through the column in milliliters per minute, A is the cross-sectional area in square centimeters, $(P_1 - P_2)$ is the pressure difference in atmospheres between the ends of the column, and L is the length in centimeters. When the driving pressure, P, is expressed in millimeters of mercury and Q is replaced by $V_c\alpha$, where α is the interstitial volume of the column in milliliters per millimeter, the equation can be arranged as:

$$V_c = k\ (A/760\alpha)\ P/\eta L$$

If A is calculated and α is experimentally determined, it is now possible to calculate V_c for any values of η, P, and L. The need for the determination of A and α can be avoided by grouping the constants: ($kA/760\alpha$). When the value of this expression is determined experimentally by measuring V_c under one set of conditions for a standard degree of packing, the value of V_c for any other conditions may be calculated from the values of P, L, and η without further measurements. The adsorbent is poured into the column under the full water pump vacuum and settled by tapping the sides of the column, the surface of which is made smooth without applying pressure. In describing an adsorbent, the values for both k and ($kA/760\alpha$) should be stated.

The linear relation between V_c and pressure, and the reciprocal of the column length, suggested by several authors (*2*, *3*), follows from Darcy's law. Flow in relation to these variables is illustrated in Figures 1 and 2 for the systems benzene–silicic acid and benzene-lime. From these graphs and the experimental values of A and α, it is possible to calculate the values of k and ($kA/760\alpha$) for the adsorbents. In additional experiments, given herewith, the independence of diameter, the relation of vis-

Table I. Flow Characteristics of Two Adsorbents

Adsorbent	Solvent	k, Darcys	$kA/760\alpha$	V_c for 75 Mm.-Column and 665-Mm. Pressure	
				Calculated	Experimental
Merck silicic acid	Benzene	3.1	6.2×10^{-2}	9.8	10 ± 1
Mississippi lime	Benzene	6.7	14×10^{-2}	21.9	23 ± 2

Table II. Variations in V_c Due to Column Packing Differences

(Column length 75 mm.; applied pressure 675 mm.)

Run	V_c	Run	V_c
1	9.5	6	10.9
2	10.2	7	11.0
3	10.2	8	11.1
4	10.6	9	11.5
5	10.7	10	11.7

cosity, and the size of the experimental error were determined. Values of V_c (Table II) were found to show a maximum deviation of 10% from the average value.

EXPERIMENTAL

Apparatus. The chromatographic tubes used in this study were obtained from the Scientific Glass Apparatus Company, Bloomfield, N. J. All diameters refer to the inside diameter of the tube. For the study of the effects of pressure and of length on flow rate, a tube 9 × 130 mm. was used. Suction regulated by the device described by Gilmont and Othmer (*1*) was used to draw the developing solvent through the columns. For some determinations a layer of benzene about 10 mm. deep was maintained on the top of the column by addition of the solvent from a buret. In this case no correction was made for the slight liquid head; for other determinations a buret was attached to the top of the column and a correction was necessary. The average barometric pressure in these determinations was 765 mm. of mercury and the temperature was about 31° C. For the lower pressures it was necessary to cool the receiver in ice.

Adsorbent. Merck reagent silicic acid and hydrated lime, obtained from the Mississippi Lime Company, Alton, Ill., were used. The adsorbents were not prewashed (*4*). (Evidence just obtained indicates that prewashing may cause a considerable increase in V_c.)

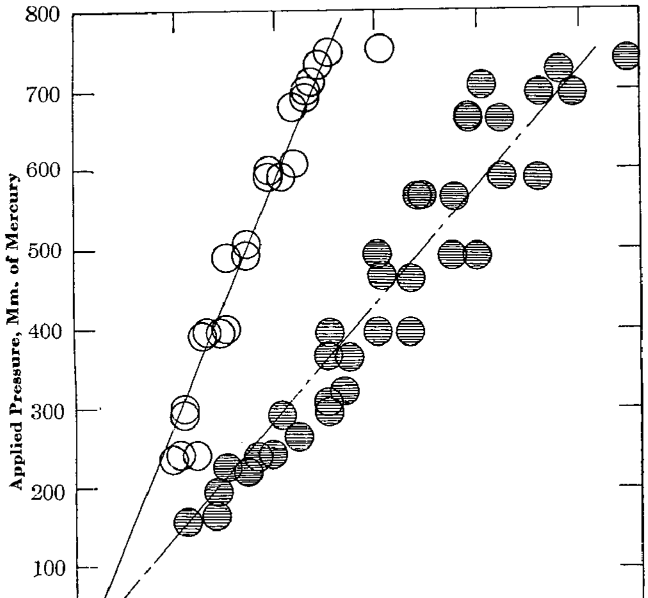

Figure 1 Relation between Chromatographic Flow Rate and Pressure

Benzene–silicic acid, ○; benzene–lime, ●

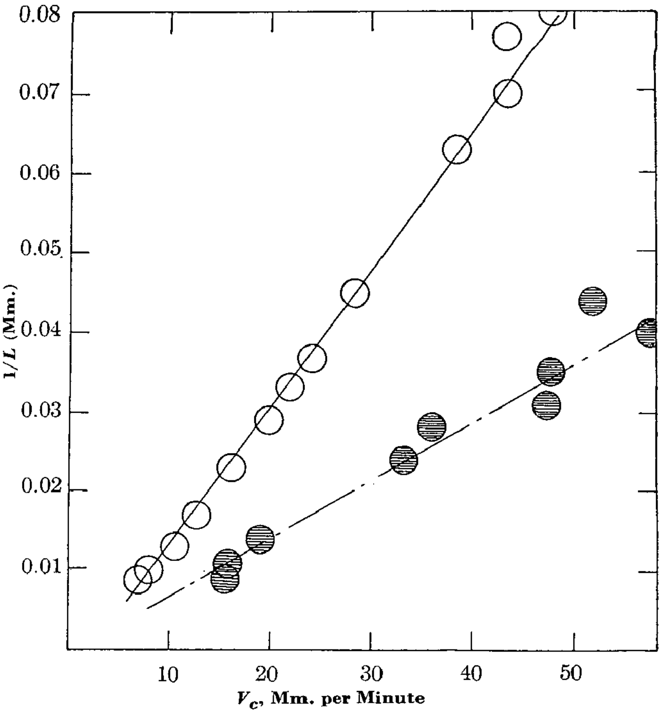

Figure 2 Relation between Chromatographic Flow Rate and Column Length

Benzene–silicic acid, ○; benzene–lime, ●

Data. The data for variation of V_c with pressure or column length are given in Figures 1 and 2. For the study of pressure four columns were run for the silicic acid and five for the lime. The flow rate for each column was determined at successively lower pressures, and these points were plotted. Each point on the V_c-length graph represents a separate chromatographic column of length indicated.

The V_c values obtained for ten columns run under the same conditions, with only the degree of packing as a variable and with special care to try to obtain the same packing, are shown in Table II. Table III gives the rate of flow for ten columns of equal length but different diameter.

In order to test the validity of the inclusion of viscosity in the formula for flow rate through a column, four columns were run using ligroin (boiling point 60° to 70° C.) in place of benzene. The V_c values thus obtained were: 19.6, 18.2, 16.5, and 18.3; the average value was 18.2 as compared with a calculated value of 18.7.

Table III. Variation of V_c with Column Diameter

(Column length 75 mm.; applied pressure 675 mm.)

Tube Diameter, Mm.	V_c
9	10.7
18	10.5
34	12.5
44	9.7
53	11.4
78	10.6

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Colorimetric Determination of Red Lead (Minium)

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Many unsuccessful attempts have been made to determine red lead in mixed paint pigments. Results are difficult to duplicate in the analysis of commercial red lead by recognized methods. These analyses can now be made quickly and accurately by a simple colorimetric procedure.

THE Diehl-Topf, Figg, Schaeffer, and other methods for analysis of red lead are to a great extent applicable to unmixed red lead but not to mixed pigments containing red lead. These methods depend on the liberation of iodine by red lead or on the reduction of red lead by hydrogen peroxide, oxalic acid, arsenious oxide, etc., and thus can be used only in the absence of substances other than oxides of lead that liberate iodine or reduce peroxides under the conditions of the analysis. In the iodometric methods, light causes the liberation of iodine in excess of the anticipated amount when analysis of mixed pigments is attempted. This effect is seemingly increased when lead chromate pigment is present. In attempting to analyze mixed pigment the necessary filtration is an additional source of error.

Red lead, mixed or unmixed, has been successfully determined by a simple colorimetric procedure in which the decomposition of lead tetraacetate by sufficient water to reduce the acidity of the final solution to 0.2 *N* or less, results in a clear yellow to red colloidal suspension of insoluble lead dioxide. The following equations describe the reaction:

$$Pb_3O_4 + 4CH_3COOH = Pb(CH_3COO)_4 + 2PbO + 2H_2O$$

$$Pb(CH_3COO)_4 + 2H_2O = PbO_2 + 4CH_3COOH$$

ANALYTICAL PROCEDURE

The analytical procedure varies slightly, depending on whether red lead under analysis is isolated or mixed with other pigments. Both methods are given, since the establishing of color standards is identical with the analysis of the isolated red lead.

For Red Lead (Unmixed). The red lead powder is dried for several hours at 125° C. under full vacuum and 0.5 gram is weighed to 4th decimal accuracy into a predried 125-ml. glass-stoppered flask. Exactly 20 ml. of fresh, glacial acetic acid are added from a precision buret, and the flask is quickly stoppered and swirled at room temperature for a few minutes until the lumps are finely divided. A small strip of paper is inserted at one side of the stopper and the flask is placed in a water bath at 60° C. and swirled every few minutes until red lead has completely dissolved. Vigorous shaking of the tightly stoppered flask may be necessary to effect solution. When cooled, the solution should be clear. If a slight cloudiness or dark coloration appears, conditions or materials have not been anhydrous.

This red lead solution is transferred to a microburet and an exact aliquot of not less than 0.25 ml. and not more than 3.0 ml. is drawn off into a 600-ml. beaker. Without delay, 5 ml. of absolute alcohol for each 0.25 ml. of aliquot are added from a graduate and the mixture is quickly swirled for 2 or 3 seconds. About 225 ml. of cool distilled water are quickly added from a graduate with immediate and rapid stirring. Color will develop at once. If any appreciable color appears when the alcohol is added, water is present in either the alcohol or the acetic acid and erroneous results will be obtained. The solution is next transferred to a 250-ml. volumetric flask, brought to volume with water, and compared to colored standards containing known amounts of red lead, developed by the same procedure. The color comparison should be made immediately and the use of Fisher electrophotometer with green light filter is recommended. A graph developed in this way is a straight line if the logarithmic scale of the instrument is used. This graph should be prepared by following the procedure through with exactly 0.5 gram of red lead of known high purity, 99% or higher, and developing colored standards by drawing off a series of aliquots ranging from 0.25 to 3.0 ml.

For Mixed Pigments Containing Red Lead. The pigment is extracted from the wet paint by the usual centrifuge method, except that anhydrous ethyl ether (technical) is used as the extraction solvent.

The finely ground and sifted pigment (100-mesh sieve) is dried for several hours at 125° C. under full vacuum and a sample containing not less than 0.2 gram of red lead is weighed into a predried 50-ml. centrifuge tube having a constricted neck. Exactly 20 ml. of glacial acetic acid are added from a precision buret. The tube is quickly stoppered with a rubber stopper and shaken for a few minutes at room temperature, then placed in a water bath at 60° C. The stopper is loosened momentarily to release pressure and the tube is vigorously shaken every few minutes. It is removed from the bath after 15 minutes, then centrifuged until the solution is clear and can be drawn off. The clear liquid is transferred to a microburet by means of a pipet and exactly 1 ml. is drawn off into a 600-ml. beaker. Then 20 ml. of absolute ethyl alcohol are added quickly from a graduate, the mixture is swirled for 1 second, and 200 ml. of distilled water are added immediately with constant and rapid stirring. Speed of addition of alcohol and water, respectively, is very important at this point. Alcohol prevents cloudiness which may appear when small amounts of red lead are present.

The colored solution is then transferred to a 250-ml. volumetric flask, diluted to volume with water, and compared on the electrophotometer at once. Fading will begin in 10 or 15 minutes and is accelerated by a delay in adding water to the aliquot following addition of alcohol. If the color formed is faint a larger aliquot may be used from the buret, provided 5 ml. of alcohol are added for each 0.25 ml. of aliquot used. Per cent of red lead is calculated from a graph prepared from standards as outlined above.

ACCURACY METHOD

A pigment mixture duplicating the minimum requirements of U. S. Army specification 3-181, O. D. enamel, was prepared from pigments predried at 125° C. under vacuum. This mixture contained precisely 17% red lead by weight. Baker's analyzed C.P. powder, analyzing 99.9% red lead was used. The approximate composition of the mixture was as follows: lead chromate 35%, red lead 17%, zinc oxide 8%, extenders and tinting pigments (magnesium silicate, carbon, etc.) 40%.

Triplicate samples weighing exactly 2, 3, and 4 grams were taken and the analysis proceeded according to the method given for mixed pigments. Results are as charted.

Weight of Sample	Aliquot Used	Colorimetric Readings	Red Lead
Grams	*Ml.*		%
2	1	7.6, 7.6, 7.5	17.25
2	1	7.4, 7.4, 7.4	16.75
2	2	16.2, 16.1, 16.2	17.0
3	1	11.8, 11.8, 11.7	17.0
3	1	11.7, 11.8, 11.7	16.87
3	2	24.9, 24.9, 25.0	17.0
4	1	16.2, 16.2, 16.3	17.05
4	1	16.0, 16.2, 16.2	17.0
4	2	33.5, 33.6, 33.6	17.05

It is notable that accuracy increases as the red lead content of the aliquot taken approaches 50 mg. Results are reproducible to 0.05% when the aliquot contains 30 to 60 mg. of Pb_3O_4.

DISCUSSION

This method is specific, since red lead is the only compound used as a paint pigment that is completely soluble in glacial acetic acid and develops color when diluted under the conditions given. Litharge is soluble under the conditions but remains in solution when diluted. Lead dioxide is insoluble in glacial acetic acid. To attempt to separate red lead from mixed pigments with glacial acetic acid and determine the total lead in the extraction would require correction for any litharge present. In the analysis of extracted pigments, some loss of red lead must be anticipated, since it is a highly reactive pigment and readily forms lead soaps with fatty acids of the vehicle. The unreacted red lead in the pigment would vary with the type of pigment and vehicle.

Determination of Calcium by Potentiometric Titration

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A new method is proposed for the determination of calcium by potentiometric titration. The method is based on the precipitation of calcium ions by potassium fluoride solution and the use of the oxidation-reduction potential of ferric-ferrous ion as an indicator for the determination of the equivalence point. The estimation is carried out in a 50% alcoholic solution saturated with sodium chloride. The method can be used to determine the sum of calcium and magnesium.

NO satisfactory potentiometric method for the determination of calcium can be found in the literature. Most methods are based on the use of third-class electrodes such as $Ag/Ag_2C_2O_4/CaC_2O_4/Ca^{++}$, $Pb/PbC_2O_4/CaC_2O_4/Ca^{++}$, and $Ag/Ag_3PO_4/Ca_3(PO_4)_2/Ca^{++}$ (*1*).

The method proposed here for the estimation of calcium was originally suggested by Treadwell (*2*) some 15 years ago for the determination of mixtures of magnesium and aluminum. It is based on the fact that ferric but not ferrous ion forms a stable complex with fluoride. If a solution of calcium chloride containing ferrous and a small quantity of ferric ion is titrated with potassium fluoride, the fluoride added is first precipitated as calcium fluoride. At the end point, the Fe^{+++} is converted to FeF_6^{---}, causing an abrupt drop in the oxidation-reduction potential measured by means of a bright platinum electrode immersed in the solution. It is not practicable to work in a purely aqueous solution, owing to the considerable solubility of calcium fluoride and it is probably for this reason that the method, though allowing the rapid determination of calcium, has not been suggested so far. Accurate results were, however, obtained by working in a 50% ethyl alcohol solution saturated with sodium chloride. The method can also be applied to the estimation of the sum of calcium and magnesium (a separate estimation of the two in a mixture was not practicable under the working conditions), and thus by the additional determination of one of the components by usual analytical methods, the proposed potentiometric method may be used to ascertain the amount of both calcium and magnesium, an important fact considering the analytical importance of solutions of these ions. In the determination of the sum of calcium and magnesium the potential drop is less distinct than in the case of pure calcium chloride solutions, but the error never exceeds ±1%. This disadvantage is partly offset by the ease and speed of the determination, since ordinarily in this separation many difficulties have to be overcome.

EXPERIMENTAL

All substances used were Schering-Kahlbaum products (puriss. or for analysis) except ferrous chloride which was obtained from Riedel de Haën. The potentiometric cell may be indicated as follows:

Pt	Sample solution	KCl (satd.)-agar-agar bridge	KCl, Hg_2Cl_2 (satd.) reference electrode	Hg

The calcium chloride solution was kept in a Pyrex beaker covered with an ebonite block which could be fixed in a thermostat. The measurements were in general carried out at a temperature of 0° C. The ebonite block contained a number of holes for a stirrer, electrode, and electrolytic bridge and for the introduction of the solutions and addition of titrant solution from a 10-ml. microburet divided into 0.01 ml. The bright platinum electrode had the form of a square of 1 sq. cm. area and when not in use was kept immersed in distilled water. The e.m.f. of the cell was measured with a Hellige Roehrenpotentiometer. This apparatus is based on the following principle:

The potential to be measured is applied to the grid of a triode valve, and causes a change in the anode current. This change is measured by means of a dial-galvanometer. Thus it is possible to read directly (in millivolts) the value of the potential applied to the grid. As the accuracy is reduced when more than 200 mv. are applied to the grid, the apparatus possesses an arrangement whereby back e.m.f.'s of 200, 400, 600, 800, 1000 mv., respectively, can be applied. These back e.m.f.'s are obtained from a series of resistances connected to a special standard cell in

Table I. Potentiometric Titration of 50 Ml. of 0.05 *M* Calcium Chloride with *M* Potassium Chloride

(Solvent 91% by volume ethyl alcohol saturated with Na Cl)

M KF, Ml.	*E*, mv.	$\Delta E/\Delta V$
0.00	+146	...
0.50	+148	...
2.50	+148	...
3.50	+146	...
4.50	+125	...
4.80	+102	
		200
4.90	+82	
		525
4.98	+40	
		600
5.06	−8	
		500
5.14	−48	
		150
5.22	−60	

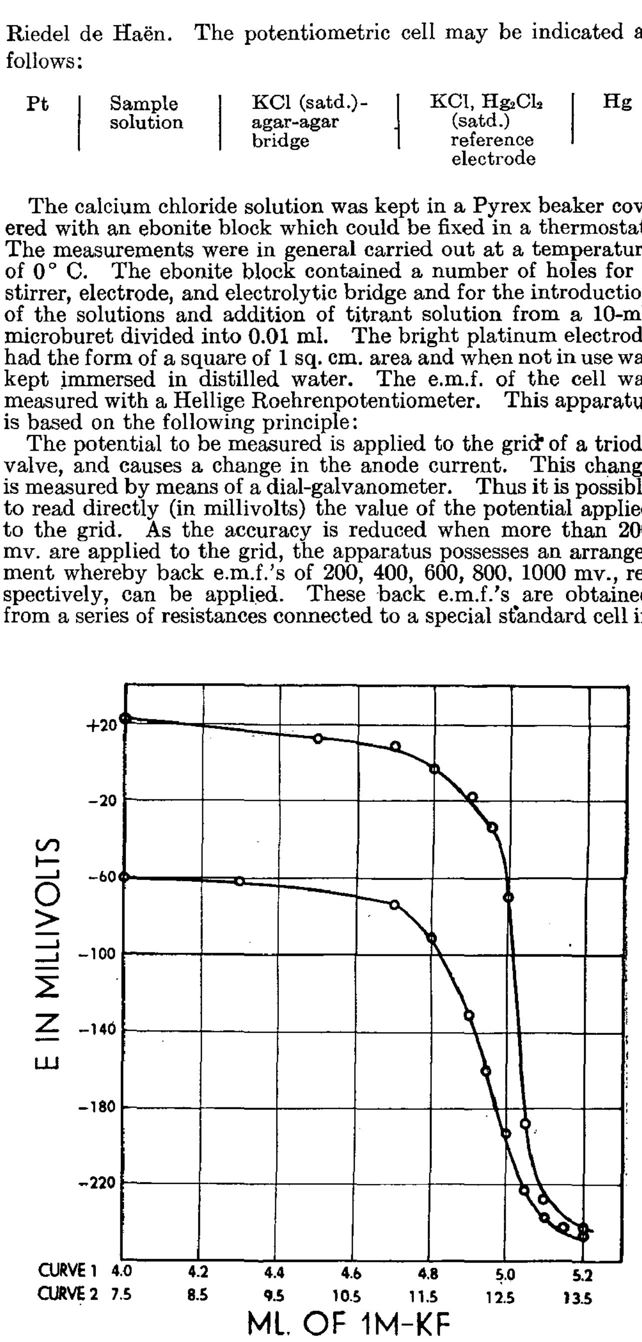

Figure 1. Potentiometric Titrations

1. 50 ml. of 0.05 *M* calcium chloride with 1 *M* potassium fluoride. $\Delta E/\Delta V$ maximum obtained at 5.025 ml. of potassium fluoride
2. 50 ml. of 0.05 *M* calcium chloride and 0.05 *M* magnesium chloride with 1 *M* potassium fluoride. $\Delta E/\Delta V$ maximum obtained at 12.4 ml. of potassium fluoride
Solvent 50% ethyl alcohol saturated with sodium chloride

Table II. Precision and Accuracy of Determination of Calcium under Routine Conditions

Test No.	M KF Found, Ml.	Deviation (d)	$d^2 \times 10^6$	Error[a] %
Sample 1 (theoretical value 5.00 ml. of M KF)				
1	5.025	+0.016	256	+0.5
2	5.010	+0.001	1	+0.2
3	5.035	+0.026	676	+0.7
4	4.085	−0.024	576	−0.3
5	4.090	−0.019	361	−0.2
6	5.010	+0.001	1	+0.2
	Av. 5.009	$d_{av.}$ 0.015	$\sqrt{\frac{\Sigma d^2}{5}}$ 0.019	
Sample 2 (theoretical value 7.50 ml. of M KF)				
1	7.530	+0.020	400	+0.4
2	7.505	−0.005	25	+0.1
3	7.480	−0.030	900	−0.3
4	7.540	+0.030	900	+0.5
5	7.475	−0.035	1225	−0.3
6	7.530	+0.020	400	+0.4
	Av. 7.510	$d_{av.}$ 0.023	$\sqrt{\frac{\Sigma d^2}{5}}$ 0.028	

[a] Concentrations determined by gravimetric analysis were considered as theoretical standard.

the apparatus. This cell also supplies the e.m.f. of 200 mv. which is needed for the preliminary adjustment of the galvanometer sensitivity. The apparatus has a very constant zero reading, and its over-all accuracy is 1 mv. The concentrations of all the standard solutions used were determined gravimetrically: the calcium was determined as $CaC_2O_4.H_2O$, the magnesium as $Mg_2P_2O_7$, and the potassium fluoride as PbClF.

Curve 1 (Figure 1) shows the change of potential in the titration of 0.05 M calcium chloride with 1 M potassium fluoride. Below a concentration of 0.01 M calcium chloride the potential drop is no longer distinct. It is necessary to wait at least 3 minutes before each measurement of the e.m.f. in order to obtain a constant value. Thus a titration generally takes about half an hour. The accuracy in the determination of calcium is within the limits of ±0.5%.

Curve 2 shows the change of potential in the determination of the sum of calcium and magnesium (magnesium is not precipitated as magnesium fluoride but as Me^IMgF_3). It can be seen that here the potential drop is less marked. A 50% ethyl alcohol solution saturated with sodium chloride formed a very suitable medium for the estimation. In each experiment 0.02 gram of ferrous chloride containing 0.4 mg. of ferric chloride was added to the solution before titration. At higher concentrations of ethyl alcohol (>70%), the potential drop is less pronounced. Data presented in Table I show the course of the potential change using 91% ethyl alcohol as solvent. By comparing the data in Table I with curve 1 (Figure 1) it can be seen that in the latter case the potential drop is less distinct, though even under these conditions the error does not exceed ±1%. In solutions containing less than 30% ethyl alcohol no results clear enough to allow the determination of calcium were obtained.

PROCEDURE FOR DETERMINATION OF CALCIUM

Dilute a solution of calcium chloride with distilled water and ethyl alcohol so that its final concentration of calcium chloride is between 0.05 M and 0.2 M, and that of the alcohol 50% by volume. Then add 0.02 gram of ferrous chloride containing 0.4 mg. of ferric chloride and saturate with sodium chloride (add 6 grams of sodium chloride per 50 ml. of solution) and titrate with a molar potassium fluoride solution. Stir the solution well and keep it in an ice-water mixture during titration (this cooling is not compulsory when the room temperature is below 16° C.). Be careful to wait until constant potential is obtained after each addition of potassium fluoride, especially in the proximity of the equivalence point. Ascertain by graph or by calculation the amount of potassium fluoride added for which $\Delta E/\Delta V$ becomes a maximum. One milliliter of M potassium fluoride corresponds to 0.5 ml. of M calcium chloride or 20.04 mg. of calcium in the tested solution.

Table II shows the precision and accuracy of the analytical method under routine conditions.

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Simultaneous Determination of Carbon, Fluorine, and Chlorine in Halocarbons

Semimicromethod

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Carbon, fluorine, and chlorine (and bromine) can be determined simultaneously in halocarbons, which do not contain hydrogen, by a combustion method. After decomposition of the compound at 1000° C. in a stream of oxygen, the chlorine reacts with silver in an absorption tube maintained at 295° C. (if bromine is present, it reacts simultaneously). Fluorine reacts with quartz to form silicon tetrafluoride, which is absorbed on alumina at 175° C. Carbon dioxide is absorbed by Ascarite as in the conventional carbon and hydrogen determinations.

PARR bomb fusions of fluorocarbons with sodium peroxide have not yielded reproducible analytical results, and on a large number of occasions extremely high values for the halogen content (100 to 300% of the theoretical) were obtained, even though halogen-free reagents were used in all cases. Fusion of these compounds with potassium for 30 minutes at 400° C. in sealed Pyrex tubes has been recommended (*2*). It was found by Kimball and Tufts (*6*) that such conditions were not sufficiently vigorous for the quantitative decomposition of some compounds; they reported a fusion with potassium in specially designed nickel bombs. Simons and Block (*9*) suggested decomposition of fluorine-containing organic compounds by fusion with sodium in quartz at red heat; more convenient sodium fusions have been reported in the Manhattan Project literature (*4*, *5*).

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Table I. Analysis of Standard Halocarbons

Compound	By Analysis			Theoretical		
	% C	% Cl	% F	% C	% Cl	% F
$FCl_2C\text{-}CF_2Cl$ (Freon-113)	12.76	55.60	30.69	...	...	...
	12.83	56.45	31.90	...	...	...
	13.19	56.47	29.96	...	...	...
	13.16	57.36	32.40	...	...	...
	12.92	56.49	30.18	...	...	...
Av.	12.97 ±0.16	56.47 ±0.36	31.03 ±0.90	12.80	56.80	30.40
C_8F_{16} (Perfluorodimethylcyclohexane)	24.1		72.2	...		...
	23.8		73.8	...		...
	24.0		73.5	...		...
	24.0		73.3	...		...
	23.5		74.6	...		...
	23.7		74.0	...		...
	24.0		72.2	...		...
Av.	23.9 ±0.17		73.4 ±0.69	24.0		76.0

Miller and McBee (*7*) have reported a pyrolysis method for the determination of carbon in halocarbons. Fluorine was removed from the gas stream by reaction with quartz to form silicon tetrafluoride, which was absorbed on alumina contained in the combustion tube. The alumina was maintained between 625° and 650° C.

Hubbard and Henne (*3*) had previously determined fluorine in organic compounds by quantitatively absorbing the silicon tetrafluoride formed in this manner in water and then determining the fluoride present in the aqueous solution.

Since fluorine can be quantitatively converted to silicon tetrafluoride, and this compound can be quantitatively absorbed by the alumina, it should be possible to determine the fluorine by weighing an absorption tube filled with alumina on which silicon tetrafluoride is absorbed. The alumina has to be used at an elevated temperature to prevent absorption of some of the carbon dioxide. Since silver is used to remove all chlorine quantitatively in the usual carbon and hydrogen determinations, it should also be possible to determine the chlorine content of a halocarbon sample by weighing an absorption tube filled with silver. If bromine is present in the compound, it would also react with the silver.

EQUIPMENT AND MATERIALS

Quartz combustion tube, 69 cm. long, 11 mm. in outside diameter (7 mm. in inside diameter). Side arm, 6 mm. in outside diameter (2 mm. in inside diameter), attached about 4 cm. from the large end of the tube. Capillary tip, 3.5 cm. long, 3.5 mm. in outside diameter (2 mm. in inside diameter).

Combustion tube filling, 6 rolls of platinum gauze, 3.5 cm. long. Crushed quartz.

Two soft-glass carbon and hydrogen absorption tubes, 31 cm. long. One soft-glass carbon and hydrogen absorption tube, 20 cm. long. Two Fisher microcombustion furnaces. Furnace, 175–180° C., 17 cm. long. Furnace, 175–180° C., 7 cm. long. Furnace, 295° C., 21 cm. long. Roll of iron wire gauze, 7 cm. long. Oxygen purification train.

PROCEDURE

The oxygen purification train and pressure regulator, *A*, Figure 1, is set up as in the ordinary carbon and hydrogen train. The combustion tube, *B*, is filled with alternating zones of crushed quartz and platinum gauze, spaced so that a roll of platinum is at the entrance of the high-temperature furnace as well as at the junction between the high-temperature furnace, *C*, and the 175° C. furnace, *D*, 7 cm. long, which surrounds the exit end of the combustion tube. The other four rolls of platinum are distributed evenly throughout the section of the combustion tube which is in the high-temperature furnace. The platinum serves as a combustion catalyst, and the quartz by reaction with the fluorine forms silicon tetrafluoride which is absorbed, or otherwise retained, in an absorption tube containing activated alumina (indicating type) at 175° C. The 175° C. furnace covering the exit end of the combustion tube is used to provide a temperature gradient to protect the rubber connection between the combustion tube and the absorption tube, which contains the silver wire.

Attached to the combustion tube is a soft-glass absorption tube, 31 cm. long, which contains clean silver wire cut into 2- to 4-mm. lengths and packed as tightly as possible. The 295° C. furnace, *E*, 21 cm. long, covers the absorption tube containing the silver.

The silicon tetrafluoride absorption tube which contains alumina, sodium fluoride, and Drierite is attached to the silver-containing tube. The furnace, *F*, which covers this absorption tube, is 17 cm. long; it actually consists of two 175° C. thermostatic sleeves. The alumina is placed only in the section of the absorption tube covered by the furnace and must be dried in a stream of oxygen at 175° to 180° C. for 4 hours before the packing of the tube is completed with sodium fluoride and Drierite. The sodium fluoride is principally used to separate the Drierite from the hot region near the furnace, but will also remove any hydrogen fluoride which may have passed through the alumina. If the alumina is permitted to extend out of the furnace, there is danger of absorption of carbon dioxide by the alumina. The indicating Drierite is placed in the exit end of the tube to absorb any moisture which may be given off by the alumina during the combustion. The Drierite is placed at the end of the tube which is most conveniently opened, as it must be replaced after about four determinations, while the alumina is not exhausted before 20 to 25 determinations have been made.

The carbon dioxide absorption tube, *G*, containing Ascarite and a small amount of Drierite, is connected to the tube containing the alumina. A safety tube, *K*, containing Ascarite and Drierite is attached at the end of the train.

All connections are glass to glass held in place by heavy-walled paraffin-impregnated rubber capillary tubing.

A 20- to 30-mg. sample is weighed in a Pyrex capillary tube if the sample is a liquid or a low-melting solid. Other solids are weighed in a platinum microboat. The capillaries are prepared in the laboratory from Pyrex tubing 3.5 mm. in outside diameter and, except for a slight variation, are made like the usual weighing microcapillaries. Instead of a straight capillary, a hook is formed at the closed end to facilitate their removal from the combustion tube.

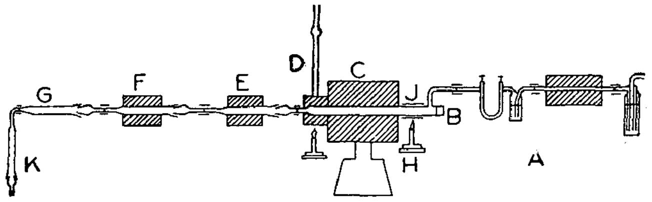

Figure 1. Combustion Train

The absorption tubes are weighed and connected to the train in proper order about 10 minutes before the sample is introduced, so as to allow the furnaces to heat the absorption tubes to constant temperature.

The section of the combustion tube which is to contain the sample is wrapped with a piece of moist chamois to cool this section before introduction of the sample. The tip of the capillary is scratched with a file and inserted into the end of the combustion tube, then broken by applying pressure with a microspatula. The combustion tube is then stoppered immediately. These precautions are necessary because many fluorine-containing halocarbon samples are extremely volatile.

After removal of the wet chamois, a very low flame from a microburner, *H*, placed about 7.5 cm. (3 inches) below and 2.5 cm. (1 inch) behind the section containing the sample, vaporizes the organic compound. The burner is gradually moved forward until all the sample has been vaporized from the capillary or boat. The gauze, *J*, is then moved into place over the capillary and is heated directly with the microburner with the maximum flame possible. The flame and gauze are gradually moved towards the furnace. After the sample has been completely vaporized, 20 minutes are allowed for thorough sweeping through with oxygen flowing at 10 ml. per minute.

After combustion is complete, the absorption tubes are removed, wiped, and allowed to cool for about 20 minutes before weighing. The weight gained by the silver-containing tube represents the actual weight of the chlorine. When both chlorine and bromine are present, the weight gained by the silver tube represents the sum of chlorine and bromine. Presumably these combined silver halides could be extracted from the surface of the silver wire and be determined individually if necessary.

The weight gained by the alumina-containing tube represents the weight of silicon tetrafluoride and the per cent fluorine is calculated from the weight of silicon tetrafluoride obtained. If hydrogen is present in the compound, the water which is formed will be picked up by the alumina or the Drierite in the alumina-containing absorption tube. This method of fluorine determination, therefore, does not give correct fluorine values in hydrogen-containing compounds. However, if the hydrogen content has been estimated by some other method—i.e., neutron scattering (*1*)—the weight of water expected from the hydrogen can be subtracted from the total weight gain of the alumina tube; the remainder of the weight gain is considered to be silicon tetrafluoride.

Table II. Halocarbon Analyses

Molecular Formula	Structural Formula	Theory C	Theory F	Theory Cl	Theory Br	Theory Cl + Br	By Analysis C	By Analysis F	By Analysis Cl	By Analysis Br	By Analysis Cl + Br[a]
C_4Cl_6	$CCl_2{=}CCl{-}CCl{=}CCl_2$[b]						18.73 ..... 18.86 17.68		82.24 81.19		
		18.42	...	81.58	...	...	18.42 ±0.50	.....	81.71 ±0.58	....	....
C_4Cl_6	$CCl_2{=}CCl{-}CCl{=}CCl_2$[b]						18.45 18.91		80.02 83.77		
		18.42	...	81.58	...	...	18.68 ±0.23	.....	81.90 ±1.87 81.32[c]	....	....
$C_4Cl_4F_6$	$CF_2Cl{-}CFCl{-}CFCl{-}CFCl_2$						16.40 15.74 15.71	37.34 38.37 38.13	44.44 45.33 44.92		
		15.81	37.52	46.67	...	...	15.95 ±0.30	37.95 ±0.40	44.90 ±0.30 45.27[c]	....	....
$C_3F_5Cl_3$	$CF_2Cl{-}CFCl{-}CF_2Cl$						15.60 15.33	40.22 40.36	46.84 43.79		
		15.18	40.01	44.81	...	...	15.47 ±0.15	40.29 ±0.07	45.32 ±1.52 45.47[c]	....	....
C_2F_3-$ClBr_2$	$CF_2BrCFClBr$						8.97 8.76	20.32 20.85			82.24 81.19
		8.69	20.63	12.83	57.85	70.67	8.87 ±0.10	20.57 ±0.24	11.83[d]	53.33[e]	81.71 ±0.58
C_4F_6-Cl_2Br_2	$CF_2BrCFBr{-}CFClCF_2Cl$						12.36 12.33 12.40	..... 28.89 28.78			59.58 58.45 57.42
		12.23	29.02	18.06	40.69	58.74	12.36 ±0.02	28.83 ±0.05	20.74[c]	46.75[f]	58.47 ±0.73
$C_4Cl_3F_7$							17.75 17.43 15.22 16.51	45.77 45.93 ..... 47.92	39.01 36.38 ..... 35.02		
		16.71	46.28	37.01	...	...	16.73 ±0.86	46.54 ±0.92	37.70 ±2.00 37.16[c]	....	....
$C_3Cl_4F_4$							14.32 14.70 15.14	30.79 ..... 28.99	54.23 ..... 56.60		
		14.19	29.94	55.87	...	...	14.72 ±0.28	29.89 ±0.90	55.42 ±1.18 50.46[d]	....	....
$C\ Br_2$-ClF_5	Probably $CF_2Cl{-}CFBr{-}CF_2Br$						12.12 11.34 11.02	28.67 28.49 28.40			62.71 59.21 58.65
		11.04	29.11	10.87	48.98	59.85	11.49 ±0.42	28.52 ±0.10	13.06[c]	58.89[f]	60.19 ±1.68
$C_8F_{12}Cl_6$							17.97 18.15	42.06 42.69	40.32 41.43		
		17.90	42.47	39.63	...	...	18.06 ±0.09	42.38 ±0.31	40.88 ±0.56 39.72[c]	....	....
$C_8F_{12}Cl_4$							21.34 20.79 20.74	48.94 49.31 48.93	31.52 29.46 30.67		
		20.62	48.94	30.44	...	...	20.96 ±0.26	49.06 ±0.17	30.55 ±0.73 30.69[c]	....	...
$C_4F_6Cl_2$	$CF_2{-}CFCl{-}CFCl{-}CF_2$						20.62 21.26	49.07 47.52	..... 31.47		
		20.62	48.94	30.44	...	...	20.94 ±0.32	48.30 ±0.77	31.47 30.67[c]	....	....

[a] Determined by combustion.
[b] The two C_4Cl_6 samples were prepared independently.
[c] Gravimetric determination after Parr bomb fusion.
[d] Titrimetric determination after Parr bomb fusion.
[e] Titrimetric determination of chlorine plus bromine. Bromine calculated from the Br-Cl ratio.
[f] Gravimetric determination of chlorine plus bromine. Bromine calculated from the Cl-Br ratio.
[g] Exact structure unknown.
Chlorine and bromine contents after Parr bomb fusions were determined in S.A.M. Laboratories.

When both hydrogen and fluorine are present in the compound, some hydrogen fluoride is apparently formed which etches the capillary tips of the absorption tube containing the silver wire. What effect this has on the analytical results could not be determined because a pure hydrogen-containing halocarbon was not available. It would seem that if hydrogen is present in the compound, the weight of the chlorine absorption tube will be affected. Removal of some fluorine in the form of hydrogen fluoride may affect the fluorine results, unless all the hydrogen fluoride reacts with the glass to form silicon tetrafluoride under the conditions existing in the absorption tubes. If the glass of the silver-containing tube furnishes the silicon for the silicon tetrafluoride, produced by the reaction with hydrogen fluoride, an error will also be introduced in the chlorine determination.

The gain in weight of the Ascarite tube is the weight of carbon dioxide and the per cent carbon is calculated directly from this value.

DISCUSSION

Most of the halocarbon compounds are difficultly combustible and it is necessary to use a temperature of about 1000° C. in order to obtain satisfactory results. Initially a temperature of 925° to 950° C. was used, but less satisfactory analyses were obtained. Two Fisher microcombustion furnaces were used for the high-temperature furnace because these were the only ones available at the time this method was developed. The highest temperature attainable was 1010° C., but a furnace built for operation near 1100° C. might yield better results.

The small 175° C. furnace (maintained at temperature by *p*-cymene at its boiling point) at the end of the combustion tube was installed to protect the rubber connection from the high temperature of the large furnaces. Specially designed combustion and absorption tubes with ground-glass joints would eliminate this hazard, and might otherwise improve results.

The silver wire used for chlorine and bromine absorption does not absorb any fluorine-containing compound. When compounds containing only carbon and fluorine are analyzed, there is no change in the weight of the silver-containing tube.

Since silver wire has a relatively small surface area, the silver-containing absorption tube has to be repacked after about four combustions. If very finely divided silver could be deposited on a porous medium (to permit an adequate oxygen flow), this difficulty could be obviated.

It was found that alumina would absorb silicon tetrafluoride at room temperature but would then also absorb from 25 to 75% of the carbon dioxide. A temperature of 175° to 180° C. was used because two Fisher microthermostatic sleeves were the only small furnaces available. It is probably advisable to make a more complete study of the temperature dependence of the relative absorption of silicon tetrafluoride and carbon dioxide by alumina.

Alumina, removed from a quartz absorption tube which had been used at 650° C., was examined roentgenographically (*8*). The contents of the tube were divided into three sections, the middle and the two ends. A sample of the alumina before use for silicon tetrafluoride absorption was also examined. The original alumina was found to consist of α-$Al_2O_3.H_2O$ and a small amount of anhydrous γ-Al_2O_3. The section at the entry of the tube contained anhydrous γ-Al_2O_3 and a small amount of α-$Al_2O_3.H_2O$; the other two sections contained anhydrous γ-Al_2O_3 only. While the center section was in the hottest part of the furnace, the temperatures in the two end sections were approximately the same. The alumina was dried in a stream of oxygen at 650° C. for 24 hours before being used. Although it was impossible to identify an x-ray pattern of a known fluorine or silicon compound on the alumina after the silicon tetrafluoride absorption, there was a slight change in the γ-Al_2O_3 pattern.

Miller and McBee (*7*) had found that a temperature in excess of 600° C. was required for complete absorption of the silicon tetrafluoride by their sample of alumina, while apparently all the silicon tetrafluoride was absorbed by this sample of alumina at 175° C. The temperature for a quantitative reaction of alumina and silicon tetrafluoride appears to be related to the surface condition of the alumina. A possible mechanism for the reaction is:

$$2H_2O + SiF_4 = SiO_2 + 4HF$$

$$6HF + Al_2O_3 = 2AlF_3 + 3H_2O$$

Only a small amount of water (from the partially hydrated alumina) would be required initially, as more water would be formed during the course of the reaction. Probably a complex aluminum fluosilicate would be formed rather than aluminum fluoride and silica. The Drierite in the end of the alumina absorption tube was actually used up more rapidly than the alumina. This may substantiate the mechanism suggested above. That this reaction may be due to adsorption on the surface of the alumina without such chemical reactions is suggested by the Fresenius method (*10*) for fluoride determination in inorganic compounds, in which silicon tetrafluoride is absorbed on pumice.

RESULTS

Samples of carefully purified and fractionated perfluorodimethylcyclohexane (the isomeric mixture), C_8F_{16}, and Freon-113, $C_2Cl_3F_3$, were analyzed by this method (Table I). The perfluorodimethylcyclohexane samples were analyzed at the lower temperature (925° to 950° C.) and thus the results may not be truly indicative of the fluorine analyses which can be obtained by this method. but do indicate the reproducibility of the method.

Freon-113 (1,1,2-Trichlorotrifluoroethane). The unsaturated compounds, acid chlorides and fluorides, hydrogen fluoride, and hydrogen chloride, usually found in commercial Freon-113 are removed by refluxing with an aqueous potassium permanganate solution for 3 or 4 days. The Freon layer is neutral at the same time that it is free of unsaturates. A test for completeness of removal of the unsaturates is to warm a mixture of 2 volumes of Freon, 1 volume of acetone, and 2 or 3 drops of aqueous permanganate solution. If any impurities remain, a brown color develops quickly. When this test is negative, the Freon is separated from the aqueous layer. It was then fractionated in a column (packed with $^1/_{16}$ inch nickel helices), with 40 theoretical plates. The material used had boiling point 47.8° C., freezing point $-36.40°$ C.

Perfluorodimethylcyclohexane. After fractionation in the same column as was used for the Freon, the material used had a boiling range of 101.6° to 102.1° C. The boiling points of the ortho, meta, and para isomers are 102.1–102.4°. 101.7°, and 100.5° C., respectively.

A large number of other halocarbons have also been analyzed. Results for a representative group are given in Table II, together with any other pertinent data available. These compounds were prepared by a group under the supervision of W. T. Miller, S.A.M. Laboratories, Carbide and Carbon Chemicals Corporation, New York, N. Y. The compounds containing carbon, fluorine, and chlorine were fractionated in a column with 60 theoretical plates; those containing bromine, in a column with 10 theoretical plates.

It must be strongly emphasized that the spread of values in successive determinations is undoubtedly due to changes in experimental technique. It was necessary to analyze compounds and to develop the method simultaneously in order to complete the analyses before the closing date of the laboratory.

Some additional work is necessary to determine the ideal conditions of combustion. However, these will not be much different from the conditions here reported. Additional work is also indicated for the mechanism of absorption of silicon tetrafluoride by alumina, the ideal temperature of absorption, and the effects of variations in the surface of the alumina.

CONCLUSIONS

A semimicromethod for the simultaneous determination of carbon, fluorine, and chlorine (and bromine) in halocarbons by combustion is reported. This method is estimated to give results which are at present ±0.3% in the carbon content, ±0.4% in the fluorine content, and ±0.9% in the chlorine (and bromine) content.

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BASED on work performed under Contract No. W-7405-eng-26 for the Manhattan Project; the information presented herein will appear in Division VIII of the Manhattan Project Technical Series as part of the contribution of the S.A.M. Laboratories, Carbide and Carbon Chemicals Corp. This material was originally reported on March 22, 1946, in Report A-3843 (DB-R-17) by R. Teston and F. E. McKenna.

Amperometric Titration of Thiodiglycol with Electrolytically Generated Bromine

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Electrolytically generated bromine can be used for the titration of microgram quantities of thiodiglycol. The presence of excess bromine can be detected and its concentration can be determined by observing the current flow between two platinum indicator electrodes which have a potential difference of approximately 0.3 volt impressed across them.

THE oxidation of thiodiglycol in 50% acetic acid by bromine to give thiodiglycol sulfoxide has been used as a means of titrating solutions of hydrolyzed bis(2-chloroethyl) sulfide. The work reported in this paper was undertaken to investigate, first the determination of the end point of this titration by means of a pair of platinum electrodes having a potential difference impressed across them and, second, the electrolytic generation of the titrating bromine. The method for determining the end point was first called to the authors' attention by investigators in the Australian Munitions Supply Laboratories, Marybyrnong, Victoria. The electrolytic generation of the bromine was suggested by Philip A. Shaffer, Jr., who was using it for similar purposes, and appears to have been first used by Szebellédy and Somogyi (*3*) for various other titrations.

If two platinum electrodes are immersed in a solution containing bromide ion and a suitably small potential difference is applied between them, an appreciable current (more than 0.5 microampere) flows only when the solution contains bromine. Under proper conditions the current is proportional to the bromine concentration and the amount of bromine present at the conclusion of the titration can be determined. A similar behavior in iodide-iodine systems has been utilized by Foulk and Bawden (*1*) to determine the end point of certain iodometric titrations, although these investigators made no attempt to obtain a quantitative measure of the iodine concentration. More recently Laitinen and Kolthoff (*2*) have used a rotating platinum microelectrode in conjunction with a calomel reference electrode (to measure bromine concentration) for the amperometric titration of arsenious acid with bromate in the presence of hydrogen bromide.

Preliminary experiments on the titration of thiodiglycol showed that the electrolytic generation of bromine in the solution was equivalent to the introduction of a corresponding amount of bromine in 50% acetic acid. This made possible the elimination of unstable bromine solutions, which require frequent restandardization, and also permitted a permanent calibration in terms of electrical units.

EXPERIMENTAL

Apparatus. The arrangement of the two pairs of platinum electrodes used in this work is shown in Figure 1. The generator electrodes were 0.5 to 1.0 sq. cm. each, and the indicator electrodes varied from 4 to 9 sq. cm. each. The indicator electrodes were always within 30% of equal size; if one was larger than the other, it was placed in position II. All the electrodes were constructed of platinum foil welded to platinum wire supports, which in turn were sealed through soft-glass tubing; a mercury pool in the tubing was used to make contact with the external circuit. The generator anode and its wire support were immersed as deeply as possible to prevent loss of bromine from the solution.

The two separate electrical circuits employed, one for the indicator electrodes and the other for the generator electrodes, are shown in Figure 2. The generator circuit contained series resistors (R_3-R_8) for generating rates of 0.8, 4, and 10 micrograms of bromine per second and corresponding shunts (R_9-R_{11}) which were adjusted so that the milliammeter scale reading was between 0.9 and 1.0 at each generating rate. To calibrate the milliammeter and shunts the generator electrodes were replaced by a standard resistor and the voltage drop was measured with a potentiometer. The correct resistor values for other generating rates or for other supply voltages can be calculated.

Any 1.5-volt dry cell, from standard flashlight size upward may be used to furnish the operating potential for the indicator electrodes. A Burgess No. 2308 45-volt B-battery was used to supply the generator current and was used for more than 200 titrations over a 2-month period without noticeable deterioration.

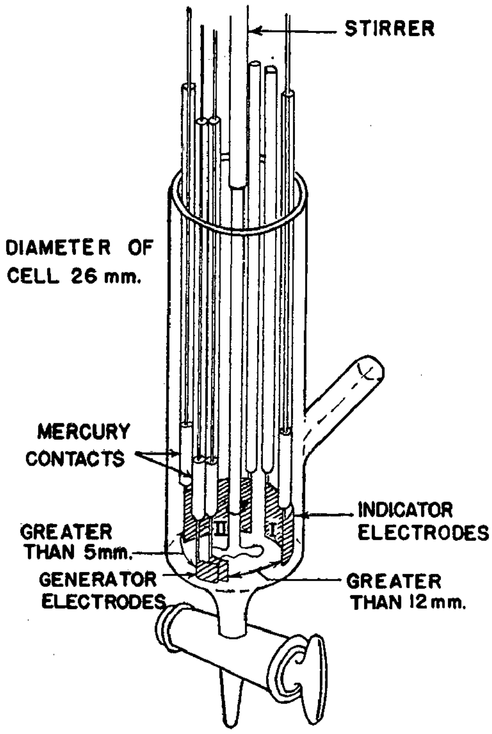

Figure 1. Electrodes and Titration Cell

Preliminary Adjustment. Ten milliliters of 50% acetic acid and 1 ml. of 1 formal aqueous potassium bromide were pipetted into the titration cell, the stirrer was started, and switch S_1 was snapped to the on position. The generating current switch, S_2, was closed until an indicator current of at least 20 microamperes was obtained; if the system had not been operated for some time or if a new battery had just been installed, the generating rate selector switch, S_3, was set to each of the titrating rates in turn, beginning with the lowest rate, and the generating current was adjusted in each case to the proper value with the separate generating current adjusting resistors. Final adjustment in stirrer speed was made during this period; too vigorous stirring causes the indicator current to decrease rapidly with time (more than 1 microampere per minute) while insufficient stirring is evidenced by the flow of significant indicator current (more than 1 microampere) before the end point is reached. The cell was drained

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and, if an indicator current of more than 60 microamperes had been obtained during these preliminary adjustments, was rinsed with 15 ml. of 50% acetic acid.

Titration. Ten milliliters of 50% acetic acid solution and 1 ml. of 1 formal aqueous potassium bromide were pipetted into the titration cell. The generating rate selector switch was set to a suitable rate and the titration was begun by closing the generating current switch and simultaneously starting a stopwatch. Immediately the generating current was noted, and, if necessary, readjusted to the proper value; further adjustment was sometimes required during long titrations at high rates of bromine generation.

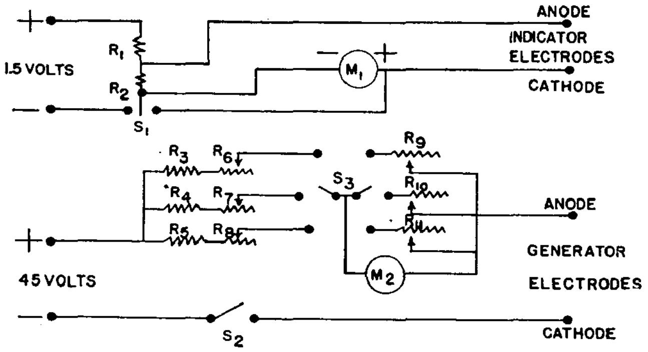

Figure 2. Electrical Circuits Employed

S_1 = SPDT, on-off switch
S_2 = SPST, generating current switch
S_3 = Two-gang rotary switch; generating rate selector switch
R_1 = 300 ohms
R_2 = 75 ohms
R_3 = 35,000 ohms
R_4 = 7000 ohms
R_5 = 3000 ohms
R_6 = 15,000 ohms, variable
R_7 = 3000 ohms, variable generating current adjusting resistors
R_8 = 1000 ohms, variable
R_9 = 500 ohms, semivariable
R_{10} = 30 ohms, semivariable
R_{11} = 15 ohms, semivariable
M_1 = 0–100 microammeter; internal resistance less than 3000 ohms
M_2 = 0–1 milliammeter; internal resistance approximately 100 ohms

When the indicator current began to rise continuously or dropped to a negative value, the titration was stopped. The time of bromine generation, the rate of generation, and the maximum value of the indicator current were recorded; the indicator current was allowed 15 to 20 seconds to attain a steady value. If the indicator current was less than 3 microamperes, the generating rate selector switch was set to 1 microgram per second and the titration was continued until the indicator current rose continuously.

At the end of each titration the end-point correction factor was determined by noting the indicator current, generating 10 micrograms of bromine, and again noting the indicator current. Division of the current increase into 10 gave a factor "micrograms of bromine per microampere of indicator current", whose product with the value of the indicator current at the end of the titration gave the end-point correction. This end-point correction and a blank correction for the 50% acetic acid being used were subtracted from the product of the generating rate and the time of generation to give the amount of bromine consumed in the titration.

The solution was drained off and, if an indicator current greater than 60 microamperes had been obtained, the cell was rinsed with 15 ml. of 50% acetic acid before beginning the next titration. After the last titration the cell and electrodes were rinsed with 15 ml. of 50% acetic acid and the solvent was drained off. The stirrer was stopped and switch S_1 was turned off.

DISCUSSION

Indicator Electrode System. Typical plots of indicator electrode current against bromine concentration, obtained with the experimental apparatus described above, are shown in Figure 3.

The linear relationship is the same as is obtained with the conventional electrode systems employed in amperometric titrations—namely, a calomel reference electrode and either a dropping mercury electrode or a rotating platinum microelectrode. In the presence of 0.09 formal bromide ion and at impressed potential differences of less than 0.36 volt, the current which flows is proportional to the bromine concentration and independent of the applied potential. Departures from linearity at large currents result when the voltage drop in the external circuit resistance becomes large in relation to the impressed potential; for a given external resistance an increase in the applied potential difference increases the length of the linear portion of the curve without changing the slope. The impressed potential difference should therefore be as large as possible without being great enough to cause a significant current (more than 1 microampere) to flow between the indicator electrodes before the end point is reached. With the electrolyte used in these experiments (10 ml. of 50% acetic acid and 1 ml. of aqueous 1 formal potassium bromide) the upper limit of the potential was approximately 0.36 volt.

Table I. Indicator Current as a Function of Electrode Size

Cathode Size	Anode Size	Microamperes/Micrograms of Bromine per Ml.
Sq. cm.	*Sq. cm.*	
0.04[a]	14.9	1.5
0.8	14.9	4.2
0.8	0.8	4.2
2.1	3.0	16.0
6.5	8.4	21.8
8.4	6.5	24.3
14.9	0.8	46.3

[a] Rotating microelectrode.

Table II. Apparent Resistance of Generator Electrodes

Generating Rate	Apparent Resistance After 30 seconds	Apparent Resistance After 360 seconds
Micrograms of bromine per second	*Ohms*	*Ohms*
0.8	1270[a], 1460[b]	1385[a], 1700[b]
4.0	358[a], 458[b]	388[a], 498[b]
10.0	178[a], 282[b]	203[a], 317[b]

[a] 0.80 sq. cm. cathode and 0.85 sq. cm. anode.
[b] 0.10 sq. cm. cathode and 0.85 sq. cm. anode.

As might be expected, the slope of the current *vs.* bromine curve is dependent upon the size of the indicator electrodes and especially that of the cathode (see Table I). Present work has been limited to systems having a total anode and cathode area of not over 15 sq. cm. because this was the maximum electrode area that could be immersed conveniently in 11 ml. of solution. While greater sensitivity can be obtained by making the cathode larger the indicator current is unstable if the cathode area is very large in comparison with the anode area and as a result accurate measurement of the bromine concentration is difficult. The best compromise between sensitivity and current stability is apparently offered by electrodes of 6 to 9 sq. cm. area each, with the cathode area 100 to 150% that of the anode. If volumes larger than 10 ml. are to be titrated, the use of larger electrodes should lead to an increase in sensitivity.

The arrangement of the indicator electrodes was dictated by the desire to titrate aliquots of only 10 ml. and to generate the bromine electrolytically. The most suitable of the experimental configurations tested (Figure 1) allows the use of reasonably large indicator electrodes in a spatial configuration which gives adequate isolation from the generator electrodes and in addition permits effective stirring. The stirrer is rotated counterclockwise, viewed from above, so that the flow of solution is from the generator electrodes toward indicator electrode 1.

If the minimum spacings specified were not observed, large currents were found to flow between the indicator electrodes during titrations; the direction depended upon the polarities of the interacting electrodes. These currents should not be confused with normal, momentary displacements of 5 to 10 microamperes which occur when the generator current is turned on or off.

It is important that indicator electrode II be made the cathode; otherwise, during titrations at high rates (4 to 10 micrograms of bromine per·second) an indicator current will flow before the equivalence point is reached. Furthermore, a satisfactory "current reversal" may not be observed at these high titrating rates; "current reversal" is the name applied to a momentary current which is observed just before the equivalence point is reached and which flows in a direction opposite to that expected. If the generating current is stopped when the first signs of current reversal appear, instead of when a normally rising indicator current is detected, and if the electrodes are allowed 5 to 15 seconds to reach a steady state, it will be found either that the solution is within 5 to 10 micrograms of bromine of the end point or that only a slight excess (under 10 micrograms of bromine) is present in the solution. This behavior is of extreme importance in titrations at 4 and 10 micrograms per second, since without its aid the finite time required for electrode response results in excess bromine concentrations of 1 to 5 micrograms per ml. and a serious decrease in the precision with which the end point can be determined. At the lowest generating rate employed (0.8 microgram per second) no usable current reversal has been observed, but this is of no consequence, since bromine excesses of more than 0.5 microgram per ml. are not encountered.

Generator Electrode System. Generator current was supplied from a 45-volt B-battery by means of the circuit of Figure 2. The series resistors necessary with this potential were large in comparison with changes in apparent resistance of the generator electrodes during titrations and gave a much more constant current than could be obtained with a lower voltage battery. The current was constant to within 0.5% at bromine generation rates of 0.8 microgram per second under all conditions and also at 4 micrograms per second, except when using an old battery. In this latter case and at 10 micrograms per second occasional minor adjustments were necessary to hold the current within 0.5%. No measurements were made at higher generating rates, since the indicator electrodes did not perform satisfactorily at 20 micrograms per second.

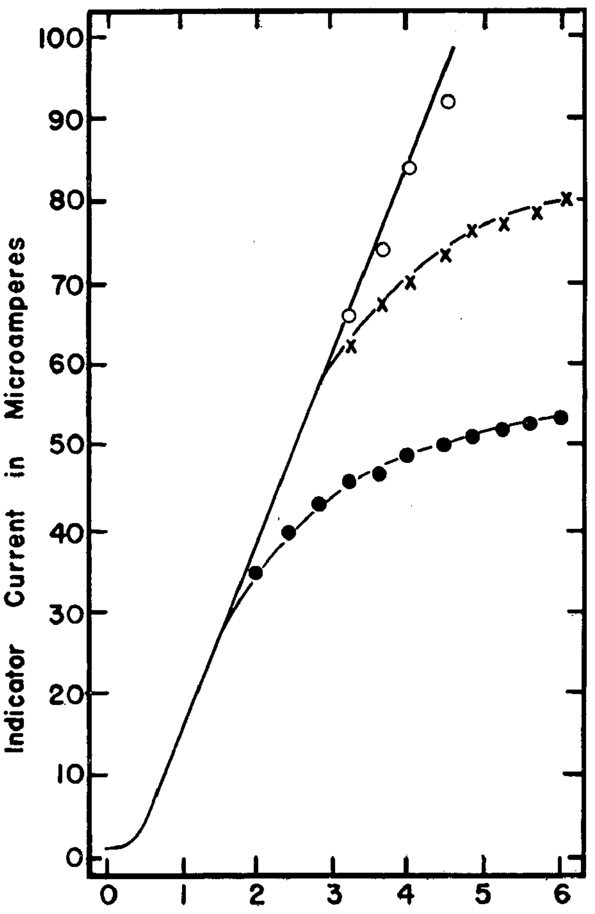

Figure 3. Indicator Current *vs.* Bromine Concentration

O Polarizing potential 0.3 volt
X Polarizing potential 0.15 volt
● Polarizing potential 0.1 volt
External resistance approximately 1500 ohms in all cases; cathode 8.4 sq. cm. and anode 6.5 sq. cm.

Numerous titrations have been carried out at rates of bromine generation of 0.8, 4, and 10 micrograms per second without any observed deviation from stoichiometry. The uncertainties of the measurements involved were estimated to be ± 2% for the standard thiodiglycol solutions used and ±0.5% for the electrolytic current.

While unimportant from the stoichiometric viewpoint, variations in generator electrode size have a pronounced effect on the apparent resistance (impressed voltage divided by current flowing) of the electrodes and on its constancy during a titration. The exact value of the apparent resistance is not important, provided that an adequate supply voltage is available and that the maximum current density encountered is not sufficient to cause objectionable overvoltages. On the other hand, changes in the apparent resistance during a titration are undesirable, since, if the external resistance is not readjusted to keep the total resistance of the generator circuit constant, a decrease in current results. The magnitude of such resistance changes is shown in Table II for two typical pairs of generator electrodes. While the apparent resistance becomes more stable as the generator electrode size is increased, the use of a generator cathode larger than 1 sq. cm. is not recommended, since the bromine diffusion current at the generator cathode would become significant in comparison with the total current at low generating rates and bromine generation would no longer be stoichiometric.

Sufficient time was not available to construct and test an electronic current regulator, but such a device should make possible current constancy to within 0.1 or 0.2% without any manual readjustments.

Results Obtained. Several hundred titrations have been carried out with 10-ml. portions of 50% acetic acid containing amounts of thiodiglycol [hydrolyzed from bis(2-chloroethyl) sulfide] of from 0 to 1420 micrograms. Typical results obtained by two individuals over an 11-day period are given in Table III. The precision for blanks and amounts of thiodiglycol below 100 micrograms was found to be approximately ±0.5 microgram, provided that the correction for excess bromine at the end of the titration was not more than 5 micrograms; this error is due to the uncertainty with which the end point can be determined. With larger amounts of thiodiglycol the results in general agreed to within 0.5% and in this range the constancy of the generating current limits the precision.

Unfortunately, the errors involved in the preparation of the

Table III. Titration of Unknowns

Thiodiglycol Content	
Calculated *Micrograms*	Found *Micrograms*
700	698.5, 699.5, 700
466	467
233	231.5
384	375.5, 375, 377, 376, 376
153.5	149
76.5	74
38.5	37.5, 38
0	0, 0.5
1714[a]	1732[a]
342.5[a]	344, 343.5, 343.5, 343[a]
68.5[a]	67.5, 67

[a] Figures for unhydrolyzed bis(2-chloroethyl) sulfide.

Table IV. Specificity of Titration

Compound Titrated	Moles of Mustard Found per Mole of Compound Titrated
Mustard, unhydrolyzed	0.998
Bis(2-chloroethyl) disulfide	4.9
Bis(2-chloroethyl) trisulfide	7.7
Bis(2-chloroethyl) pentasulfide	11.6
Bis(2-chloroethyl) sulfoxide	0.0
Bis (2-chloroethyl) sulfone	0.0

standard thiodiglycol solutions [from weighted amounts of bis(2-chloroethyl) sulfide] and in the measurement of the absolute value of the generating current make the appraisal of the accuracy of the titration uncertain, except that it is within 2%.

The results of titrations with several compounds closely related to thiodiglycol are summarized in Table IV. Although freshly prepared bis(2-chloroethyl) sulfide solutions which had not had time to hydrolyze were stoichiometrically equivalent to hydrolyzed solutions, they reacted so slowly with bromine that appreciable bromine concentrations were obtained during the titrations. The corresponding disulfide, trisulfide, and pentasulfide consume large amounts of bromine and react so slowly that extreme difficulty is experienced in determining the end point. As might be expected, the sulfoxide and sulfone do not react with bromine.

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Amperometric Methods in the Control of Water Chlorination

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Using rotating platinum electrodes, current-voltage curves have been obtained for solutions of chloramines and of hypochlorous acid at several pH values. They are compared with similar curves for dissolved oxygen. A limiting current was found even at the low chlorine concentrations that exist in drinking water when the electrode area was sufficient and other conditions were right. These results serve as a basis for discussion of the applications and limitations of the amperometric methods that have been used for both continuous recording and amperometric titration of chlorine residuals, even though the electrodes used have not been shown to give a limiting current.

THE determination of "residual" chlorine in water by an electrometric method that could be adapted to continuous automatic indication and recording has long been recognized as an important objective by numerous investigators. In several attempts to use an amperometric method, concentration has been measured by the amount of current flowing through a cell containing one polarized electrode. No particular attention has been paid to the possible existence of a limiting current and there has been no publication of current-voltage curves for hypochlorous acid or chloramine.

Rideal and Evans (*18*) used a polarized electrode consisting of a platinum rod extending axially through a copper tube. The water flowed through the latter, which was connected through an ammeter to the platinum and acted as the nonpolarizable electrode. Ornstein (*17*) patented the modification in which the two electrodes were separated by a porous diaphragm and the less noble electrode was immersed in a sample of unchlorinated water. Wallace (*19*) perfected a design which provided continuous abrading of the electrode surface and in which an external source was used to impress an unvarying voltage of substantial magnitude. Low electrical resistance and a constant environment for the nonpolarizable electrode were added by Marks (*15*) in a modification discussed by Baylis *et al.* (*1*).

The amperometric titration (*11*) of Foulk and Bawden (*6*) was applied to the determination of dissolved oxygen in water by Hewson and Rees (*7*) and Evans and Simmons (*5*). By the use of a special electrode and a different reagent Marks and Glass (*16*) adapted the method to the determination of chlorine residual in water.

In order to gain a better understanding of the results obtained with the direct amperometric method and the amperometric titration and to define their limitations more clearly, current-voltage curves have been determined employing several types of electrodes in very dilute solutions of hypochlorous acid and chloramines.

CURRENT-VOLTAGE CURVES

Dropping Mercury Electrode. Hypochlorous acid was found to react too rapidly with mercury to obtain satisfactory curves. Solutions of chloramines containing 50 to 100 p.p.m. of "available" chlorine gave polarographic waves with apparatus similar to that shown in Figure 1 in which the rotating electrode was replaced by a conventional dropping mercury electrode, the mercury falling into a funnel opening and being siphoned off to minimize contact with the solution. Since the curves have characteristics very similar to those obtained with the rotating platinum electrodes, they are not shown.

Experimental. The rotating platinum microelectrode (*9*) and cell are shown in Figure 1. The container was a glass jar approximately 7 cm. in diameter and 9 cm. high, fitted with a rubber stopper. The platinum electrode was incorporated into the plunger of a hypodermic syringe as shown. As finished, the exposed portion was a circular area 2 mm. in diameter on the surface of a projecting knob of glass. The other end of the plunger was centered in a gear driven at 600 r.p.m. by a laboratory motor and rotated within the cylinder of the syringe as a close-fitting bearing. Electrical connection was made by a stationary tube with sealed-in platinum wire dipping into mercury as indicated. The anode was "fine" silver wire 0.5 mm. in diameter and 18 cm. long, and the porous anode container was a Coors porcelain thimble No. 735, size 1.

The large rotating platinum electrode shown in Figure 2 was mounted in the syringe plunger and used interchangeably with the microelectrode in the cell of Figure 1. The electrode was in the form of a band 0.4 mm. thick, 29 mm. in outside diameter, and 11.8 mm. high cemented to the Lucite holder. Electrical contact was made by soldering one end of a platinum wire to the

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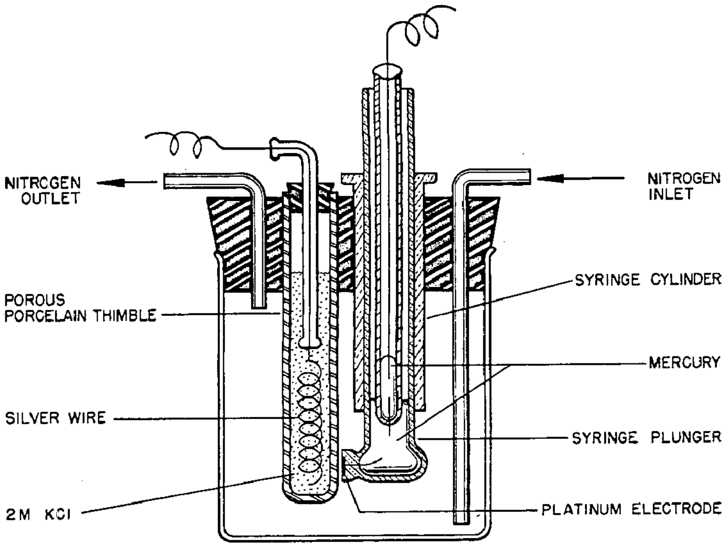

Figure 1. Rotating Platinum Microelectrode

stainless steel shaft and the other to a platinum rivet forced into a small hole in the platinum band.

Measurements with the microelectrode were made on a Sargent Heyrovský polarograph Model XI, the drum being turned by hand and current readings taken from the galvanometer without photographing because of the time required for equilibrium.

The electrical circuit used with the large rotating electrode was essentially the same as given by Kolthoff and Lingane (*8*), except that the voltage drop across the resistance in series with the cell, R_2, was recorded by a Leeds & Northrup Micromax recorder, 10 mv. full scale, instead of a galvanometer and shunt. This was convenient, since it required 20 to 30 minutes to establish equilibrium at each point. A silver–silver chloride–2 M potassium chloride electrode constructed according to Brown (*2*) was inserted into the cell of Figure 1, making contact with the solution through porous porcelain. At each point the potential of the rotating electrode was measured with respect to this reference. The cells were immersed in a water bath maintained at a temperature of 25° ± 0.1° C.

Solutions were made 0.1 M in potassium chloride, and 0.01 M in phosphates for pH 7, 0.01 M in acetate for pH 5, or 0.0025 M in borate for pH 9, and were treated with chlorine until "demand free". Just before use the chlorine concentration was brought to the desired point, the pH adjusted using a Hellige, Inc., glass electrode, and oxygen removed by treatment with tank nitrogen purified by passage through alkaline pyrogallol, sulfuric acid, and water containing a slight amount of "residual" chlorine. Using the same inlet and outlet tubes nitrogen pressure was used to force the solution through the cell at the rate of about 20 ml. per minute for the microelectrode and 60 ml. per minute for the large electrode. At each setting of potential the current was read only after equilibrium had been obtained, 5 to 10 minutes for the microelectrode and 20 to 30 minutes for the large electrode, and the potential was measured with a Leeds & Northrup portable potentiometer. Throughout each run the concentration of available chlorine was determined by amperometric titration with sodium arsenite (*16*). The curves were not sufficiently reproducible in going from negative to positive potentials. In all experiments reported the potential was changed in the negative direction, which resulted in good reproducibility.

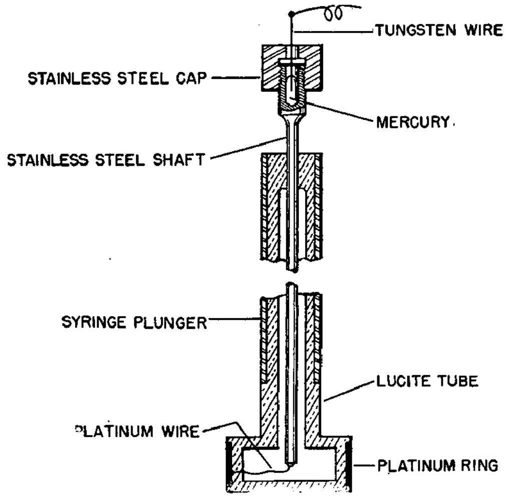

Figure 2. Rotating Platinum Cylindrical Electrode

Results. Representative examples of current-voltage curves obtained with the microelectrode, given in Figure 3, show that down to concentrations of 0.5 p.p.m. available chlorine there was a well-defined region of diffusion current. Except for the lowest concentrations the current was linear in the available chlorine concentration, as shown in Table I. The shapes of the curves are very different from those calculated on the assumption that the current is limited only by concentration polarization as found by Laitinen and Kolthoff for the reduction of oxygen and of bromine in acid solution (*13*). In addition, the reduction is an irreversible process—for example, note the length of time required for equilibrium—so that no precise significance can be attached to the half-wave potentials. The latter apparently shift slightly in the positive direction with increase in concentration, but they become markedly less positive as the hypochlorous acid is made less easily reducible by increasing the pH. When the available chlorine is made still more difficult to reduce by being converted to chloramine, the half-wave potential becomes much more negative, as shown in Figure 4. In this figure is also included a curve obtained with a buffered electrolyte solution (pH 7) saturated with air. The half-wave potential is even more negative than that for chloramine.

The necessity of measuring the small currents given by the microelectrode at low concentrations of available chlorine can be avoided by the use of the large rotating electrode. Diffusion currents have been obtained using large rotating electrodes in solutions of other oxidizing or reducing agents, as reviewed and discussed by Levich (*14*). Typical current-voltage curves for hypochlorous acid are given in Figure 5, which shows that well-de-

Table I. Relation between Available Chlorine Concentration and Diffusion Current with Rotating Microelectrode at pH 7.0 and 25° C.

Concentration *P.p.m.*	I *Microamperes*	I/c
0.52	0.57	1.1
0.90	0.92	1.02
2.00	1.90	0.95
4.97	4.71	0.95
9.95	9.25	0.93
19.7	18.8	0.95

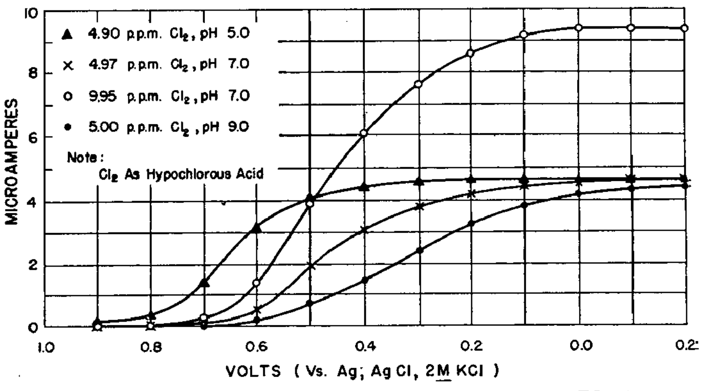

Figure 3. Current-Voltage Curves of Rotating Platinum Microelectrode at 25° C.

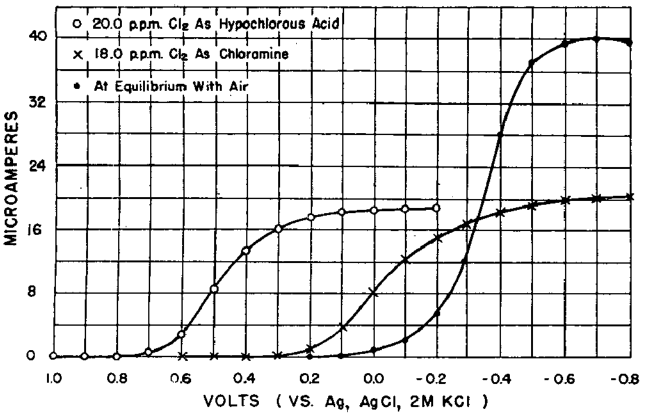

Figure 4. Current-Voltage Curves of Rotating Platinum Microelectrode at pH 7 and 25° C.

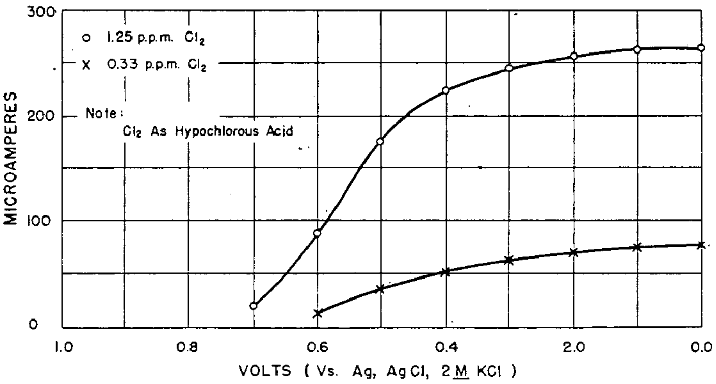

Figure 5. Current-Voltage Curves of Rotating Platinum-Silver Cylinder at pH 7 and 25° C.

fined diffusion currents are obtained. Table II shows further that the diffusion current is proportional to concentration within about 5%. The reproducibility, general shapes of the current-voltage curves, and effect of concentration and pH on half-wave potentials are in essential agreement with the results obtained with the microelectrode.

While the results obtained with oxygen at this electrode were not so reproducible as for the microelectrode, in both cases it was possible to obtain separable waves on air-saturated solutions at pH 5 and 7, but not at pH 9. Apparently the reduction potential of oxygen does not shift with pH. Laitinen and Kolthoff (*12*) obtained the same result employing a stationary microelectrode.

While these procedures would be lengthy and cumbersome as routine analytical methods and would apply only to special conditions, they show that a diffusion current can be obtained by employing solid electrodes in very dilute solutions of hypochlorous acid or chloramines.

CONTINUOUS INDICATION AND RECORDING

Conditions encountered in continuous measurement on a water supply are less favorable for the existence of a limiting current, for various reasons. The solution is comparatively poorly buffered and the low electrolyte content is particularly unfavorable for the existence of a diffusion current. Practical considerations, such as maintenance of a clean surface, frequently require methods of operation which do not allow the degree of concentration polarization necessary to give a diffusion current. The system discussed by Baylis (*1*) included an electrode in the form of a perforated disk placed so that the stream of incoming sample impinged on one flat surface, the other being insulated. As the liquid stream entered the cell, it entrained Carborundum particles which abraded the electrode surface to prevent fouling. The nonpolarizable electrode was silver immersed in 2 *M* potassium chloride, separated from the water by means of a porous porcelain diaphragm which contacted the insulated side of the electrode to minimize the length of the electrical path through the water and therefore the effect of its variable conductivity.

With this cell operating on the tap water of Newark, N. J., it has not been possible to obtain a well-defined diffusion current. Nevertheless, at any suitable and substantially constant value of imposed potential a linear relation between current and concentration is obtained in the range of ordinary chlorine residuals. In Table III are shown typical results obtained with such a cell in which the imposed potential was -0.075 volt, which should be sufficiently negative to give a limiting current even at pH 9 and permit the perforated cathode to be of copper. It is only at concentrations above 1 p.p.m. that the current does not [illegible] to follow the linear relation.

If other conditions were favorable for a limiting current, results with the microelectrode indicate further that pH should have no effect on its magnitude. While the change in current per unit change in concentration does not vary greatly with pH, the absolute values of current do. The current at zero chlorine concentration increases about 30% as the pH is lowered from 7 to 6 and decreases about 30% as it is raised from 7 to 8. That this is not an extraneous chemical reaction of the copper is shown by the fact that a gold electrode gives similar results. This result is expected when conditions are such that the current-voltage curve continues to rise indefinitely instead of reaching a limiting value. With regard to temperature coefficient, the change in current per unit change in concentration exhibits a direct variation of only about 2% per degree centigrade in the range of 10° to 20° C., which is about the expected value for a diffusion-controlled process (*10*). In addition to this, the current at zero concentration increases by 3 to 4% per degree, giving a total increase of 5 to 6% per degree in absolute current, which again can be attributed to the lack of a limiting current. For the same reason, it is to be expected that the pH and temperature coefficients will be somewhat different at other values of impressed voltage.

The potential range of -0.075 to -0.1 volt has been used because this instrument has been employed in the determination of total "chlorine residual" whether in the form of chloramine or hypochlorous acid. It has been found, in agreement with the results in Figure 4, that this potential range is sufficiently negative to permit a response of practical magnitude to changes in chloramine concentration with only a moderate response to changes in dissolved oxygen content. Since the current is not truly diffusion-controlled, conversion of hypochlorous acid to

Table II. Relation between Available Chlorine Concentration and Diffusion Current with Large Rotating Electrode at pH 7.0 and 25° C.

Concentration *P.p.m.*	*I* *Microamperes*	*I/c*
0.33	68	206
1.25	260	208
2.80	530	190
6.20	1280	206

Table III. Relation between Available Chlorine Concentration and Diffusion Current with a Bombarded Electrode at pH 6.7 and 17° C.

Concentration *P.p.m.*	*I* *Microamperes*	$I - I_0/c$
0	35	...
0.55	120	155
0.70	145	157
0.90	175	156
1.0	185	150
1.8	240	114

chloramine might be expected to decrease the current by more than the 30% found for the rotating microelectrode. However, the shapes of the current-voltage curves apparently change with concentration in such a way that, in the vicinity of 0.5 p.p.m. the decrease in current amounts to no more than 30%.

In a water supply changes in pH, temperature, and dissolved oxygen content ordinarily occur slowly and in many cases the distribution of "available chlorine" between hypochlorous acid and chloramine changes only periodically. In practice it is sometimes found that the calibration changes more rapidly than could be caused by these factors, probably because of alterations in the nature of the electrode surface. The catalytic activity of this surface is a factor, since the current is controlled not only by diffusion but partially by other processes such as reaction rates. In spite [illegible] number of variables which tend to change the calibration, this electrode is serving a useful purpose. With periodic recalibration against an independent method, it provides a means of obtaining a continuous record of chlorine residual and shows up variations which are not apparent from periodic tests by the usual methods.

More recently an arrangement similar to the rotating electrode of Figure 2, shown in Figure 6, has been used in the experimental recording of chlorine residuals on several water supplies. The electrode rotates within a rather close-fitting porous porcelain diaphragm which serves as a salt bridge arranged to minimize electrical resistance. The electrode is easily removed for cleaning and because the flow of sample is used for neither abrading nor agitating, it can be small enough to permit continuous treatment with a small amount of buffer to keep the pH constant. Preliminary experiments indicate that under some conditions a limiting current exists and correspondingly less frequent calibration may be needed.

In Figure 7 is shown another modification of this cell which is suitable for amperometric titration of chlorine residuals with sodium arsenite. The basic cell elements, procedure, precision in determining chlorine residuals, and the method for distinguishing between chloramine and hypochlorous acid, are essentially as described by Marks and Glass (*16*). Since current change rather than absolute value is used to detect the end point, the existence of a limiting current is not so important here. However, this type of electrode gives a more rapid response and a steadier current flow, so that the end point can be detected more easily and rapidly.

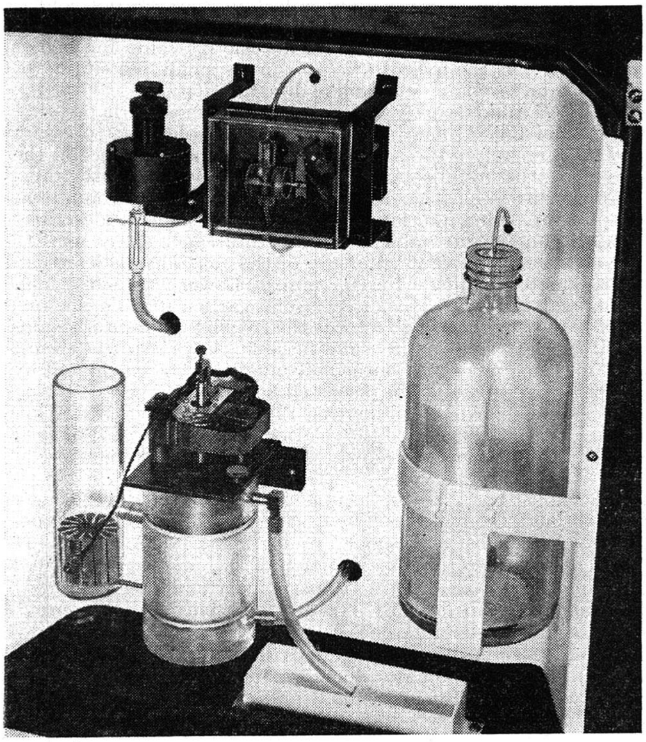

Figure 6. Rotating Platinum Electrode for Continuous Recording

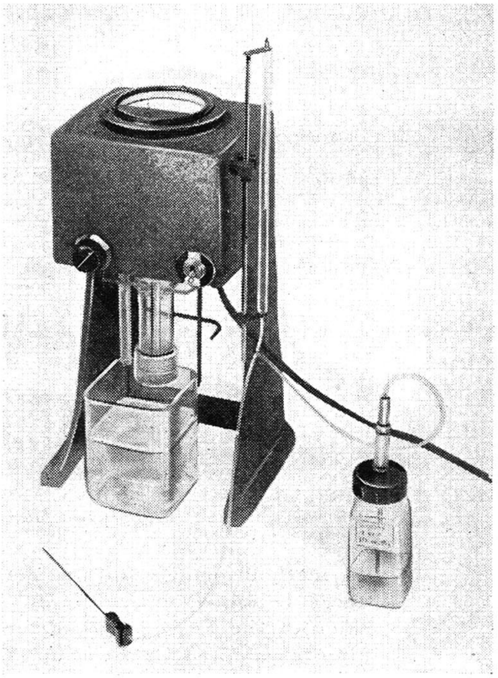

Figure 7. Amperometric Titrator

Reference to Figure 4 indicates that the waves for hypochlorous acid and chloramine are separable, so that it is possible with a noble metal cathode to operate in a potential range that is sufficiently positive to include only the former. The germicidal activity of chloramine is comparatively small (*3*), so that in recent work greater attention has been paid to measurement of "free available chlorine" (hypochlorous acid) with which dissolved oxygen does not interfere. The degree of sterilization to be expected is probably indicated more reliably by a measurement of this quantity, for example, than of a complex quantity like an electrode potential (*4*).

CONCLUSIONS

Current-voltage curves obtained with rotating platinum electrodes in buffered solutions of hypochlorous acid or chloramine containing sufficient indifferent electrolyte exhibit a limiting current. Even with large electrode area at chlorine concentrations encountered in drinking water the limiting current is linear with respect to concentration. This linear relationship is approximately the same for hypochlorous acid, hypochlorite ion, and chloramine. However, the reduction potential becomes more negative on increase of pH or conversion of hypochlorous acid to chloramine. Current proportional to concentration of hypochlorous acid can be obtained in a potential range where chloramine is without any effect, an interesting possibility in view of the much greater importance of the former in rapid sterilization.

Greater variations in current due to changes in pH, temperature, ratio of chlorine and ammonia, and the nature of the electrode surface can be expected from the fact that the electrodes that have been used for recording chlorine residuals do not give limiting currents. In addition, some current due to oxygen reduction is obtained in the potential range that includes chloramine. Accordingly, it is necessary to recalibrate against an independent method at regular periods. In spite of this the method has proved useful in giving a continuous, permanent record.

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Determination of the Vapor Pressure of Liquids on a Milligram Scale

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A method for determining the vapor pressure and the heat of vaporization of organic liquids on a milligram scale is described. The procedure is a modification of the Emich method for determination of the boiling point of organic liquids adapted for use at applied pressures less than one atmosphere.

CONSIDER a column of liquid contained in the mid-section of a glass tube sealed at one end and connected to a manometer and vacuum source at the other end. Let

p_t^{o} = observed pressure above the liquid column at temperature t
l_t = length of the liquid column at temperature t
d_t = density of the liquid at temperature t
t_0 = lowest observed temperature
$p_t^c = p_t^a + p_t^s$
where
p_t^a = pressure of air in the space below the liquid column
p_t^s = vapor pressure of the substance in the space below the liquid column

With the top of the liquid column at some reference point on the glass tube and when equilibrium is established, we have

$$p_t^{o} + \frac{l_t \mathrm{d}_t}{13.6} = p_t^c \qquad (1)$$

If the pressure of the air in the space below the liquid column is known at any one temperature, its pressure at any other temperature can be calculated from Charles' law. The vapor pressure of the substance can then be obtained with the aid of Equation 1.

In practice two cases are encountered, one in which the vapor pressure of the substance is less than the reading error of the manometer (0.2 mm.) at the lowest convenient working temperature, and the other where the vapor pressure of the substance is greater than this value. We shall consider the two cases separately.

Case I. Liquids whose boiling points at atmospheric pressure are greater than 190° C. will usually have a vapor pressure of less than 0.2 mm. at 25° C. Therefore at this latter temperature p_t^s may be ignored and we may take $p_t^c = p_t^a$. We then have

$$p_{t_0}^a = p^{o}_{\,0} + \frac{l_{t_0} \mathrm{d}_{t_0}}{13.6} \qquad (2)$$

and

$$p_t^s = p_t^{o} + \frac{l_t \mathrm{d}_t}{13.6} - \frac{273 + t}{273 + t_0}\, p_{t_0}^a \qquad (3)$$

Thus by observing the ambient temperature, the pressure above the liquid column, and the length of the liquid column when the top of the liquid column coincides with the reference point on the glass tube it is possible to determine the vapor pressure of a substance at selected temperatures. If no liquid is lost by vaporization, the hydrostatic pressure $l\mathrm{d}/13.6$ is independent of the temperature. However, if liquid is lost by vaporization and if the density of the substance is not known for all selected values of t, no large error is introduced by using the d_{t_0} value for higher temperatures, as the hydrostatic pressure is small, amounting to only 0.37 mm. for 5 mm. of liquid of $\mathrm{d} = 1.0$.

Case II. Liquids whose boiling points at atmospheric pressure are less than 190° C. may possess an appreciable vapor pressure at 25° C. Therefore the partial pressure of the substance in the space below the liquid column cannot be neglected and the pressure of the air in the space below the liquid column at room temperature cannot be determined in the direct manner described in Case I, unless the ambient temperature can be decreased to the point where the vapor pressure of the substance is less than the manometer reading error (0.2 mm.). Lower values of t_0 may be obtained with the aid of ice or solid carbon dioxide–acetone baths, as the only limiting factor is the freezing point of the sample. If this latter procedure is not feasible, the pressure of the air at the lowest temperature measured must then be calculated by the series of approximations discussed below.

It is assumed that p_t will increase rapidly with increasing temperature in accordance with the relation $\log P = A/(273 + t) + B$ and that p_t^a will increase slowly with increasing temperature as suggested by $P_t = (273 + t)/(273 + t_0)P_{t_0}$. When $\log p_t$ is plotted against $1/(273 + t)$, the upper portion of the smooth curve drawn through the points will be nearly straight if the true vapor pressure of the substance is given by $\log P = A/(273 + t) + B$. A tangent drawn to the upper portion of the curve will be a first approximation to the slope of the assumed vapor pressure curve. This tangent extrapolated to $1/(273 + t_0)$ defines the first approximation to $p_{t_0}^s$ and the difference between $p_{t_0}^c$ of the experimental curve and $p_{t_0}^s$ given by the tangent is the first approximation of $p_{t_0}^a$. Using this approximate value for $p_{t_0}^a$, new values of p_t^s are calculated with the aid of Equation 3 and a second approximation to $p_{t_0}^a$ is made as described above. After a series of approximations (usually two are sufficient) subsequent changes in the converging $p_{t_0}^a$ values become less than 0.5 mm. and the last value of $p_{t_0}^a$ so obtained is used to calculate final values of p_t^s.

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The accuracy of the above procedure is dependent not only upon the extent to which the substance satisfies the relation log $P = A/(273 + t) + B$ but also on the accuracy of the measurements of the pressure at the upper and lower portions of the curve.

EXPERIMENTAL

Apparatus. The assembly diagrammed in Figure 1 was employed. The manometer, constructed from 15-mm. outside diameter tubing with arms 150 mm. in length, is equipped with a 100-mm. sliding scale. The trap, constructed from 20-mm. outside diameter tubing, contains potassium hydroxide pellets in the arm adjacent to the manometer and 8- to 12-mesh activated carbon in the other arm. The two components in the trap are separated with a plug of glass wool. A Hershberg melting point apparatus (*2*), equipped with a 7.6-cm. (3-inch) immersion 0° to 250° C. thermometer and modified so that it can be heated with two 50-watt Chromalox cartridge heaters, is used as a bath. A modified Emich boiling point tube is prepared by forming a uniform 1-mm. inside diameter capillary at least 15 cm. in length on one end of a 7-mm. outside diameter soft-glass tube, the other end of which is joined to a standard taper. The end of the 1-mm. inside diameter capillary is then drawn out to form a tip of 0.2-mm. inside diameter and 10 mm. long. The tube so prepared is bent to form a right angle as shown in Figure 1.

Procedure. The capillary tip of the boiling point tube is brought into contact with a drop of freshly distilled liquid and the liquid is allowed to rise in the tube until a 5-mm. length is obtained in the 1-mm. section of the tube. The tip is then withdrawn from the liquid and wiped clean with absorbent paper, and the capillary end is sealed by heating it quickly in the edge of a hot flame. Satisfactory results will usually be obtained if the length of the gas bubble in the 0.2-mm. capillary end of the tube is about 1 mm. A piece of black thread is then tied around the tube 10 cm. from the bottom of the tube and the tube is connected to the trap and vacuum system. The bath is placed in position, care being taken to locate the tube in the center of the ascending column of bath liquid and immediately adjacent to the thermometer. The thread marker should be 3 to 5 mm. below the surface of the bath liquid. In the cases of liquids having a boiling point of 100° to 190° C. at atmospheric pressure, it is recommended that the initial pressure measurements be made at 0° C. rather than at room temperature. For observations at 0° an ice bath contained in a large test tube was found to be satisfactory.

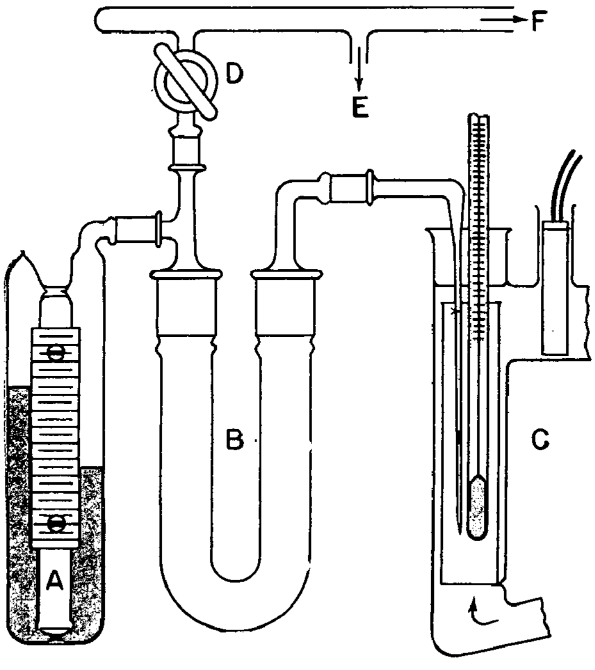

Figure 1. Apparatus

- *A.* **Manometer**
- *B.* **Trap**
- *C.* **Modified Hershberg melting point apparatus**
- *D.* **2-mm. oblique bore stopcock**
- *E.* **To needle valve**
- *F.* **To vacuum pump**

Table I. Vapor Pressure Data

Compound	Temperature	Vapor Pressure Observed	Vapor Pressure Literature	Mean ΔH^a Observed	Mean ΔH^a Literature
	°*C.*	*Mm.*	*Mm.*	*K cal.*	*K cal.*
Aniline	57.3	5	5[b]	..	..
	85.0	22	23[b]		
	94.8	35	36[b]		
	105.2	56	56[b]		
	110.7	64	71[b]		
	115.0	84	83[b]		
Toluene	26.0	26	31[b]	10.1	8.7
	41.0	57	62[b]		
	45.5	70	76[b]		
	47.0	76	81[b]		
	49.0	84	88[b]		
β-Chlorovinyl-dichloroarsine	66.5	3	6[c]	12.6	12.1
	79.2	11	12[c]		
	87.0	14	17[c]		
	92.2	19	23[c]		
	98.2	26	30[c]		
	103.0	32	38[c]		
	105.3	36	41[c]		
	110.0	45	51[c]		
Ethyl iodoacetate	28.8	1	0.9[c] (30° C.)	12.2	..
	40.8	2	..		
	51.4	3	..		
	60.0	6	..		
	72.0	13	16[c] (76–78° C.)		
	88.6	29	..		
Chloropicrin	25.5	24	25[c]	9.4	9.3
	37.8	39	46[c]		
	40.2	49	50[c]		
	42.0	54	57[c]		
	46.2	65	68[c]		
	55.0	100	101[c]		
α-Bromobenzyl-cyanide	85.0	1	..	14.5	..
	105.8	4	..		
	121.6	10	12[c] (132–134° C.)		
	143.0	25	..		
	151.8	37	..		
	159.2	50 (decomp.)	..		

[a] Calculated from vapor pressure data over temperature range shown in column 2.

[b] Interpolated from data given in (*3*).

[c] Interpolated from data given in (*4*).

Observations are made by decreasing the pressure in the vacuum manifold with the aid of a needle valve leak until the top of the liquid column in the capillary tube coincides with the thread marker. The stopcock between the vacuum manifold and the trap is slowly closed until the rapid oscillation of the liquid column, caused by pulsations from the vacuum pump, is damped just sufficiently to permit accurate observation of its position. The pressure in the manifold is then increased until the liquid column is displaced downward and then decreased until the top of the liquid column coincides with the marker. The manometer is read and the operation repeated until reproducible results are obtained. The initial readings at t_0 may be found to be high, owing to the removal from the liquid of volatile pyrolysis products formed when the tube is sealed. However, with pure substances reproducible values are soon obtained.

With reproducible values of $p^\circ_{t_0}$ at hand the length of the liquid column is determined and the temperature of the bath raised to selected values where corresponding values for p°_t and l_t are again determined. If, during a measurement at a constant bath temperature and a constant observed pressure, the liquid column rises slowly above the marker the liquid is decomposing to give more volatile products. To determine whether or not decomposition has occurred during the course of an experiment a redetermination of $p^\circ_{t_0}$ is advisable. If the value for $p^\circ_{t_0}$ is essentially the same as that obtained initially it can be concluded that no significant decomposition has occurred. Values of d_{t_0} determined with the aid of a micropycnometer may be used for all values of t without introducing a large error. Information in regard to the boiling point of the substance under investigation may be obtained with the aid of the conventional Emich method.

DISCUSSION

The above method for the determination of the vapor pressure of a liquid is essentially the Emich method (*1*, *5*) for the determination of boiling points adapted for applied pressures less than 100 mm. of mercury. The observed pressure is corrected for the hydrostatic pressure of the liquid column and the partial pressure of the air in the space below the liquid column. These factors are and can be ignored in the conventional boiling point determinations at atmospheric pressure

Reliable vapor pressure data can be obtained with the method described above and a number of results are presented in Table I. In each case the observations are made on a sample of approximately 5 cu. mm. Studies on the application of the method were restricted to conditions under which the highest vapor pressure measured was less than 100 mm., principally because the vapor pressure measurements were subsequently used to define the optimum conditions for the purification and separation of certain organic liquids by vacuum distillation. There is no reason why the method cannot be applied over greater pressure and temperature ranges, although at higher pressures distillation from the liquid column may limit the number of observations that can be made from any one sample.

As observations made on a sample of approximately 5 cu. mm. permit the construction of a vapor pressure versus temperature curve, it is clear that the heat of vaporization of an organic liquid can also be determined on a milligram scale.

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Colorimetric Micromethod for Determination of Formic Acid

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The sensitivity of the mercurous chloride method for formic acid determination can be increased approximately one hundredfold by means of a colorimetric procedure based on the reduction of a mixture of phosphomolybdic and phosphotungstic acids. This method may be used to determine formic acid in blood.

METHODS frequently employed for the determination of formic acid consist of the measurement of the amount of mercurous chloride or of carbon dioxide formed in the reaction of formic acid with mercuric chloride. Both gravimetric (*1, 3, 10*) and oxidative titrimetric (*6, 7, 11*) procedures have been used to measure the mercurous chloride, but neither procedure is successfully applicable to the determination of less than milligram quantities of formic acid (*4, 12*). Quantities in the range of 0.1 to 1 mg. can be determined by the carbon dioxide method (*9*). To increase the sensitivity of the mercurous chloride method, a colorimetric procedure has been developed which permits the determination of quantities of formic acid as small as 5 to 30 micrograms in 1 ml. with an accuracy of ±1 microgram. The present method is based on the chromogenic reduction of a mixture of phosphomolybdic and phosphotungstic acids by the washed mercurous chloride precipitate from the formic acid–mercuric chloride reaction. Formic acid itself does not give a color with the reagent.

REAGENTS

Mercuric Chloride Reagent. An aqueous solution is employed containing 20 grams of mercuric chloride, 30 grams of sodium acetate, and 8 grams of sodium chloride in 100 ml., as generally used by others.

Suspension of Diatomaceous Earth. A mixture of 20 mg. of Dicalite laboratory Filteraid and 100 ml. of water is shaken up each time before use.

Alcohol. U.S.P. 95% ethyl alcohol is mixed with activated charcoal and filtered to remove any suspended impurities which may interfere with the analysis.

Chromogenic Reagent. Ten grams of phosphotungstic acid and 130 grams of phosphomolybdic acid are dissolved in sufficient water at room temperature to give a volume of 400 ml., and then 50 ml. of concentrated hydrochloric acid and 50 ml. of 85% phosphoric acid are added. Although a small sediment forms, the supernatant light yellow solution is stable for several weeks in a stoppered Pyrex bottle. The gradual appearance of a green tinge is attended by a slight increase in the color of the blank.

Sodium Formate Standard. A freshly prepared solution is used containing 44.4 mg. of sodium formate per liter, which is equivalent to 30 micrograms of formic acid per milliliter.

Sodium Carbonate, saturated aqueous solution.

PROCEDURE

For determining the relationship of colorimetric reading to formic acid concentration a series of dilutions of standard sodium formate solution is prepared containing the equivalent of 0 to 30 micrograms of formic acid per ml.

One milliliter of each solution is placed in a 15-ml. conical centrifuge tube with 0.5 ml. of mercuric chloride reagent and the mixture is heated on a steam bath for 3 hours. The upper two thirds of the tubes should be protected from excessive heating in order to prevent evaporation. (A satisfactory steam bath cover and tube support for this purpose consist of a sandwich of sponge rubber between aluminum plates with perforations into which the tubes fit snugly.) The tubes are next allowed to cool completely and 2 ml. of diatomaceous earth suspension are added to increase the bulk of the precipitate.

To overcome the tendency of some of the particles to stay in a

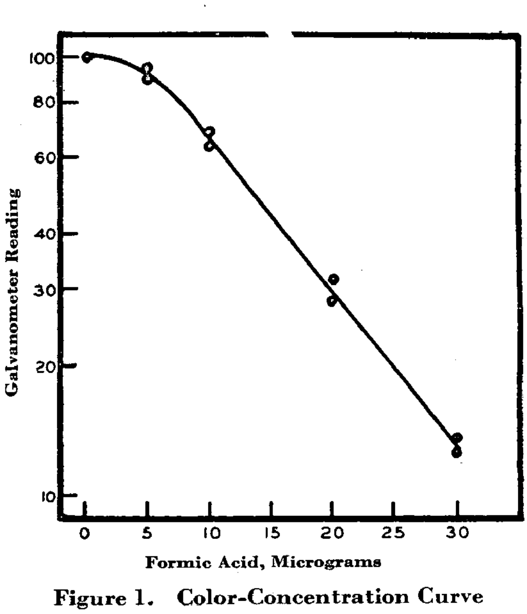

Figure 1. Color-Concentration Curve

surface film, approximately 10 ml. of alcohol are mixed with the suspension by running it in rapidly from a coarse buret tip. The tubes are centrifuged for 10 minutes at 2000 r.p.m., after which the fluid can be decanted without loss of precipitate. Two water washings are performed by twice adding 10 to 15 ml. of water, centrifuging, and decanting. To each washed precipitate is then added 1 ml. of chromogenic reagent. The end of each tube is flipped with the finger to stir up the precipitate and the mixture is heated on the steam bath for 15 minutes. Without waiting for the tubes to cool, 4 ml. of saturated sodium carbonate solution are added and the blue color which results is measured photoelectrically. No effort is made to eliminate residual diatomaceous earth, since it was not found to interfere significantly with the colorimetry. There is no appreciable variation in color density for at least 10 minutes and no appearance of turbidity when the mercurous chloride precipitate has been adequately washed.

A color-concentration curve obtained using a Cenco Photelometer with its red filter is given in Figure 1.

Unknown samples to which the mercuric chloride method can be directly applied are treated in the same manner as the standards and the formic acid concentration is determined by comparison of the color density measurement with the standard values. Formic acid in biological samples such as blood is preliminarily separated from interfering substances by protein precipitation and low-temperature vacuum distillation in the presence of a strong acid. In the case of blood it was found satisfactory to centrifuge a mixture of 1 ml. of blood with 1 ml. of water and 1 ml. of 10% sulfosalicylic acid, then to add approximately 0.02 ml. of sulfuric acid to the separated supernatant and to vacuum-distill this to dryness at room temperature. This distillation can be conveniently carried out in an appropriate evacuated and sealed tube (*5*) with the condenser portion cooled in a dry ice bath. When blood samples were treated in this way, recoveries of added formic acid in amounts of 30 to 1000 micrograms per ml. averaged 98% in nine single analyses, with an average absolute deviation from the mean of 5.1%.

DISCUSSION

The curve of Figure 1 reveals a deviation from Beer's law which is most apparent at the lowest concentrations and a separation of duplicate points from the line equivalent to approximately 1 microgram. The disproportionately low color intensity in the 0- to 5-microgram range is probably due to loss of some mercurous chloride by solution in the wash waters, while the scattering may be accounted for by mechanical losses. Neither of the factors was improved through reduction of the scale of the procedure and employment of centrifuge tubes of 3-ml. volume, but slight benefit is obtainable through use of wash water saturated with mercurous chloride.

The specificity of the colorimetric procedure for formic acid is no better than that of other methods based on reduction of mercuric chloride, and samples to be analyzed must be free of other reducing substances such as ascorbic acid and formaldehyde. However, the increased sensitivity of the colorimetric method does eliminate the need for the commonly employed concentrating procedures involving lengthy distillations or evaporation of considerable volumes (*1, 2, 3, 6, 7, 12*). Such procedures constitute a recognized source of error due either to decomposition of the acid or to its formation from carbohydrates (*3, 4, 8*).

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Oxidative Bromination in the Determination of Malic Acid and Aspartic Acid

Micromethod for Determination of Beta-Alanine

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FOR the determination of malic acid in biochemical work Pucher, Vickery, and Wakeman (*21*; cf. *22*) have developed a very specific micromethod which is based upon permanganate oxidation in acid solution containing potassium bromide. The reaction product, when distilled with steam in an acid 2,4-dinitrophenylhydrazine solution, yields an insoluble dinitrophenylhydrazine derivative. This compound is filtered off, dried, and then dissolved in pyridine. On addition of sodium hydroxide to the pyridine solution and dilution with water, a measurable blue color is developed.

This method has been used as such—i.e., without previous deamination with nitrous acid (cf. *21*)—by Arhimo (*1*) for the determination of aspartic acid, and it has proved to be exceptionally specific for this purpose. Of the other amino acids tested by him, only tyrosine and dioxyphenylalanine were found to interfere, whereas glutamic acid did not. The method can be successfully employed in the determination of aspartic acid, since aspartic acid, together with glutamic acid, may be separated from the other amino acids, according to Foreman's (*7*) principle, and the organic mono- and dicarboxylic acids, including malic acid, are extractable with ether from the amino acids in solution. Subsequently Laine (*10*) calculated the extinction values for tyrosine, although the method in this case seems less appropriate because of the comparatively low extinction values.

Although considerable study has been given to the nature of the oxidation product of malic acid, a detailed explanation of the chemical reactions that occur has not yet been obtained (*21*). Arhimo (*1*) has suggested dibromoxalacetic acid as an interme-

The 2,4-dinitrophenylhydrazine derivative, formed from malic acid and obviously also from aspartic acid, β-alanine, and tyrosine, by brominating permanganate oxidation, was identified as glyoxal-2,4-dinitrophenylosazone. The latter is obtained from dibromoacetaldehyde, but not from bromal, showing that dibromoacetaldehyde, in all probability, functions as intermediate in the reaction. There is, according to Dakin's assumption, an analogy in the behavior of dichloroacetaldehyde, when aspartic acid is oxidized by chloramine-T. The micromethod for determination of malic acid developed by Pucher, Vickery, and Wakeman is based upon this reaction. The method has been applied by Arhimo to the determination of aspartic acid and may be used to determine β-alanine.

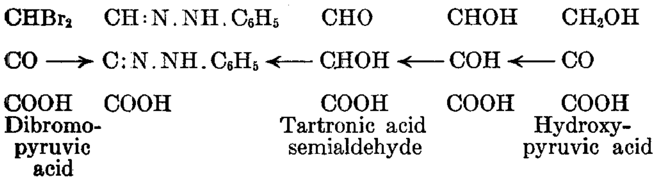
diate. Recently Greenberg (*8*) has claimed that malic acid, being first brominated to dibromomalic acid, ought to be oxidized to dibromoxalacetic acid. The dibromoxalacetic acid could then be separated by steam distillation and combined with dinitrophenylhydrazine in acid solution to yield a hydrazone which is insoluble in water. The behavior of citric acid on being converted into pentabromoacetone (*19–22*) suggests an analogous reaction mechanism in the case of malic acid—i.e., an oxidative bromination. The mechanism of this brominating and simultaneously decarboxylating oxidation in the citric acid determination, the so-called Stahre's reaction, has been elucidated by Wöhlk (*27*) and described by Kometiani (*9*). However, such a behavior of malic acid has never been mentioned.

Since the elucidation of the reaction mechanism seems to be of importance for the development and application of the excellent method of Pucher, Vickery, and Wakeman, the authors have attempted to solve this question.

The blue color, developed from the 2,4-dinitrophenylhydrazine derivative by addition of alkali, indicates that a dinitrophenylosazone is formed (cf. *2*). The authors have isolated and crystallized this compound and found it to be glyoxal-2,4-dinitrophenylosazone. This is in favor of dibromoacetaldehyde as the reaction product formed by permanganate oxidation from malic acid in the presence of bromine.

Dibromoacetaldehyde reacts with hydroxylamine hydrochloride to form glyoxime, as proposed by Wittorf (*26*). Since the permanganate oxidation of tyrosine yields acetic acid (*5*), the formation of dibromoacetaldehyde from tyrosine is also conceivable. The hydration of dibromoacetaldehyde in aqueous solution (*18*) retains it in the water phase on extraction with petroleum ether to remove the water-insoluble pentabromoacetone. This is in agreement with the appearance of dibromoacetaldehyde as an intermediate in the malic acid determination of Pucher, Vickery, and Wakeman.

Dibromopyruvic acid reacts with phenylhydrazine, yielding the phenylosazone of glyoxalcarbonic acid (*14*). At room temperature treatment of hydroxypyruvic acid with phenylhydrazine solution yields this compound via tartronic acid semialdehyde but at a higher temperature, 50° to 60° C., the reaction leads to the formation of glyoxalphenylosazone (*6, 23*).



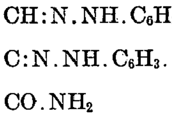
$$\begin{array}{lllll}
\mathrm{CHBr_2} & \mathrm{CH{:}N.NH.C_6H_5} & \mathrm{CHO} & \mathrm{CHOH} & \mathrm{CH_2OH}\\
\mathrm{CO} \longrightarrow & \mathrm{C{:}N.NH.C_6H_5} \longleftarrow & \mathrm{CHOH} \longleftarrow & \mathrm{COH} \longleftarrow & \mathrm{CO}\\
\mathrm{COOH} & \mathrm{COOH} & \mathrm{COOH} & \mathrm{COOH} & \mathrm{COOH}
\end{array}$$

Dibromopyruvic acid Tartronic acid semialdehyde Hydroxypyruvic acid

If dibromopyruvic acid functions as an intermediate in malic acid determination, glyoxaldinitrophenylosazone would be formed when the steam-volatile oxidation product reacts with dinitrophenylhydrazine. It is also possible that heating the oxidation solution preceding the distillation decarboxylates the primary oxidation product. Considering these alternatives, the authors have prepared the dinitrophenylhydrazine derivative by adding dinitrophenylhydrazine on the one hand to the oxidation solution directly, and on the other hand to the cold distillate, obtained by distillation through a spiral condenser. In either case they have established by titration that the dinitrophenylhydrazine derivative did not contain a carboxyl group.

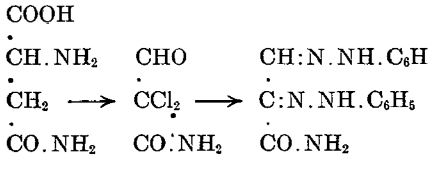
The decomposition points of the *p*-nitrophenylosazones of glyoxal and of glyoxalcarbonic acid differ very little from each other, the decomposition point of glyoxal-*p*-nitrophenylosazone being 310–11° C. (*25, 28*) and that of glyoxalcarbonic acid *p*-nitrophenylosazone 310° C. (*4*). Since the same similarity may exist with regard to the 2,4-dinitrophenylosazones, the authors have solved the problem by using phenylhydrazine. According to the latest report of Sprinson and Chargaff (*23*; cf. *6, 12*) the difference between the decomposition points of the two phenylosazones is considerable, glyoxalphenylosazone being decomposed at 169° C., and glyoxalcarbonic acid phenylosazone at 222–223° C. The phenylosazone isolated by the authors from the oxidation solution and from the distillate proved to be the derivative of glyoxal.

Although asparagine reacts very poorly in the determination according to Pucher, Vickery, and Wakeman a dinitrophenylhydrazine derivative can be separated from the oxidation solution with good yields. However, the authors have not succeeded in crystallizing this compound. The fact that the oxidation product of asparagine is not volatile with steam, and that its dinitrophenylhydrazine derivative is an osazone, giving a blue color when alkali is added, suggests the possibility that it may be the 2,4-dinitrophenylosazone of glyoxalcarbonic acid amide:



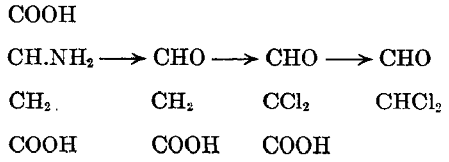
$$\begin{array}{l}
\mathrm{CH{:}N.NH.C_6H_3.(NO_2)_2}\\
\mathrm{C{:}N.NH.C_6H_3.(NO_2)_2}\\
\mathrm{CO.NH_2}
\end{array}$$

On oxidation of asparagine with sodium hypochlorite, Langheld (*11*) obtained the corresponding phenylhydrazine derivative, and Dakin (*3*), using the sodium salt of *p*-toluenesulfonamide (chloramine-T) as the oxidizing agent, obtained both the phenylhydrazine and the *p*-nitrophenylhydrazine derivatives. Dakin describes the reaction phases as follows:



$$\begin{array}{lll}
\mathrm{COOH} & & \\
\mathrm{CH.NH_2} & \mathrm{CHO} & \mathrm{CH{:}N.NH.C_6H_5}\\
\mathrm{CH_2} \longrightarrow & \mathrm{CCl_2} \longrightarrow & \mathrm{C{:}N.NH.C_6H_5}\\
\mathrm{CO.NH_2} & \mathrm{CO.NH_2} & \mathrm{CO.NH_2}
\end{array}$$

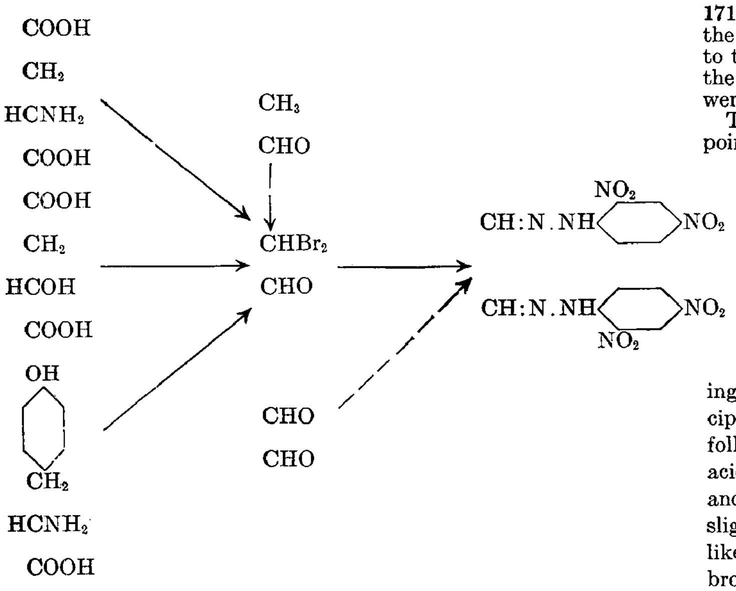
Especially remarkable in this connection is the finding that in oxidizing aspartic acid with chloramine-T, derivatives of glyoxal are separated in large amounts from the oxidation solution, when phenylhydrazine or aromatic diamines are added. According to Dakin, this oxidation of aspartic acid with chloramine-T leads to the formation of dichloroacetaldehyde, the CH_2-group being chlorinated supposedly in the following way:



$$\begin{array}{llll} \mathrm{COOH} & & & \\ \mathrm{CH.NH_2} \longrightarrow & \mathrm{CHO} \longrightarrow & \mathrm{CHO} \longrightarrow & \mathrm{CHO} \\ \mathrm{CH_2} & \mathrm{CH_2} & \mathrm{CCl_2} & \mathrm{CHCl_2} \\ \mathrm{COOH} & \mathrm{COOH} & \mathrm{COOH} & \end{array}$$

When methyl aspartic acid was used, the corresponding derivatives of methyl glyoxal were obtained.

As a summary of the foregoing the following reaction mechanism for the method of Pucher, Vickery, and Wakeman is proposed:



In order to ascertain the validity of this scheme the authors have prepared the 2,4-dinitrophenylhydrazine derivatives on the one hand from malic acid according to Pucher, Vickery, and Wakeman, and on the other hand directly from glyoxal and from dibromoacetaldehyde. If the scheme is valid, the same derivative, glyoxal-2,4-dinitrophenylosazone, ought to be obtained from all these different components.

EXPERIMENTAL

The 2,4-Dinitrophenylhydrazine Derivatives. The 2,4-dinitrophenylhydrazine derivative formed in the malic acid determination according to Pucher, Vickery, and Wakeman was prepared from malic acid (Schuchardt, pro analysi). After repeated recrystallization from glacial acetic acid its decomposition point was 322° C.

Glyoxal-2,4-dinitrophenylosazone was prepared from glyoxal sodium bisulfite (Schuchardt) in hydrochloric solution with a calculated excess of 2,4-dinitrophenylhydrazine. Various preparations, repeatedly recrystallized from glacial acetic acid, decomposed at 322–324° C.

2,4-Dinitrophenylosazone from Dibromoacetaldehyde. Dibromoacetaldehyde was prepared according to Mylo (*13*) and the fraction boiling at 135–141° C. was used for the preparation of the osazone. This, recrystallized from glacial acetic acid, decomposed at 323° C.

The osazones were all alike in appearance and crystallized from glacial acetic acid in beautiful red needles. In pyridine solution diluted with water they all yield the blue color, characteristic of the dinitrophenylosazones when alkali is added.

Neuberg and Simon (*16*) report the decomposition point of the 2,4-dinitrophenylosazone of glyoxal to be 318°, Lucas and Stewart (*12*) 323°, and Strain (*24*) 326–328° C.

2,4-Dinitrophenylhydrazine Derivative of Bromal. Bromal was prepared according to Mylo (*13*; cf. *17*), the fraction boiling between 174° and 180° C. being collected; bromal hydrate, puriss. (Schering-Kahlbaum), was also used. The dinitrophenylhydrazone of bromal crystallized from glacial acetic acid in reddish-yellow needles. Recrystallized, it decomposed at 261–262° C. In a pyridine solution diluted with water the addition of alkali precipitated it partly, the solution remaining reddish. In contrast with the glyoxalosazone, it dissolved in an alcoholic potassium hydroxide solution with a violet color.

The Phenylhydrazine Derivatives. Attempts to prepare a phenylhydrazine derivative from malic acid according to the method of Pucher, Vickery, and Wakeman, but using hydrochloric phenylhydrazine solution in the receiver, led to the formation of deeply colored products. This was induced supposedly by liberating hydrogen bromide and was avoided by using sufficient amounts of sodium acetate. The phenylhydrazine derivatives were, therefore, prepared by adding sodium acetate to the phenylhydrazine solution containing acetic acid. They were crystallized by the addition of sufficient water to their hot alcoholic solutions to produce a slight turbidity.

The phenylhydrazine derivative so obtained from malic acid decomposed at 170–172° C.; the decomposition point of the phenylosazone, derived directly from the oxidation solution, was 169–171° C. When a spiral condenser was used in the distillation and the compound was then separated by addition of phenylhydrazine to the cold distillate, the result was the same. Thus, as regards the decomposition points, all the phenylhydrazine derivatives were identical with glyoxalphenylosazone.

The decomposition points were determined with the melting-point apparatus of Dr. Linström, using rapid heating at the rate of 1° C. every 2 or 3 seconds, according to Emil Fischer.

SPECIFICITY OF METHOD AND EMPLOYMENT FOR DETERMINATION OF β-ALANINE

On the basis of the above reaction scheme the authors made some determinations of the specificity of the method. In addition to those acids which, according to Pucher, Vickery, and Wakeman, failed to give any precipitate they have found that admixtures of 25 mg. of the following substances did not interfere: ethanol, dioxytartaric acid, and dioxymaleic acid (prepared according to Neuberg and Schwenk, *15*). Acetaldehyde, on the other hand, interferes slightly and so does ascorbic acid, although the latter behaves like carbohydrates, yielding a precipitate even if no potassium bromide is added.

Of the amino acids, α-alanine does not interfere and asparagine only slightly. β-Alanine, however, reacts in a manner analogous to malic acid. Since only small quantities of β-alanine were available, the authors were compelled to perform the determinations with commercial preparations which evidently were not completely pure. The results, on a malic acid basis, suggested a purity of 95% with Schuchardt's β-alanine and 93% with Schering-Kahlbaum's preparation.

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Recommended Specifications for Analytical Reagent Chemicals

Benzine (petroleum benzine, petroleum ether), mercuric iodide red, mercuric oxide red, methyl orange, methyl red, nitric acid fuming, sodium cobaltinitrite, sodium phosphate dibasic (suitable for buffer solutions), starch soluble (for iodometry)

EDWARD WICHERS, A. Q. BUTLER, W. D. COLLINS, F. S. EISENHAUER, J. F. FLAGG, R. A. OSBORN, JOSEPH ROSIN, J. F. ROSS, AND JOHN WOLF

Committee on Analytical Reagents, AMERICAN CHEMICAL SOCIETY

THE specifications given below comprise the fourteenth group to be published by the committee since 1925, and the second to supplement and amend those appearing in the twelve earlier publications (*1–12*), which were contained in the book, "A.C.S. Analytical Reagents", published in 1941.

The specifications are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for the improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (*1–13*) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (*3*). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

Benzine (Petroleum Benzine, Petroleum Ether)

Note. Dangerously flammable. Should be kept away from flame and be stored in a cool place in tight containers.

REQUIREMENTS

Appearance and Color. To pass test.
Odor. To pass test.
Boiling Range. 30–65° C.
Nonvolatile Matter. Not more than 0.0015%.
Acid. To pass test.
Heavy Oils and Fats (Spot Test). To pass test.

TESTS

Appearance and Odor. Mix the material in the original container and pour 10 ml. into a test tube (150 by 20 mm.). The liquid should be clear and free from suspended matter or sediment. The color should be no more than the color of a standard prepared by dissolving 0.0025 gram of potassium dichromate in 1 liter of water.

Odor. The odor should not be disagreeable or sulfuretted.

Boiling Range. Determine by the method of the U. S. Pharmacopoeia using 100 ml. of the benzine. None should distill below 30° C. and not less than 90% should distill between 30° and 65° C.

Nonvolatile Matter. Evaporate 100 ml. at 70–80° C. Dry for 30 minutes at 105° C. The weight of the residue should not exceed 0.0010 gram.

Acid. Thoroughly shake 10 ml. with 5 ml. of water for 2 minutes and allow to separate. The aqueous layer should not turn blue litmus paper red in 15 seconds.

Heavy Oils and Fats (Spot Test). Pour gradually 10 ml. onto the center of a clean filter paper. After 30 minutes there should be no greasy stain visible on the paper and it should have no disagreeable odor.

Mercuric Iodide, Red (HgI_2)

REQUIREMENTS

Assay. Not less than 99% HgI_2.
Solution in Potassism Iodide Solution. To pass test.
Nonvolatile Matter. Not more than 0.050%.
Foreign Metals (as Pb). Not more than 0.001%.
Mercurous Mercury (as Hg). Not more than 0.10%.
Soluble Mercury Salts (as Hg). Not more than 0.05%.

TESTS

Assay. Dry about 1 gram over sulfuric acid overnight. Place 0.5 gram of the dried sample in a glass-stoppered Erlenmeyer flask, and add 30 ml. of hydrochloric acid, 20 ml. of water, and 5 ml. of chloroform. Rotate the flask until the mercuric iodide is dissolved, then titrate the solution with 0.05 molar potassium iodate until the iodine color is discharged from the aqueous layer. Stopper the flask, shake well for 30 seconds, then continue the titration, shaking vigorously after each addition of the potassium iodate until the chloroform is free of iodine color. 1 ml. of 0.05 molar potassium iodate corresponds to 0.02272 gram of HgI_2.

Solution in Potassium Iodide Solution. Dissolve 10 grams of the sample in a solution of 10 grams of potassium iodide in 100 ml. of distilled water in a glass-stoppered flask. A complete, or practically complete, solution results. Retain the solution.

Nonvolatile Matter. Add 1 ml. of sulfuric acid to 2 grams of the sample in a porcelain crucible and ignite gently *under a well-ventilated hood* to constant weight. The weight of the residue should not exceed 0.0010 gram. Retain the residue.

Foreign Metals. To the residue obtained in the test for nonvolatile matter add 1 ml. of hydrochloric acid and evaporate to dryness on the steam bath. Add 10 ml. of 10% ammonium acetate solution to the residue, cover the crucible, and heat for 30 minutes on the steam bath. Filter and wash with 20 ml. of water. Add to the filtrate 2 ml. of *N* hydrochloric acid and 10 ml. of hydrogen sulfide water. Any darkening produced is not greater than is produced in a blank made with a quantity of lead nitrate corresponding to 0.02 mg. of Pb.

Mercurous Mercury. Add 5 ml. of 0.1 *N* iodine to the solution obtained in the test for solution in potassium iodide, and follow with 3 ml. of *N* hydrochloric acid. Allow to stand in a dark place for one hour, agitating every 15 minutes; then titrate the excess of iodine with 0.1 *N* sodium thiosulfate, adding starch solution toward the end. Not more than 0.5 ml. of the 0.1 *N* iodine should have been consumed, correction being made for a blank.

Soluble Mercury Salts. Shake 1 gram of the sample with 20 ml. of water for 2 minutes, and filter. Dilute 10 ml. of the filtrate to 30 ml. with water and add 10 ml. of hydrogen sulfide water.

The color produced is not darker than that which is produced by the addition of 10 ml. of hydrogen sulfide water to a solution containing 0.34 mg. of mercuric chloride in 40 ml. of water.

Mercuric Oxide, Red (HgO)

REQUIREMENTS

Insoluble in Hydrochloric Acid. Not more than 0.030%.
Nonvolatile Matter. Not more than 0.025%.
Chloride (Cl). Not more than 0.025%.
Sulfate (SO_4). Not more than 0.020%.
Total Nitrogen (N). Not more than 0.005%.
Iron. Not more than 0.005%.

TESTS

Insoluble in Hydrochloric Acid. Dissolve 3 grams in 30 ml. of dilute hydrochloric acid (1 + 3) and heat on the steam bath for 1 hour. Filter through a tared filtering crucible, wash well with water, and dry at 105–110° C. The weight of the insoluble residue should not exceed 0.0009 gram.

Nonvolatile Matter. Ignite 4 grams in a weighed porcelain dish in a well-ventilated hood, cool, and weigh. The weight of the residue should not exceed 0.0010 gram. Save the residue for the determination of iron.

Chloride. Dissolve 1 gram in 50 ml. of water and 1 ml. of formic acid. Add, dropwise, a 10% solution of sodium hydroxide until a small amount of permanent precipitate is formed. Digest under a reflux condenser until all the mercury is reduced to metal and the solution is clear. Cool, filter through a paper that has been washed free of chlorides, and dilute to 100 ml. Dilute 20 ml. of this solution to a total volume of 50 ml. containing 1 ml. of nitric acid and 1 ml. of 0.1 *N* silver nitrate. Any turbidity should not be more than that in an equal volume of solution containing 0.05 mg. of chloride and the quantities of reagents used in the test.

Solution A. Dissolve 5 grams in 50 ml. of water and 3 ml. of formic acid. Digest under a reflux condenser until all the mercury is reduced to metal and the supernatant liquid is clear. Cool, filter through a well-washed paper, and dilute to 100 ml.

Sulfate. To 10 ml. of solution A add 0.01 gram of sodium carbonate and evaporate to dryness. Dissolve the residue in 10 ml. of water and add 1 ml. of 1 *N* hydrochloric acid. Filter if necessary and add 1 ml. of a 10% solution of barium chloride. Any turbidity should not be more than that produced in a solution containing 0.10 mg. of sulfate, 0.6 ml. of formic acid, and 0.01 gram of sodium carbonate treated in the same way as the solution of the sample.

Total Nitrogen. Dilute 10 ml. of solution A to 55 ml. in a flask suitable for an ammonia distillation, and add 15 ml. of a 10% solution of sodium hydroxide and 1 gram of aluminum wire or small chips. Connect the flask through a spray trap to a condenser, the tip of which dips below the surface of 10 ml. of 0.1 *N* hydrochloric acid. Distill over 35 ml. and add 5 ml. of a 10% solution of sodium hydroxide and 2 ml. of Nessler's solution. Any color produced should not be greater than that produced in a solution containing 0.030 mg. of ammonia and 0.30 ml. of formic acid treated in the same way as the solution of the sample.

Iron. Dissolve the residue from the test for nonvolatile matter by warming with 9 ml. of hydrochloric acid and dilute to 200 ml. To 50 ml. of this solution add a few crystals of ammonium persulfate (30 to 50 mg.) and 3 ml. of a 30% solution of ammonium thiocyanate. Any red color should not be more than that produced by 0.05 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Methyl Orange (Sodium *p*-Dimethylaminoazobenzenesulfonate)

REQUIREMENTS

Insoluble Matter. To pass test.
Range of pH. 3.0 to 4.6.
Sensitiveness. To pass test.

TESTS

Insoluble Matter. Dissolve 0.1 gram in 100 ml. of water. The resulting solution should be free of turbidity or insoluble residue.

Range of pH. Add 0.10 ml. of the solution obtained in the test for insoluble matter to each of three buffer solutions, prepared as follows: Solution A (pH 3.0), 25 ml. of 0.2 *N* potassium acid phthalate and 10.20 ml. of 0.2 *N* hydrochloric acid diluted to 100 ml. Solution B (pH 3.8), 25.00 ml. of 0.2 *N* potassium acid phthalate and 1.32 ml. of 0.2 *N* hydrochloric acid diluted to 100 ml. Solution C (pH 4.6), 25.00 ml. of 0.2 *N* potassium acid phthalate and 6.00 ml. of 0.2 *N* sodium hydroxide diluted to 100 ml. Solution A should be red, solution B orange (yellowish red), and solution C yellow.

Sensitiveness. Add 0.1 ml. of the solution obtained in the test for insoluble matter to 100 ml. of water. The yellow color should be changed to reddish by the addition of not more than 0.1 ml. of 0.1 *N* acid.

Methyl Red (*p*-Dimethylaminoazobenzene-*o*-carboxylic acid)

REQUIREMENTS

Insoluble Matter. To pass test.
Range of pH. 4.2 to 6.2.
Sensitiveness. To pass test.

TESTS

Insoluble Matter. Dissolve 0.1 gram in 100 ml. of 95% alcohol. The resulting solution should be free of turbidity or insoluble matter.

Range of pH. Add 0.10 ml. of the solution obtained in the test for insoluble matter to each of three buffer solutions prepared as follows: Solution A (pH 4.2), 25 ml. of 0.2 *N* potassium acid phthalate and 1.82 ml. of 0.2 *N* sodium hydroxide diluted to 100 ml. Solution B (pH 5.2), 25 ml. of 0.2 *N* potassium acid phthalate and 14.88 ml. of 0.2 *N* sodium hydroxide diluted to 1 ml. Solution C (pH 6.2), 25 ml. of 0.2 *M* potassium dihydrogen phosphate and 4.28 ml. of 0.2 *N* sodium hydroxide diluted to 100 ml. Solution A should be red, solution B orange (yellowish red), and solution C yellow.

Sensitiveness. Add 0.1 ml. of the solution obtained in the test for insoluble matter to 100 ml. of carbon dioxide–free water. A yellow color should be produced which is changed to reddish by the addition of not more than 0.05 ml. of 0.02 *N* acid.

Nitric Acid, Fuming (Specific Gravity Approximately 1.5) (HNO_3)

REQUIREMENTS

Assay. Not less than 90% HNO_3.
Dilution Test. To pass test.
Nonvolatile Matter. Not more than 0.002%.
Dissolved Oxides. To pass test (limit about 0.010% as N_2O_3).
Chloride. Not more than 0.0005%.
Sulfate. Not more than 0.0005%.
Arsenic. Not more than 0.00003%.
Heavy Metals. To pass test (limit about 0.0005% as lead).
Iron. Not more than 0.0002%.

TESTS

Assay. Tare a small glass-stoppered Erlenmeyer flask, containing about 15 ml. of water. Quickly introduce about 2 ml. of the sample, stopper, cool, and weigh. Dilute with 40 ml. of water and titrate with 1 *N* sodium hydroxide solution, using methyl orange indicator. One milliliter of 1 *N* sodium hydroxide corresponds to 0.06302 gram of HNO_3.

Dilution Test. Pour 1 volume of acid into 3 volumes of water. No turbidity or precipitate should be observed within 1 hour.

Nonvolatile Matter. To 33 ml. add 0.10 ml. of sulfuric acid, evaporate to dryness in a platinum dish, ignite at cherry redness for 5 minutes, cool, and weigh. The weight of the residue should not exceed 0.0010 gram.

Dissolved Oxides. Add 10 grams of the sample (6.6 ml.) to 150 ml. of cold water in a casserole. Add 20 ml. of dilute sulfuric acid (1 + 4) and titrate with 0.1 *N* potassium permanganate, rapidly at first, then slowly till the pink color lasts 3 minutes. Not more than 5.0 ml. of the permanganate solution should be required. One milliliter of 0.1 *N* $KMnO_4$ equals 0.0019 gram of N_2O_3.

Chloride. Dilute 2 ml. to 50 ml. and add 1 ml. of a 0.1 *N* solution of silver nitrate. The turbidity should not be greater than that produced by 0.015 mg. of chloride in an equal volume of solution containing 1 ml. of nitric acid and 1 ml. of a 0.1 *N* solution of silver nitrate.

Sulfate. To 7 ml. add 0.01 gram of sodium carbonate and evaporate to dryness. Take up in water, filter if necessary, dilute to 10 ml., and add 1 ml. of *N* hydrochloric acid and 1 ml. of a 10% solution of barium chloride. The turbidity after 10 minutes should not be greater than is obtained in an equal volume of water containing 0.01 gram of sodium carbonate neutralized with hydrochloric acid, 0.05 mg. of sulfate, and the quantities of reagents used in the test.

Arsenic. To 13 ml. in a 150-ml. beaker add 5 ml. of sulfuric acid and evaporate to strong fumes, cool, dilute with water and evaporate to fumes again, repeating this evaporation if necessary to remove all the nitrate. Cool and determine arsenic by the modified Gutzeit method. The stain should not exceed that produced by 0.006 mg. of arsenic.

Heavy Metals. Evaporate 7 ml. to dryness, add 0.05 ml. of acetic acid, dilute to 45 ml., and add 5 ml. of hydrogen sulfide water. The brown color produced should not be more than that produced by 0.05 mg. of lead in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Evaporate 7 ml. to dryness, add 3 ml. of hydrochloric acid, dilute to 50 ml., and add a few crystals of ammonium persulfate (30 to 50 mg.) and 3 ml. of a 30% solution of ammonium thiocyanate. The red color should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Sodium Cobaltinitrite (for Determination of Potassium)

REQUIREMENTS

Insoluble Matter. Not more than 0.02%.
Sensitiveness. To pass test.

TESTS

Insoluble Matter. Dissolve 5 grams in 25 ml. of water, add 1 ml. of acetic acid, and allow to stand overnight. Filter through a tared filtering crucible, wash with cold water, dry at 105° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Sensitiveness. Dissolve 3 grams in 10 ml. of water and add the solution to a mixture of 1 ml. of acetic acid and 5 ml. of water containing 0.5 mg. of potassium (as KCl). A distinct precipitate should be produced in 1 hour.

Sodium Phosphate, Dibasic (Disodium Hydrogen Phosphate), Anhydrous (Suitable for Buffer Solutions) (Na_2HPO_4)

REQUIREMENTS

Insoluble Matter. Not more than 0.010%.
Moisture (loss at 105–110° C.). Not more than 0.3%.
pH of 0.1-molar Solution. 9.1 to 9.2 at 25° C.
Chloride (Cl). Not more than 0.002%.
Nitrogen Compounds (as N). Not more than 0.002%.
Sulfate (SO_4). Not more than 0.010%.
Iron (Fe). Not more than 0.002%.
Heavy Metals (as Pb). To pass test (limit about 0.002%).

TESTS

Insoluble Matter. Dissolve 10 grams in 100 ml. of hot water and allow to stand on the steam bath for 1 hour. Filter through a tared filtering crucible, wash well with hot water, dry at 105–110° C., cool, and weigh. The weight of the residue should not exceed 0.0010 gram.

Moisture. Accurately weigh about 2 grams and dry at 105–110° C. to constant weight. The loss in weight should not exceed 0.3%. Save the material for the determination of pH.

pH of 0.1 Molar Solution. Dissolve 1.42 grams of the previously dried sample and make up to 100 ml., using water with pH of 6.5 to 7.4. The pH determined with a glass electrode should be from 9.1 to 9.2 at 25° C.

Chloride. Dissolve 1 gram in 30 ml. of water, add 3 ml. of nitric acid, dilute to 50 ml., and add 1 ml. of 0.1 *N* silver nitrate solution. The turbidity should not be more than that produced by 0.02 mg. of chloride (Cl) in an equal volume of solution containing the quantities of reagents used in the test.

Nitrogen Compounds. Dissolve 0.5 gram in 60 ml. of water, add 20 ml. of a 10% solution of sodium hydroxide and 0.5 gram of aluminum wire in small pieces; allow to stand for 1 hour protected from absorption or loss of ammonia. Connect the flask through a spray trap to a condenser, the lip of which dips below the surface of 10 ml. of 0.1 *N* hydrochloric acid, and slowly distill 40 ml. To the distillate add 2 ml. of a 10% solution of sodium hydroxide and 2 ml. of Nessler's reagent. Any color produced should not be more than that produced when a solution containing 0.01 mg. of combined nitrogen is treated exactly like the sample, starting with the reduction by aluminum in sodium hydroxide solution.

Sulfate. Dissolve 5 grams in 100 ml. of water, add 7 ml. of hydrochloric acid, and heat to boiling. Filter and reheat the filtrate to boiling. Add 5 ml. of a 10% solution of barium chloride and allow to stand overnight. If a precipitate is formed, filter, wash, ignite, and weigh. The weight should not be more than 0.0012 gram greater than the weight of the ignited precipitate from a blank made with the quantities of reagents used in the test, including filtrations and ignition.

Iron. Dissolve 5.5 grams in water and dilute to 100 ml. Dilute 10 ml. of this solution to 40 ml., and add 1 ml. of ammonium hydroxide and 10 ml. of hydrogen sulfide water. Any color should not be more than is produced by 0.01 mg. of iron in an equal volume of solution containing 1 ml. of the solution of the sample and the quantities of reagents used in the test.

Heavy Metals. Dissolve 2 grams in 40 ml. of water and exactly neutralize the solution with normal sulfuric acid, using 3 drops of phenolphthalein as indicator. Add 15 ml. of 1 *N* sulfuric acid and 5 ml. of hydrogen sulfide water, and dilute to 100 ml. Any brown color which is immediately developed should not be more than is produced by 0.04 mg. of lead in 100 ml. of water on the addition of 15 ml. of 1 *N* sulfuric acid and 5 ml. of hydrogen sulfide water.

Starch, Soluble (for Iodometry)

REQUIREMENTS

Solubility. To pass test.
Neutrality (pH of 2% solution at 25° C.) Between 4.5 and 6.0.
Residue on Ignition. Not more than 0.3%.
Sensitiveness. To pass test.

TESTS

Solubility. Dissolve 2 grams in 100 ml. of hot water. The solution is not more than opalescent, and it remains mobile on cooling.

Neutrality. Determine the pH of the solution obtained in the test for solubility, using a glass electrode. The pH at 25° C. should be more than 4.5 and less than 6.0.

Residue on Ignition. Ignite 1 gram, cool, and weigh. The weight of the ignited residue should not exceed 0.0030 gram.

Sensitiveness. Prepare a paste of 1.0 gram of the sample with a little cold water and add to it with stirring 200 ml. of boiling water. Add 5 ml. of this cooled solution to 100 ml. of water, containing 50 mg. of potassium iodide, and add 0.05 ml. of 0.1 *N* iodine solution. A deep blue color should be produced which will be discharged by 0.05 ml. of 0.1 *N* sodium thiosulfate solution.

Corrections for Published Specifications

Acid, Hydrochloric (*1*)

REQUIREMENT

Iron. Not more than 0.00005%.

TEST

Iron. Evaporate 17 ml. of the acid in porcelain or glass practically to dryness on the steam bath. Add about 40 ml. of water, 1 ml. of the acid and a few small crystals of ammonium persulfate (30 to 50 mg.). Add 3 ml. of a 30% solution of ammonium thiocyanate and make up to 50 ml. Any red color should not be more than is produced by 0.01 mg. of iron in an equal volume of solution containing 1 ml. of the sample and the quantities of persulfate and thiocyanate used in the test.

Acid, Molybdic, Anhydride (*4*). Acid, Molybdic, 85% (*4*)

TEST

Insoluble in Ammonium Hydroxide. Dissolve 10 grams in a mixture of 50 ml. of water and 20 ml. of ammonium hydroxide, digesting on the steam bath for about 2 hours. Filter through asbestos in a Gooch crucible, wash, dry at 105° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Alcohol, Ethyl 95%, and Alcohol, Absolute (*5*)

REQUIREMENT

Alkalinity. Not more than 0.0003% as NH_3.

Ammonium Thiocyanate (*1*)

TEST

Chloride. Dissolve 1 gram in 20 ml. of water in a small flask. Add 10 ml. of dilute sulfuric acid (1 + 4) and 7 ml. of 30% hydrogen peroxide. Concentrate to 20 ml. by boiling *in a well-ventilated hood.* Restore to volume with water and evaporate again.

Repeat till all the cyanide has been volatilized. Cool and dilute to 100 ml. Dilute 10 ml. of this solution to 50 ml., and add 1 ml. of nitric acid and 1 ml. of a 0.1 *N* silver nitrate solution. The turbidity produced should not be more than is produced by 0.02 mg. of chloride in an equal volume of solution containing the quantities of reagents used in the test.

Amyl Alcohol (*2*)

TEST

Substances Darkened by Sulfuric Acid. Cool 10 ml. of the alcohol and 10 ml. of sulfuric acid to 10° C., mix carefully, and shake for 1 minute. The color should not exceed that of a standard prepared by mixing 5 ml. of a 1% solution of cobalt chloride ($CoCl_2.6H_2O$), 0.35 ml. of a 1% solution of potassium dichromate ($K_2Cr_2O_7$), and 15 ml. of water.

Barium Acetate (*9*)

REQUIREMENT

Calcium and Strontium Salts (as sulfates). Not more than 0.15%.

TEST

Calcium and Strontium Salts. Dissolve 2 grams in 15 ml. of hot water, add 10 ml. of hydrochloric acid, and evaporate to dryness. Dissolve the residue in 10 ml. of water, add 10 ml. of hydrochloric acid, and again evaporate to dryness. Dry for 2 hours at 105° C. Powder the residue, transfer to a small glass-stoppered flask, add 20 ml. of absolute alcohol, and allow to stand for 30 minutes with occasional shaking. Filter through a glass filter of fine porosity and wash with two 5-ml. portions of absolute alcohol. To the combined filtrate and washings add 0.1 ml. of sulfuric acid, evaporate to dryness, and ignite. The weight of the residue should not exceed 0.0030 gram.

Barium Carbonate (*3*)

REQUIREMENT

Calcium and Strontium Salts (as sulfates). Not more than 0.50%.

TEST

Calcium and Strontium Salts (as sulfates). Dissolve 2 grams in 20 ml. of water and 3 ml. of hydrochloric acid, evaporate the solution to dryness, and dry the residue at 105° C. for 2 hours. Powder the residue, transfer to a small glass-stoppered flask add 20 ml. of absolute alcohol, and allow to stand 30 minutes with occasional shaking. Filter through a glass filter of fine porosity and wash with two 5-ml. portions of absolute alcohol. To the combined filtrate and washings add 0.1 ml. of sulfuric acid, evaporate to dryness, and ignite. The weight of the ignited residue should not exceed 0.0100 gram.

Barium Chloride (*1*)

REQUIREMENT

Calcium Strontium Salts (as sulfates). Not more than 0.15%.

TEST

Calcium and Strontium Salts (as sulfates). Dry 2 grams at 105° C. for 2 hours, powder the residue, transfer to a small glass-stoppered flask, add 20 ml. of absolute alcohol, and allow to stand 30 minutes with occasional shaking. Filter through a glass filter of fine porosity and wash with two 5-ml. portions of absolute alcohol. To the combined filtrate and washings add 0.1 ml. of sulfuric acid, evaporate to dryness, and ignite. The weight of the ignited residue should not exceed 0.0030 gram.

Barium Nitrate (*4*)

REQUIREMENT

Calcium and Strontium Salts (as sulfates). Not more than 0.15%.

TEST

Calcium and Strontium Salts (as sulfates). Dissolve 2 grams in 15 ml. of hot water, add 10 ml. of hydrochloric acid, and evaporate to dryness. Dissolve the residue in 15 ml. of water, add 10 ml. of hydrochloric acid, and again evaporate to dryness. Dry for 2 hours at 105° C. Powder the residue, transfer to a small glass-stoppered flask, add 20 ml. of absolute alcohol, and allow to stand for 30 minutes with occasional shaking. Filter through a glass filter of fine porosity and wash with two 5-ml. portions of absolute alcohol. To the combined filtrate and washings add 0.1 ml. of sulfuric acid, evaporate to dryness, and ignite. The weight of the ignited residue should not exceed 0.0030 gram.

Cadmium Chloride (*8*)

REQUIREMENTS

Iron. Not more than 0.001%.

Substances Not Precipitated by Hydrogen Sulfide (as sulfates) (change from ammonium sulfide). Not more than 0.2%.

TESTS

Iron. Dissolve 2 grams in 40 ml. of water, and add 5 ml. of hydrochloric acid, a few crystals of ammonium persulfate (30 to 50 mg.) and 3 ml. of a 30% solution of ammonium thiocyanate. Any red color produced should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Substances Not Precipitated by Hydrogen Sulfide. Dissolve 2 grams in 150 ml. of water containing 15 ml. of approximately normal sulfuric acid. Heat to boiling and pass a rapid stream of hydrogen sulfide through the solution as it cools. Filter, take 75 ml. of the clear filtrate, add 5 drops of sulfuric acid, evaporate to dryness, and ignite gently. The weight of the ignited residue should not exceed 0.0020 gram.

Cadmium Sulfate (*9*)

REQUIREMENTS

Iron. Not more than 0.001%.

Substances not Precipitated by Hydrogen Sulfide (as sulfates) (change from ammonium sulfide). Not more than 0.2%.

TESTS

Iron. Dissolve 2 grams in 40 ml. of water, and add 5 ml. of hydrochloric acid, a few crystals of ammonium persulfate (30 to 50 mg.), and 3 ml. of a 30% solution of ammonium thiocyanate. Any red color produced should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Substances Not Precipitated by Hydrogen Sulfide. Dissolve 2 grams in 150 ml. of water containing 15 ml. of approximately normal sulfuric acid. Heat to boiling and pass a rapid stream of hydrogen sulfide through the solution as it cools. Filter, take 75 ml. of the clear filtrate, add 5 drops of sulfuric acid, evaporate to dryness, and ignite gently. The weight of the ignited residue should not exceed 0.0020 grams.

Cuprous Chloride (*7*)

TEST

Assay. Use 30 ml. of the ferric ammonium sulfate solution instead of the 25 ml. prescribed in the original directions for solution of the sample.

Potassium Biphthalate (*11*)

TEST

Assay. The first sentence should read: "Finely pulverize a sample, dry for 1 hour at 105–110° C. and cool in a desiccator containing a good desiccant."

Potassium Bromide (*3*)

TEST

Nitrogen Compounds. Dissolve 1 gram in 60 ml. of water, add 20 ml. of a 10% solution of sodium hydroxide and 0.5 gram of aluminum wire in small pieces, and allow to stand for 1 hour protected from absorption or loss of ammonia. Connect the flask through a spray trap to a condenser, the lip of which dips below the surface of 10 ml. of 0.1 *N* hydrochloric acid, and slowly distill 40 ml. To the distillate add 2 ml. of a 10% solution of sodium hydroxide and 2 ml. of Nessler's reagent. Any color produced should not be more than that produced when a solution containing 0.01 mg. of combined nitrogen is treated exactly like the sample, starting with sodium hydroxide and aluminum.

Potassium Carbonate, Anhydrous (*2*)

REQUIREMENT

Silica and Ammonium Hydroxide Precipitate. Not more than 0.010%.

TEST

Silica and Ammonium Hydroxide Precipitate. Dissolve 10 grams in 100 ml. of water. Cautiously add 12 ml. of sulfuric acid to 12 ml. of water, cool, add the mixture to the solution of the sample, and evaporate to strong fuming. Cool, dissolve the residue in 130 ml. of hot water, and add ammonium hydroxide until the solution is just alkaline to methyl red. Heat to boiling and filter, reserving the filtrate for the calcium and magnesium test. Wash with hot water, rejecting the washings, ignite, and weigh the precipitate. The weight of the ignited precipitate should not exceed 0.0010 gram. The precipitate includes some, but not all, of the silica in the sample.

Potassium Hydroxide (*1*)

TEST

Silica and Ammonium Hydroxide Precipitate. Weigh about 10 grams and dissolve in about 100 ml. of water. Cautiously add 12 ml. of sulfuric acid to 12 ml. of water, cool, add the mixture to the solution of the sample, and evaporate to strong fuming. Cool, dissolve the residue in 130 ml. of hot water, and add ammonium hydroxide until the solution is just alkaline to methyl red. Heat to boiling, filter, wash with hot water, and ignite. The weight of the ignited precipitate should correspond to not more than 0.020% of the weight of the sample. The precipitate includes some, but not all, of the silica in the sample.

Potassium Sulfate (*2*)

TEST

Nitrogen Compounds. The standard for comparison should be prepared by starting with a quantity of ammonium chloride corresponding to 0.015 mg. of nitrogen, to be treated with sodium hydroxide and aluminum in a volume of 45 ml. exactly as the sample is treated.

Silver Nitrate (*1*)

TEST

Free Acid. Dissolve 5 grams in 50 ml. of water, add 5 drops of bromocresol green (0.04%), and mix well. The solution should be colored blue, not green or yellow.

Sodium Carbonate, Anhydrous (*2*)

TEST

Ammonium Hydroxide Precipitate. Dissolve 10 grams in 100 ml. of water. Cautiously add 15 ml. of sulfuric acid to 15 ml. of water, cool, add the mixture to the solution of the sample, and evaporate to strong fuming. Cool, dissolve the residue in 130 ml. of hot water, and add ammonium hydroxide until the solution is just alkaline to methyl red. Heat to boiling and filter, reserving the filtrate for the calcium and magnesium test. Wash with hot water, rejecting the washings, ignite, and weigh the precipitate. The weight of the ignited precipitate should not exceed 0.0010 gram. The precipitate includes some, but not all, of the silica in the sample.

Sodium Hydroxide (*1*)

TEST

Silica and Ammonium Hydroxide Precipitate. Weigh about 10 grams and dissolve in about 100 ml. of water. Cautiously add 15 ml. of sulfuric acid to 15 ml. of water, cool, add the mixture to the solution of the sample, and evaporate to strong fuming. Cool, dissolve the residue in 130 ml. of hot water, and add ammonium hydroxide until the solution is just alkaline to methyl red. Heat to boiling, filter, and ignite. The weight of the ignited precipitate should correspond to not more than 0.020% of the weight of the sample. The precipitate includes some, but not all, of the silica in the sample.

Sodium Oxalate (*1*)

REQUIREMENT

Neutrality. To pass test.

TEST

Neutrality. *Dissolve 2 grams in 200 ml. of water, and add* 10.00 ml. of 0.01 *N* oxalic acid and 0.20 ml. of a 1% solution of phenolphthalein. Boil the solution in a flask of resistant glass for 10 minutes, passing through it a stream of air free from carbon dioxide. Cool the solution rapidly to room temperature while keeping the flow of carbon dioxide–free air passing through it. Not less than 9.2 nor more than 10.5 ml. of 0.01 *N* sodium hydroxide should be required to match the pink color of a buffer solution containing 0.20 ml. of a 1% solution of phenolphthalein. The buffer solution contains in 1 liter 3.1 grams of boric acid (H_3BO_3), 3.8 grams of potassium chloride, and 5.90 ml. of *N* sodium hydroxide.

Sodium Tungstate (*12*)

TEST

Chloride. Dissolve 1 gram in 20 ml. of water, add 3 ml. of phosphoric acid, mix well, add 3 ml. of nitric acid, and dilute to 50 ml. Dilute 10 ml. of this solution to 50 ml. and add 1 ml. of a 0.1 *N* solution of silver nitrate. The turbidity should not be more than is produced by 0.02 mg. of chloride in an equal volume of solution containing the quantities of reagents used in the test.

Zinc Chloride (*5*)

REQUIREMENTS

Iron. To pass test (limit about 0.001%).
Lead. Not more than 0.005%.

TESTS

Ammonia. Dissolve 1 gram in 50 ml. of water, pour 10 ml. into 25 ml. of a 10% solution of sodium hydroxide, dilute to 50 ml., and add 2 ml. of Nessler's solution. Any color produced should not be more than is produced by 0.01 mg. of NH_3 in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Dissolve 2 grams in 45 ml. of water, and add 2 ml. of hydrochloric acid, a few crystals of ammonium persulfate (30 to 50 mg.), and 3 ml. of a 30% solution of ammonium thiocyanate. Any red color produced should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Lead. Dissolve 1 gram in 10 ml. of water and a few drops of nitric acid. Add ammonium hydroxide dropwise with constant stirring until a faint but permanent precipitate is produced, clear this turbidity with a few drops of dilute nitric acid (1 + 10), and dilute to 50 ml. Add 10 ml. of this solution to 20 ml. of a 10% solution of sodium cyanide, stirring constantly during the addition. Add 0.2 ml. of a 10% solution of sodium sulfide and transfer to a Nessler tube. The color produced should not be more than is produced by 0.01 mg. of lead in an equal volume of solution containing the quantities of reagents used in the test.

Zinc Oxide (*12*)

REQUIREMENT

Iron. To pass test (limit about 0.001%)

TEST

Iron. Dissolve 1 gram in a mixture of 5 ml. of hydrochloric acid and 5 ml. of water. Dilute to 50 ml., and add a few crystals of ammonium persulfate (30 to 50 mg.) and 3 ml. of a 30% solution of ammonium thiocyanate. Any red color should not be greater than that produced by 0.01 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Zinc Sulfate (*7*)

REQUIREMENTS

Arsenic. Not more than 0.0001%.
Iron. To pass test (limit about 0.001%).

TESTS

Ammonia. Dissolve 1 gram in 25 ml. of water, pour into 25 ml. of a 10% solution of sodium hydroxide, and add 2 ml. of Nessler's solution. Any color produced should not be more than is produced by 0.01 mg. of NH_3 in an equal volume of solution containing the quantities of reagents used in the test.

Arsenic. Test 1 gram by the Gutzeit method.

Iron. Dissolve 2 grams in 45 ml. of water, and add 2 ml. of hydrochloric acid, a few crystals of ammonium persulfate (30 to 50 mg.), and 3 ml. of a 30% solution of ammonium thiocyanate. Any red color produced should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Specifications Previously Published

(1) Committee on Analytical Reagents, *Ind. Eng. Chem.*, 17, 756 (1925).
(2) *Ibid.*, 18, 636, 759 (1926).
(3) *Ibid.*, 19, 645 (1927).
(4) *Ibid.*, 19, 1369 (1927).
(5) *Ibid.*, 20, 979 (1928).
(6) Ind. Eng. Chem., Anal. Ed., 1, 171 (1929).
(7) *Ibid.*, 2, 351 (1930).
(8) *Ibid.*, 3, 221 (1931).
(9) *Ibid.*, 4, 154 (1932).
(10) *Ibid.*, 4, 347 (1932).
(11) *Ibid.*, 5, 289 (1933).
(12) *Ibid.*, 12, 631 (1940).
(13) *Ibid.*, 16, 281 (1944).

Presented in connection with the report of the Committee on Analytica Reagents at the 109th Meeting of the American Chemical Society, Atlantic City, N. J.

NOTES ON ANALYTICAL PROCEDURES . . .

Preparation of Holocellulose from Nonwoody Plant Material

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HOLOCELLULOSE or "skelettsubstanz" represents the entire carbohydrate fraction of extracted plant material in a single unit. The need for such a fraction as a source material for research on cell-wall constituents and need for such a product in furthering a similar type of research on economic plants of less woody nature have long been recognized by wood chemists who have succeeded in making it a reality for wood (*2*, *3*, *5*, *6*). The object of this investigation was to determine the adaptability of methods now in use for wood to some other plants.

Plant material is usually prepared for the extraction of hemicelluloses (*1*) by a laborious procedure requiring several days and yielding an unsatisfactory product. The method reported here yields a product known as holocellulose which is almost snow white, substantially free of lignin, contains nearly all the hemicelluloses, and can be obtained in a few hours. Such a material will obviously be of value in cell-wall research. In order to test the efficiency of established procedures, the percentage of furfural retained by the holocellulose and the color of the product were used as indexes, a nearly white color being desirable. Since the nitrogen content of grasses is higher than that of wood, the amount of nitrogen retained in this fraction was determined.

EXPERIMENTAL

One should become familiar with the toxic nature of sodium chloride before using it (*4*), and should perform all work under the hood. The material used and the determinations made are indicated in Table I.

Material passing a 25-mesh screen but retained by the 50-mesh screen was used in all cases. Holocellulose was determined substantially as outlined by Wise, Murphy, and D'Addieco (*6*). To 4 grams of plant material in a 250-ml. beaker, 1.2 grams of sodium chlorite, 8 drops of concentrated acetic acid, and 125 ml. of distilled water were added and stirred until the chlorite dissolved. The beaker was then covered with a watch glass and placed on a steam bath at 80° C. for 1 hour with occasional stirring. The same amounts of reagents were added to the beaker every hour for 2 more hours, making a total digestion period of 3 hours. The beaker and contents were cooled to 10° C. in ice water, then filtered through a coarse grade Selas crucible. The material was now nearly completely white and contained only a trace of lignin. The residue was washed six times with ice water and partially dried over calcium chloride in a vacuum desiccator. Final drying was completed in an oven at 105° C. The pH of the initial and final suspension was approximately 4.3 at 25° C. Samples of holocellulose which were to be subjected to a furfural determination were filtered through poplin cloth folded as a filter paper. The dry material was removed from the cloth for analysis.

The original or control material was extracted with a solution of alcohol-benzene for 6 hours, then with ether for 1 hour. Furfural was determined by the phloroglucinol method. Total nitrogen was determined by the conventional Kjeldahl method.

The results of the investigation are shown in Table I as the holocellulose appears to retain a substantial content of ash, which was not removed by the treatment, weights of holocellulose were corrected accordingly. The holocellulose fraction in these cases was not all carbohydrate but contained a relatively high percentage of the original nitrogen of the plant material.

Table I. Percentage Content of Holocellulose in Plant Materials and Furfural and Total Nitrogen Retained by Holocellulose

Ash and moisture-free basis

Analyses	Kentucky Blue Grass	Corn-cobs	Oat Straw	Timothy Hay	Corn-stalks
	%	%	%	%	%
Holocellulose[a]	73.7	78.9	80.6	75.1	78.6
Furfural					
Original[b]	13.36	13.50	13.11	12.23	13.21
Holocellulose[c]	12.89	12.82	12.78	11.83	13.09
% recovery	96.5	95.0	97.5	96.7	99.1
Total nitrogen					
Original	2.44	0.34	1.55	1.34	1.14
Holocellulose	1.36	0.11	0.68	0.71	0.37
% retained	55.7	32.4	43.9	53.0	32.5

[a] Average deviation for these determinations was ±0.7%.
[b, c] Average of five or six determinations; other determinations were made in duplicate or triplicate.

CONCLUSIONS

The sodium chlorite method used for the preparation of holocellulose from wood may be adapted for the same use with nonwoody tissue. The older preliminary procedure for this kind of plant tissue involves 2 to 3 days' time, while the one described here seems to yield a product of satisfactory color and furfural content in 2 to 3 hours. However, when the product is obtained in the manner described, from 30 to 50% of the original nitrogen of the plant material may also be included.

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(5) Wise, L. E., Ind. Eng. Chem., Anal. Ed., 17, 63 (1945).
(6) Wise, L. E., Murphy, Maxine, and D'Addieco, A. A., *Paper Trade J.*, 122, No. 2, 35 (1946).

Contribution 608, Massachusetts Agricultural Experiment Station.

AIDS FOR THE ANALYST.....

Liquid Separator for Use under Vacuum.

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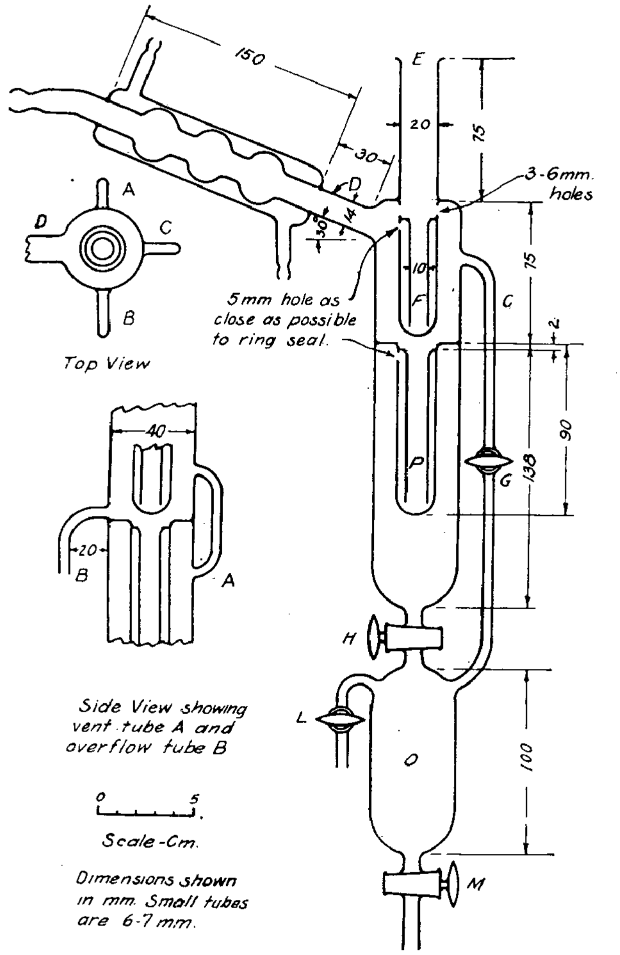
A STANDARD method for removing water from various materials and reaction mixtures is to add a liquid such as toluene which is immiscible with water, boil the mixture, condense the vapors, and separate the condensed liquids. In many cases (Gilman, "Organic Syntheses", Vol. 1, p. 412, New York, John Wiley & Sons, 1932) the organic liquid is returned to the boiling vessel, while the water is collected or discarded.

In some cases, as in the drying of a nitrocellulose mixture, it is desirable to carry out this boiling under vacuum in order to keep the temperature as low as possible. Under these conditions, when toluene is used, the separation is frequently rather slow, because of the formation of very fine droplets of the toluene in the water. The collection of the water under vacuum offers difficulty, particularly if comparatively large amounts are to be collected.



The illustration shows an all-glass apparatus which promotes complete separation of the water and toluene. It makes it possible to return the toluene to the extraction vessel and to collect the water and remove it from time to time.

The tip of the condenser from the boiling vessel or drying chamber is inserted in the top of the collecting device at *E*. The vacuum connection is made at the end of the outlet tube, *D*. The small condenser on *D* is useful in effecting the final condensation of the vapors, so that the vapor loss is as small as possible.

Stopcocks *G* and *H* are opened and *L* and *M* closed until it is necessary to remove the water which has collected. The collected water may be removed without interrupting the boiling process by closing *G* and *H*, opening *L*, and drawing off the water through *M*.

The vacuum may be re-established by closing *L* and *M*, opening *G* slowly, and allowing the water which has collected to flow into *O* by opening *H*.

The condensed liquids drop through the neck at *E* into the separation chamber, *F*, where the toluene and water have time to effect a fairly good separation. Better separation is brought about by dividing the separation chamber in two parts, *F* and *P*, than by using one longer chamber; this may be due to the fact that the liquids have to travel over the glass surface of *F* and a better separation is realized.

The return of the toluene to the boiling chamber is accomplished by connecting a return line to *B*. If continuous extraction is not desired, *B* may be connected to a receiving flask which is connected to the same vacuum line as is *D*.

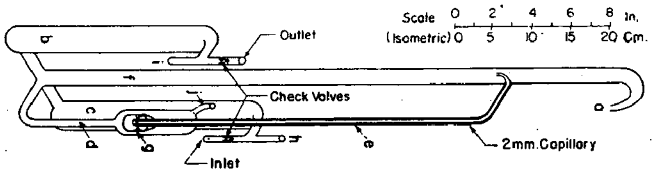
The dimensions shown have been found useful for toluene-water mixtures. Other liquids lighter than water may also be used. The apparatus may be used with liquid heavier than water if intermittent operation is used or if the heavy liquid is to be collected.

Glass Circulating Pump for Gases and Liquids.

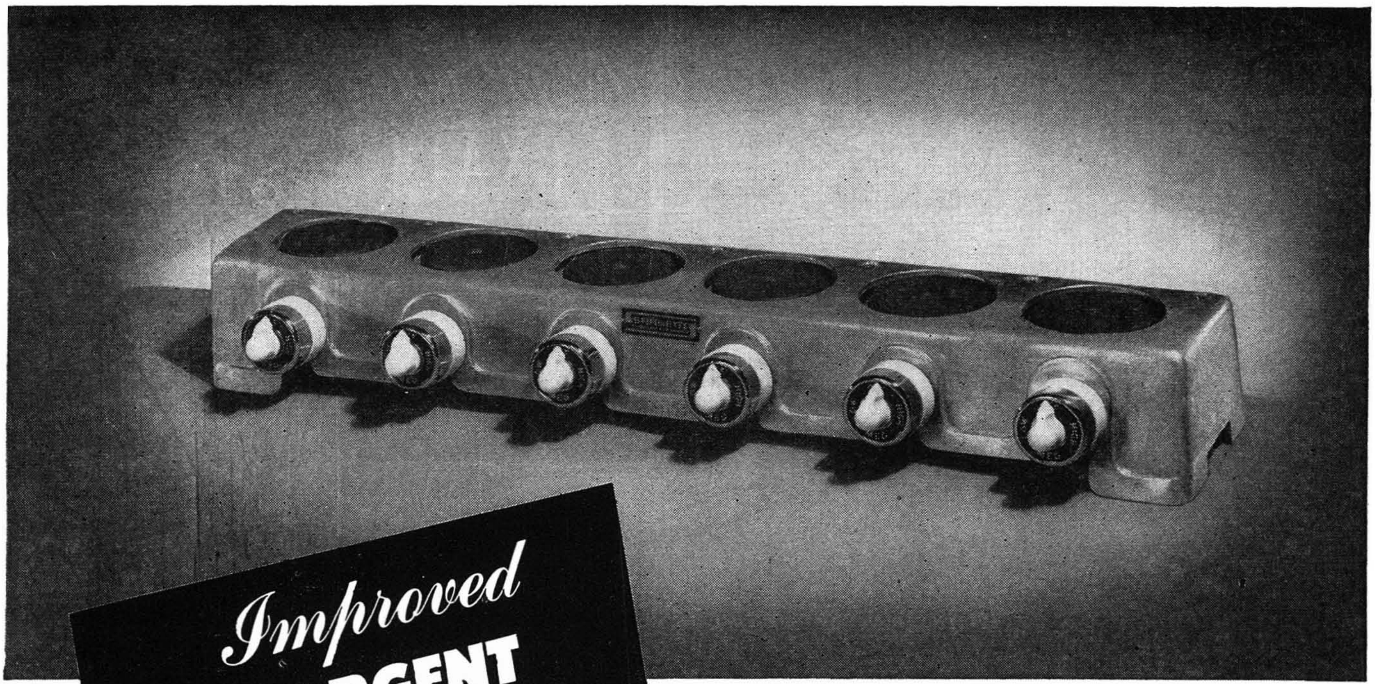
J. E. Nickels, Koppers Co., Inc., Multiple Fellowship on Tar Synthetics, Mellon Institute, Pittsburgh, Pa.

A VACUUM-operated glass pump for the circulation of gases in a closed system described by Kester [Kester, E. B., IND. ENG. CHEM., ANAL. ED., 4, 298 (1932)] finds a variety of laboratory applications. In many instances, however, the intermittent flow obtained with this pump is undesirable. To overcome this disadvantage, a modified pump has been developed that gives a nearly continuous flow and is suitable for pumping either gases or liquids. The improved design employs two mercury pistons instead of one and is more compact than the Kester device in that the pump and valves are incorporated in a single unit.

Application of vacuum at *a* causes the mercury level to fall in *b*, *c*, and *d*, and to rise in *e* and *f* until the level in cup *g* falls below the lower end of the tube *e*. As *g* becomes empty, atmospheric pressure forces the mercury from *e* into *f* and air rushes in through *e* to fill the evacuated space, thus causing the mercury to fall in *f* and rise in *b*, *c*, and *d* until it again overflows into *g*. The cycle then repeats itself. On connecting *h* and *i* to the inlet and outlet of the system through which the gas or liquid is to be circulated, there is a flow of the pumped medium through the system during both the rising and falling of mercury in pistons *b* and *c*. As a result, the flow is almost continuous, being interrupted only momentarily during each half-cycle.



The construction of the pump may be altered to enable operation by compressed air, by extending *d* below *g* far enough to maintain a mercury seal between *d* and *f*, upon applying air pressure at *j*. By modifying dimensions or rate of application of vacuum or compressed air, the pump can be made to operate over a wide range of pumping rates.



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The improved Sargent hot plate consists of a heavy cast aluminum base equipped with six solid disc heaters individually controlled by separate switches (three heat). The heaters are mounted on porcelain spools and have no direct contact with the base, thus, cool, safe, manipulation of the switches is assured. The perforated bottom baffle plate acts as a heat reflector and eliminates scorching under the hot plate. The top of the new improved Sargent hot plate is tapped to accommodate seven support rods (3/8-16), used with the crude fiber and soxhlet assemblies.

Overall dimentions: length 28½", width 5¾", height 4".

S-41315—Hot plate, Sargent, electric, for 115 volt AC/DC circuits, each **85.00**

S-41325—Ditto, but for 230 volt AC/DC circuits.... **85.00**

When used with the Crude Fiber Assembly, pictured below, seven stainless chrome steel rods are screwed into the top of the hot plate, to form uprights for the water connector clamps and the condenser support clamps. Each position in the assembly is individually controlled by a three heat switch so that any number of determinations, up to six, can be carried on simultaneously, or progressively.

The glassware for the crude fiber set-up consists of six, 600 ml, high form, Pyrex beakers without pourout, and six Sargent reflexed hemisphere condensers, designed to minimize "foaming" by causing the condensation to flow down the sides of the beaker instead of dropping directly into the refluxing mixture. The beakers may be removed from, or replaced on, the hot plate, without disturbing the condenser system.

S-31870—Crude Fiber Assembly, 6 place, electric, Sargent, 115 volt AC/DC, consisting of one S-41315 Hot Plate. Seven Rods ½" x 27" with 3/8" thread, of stainless chrome steel. Six S-4705 Beakers, high form, without pourout, Pyrex, 600 ml. Six Condensers, Sargent, reflexed hemisphere. Two Clamps, water connector. Five Clamps, condenser support. Rubber tubing........ **125.00**

S-31871—Ditto, but with S-41325 hot plate for 230 volt AC/DC circuits **125.00**

For Soxhlet Assemblies 12 new type, rubber covered spring clamps are provided, which permit easy one hand vertical adjustment of the condensers and extractors and yet insure a firm grip at all times.

S-31765—Extraction Assembly, 6 place, electric, for medium and large Soxhlet assemblies, 115 volt AC/DC circuits, consisting of, one S-41315 hot plate, seven rods ½" x 27" with 3/8" thread, of stainless chrome steel, 12 clamps, new type, Sargent, spring, rubber covered, for medium and large Soxhlet assemblies. Less glassware........ **120.00**

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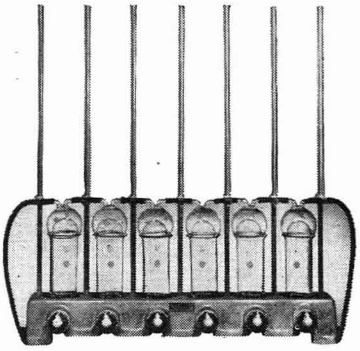
S-31767—Ditto, but with clamps for small Soxhlet assemblies 115 volt AC/DC........ **120.00**

S-31768—Ditto, but with clamps for small Soxhlet assemblies 230 volt AC/DC........ **120.00**



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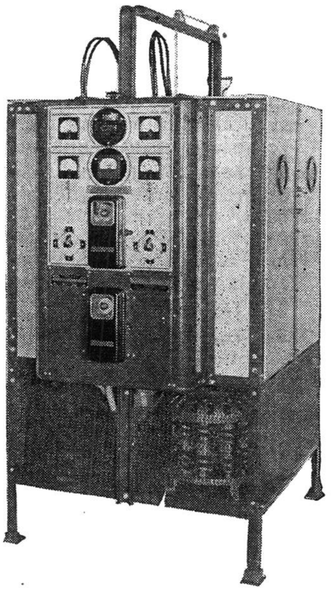

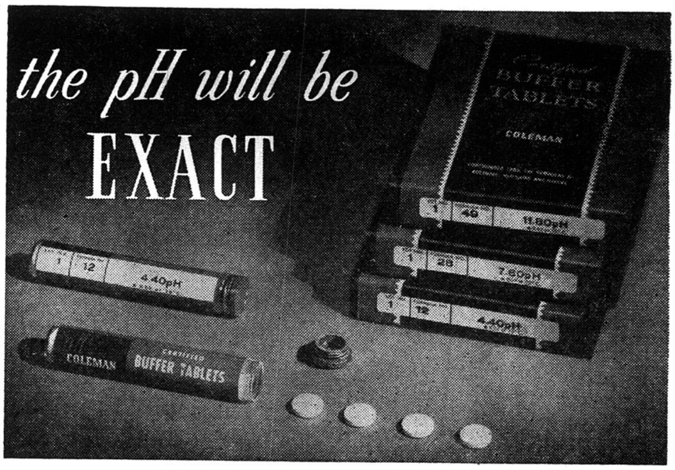
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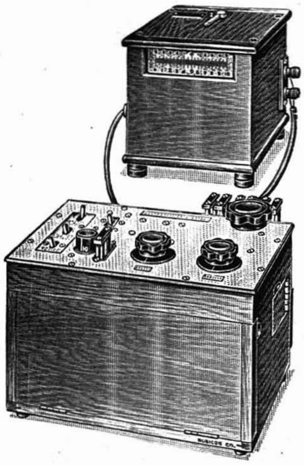

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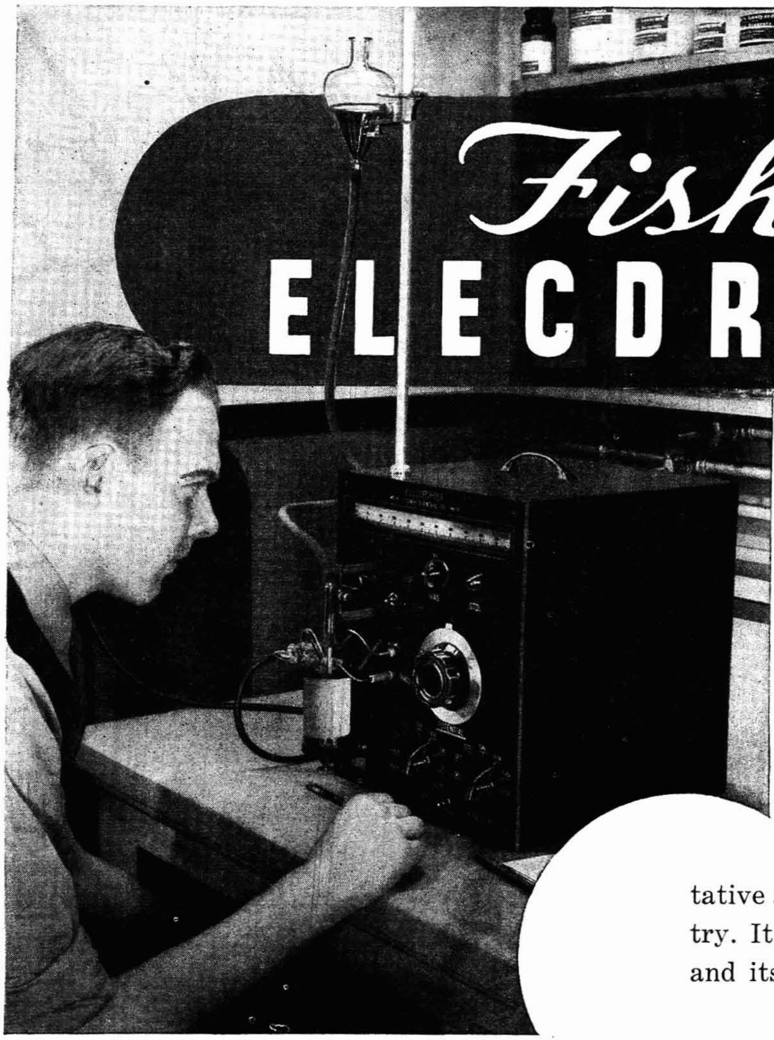

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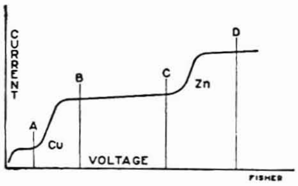

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INSTRUMENTATION

A fast bolometer, tuned amplifier, and light-chopper provide the means for an infrared spectrophotometer: another aid for the analyst

by Ralph H. Müller

A RECORDING infrared spectrometer is a useful instrument in the analytical laboratory for the purposes of identification nd establishing criteria of purity. Its value is greatly enhanced hen it can be extended to the quantitative stage wherein true pectrophotometric data can be recorded. For this purpose, a recording analytical infrared spectrophotometer is now offered by Baird Associates, University Road, Cambridge, Mass. This instrument is designed for the analysis of gases, liquids, and solids, and records absorption curves directly over the range of 2 to 16 microns when an NaCl prism is used. The entire spectrum is recorded in 12 minutes and, on the record, 1% absorption corresponds to 0.05 inch and a wave-length interval of 1 micron to 1.25 inches. The precision in absorption is ±0.01 micron.

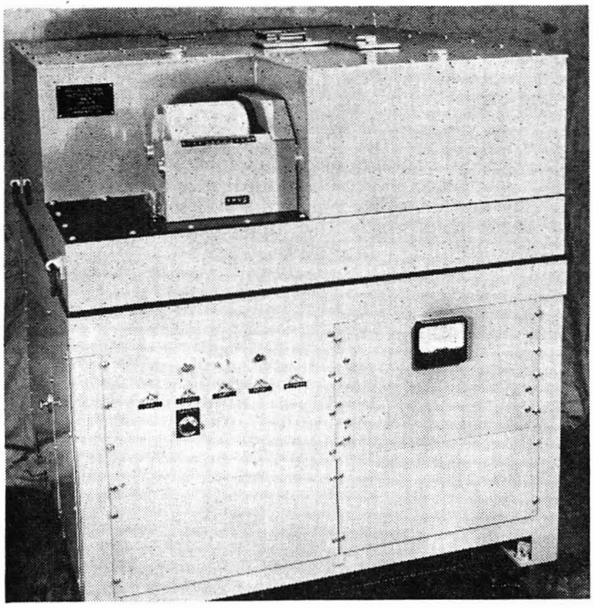

Figure 1

A general view of the instrument is shown in Figure 1. The essential controls are few in number and support the contention that the instrument is operable by laboratory technicians. The disposition of the various units in this view is readily apparent on comparison with the schematic diagram of Figure 2. Two beams from a carefully shielded Globar unit, mounted in a water-cooled housing, are focused by concave mirrors onto the entrance slit of the spectrometer along symmetrical optical paths. The absorption cell is placed in one beam and a compensating cell in the other. The spectrometer slit is illuminated alternately by the two beams by the 10-cycle rotating interrupter.

The spectrometer is of the Littrow type with a 60° rock salt prism of 10-cm. base and 8-cm. height. The bilateral slit in the collimating system is cam-controlled, varying in width from 0.1 to 2.0 mm. The collimating mirror is spherical concave, front surface aluminized of 75-cm. focal length mounted 4° off axis. The same mirror refocuses the radiation from the prism onto the bilateral exit slit and the emergent radiation is focused on the bolometer in the form of a reduced image of the exit slit. Two cams control the width of entrance and exit slits and the change in wave length is achieved by rotation of the Littrow mirror.

The bolometer, or receiving element, is a platinum ribbon approximately 7 mm. long, 0.5 mm. wide, and 0.05 micron thick. The ribbon is coated with evaporated "gold black" by the Pfund technique. The resistance of the bolometer is about 8 ohms and the sensitivity is 1 to 2 volts R.M.S. per watt of incident radiation under a "chopping" rate of 10 c.p.s. The noise level when measured at 10 c.p.s. with an amplifier of 5 c.p.s. band width is about 5 × 10^{-9} volt, and drops to about one fifth of this value

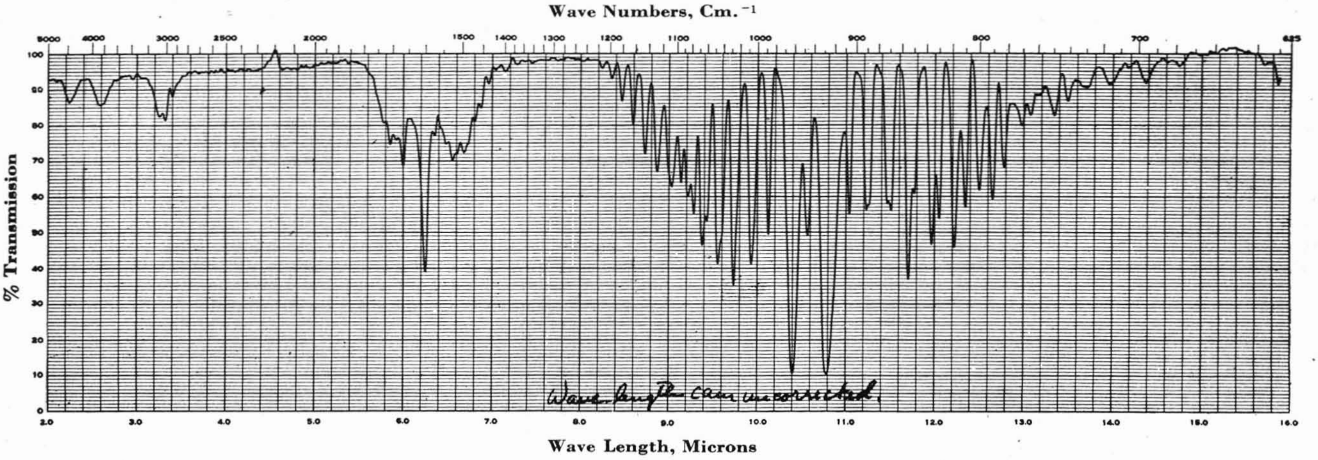

Figure 4

INSTRUMENTATION

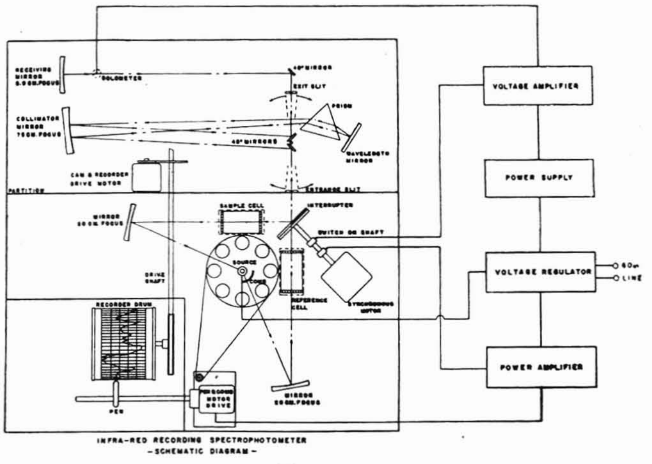

Figure 2

when no bolometer current is passing. Provision is made for evacuating the bolometer case by means of a mechanical oil pump to a pressure between 0.01 and 0.1 mm. of mercury. The sensitivity is improved and "gas microphonics" or "swish" is greatly reduced. Figure 3 illustrates the bolometer assembly.

The recording drum rotates synchronously with the rotation of the wave-length mirror. The amplified bolometer signal drives a comb-shaped diaphragm near the Globar source in such a way that it trims the reference beam until it is equal to the sample beam. The motion of the comb is coupled to the pen drive which records the transmission of the sample cell.

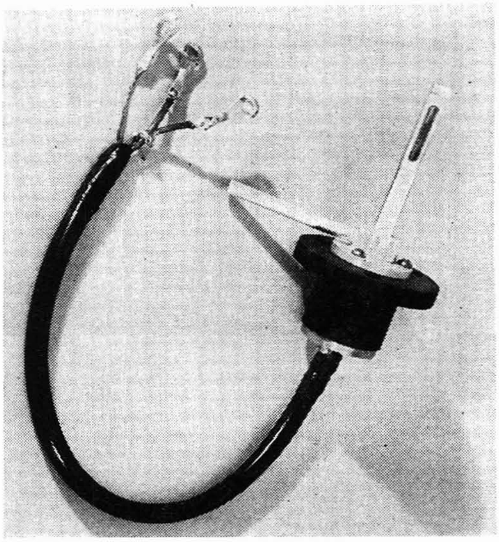

Figure 3. High-Speed Bolometer

Two amplifiers are provided. The first, a voltage amplifier, is a four-stage resistance coupled circuit tuned to 10 c.p.s. It has a gain of about 5 × 10^7 and an inherent noise level of 5 × 10^{-9} volt, the same order of magnitude as the bolometer noise. At one half of maximum gain the band pass is about 5 c.p.s. A three-stage direct current power amplifier furnishes power for the 60 c.p.s. output of the voltage amplifier after rectification by the commutator of the light beam interrupter. This amplifier has an effective gain of approximately 50 and a noise level of less than 0.3 volt.

The entire instrument measures 43 inches × 43 inches × 51 inches and weighs 300 pounds. The only utilities required are a source of 110-volt alternating current 60-cycle, single-phase and a water supply through 0.25-inch PT.

A typical record taken with this instrument is shown in Figure 4. The chart is 5 by 17.5 inches and shows the absorption of NH_3 at 100-mm. pressure in a cell 10 cm. long, recorded from 2 to 16 microns.

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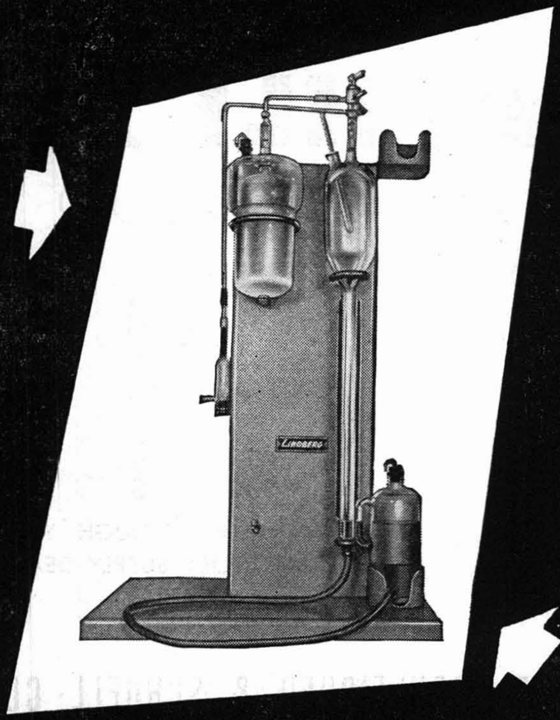

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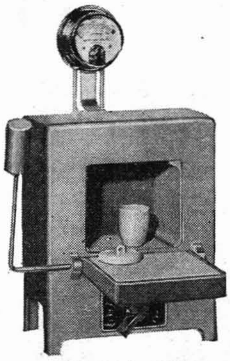


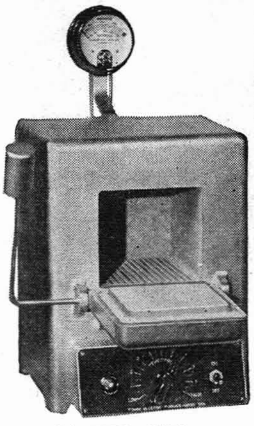
MODEL GTP

Model GTP—Cat. No. 5963—May be operated continuously from 500 to 1500° F. and intermittently to 1850° F. Temperature selected can be held by moving control knob to the desired point.

Muffle unit contains heavy gauge nickel-chromium element embedded in refractory walls assuring uniform temperatures and protection against oxidation. When necessary, entire muffle unit can be quickly removed and replaced.

Body and door are one-piece aluminum castings. Door is counterbalanced and when open serves as a shelf. Furnace weight is 15 ½ lbs. Chamber dimensions are 4″ W. × 3¾″ H. × 3¾″ D. Supplied complete with double-scale pyrometer, cord, switch and plug. Power consumption 1.2 KW.—115 volt, A. C. operation.

Price $57.50



MODEL CEA

Model CEA—Cat. No. 5964—Designed for continuous operation up to 2000° F., "Temcotrol" allows any temperature from 500 to 2000° F. to be selected and maintained.

Embedded heating element is made from special high temperature alloy and protected against damage and deterioration.

Body and door are of cast aluminum and similar to above model in design. Furnace weight is 31 lbs. Chamber dimensions are 4¾″ W. × 4¼″ H. × 6″ D. Supplied complete with double-scale pyrometer, control panel with neon signal light and toggle switch, cord and plug. Power consumption 1.55 KW.—115 volt, A. C. operation.

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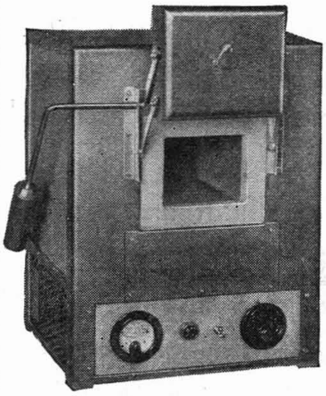

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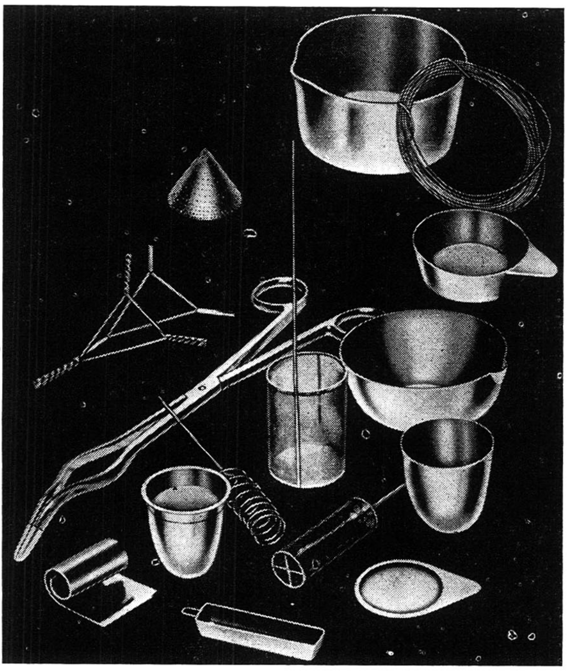

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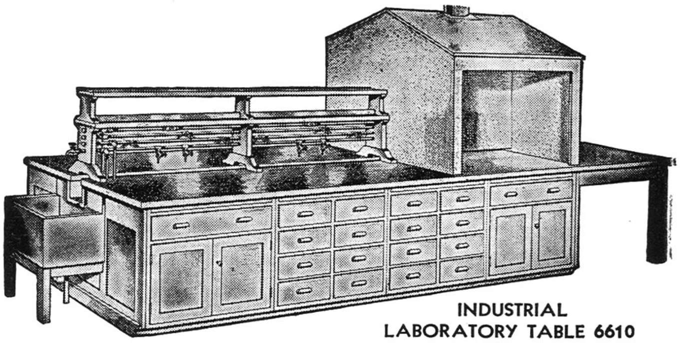

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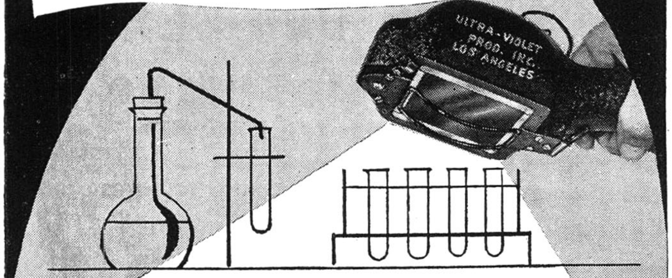
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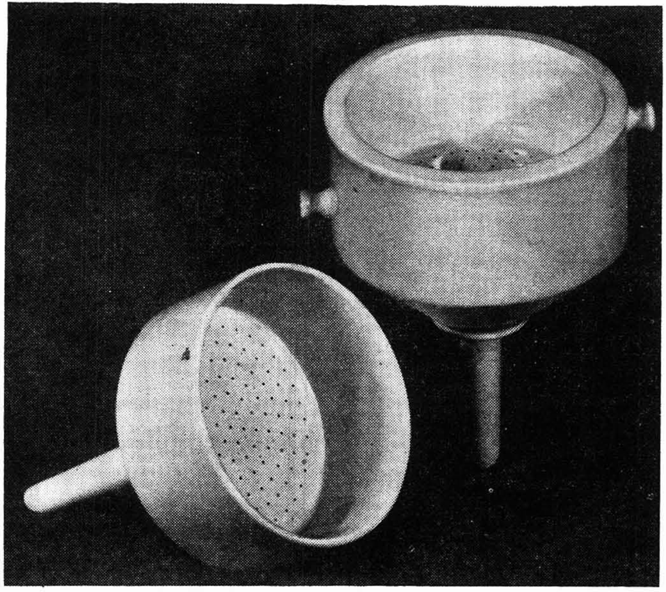

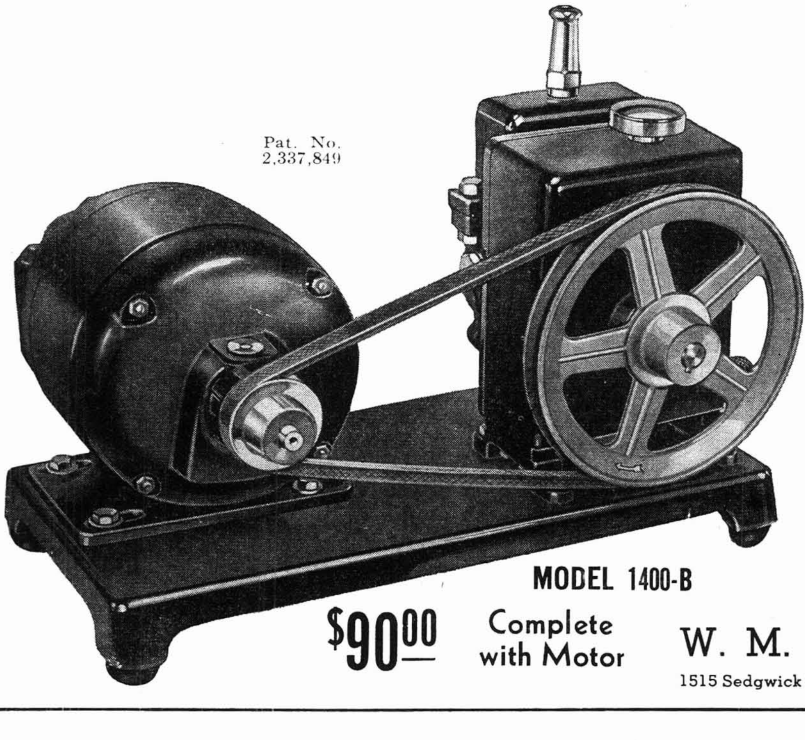
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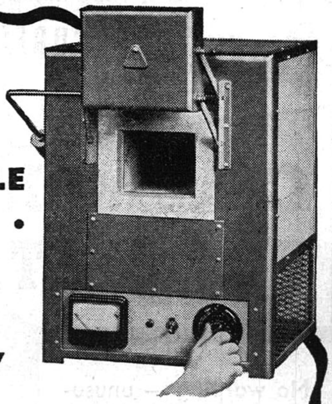

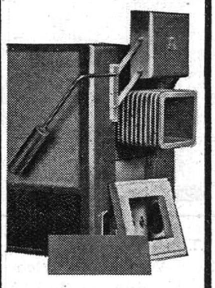

●Muffle of ceramically bonded aluminum oxide is replaceable complete with nickelchrome heating element. New coiled heating element can be furnished for rewinding old muffle core.

SPECIFICATIONS

Size—Overall 22" x 34" x 18"
Muffle chamber—6" x 5" x 10"
Operating temperature
Continuous 1600° F.
Intermittent 1900°F.
Current consumption
2300 Watts maximum
Shipping weight—170 lbs.
Price—115 V. or 230 V. **$194.00**

A sturdy, modern electric furnace, with maximum convenience and economy in operation.

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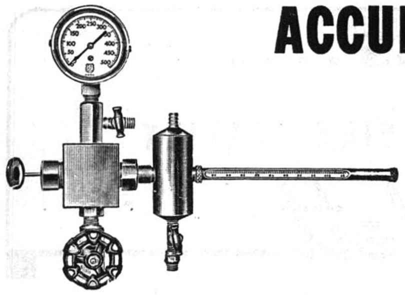

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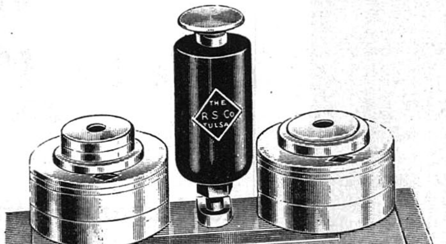

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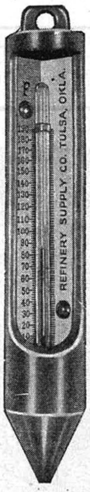

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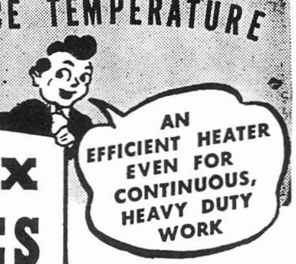
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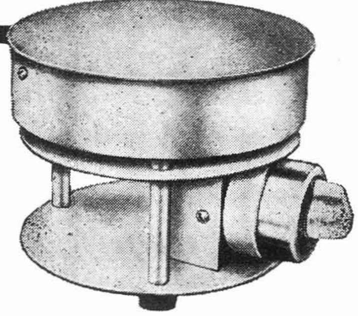
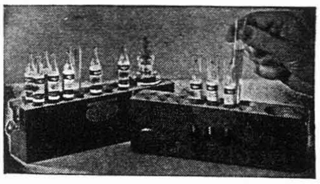
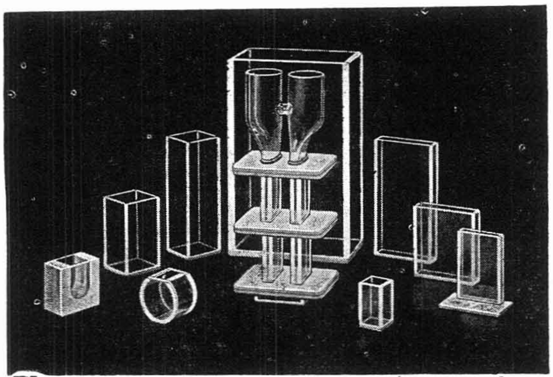
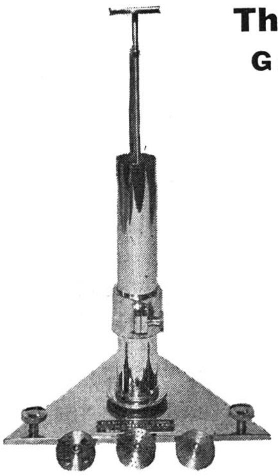



THREE-HEAT SWITCH for temperature control.





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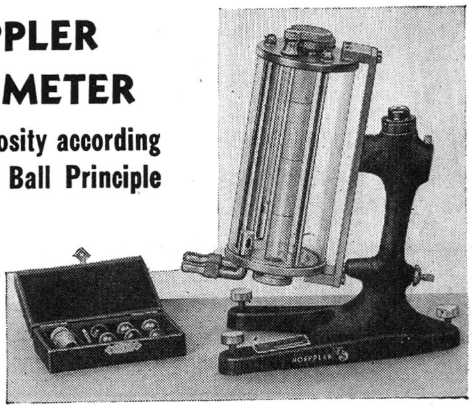

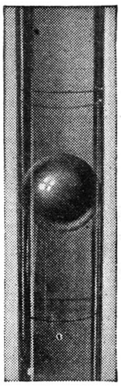

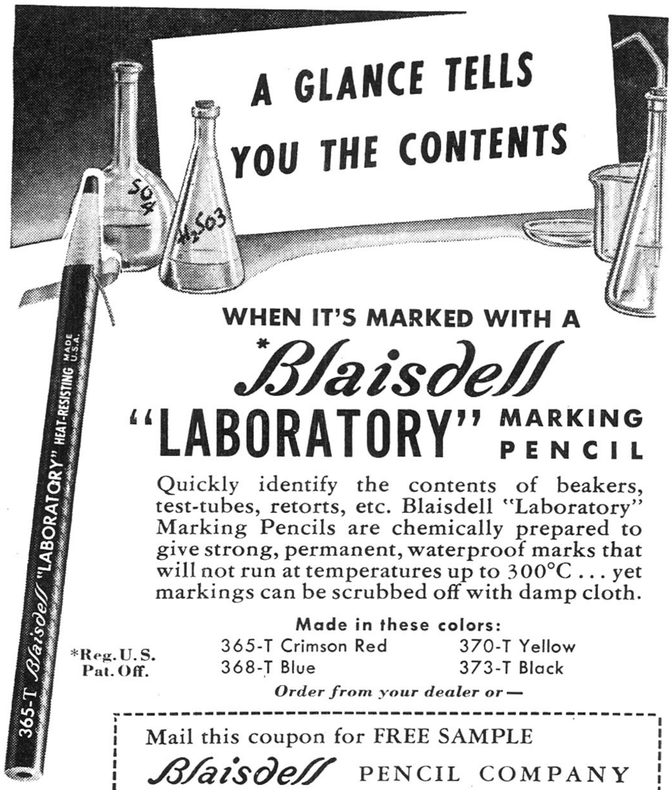

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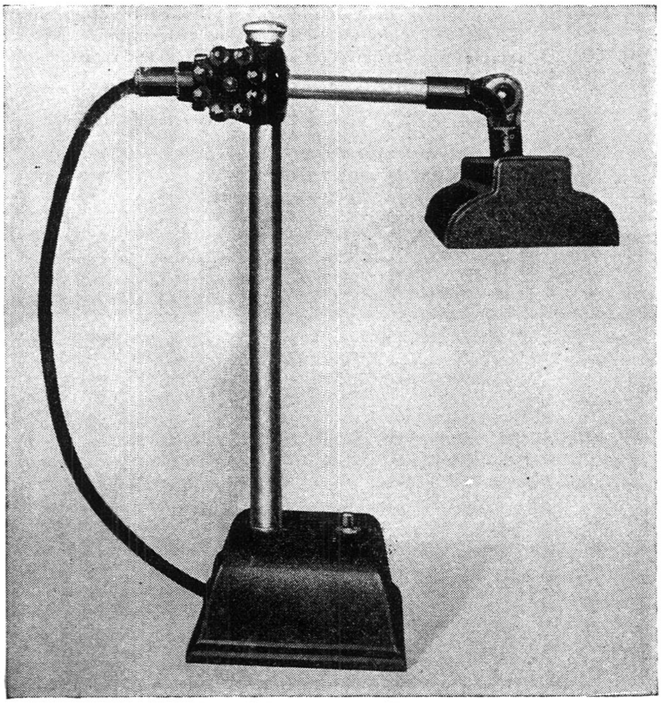

The complete "Multi-Ray" Outfit consists of an operating unit and four interchangeable lamp tubes.

Lamp Tube A provides short-wave ultraviolet—principally at 2537 Angstroms — and at an intensity sufficient for effective air, surface and liquid disinfection.

Lamp Tube B furnishes a source of long wave ultra-violet or "black-light" filtered to remove all but a trace of visible light. The energy peak of this light is close to 3600 Angstroms which is the most effective wave length for activating an extensive group of fluorescent materials. This light produces practically no radiation shorter than 3000 Angstroms.

Lamp Tube C is a white lamp yielding about 100 foot candles of illumination at close working distance. Its use converts the unit into a handy source of high intensity illumination—for the balance, for instruments, and for general laboratory purposes.

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No. 18000 Multi-Ray Laboratory Lamp complete with lamp tubes A, B, C, and D $32.00

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A bulletin illustrating the Multi-Ray Lamp and describing its many uses is available on request.

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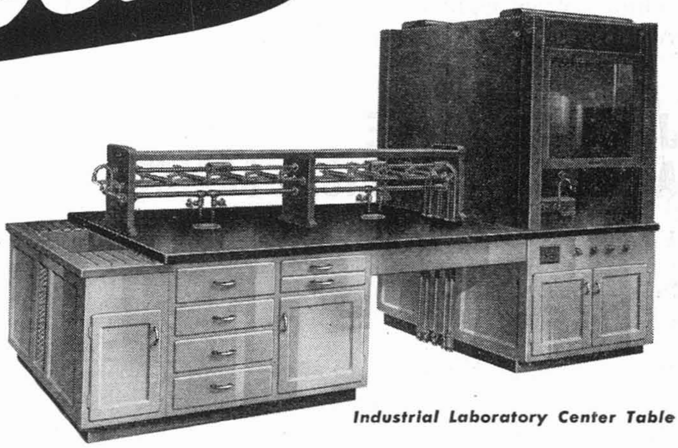

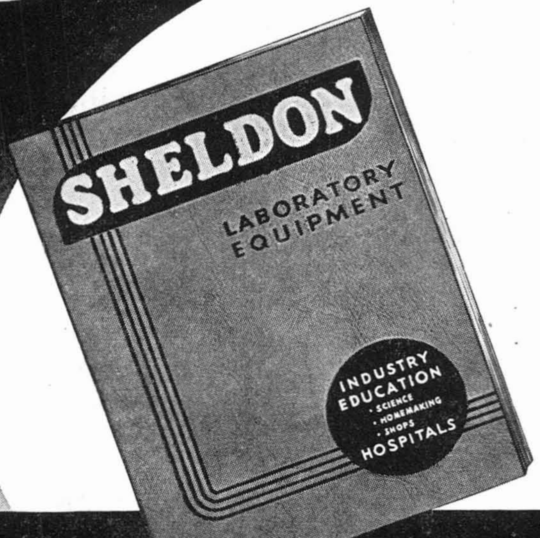
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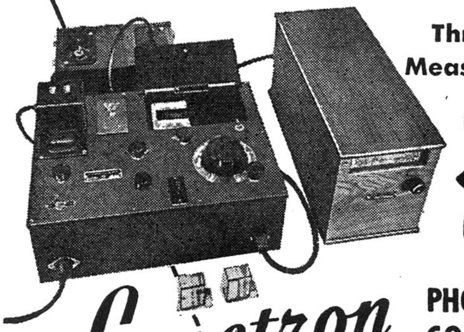

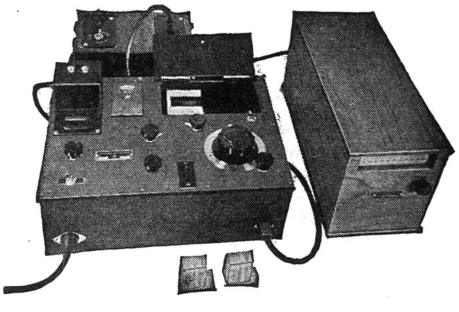

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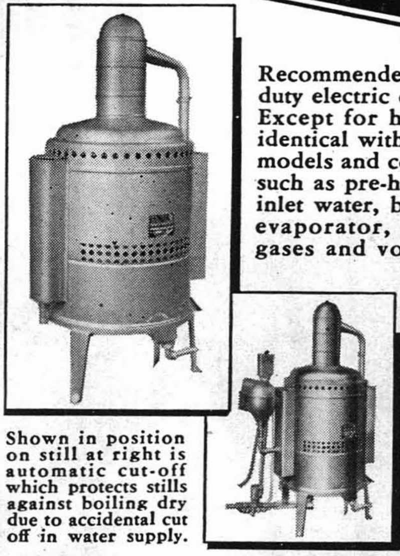

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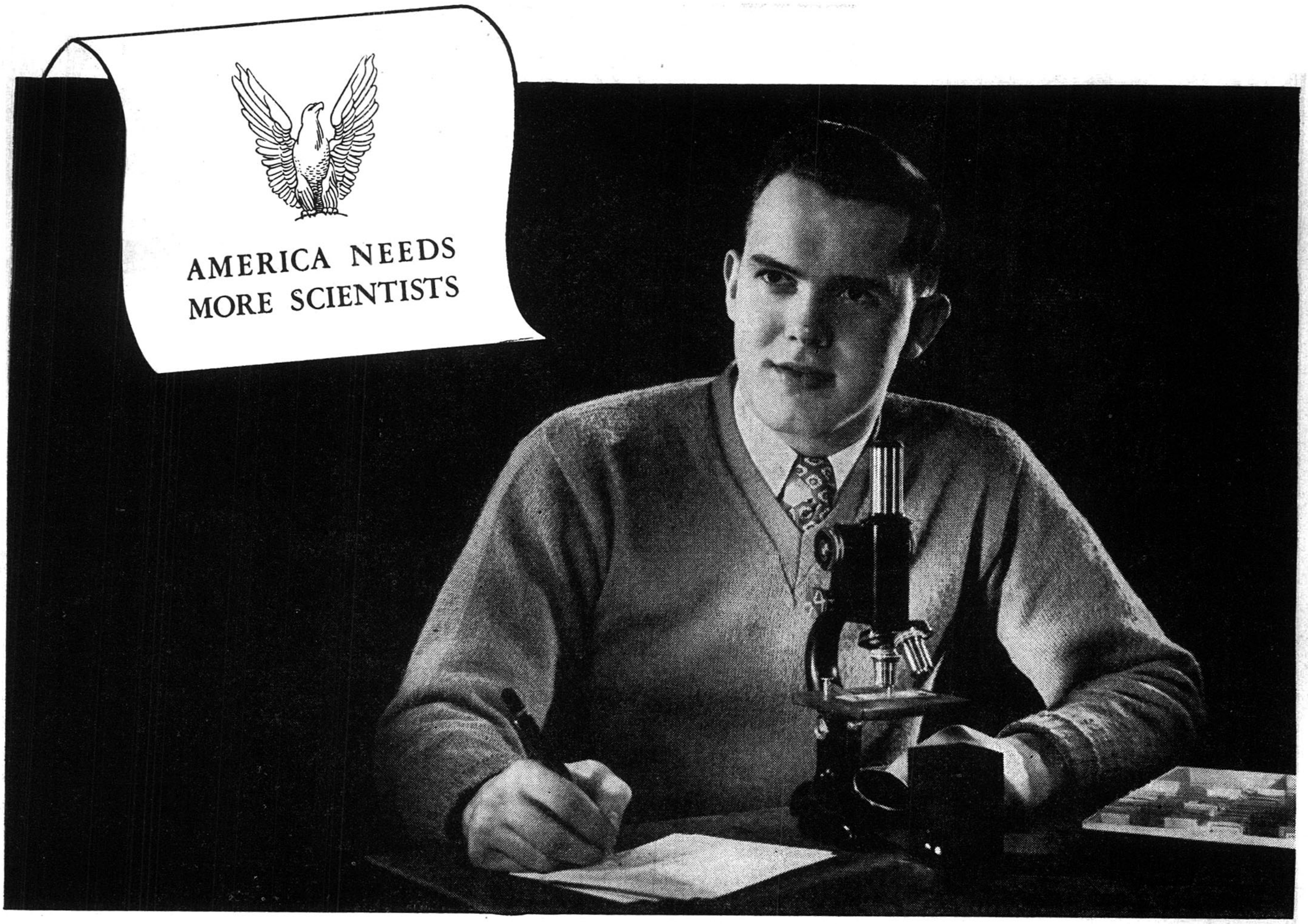
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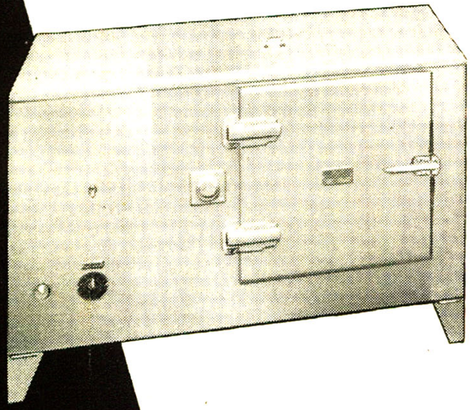

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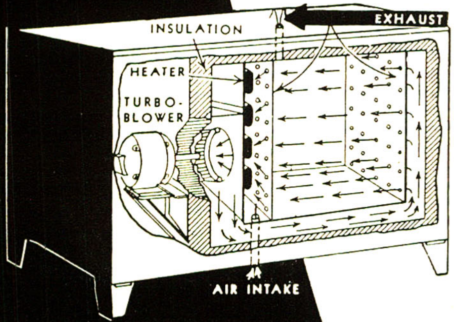

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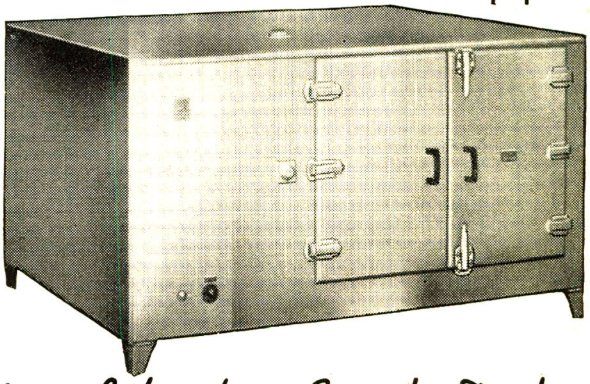

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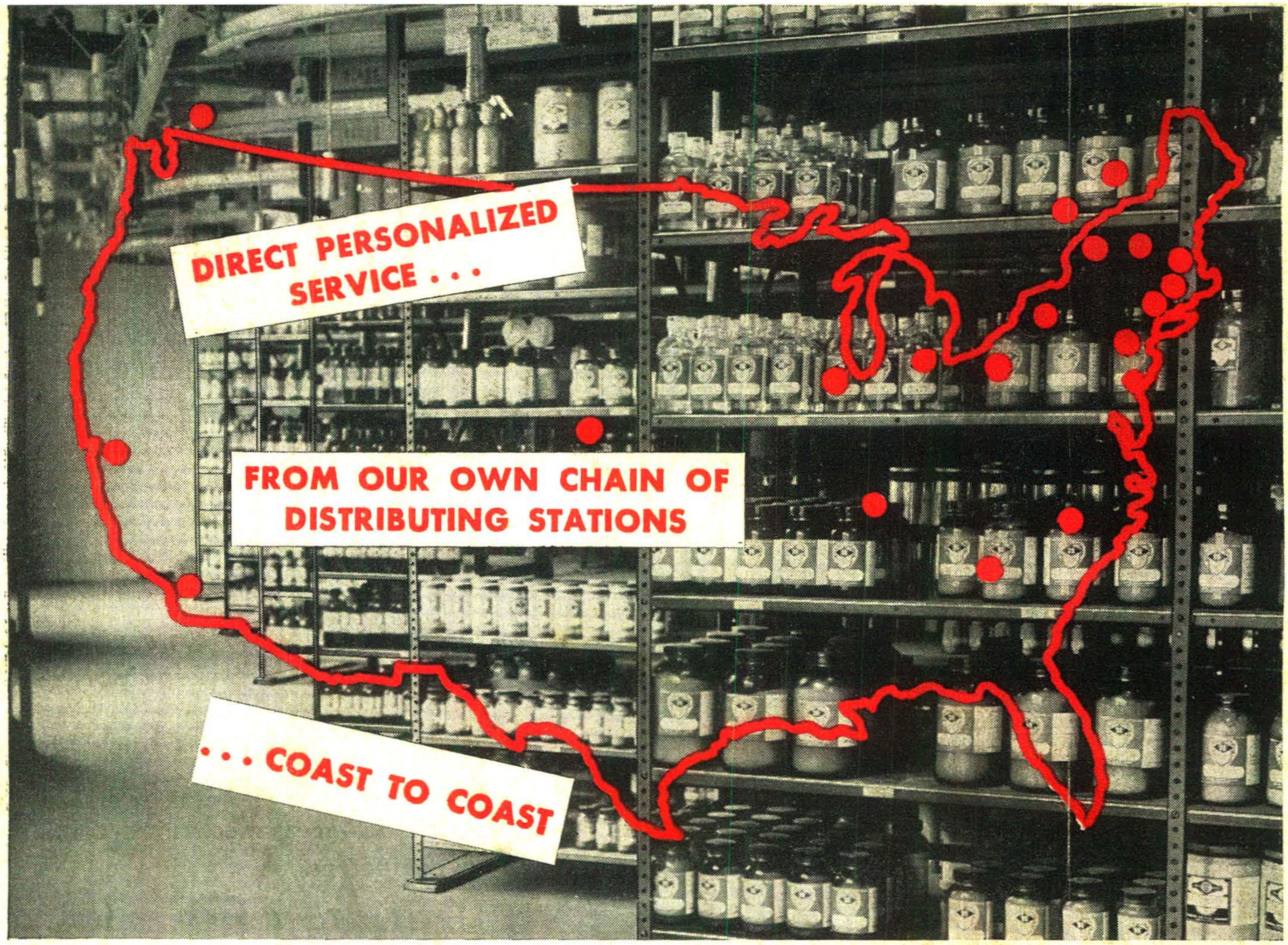

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