ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Modern Objectivity in Analysis

H. V. Churchill's address, delivered at the dinner held in conjunction with the Third Annual Analytical Symposium of the Division of Analytical Chemistry of the Pittsburgh A.C.S. Section, provided two striking examples of the evolutionary changes which instrumentation has wrought in the work of the chemical analyst and illustrated the delicate sensitivity of modern physicochemical devices now available in the field of analytical chemistry.

Speaking first of control work on aluminum alloys, Mr. Churchill pointed out that many remelting furnaces have a capacity of 35,000 pounds. From this molten metal, a sample is poured having a weight of about 60 grams. This is a sampling ratio of 1 to 260,000. When the spectrographer sparks this sample, he actually uses or consumes but 1 mg. of metal; so the ratio of sample to original material becomes 1 to 1,500,000,000. When the sample is sparked, radiation occurs, and of the total light emitted, only 30 billionths is introduced into the spectrograph and the sample fraction becomes one to 45 quadrillion or 1 to 4×10^{17}.

In another example the chief of the Analytical Division of the Aluminum Company of America cited an instance of the faith of the analytical chemist who uses the spectrograph in determining beryllium in a certain material. The maximum sample that can be presented for excitation contains 0.001 microgram of beryllium. The spectrographer promptly throws away most of the radiation and uses only 30 billionths of that emitted. Thus, he is using as his sample 30 billionths of 0.001 microgram or 10^{-15} gram.

Commenting on instrumental analysis, Mr. Churchill reminded his audience that most modern objective methods and instruments are methods and instruments for doing faster or in greater volume certain tasks which can be done more slowly and in less volume by classical or traditional methods. Illustrating this point he reviewed a case history of one of the company's plants, where the analysis of aluminum alloys developed from the use of traditional or classical methods to a stage wherein the work was done spectrochemically—that is, by photographic spectroscopy—and finally is being done by the use of direct-reading spectrographs. The speaker reported the relative productivity of workers in these three stages of evolution has been in the ratio of 4:20:60. This is a 15-fold increase in productivity and speed in changing from subjective methods to those of increasing objectivity and with an increase in both precision and accuracy.

"Is it any wonder," said Mr. Churchill, "that some of us older chemists, who experienced some little difficulty in learning to weigh to tenths of milligrams or even as microchemists to weigh to micrograms, are a bit appalled by the brash temerity of these modern-day analytical chemists who go so far into infinitesimals? No wonder we must bolster our faith with the intricate formulas of statistical analysis, and little wonder we have an almost idolatrous faith in the laws of probability."

Mr. Churchill's entertaining and instructive discussion of things analytical closed with two thoughts worth leaving with our readers. First, he criticized in no uncertain terms the poor "housekeeping" in many laboratories. As the dean of analytical chemists in an area where analytical chemists abound, his observation that too many laboratories are untidy must be accepted at its face value. Secondly, his point that recognition of status by the public while devoutly wished for is something to be earned, was sound, sane advice. "That means in the calling of analytical chemistry," he concluded, "high standards of preparation and performance. It means the maintenance of alertness of mind even after the days of academic preparation and industrial training are over. It means devotion to one's assigned tasks and their fulfillment. It means an acknowledged dynamic willingness to be a servant to the useful calling which we name analytical chemistry."

Fresenius Celebration

THE May issue of the *Zeitschrift für analytische Chemie* will celebrate the one hundredth anniversary of the founding of the world-famous Fresenius Laboratory by the old master of analytical chemistry, Karl Remigius Fresenius. The centennial celebration will include an appropriate historical review article and a large number of papers on specialized subjects written by outstanding analytical chemists located in various parts of the world. In this way the international character of the celebration will be emphasized.

The *Zeitschrift für analytische Chemie* has been closely linked with the Fresenius Laboratory and the family of Fresenius. The present director of the laboratory is the grandson of the founder. Much of the laboratory, including the extensive library, was lost during the late war.

Those desiring more specific information concerning the special issue should communicate directly with the editor, D. Kurtenacher, whose address is Verlag von J. F. Bergmann, Munich, Germany.

The first in a series of summaries of crystallographic data on compounds of interest in research and analysis is presented on page 274 of this issue.

Recording Mass Spectrometer for Process Analysis

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A recording mass spectrometer is described which has been used for making continuous analyses of the process gas stream in the uranium gaseous diffusion plant. The strategic distribution of instruments in the plant assures rapid detection of any inleaking contaminants. Modifications of the system described should prove useful in other large industrial installations.

ALTHOUGH the mass spectrometer has found considerable use as a tool for performing both isotope and gas analyses in the laboratory (*1, 3, 5*), there is no record of its application to the continuous analysis of a process gas in an industrial installation. The present paper describes the essential parts of a mass spectrometer system which was employed for analyzing the contaminants in the process stream of the Oak Ridge gaseous diffusion plant for the separation of the uranium isotopes. A recording mass spectrometer was selected for making the analyses because of its many advantages over the other instruments considered. These advantages included:

Ability to measure each component of the process stream
Negligible consumption of the extremely valuable material to be analyzed
Rapid response to changes in the composition of the gas stream
Continuous automatic recording of the principal components of the gas stream

In many respects the spectrometer resembled the conventional type instruments used in performing laboratory analyses. Figure 1 shows a schematic drawing of a typical installation. The gas to be analyzed was allowed to flow continuously past a specially designed adjustable "leak." The flow through the leak was measured by a special Pirani gage flowmeter in the line leading to the spectrometer tube. Conventional-type electronic stabilizing circuits (*3*) supplied the necessary voltages and currents to the spectrometer. Automatic switching equipment in the multipoint recorder varied the ion-accelerating potential through

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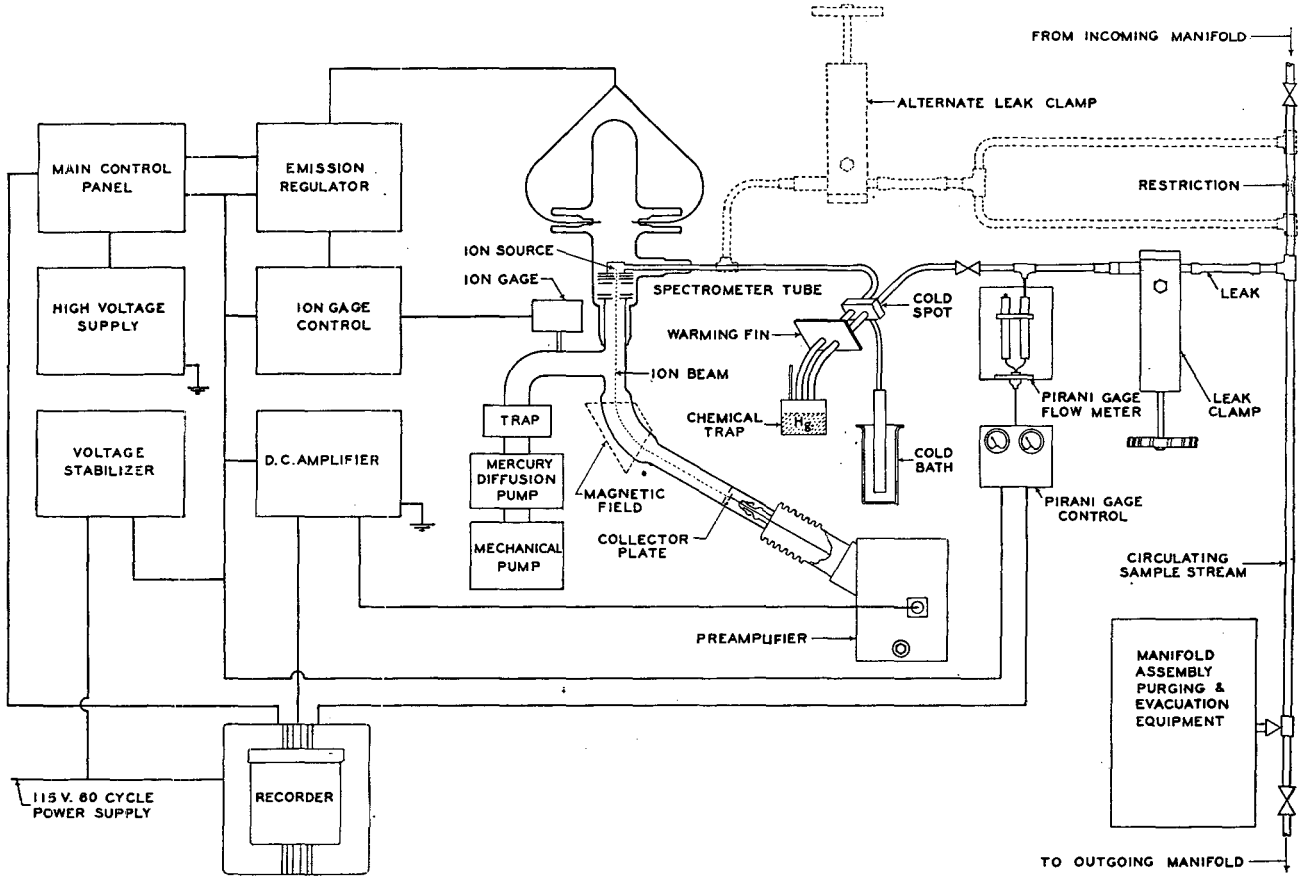

Figure 1. Schematic Diagram of Recording Mass Spectrometer, Showing Alternate Gas Inlet System and Interconnections of Component Parts

a prearranged sequence of values in order to select the masses desired for making the analysis. The ion currents were measured by an electrometer tube preamplifier followed by an inverse feedback amplifier which supplied the necessary signal to the recording potentiometer.

MASS SPECTROMETER TUBE

A drawing of the spectrometer tube is shown in Figure 2.

The sample gas enters the ionization chamber through the inlet lead. Because of the construction of the tube, the pressure in the ionization chamber is higher than in the rest of the tube. The sample gas is ionized by electrons which are emitted from the heated filament, aligned by a magnetic field, and accelerated by a potential difference between the filament and the ionization chamber. Since the useful electron beam consists of a fine pencil of electrons which is directed into the trap, the trap current is an accurate indication of the electron current. Ions formed by collision of the electrons with the gas molecules are forced through the slit in shield S and are accelerated through plates $J1$, $J2$, $J3$, $J5$, and G by the voltages on them. Plates $J1$ and $J2$, which have independently adjustable voltages, serve to bend the ion beam to one side or the other to compensate for imperfections in construction as well as for the slight bending caused by the magnetic field used in aligning the electron beam. The plates marked G are fastened to the tube body, which is electrically grounded. The ion beam is resolved in passing through the transverse magnetic field created by the permanent magnets.

The operating conditions for a typical recording mass spectrometer are as follows:

Potential between S and $J1$	Approximately 100 volts
Potential between S and $J2$	Approximately 100 volts
Potential between S and $J3$	120 volts
Potential between $J5$ and G	0.6 potential between S and G
Potential between S and T	90 volts
Potential between filament and S	75 volts
Accelerating potential between S and G	Adjustable 0 to 2500 volts
Total electron emission	100 microamperes
Total trap current	100 microamperes
Electron aligning magnet strength	250 gauss
Main magnet strength	3250 gauss
Mass 28 accelerating voltage	1050 volts

Although the ions impinging on the collector and nearby surfaces produce secondary electrons, these do not contribute to the collector current, inasmuch as a weak magnet field is present. This field is produced by a small instrument magnet.

ELECTRICAL COMPONENTS

The electrical components for the recording mass spectrometer consist of switching, regulating, and amplifying equipment. These components are separated on a functional basis and mounted on separate relay rack panels. The interconnections which are made with plug-in type cables are shown in Figure 1. All circuits, with the exception of the high-voltage supply which is self-stabilized, are operated from stabilized 115-volt, 60-cycle power.

The ionizing and accelerating voltages of the spectrometer ion source are produced by the emission regulator and high-voltage supply and are controlled by the automatic switches in the recorder which operate relays located on the main control panel. The emission regulator supplies (1) regulated current to the spectrometer filament, (2) stabilized voltage to the electron trap, and (3) stabilized voltages to the accelerating plates, S, $J1$, $J2$, and $J3$. Potentiometers and meters are used in each circuit for adjusting the voltages. The ion accelerating voltages for plates S and $J5$ are provided by the high-voltage supply. Two potential dividers, one for manual and one for automatic operation, on the main control panel permit the selection of the different accelerating voltages required to tune the spectrometer to the different mass numbers, although several specific voltages, corresponding to various components of the process gas, may be used in automatic operation.

The ion currents to the collector plate are amplified by an inverse feedback direct current amplifier. This amplifier has four stages, the first two of which, consisting of two 954 tubes and a 5×10^9 ohm input resistor, make up the preamplifier and are mounted in an aluminum box. This box is mounted on vibration insulators and connected to the spectrometer tube by a bellows assembly.

The amplified ion currents are measured by a self-balancing potentiometer-type recorder. A motor-driven switch in the recorder, operating in synchronism with the switch used to change the accelerating voltage, automatically selects any one of seven sensitivity factors between 1 and 100. The recorder has 16 channels; it records the amplifier zero and Pirani gage reading as well as the several mass ions on a 24-seconds-per-channel cycle. The entire 16 channels are used; thus some measurements are recorded more frequently than others.

An ionization gage is used to measure the pressure in the spectrometer tube. A special protective feature has been added to the ion gage control which prevents the filaments of the gage and spectrometer tube from burning out by automatically cutting off their currents when the pressure exceeds a predetermined value.

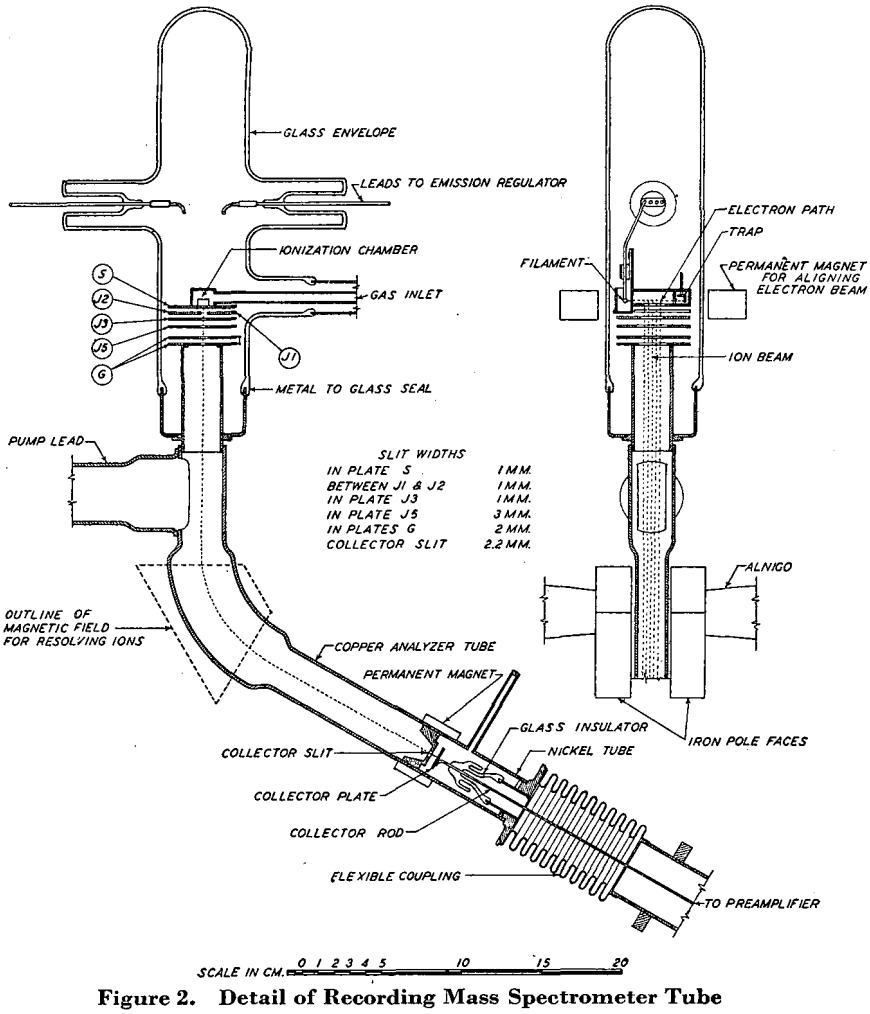

Figure 2. Detail of Recording Mass Spectrometer Tube

GAS INLET SYSTEMS

Two gas inlet systems are shown in Figure 1. The system chosen depends on the relative quantities of uranium hexafluoride in the sample stream. Since samples with high concentrations of uranium hexafluoride cause the rapid formation of insulating coatings on those electrodes in the spectrometer tube which are bombarded by electrons, they are not admitted directly into the tube but are first passed through a chemical trap which removes the uranium hexafluoride. In this system the pressure in the spectrometer is adjusted in such a way that the ion current of each constituent at the appropriate mass number is proportional to its concentration in the original mixture. This is done by building into the gas-inlet system a set of resistances and a Pirani gage; when the flow is adjusted so that the Pirani reading is held constant, the ion current of each constituent in the spectrometer is proportional to its concentration in the original mixture. This relation is strictly true only for low concentrations of impurities, and for high concentrations special calibration is required.

If the samples contain small amounts of uranium hexafluoride, the second inlet system may be used. In this system the gases are admitted directly to the tube through the alternate leak without absorption of uranium hexafluoride.

The adjustable leak with its capillary tube is an extremely low-flow nonfractionating valve. Its details are shown in Figure 3. It has been designed so that a flow rate of 25 cc. micron per second may be obtained when the absolute upstream pressure varies between 1 and 60 cm. of mercury with a downstream pressure of a few microns of mercury. The leak is adjusted by turning the handle which forces the shoes to move in and out along the inclined planes in the clamp arms, thereby closing and opening the annular space between the leak tube and the leak plug. In meeting the range requirements, the jaws move approximately 0.003 inch (0.0075 cm.) for 35 turns of the handle. A force of approximately 5000 pounds (227 kg.) is necessary to compress the leak tube. The performance of the leak depends on the accuracy with which the parts are made. The critical dimensions and their associated tolerances are given in Figure 3.

Whenever gas is allowed to flow from a high-pressure to a low-pressure region as in a mass spectrometer, extreme care must be taken to ensure that the composition of the gas in the low-pressure region—i.e., spectrometer region—bears a known relation to that on the high-pressure side—i.e., in the sample. Conventional capillary "leaks" consisting of pieces of drawnout glass tubes such as are commonly employed in the laboratory, needle valves, or other adjustable flow devices (*4*) will, in general, produce fractionation which depends upon both the composition of the gas and the pressure on the high-pressure side. In making laboratory gas analyses the problem may be eliminated by employing samples whose pressure has been reduced to a fixed value of 100 microns or less (*2*) and allowing the gas flow to take place through small holes whose diameter is small as compared with the mean free path, thus ensuring pure molecular flow. In the present instance this solution was not practical, since the manifold pressure was not always the same and not necessarily in the proper absolute range.

The problem was solved by using a length of capillary on the high-pressure side of the flowing adjustment part of the leak. The lower portion of Figure 3 shows the gas flow through the leak. There is practically no pressure drop in the capillary tube itself, essentially all taking place in the region clamped by the colletlike jaws. The capillary tube has a sufficiently large diameter so that the mean free path of gas molecules in it will always be greater, and viscous and not molecular flow will take place. It was chosen sufficiently long so that the gas just above the pinched region, containing a slight excess of heavy molecules due to the partial fractionation produced in the pinch, could not diffuse back into the circulating sample stream. The capillary diameter, while sufficiently great to ensure viscous flow within it, kept the mass flow velocity large enough to prevent back-diffusion. Thus the gas leaving the leak on the low-pressure side was representative of that in the circulating sample stream. It is apparent that the design of the leak involved a compromise between obtaining an accurately representative sample and

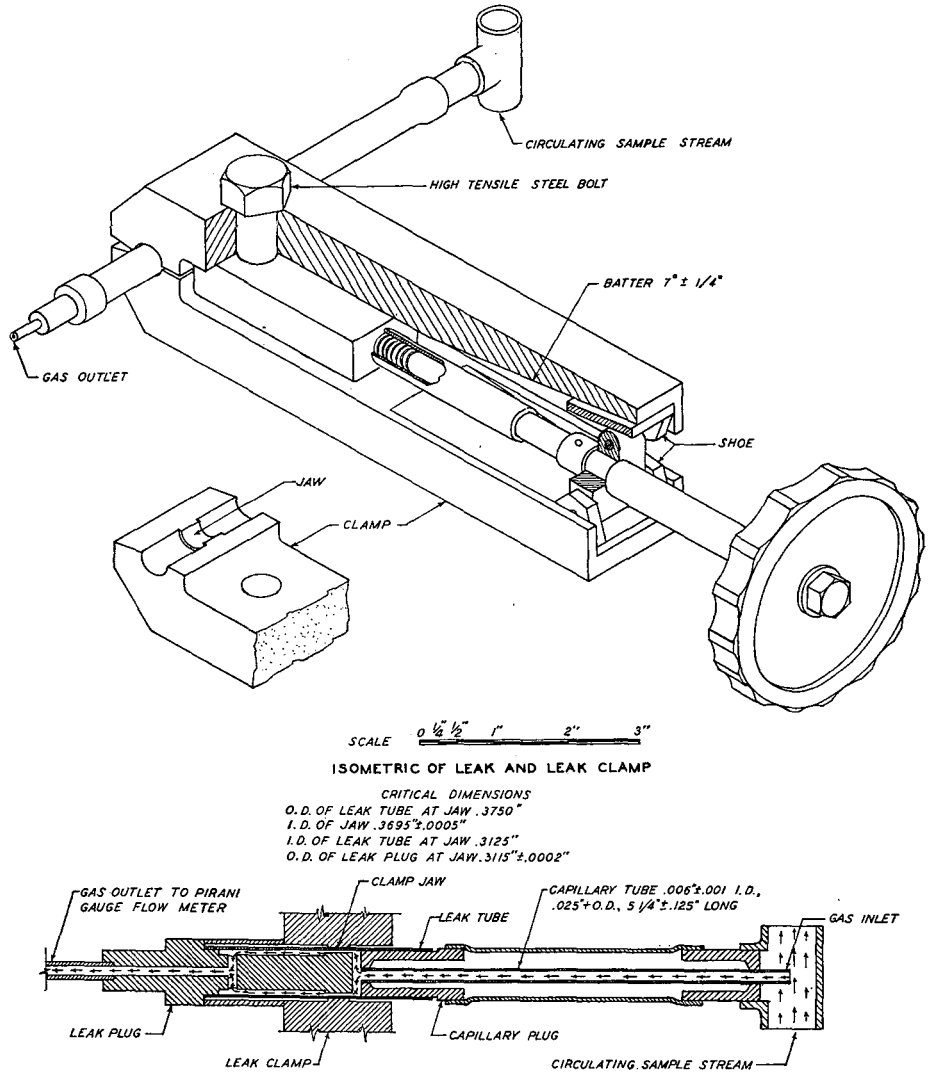

Figure 3. Schematic and Isometric Drawing of Adjustable Leak and Capillary Tube Used on Recording Mass Spectrometer

having a reasonable time response for the entire pressure and composition range. Had a longer capillary been chosen, an even more accurately representative sample would have been obtained, but at the expense of time response.

Figure 4 shows how for a given mixture of nitrogen with uranium hexafluoride the composition of the gas stream leaving the leak would vary with upstream pressure with and without the use of a capillary.

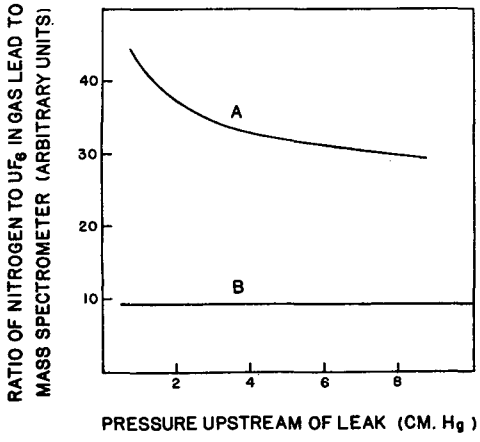

Figure 4. Effect of Capillary Tube in Compensating for Fractionating Property of Adjustable Leak

Measurements made on sample gas mixtures of N_2 and UF_6

A. **Leak without capillary tube**
B. **Leak with capillary tube**

Ordinarily in a mass spectrometer the gas passing through the leak would pass directly into the mass spectrometer. However, because of the adverse effect of uranium hexafluoride on the ion source, this component is not permitted to enter the source unless its concentration in the process stream is low. When the concentration is high this component is first absorbed by employing a "chemical trap" consisting of a small mercury reservoir shown in Figure 1.

The mercury reservoir, which is kept at room temperature, produces mercury vapor which diffuses to the cold spots, condenses, and falls back into the trap. When uranium hexafluoride is flowing into the system it meets the mercury stream at the first cold spot and a reaction takes place in which solid products are formed and accumulate on the walls of the tubing. The cold spots are held at approximately 0° C. The one in the lead to the spectrometer tube limits the mercury pressure in the tube, whereas the one in the lead to the leak confines the reaction region. To make certain that the mercury does not condense before reaching the cold spots, the warming fin is attached as shown in the diagram.

The reading of the Pirani gage depends on the composition of the gas stream as well as the pressure at the gage. For a flow of pure uranium hexafluoride the pressure is determined by the flow resistance of that portion of the gas line between the Pirani gage and the chemical trap. For a flow of nitrogen or air the pressure is determined by the resistance of that portion of the line between the Pirani gage and the diffusion pump. These resistances have been chosen so that when the Pirani gage reading is held constant the output of the amplifier corresponding to the nitrogen peak is approximately proportional to the concentration of nitrogen in the gas stream being analyzed. The instrument is calibrated with mixtures of nitrogen and uranium hexafluoride of known composition and a correction curve is provided to relate amplifier output to nitrogen concentration.

The pressure-sensitive element of the Pirani gage forms one arm of a bridge circuit. The unbalance of the bridge circuit is read on an indicating millivoltmeter as well as on the recorder. The pressure-sensitive element, consisting of a 0.003-inch nickel wire, is encased in a Monel tube and has been found stable despite the corrosive nature of the sample gases. The normal operating pressure at the gage is approximately 10 microns of mercury.

PERFORMANCE OF RECORDING MASS SPECTROMETER

Most of the recording mass spectrometers in the diffusion plant are used for automatic analysis of the process stream and are equipped with Pirani flowmeters and chemical traps for handling high uranium hexafluoride concentrations. A spectrometer chart is shown in Figure 5. Referring to the chart, a nitrogen surge is observed at approximately 1:55 A.M. Concentrations of the gases for this test are indicated in the figure. The accuracy of their measurement is approximately 5% of reading, depending on the care taken in calibrating the instrument. The concentration of hydrogen fluoride cannot be determined accurately with the standard instruments, as this gas is strongly absorbed by the gas inlet system, and hence the response of the spectrometer is extremely sluggish.

The average consumption of uranium hexafluoride is less than 40 mg. per instrument per day. Thirty seconds after the composition of the gas in the sample stream has changed, the spectrometer tube ion current reflects this change. Most of this delay is caused by the time required for the gas to pass through the capillary tube at the adjustable leak. The appearance of this change on the recorder depends on the printing cycle; for nitrogen which is printed every other point on the recorder, a change in concentration is recorded within a minute after it occurs in the sample stream.

Several of the mass spectrometers are provided with the alternate inlet system as shown in Figure 1. These are used to measure low concentrations of uranium hexafluoride and hydrogen fluoride. Concentrations of uranium hexafluoride as

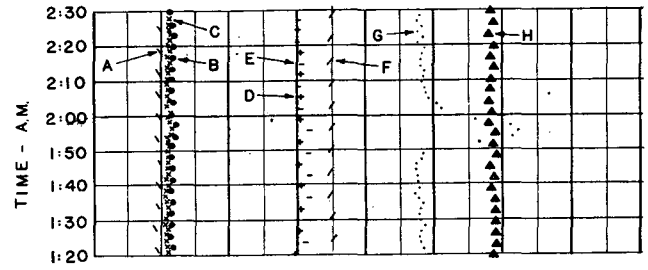

Figure 5. Typical Recording Mass Spectrometer Chart, Showing Normal Concentrations of Process Stream Components in Uranium Gaseous Diffusion Plant

A. **Amplification zero**
B. **O_2 mass 32, 0.2%**
C. **N_2 mass 14, 6%**
D. **HF mass 20, 2%**
E. **CO_2 mass 44, 0.1%**
F. **Fluorocarbon mass 69, 0.2%**
G. **N_2 mass 28, 6%**
H. **Total gas flow as measured by Pirani gage**

low as 0.1 mole % and those of hydrogen fluoride of 1 mole % may be measured with an accuracy of 10%. The response time of these instruments is appreciably less than that of the others.

The performance data cited here are by no means necessarily typical of what is to be expected in all mass spectrometer installations. For example, laboratory spectrometers which can be checked and calibrated frequently ordinarily give analyses to an accuracy of 1% or better. The present paper does demonstrate that by employing special methods such as the "chemical trap" and Pirani gage flowmeter, a mass spectrometer may even be used with highly corrosive gases under adverse circumstances. No doubt there are other commercial processes in which mass

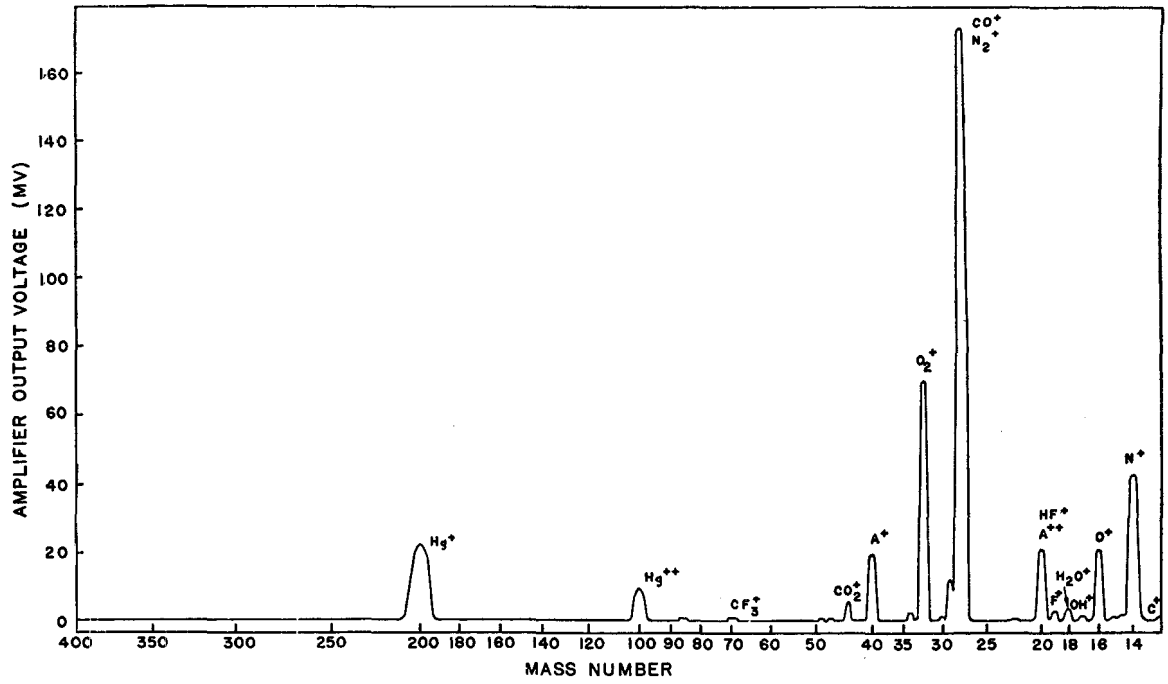

Figure 6. Typical Automatic Mass Scan of Air Taken on a Recording Mass Spectrometer Installed in Uranium Gaseous Diffusion Plant

spectrometers could be applied if modifications or extensions of the principles employed here were used.

When it is desirable to obtain a complete analysis of all impurities in the sample stream, the multipoint recorder is replaced by a single-pen recorder and the ion-accelerating voltage is varied continuously with time, so that the recorder draws a mass spectrum from mass 12 to mass 500. Figure 6 shows a portion of such a spectrum when dry air is introduced into the instrument. The spectrum included several masses such as 20 (HF), 200 (HG^{+}), and 100 (HG^{++}) which are from residual gases in the system.

ACKNOWLEDGMENT

The original design of the recording mass spectrometer was made by members of The Kellex Corporation, and after modifications to improve the reliability and facilitate the manufacture, a large number of the instruments were built by the General Electric Company.

The authors are indebted to I. R. Brenholdt for his design and construction of many of the electronic components. Much of the mechanical design, especially of the mass spectrometer tube, is due to R. B. Thorness.

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Determination of Potash in Fertilizers

Effect of Saturation of Acid-Alcohol with Potassium Chloroplatinate

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IN THE official A.O.A.C. method for determining potash in fertilizers the potassium chloroplatinate is treated with acid-alcohol and washed with 80% alcohol (*3*). A question has arisen whether this step causes low results due to the solubility of the salt in the alcohol. Although the literature contains a number of references to the solubility of potassium chloroplatinate in alcohol of various strengths (*1, 2, 5, 7*), no data have been found on the solubility in acid-alcohol. Accordingly, the purpose of the present work was to determine the practical significance of this solubility by using acid-alcohol previously saturated with potassium chloroplatinate and comparing with the official method in concurrent analysis of identical samples.

In addition to the study with acid-alcohol prepared from 80% alcohol as used in the official procedure (200 ml. of 80% alcohol plus 20 ml. of hydrochloric acid), this study includes experiments with acid-alcohol prepared from 95% alcohol (200 ml. of 95% alcohol plus 20 ml. of hydrochloric acid) which had previously been saturated with potassium chloroplatinate. The alcohol used in subsequent washing in each case was 80 and 95%, respectively. (This study also included the examination of the purity of the potassium chloroplatinate obtained with the two strengths of alcohol under the varying conditions.) At the suggestion of the general referee on fertilizer of the A.O.A.C. to the associate referee on potash, a comparison was made on one

In determining potash in fertilizers higher values can be obtained by increasing the concentration of the alcohol and saturating the acid-alcohol with potassium chloroplatinate. Comparison of the values for platinum and chlorides found by analysis with the theoretical indicates that within the limits of experimental error the values obtained represent true potassium chloroplatinate.

sample using potassium-free normal sodium acetate (1 to 2 ml.) in place of potassium-free normal sodium hydroxide. Since Hughes and Ford (*5*) reported increased solubility with rise of temperature, all work herein reported was done at 18° C. for both the acid-alcohol made from 80 and 95% alcohol and the wash alcohol. Although the official method does not specifically state whether acid-alcohol and alcohol should be 80% by volume or by weight, it is customary to report alcohol by volume and the results in this paper are on that basis.

PROCEDURE

Experiment A. Solutions of ten fertilizers were prepared according to the Lindo-Gladding official potash method. The five A.O.A.C. collaborative samples were prepared by mixing and grinding fertilizers of the same analysis from several manufacturers. The other five were the F. S. Royster Guano Company's check fertilizer samples sent monthly to 75 laboratories for analysis. In all analyses a 2.50-gram sample was used and 25-ml. aliquots were taken, so that each platinum dish contained 0.25 gram of sample. The residue was treated with exactly 6 ml. of acid-alcohol made from 80% alcohol or acid-alcohol made from 80% alcohol and saturated with potassium chloroplatinate. Identical samples were also treated with acid-alcohol made from 95% alcohol and acid-alcohol made from 95% alcohol and saturated with potassium chloroplatinate. The acid-alcohol solutions remained in contact with the residue for exactly 15 minutes. All samples were washed with approximately the same amount of alcohol (125 ml.). About one half the alcohol was used before the ammonium chloride treatment and one half after treatment. Pyrex M porosity crucibles were used in all the determinations. All potash values were determined by dissolving the potassium chloroplatinate in hot water and reweighing the crucible. The results are presented in Table I.

Experiment B. Potassium-free normal sodium acetate was used in place of potassium-free normal sodium hydroxide on one sample of fertilizer (0-12-12) using acid-alcohol made from 80% alcohol, acid-alcohol made from 80% alcohol and saturated with potassium chloroplatinate, and acid-alcohol made from 95% alcohol. The results are presented in Table II.

Table I. Effect of Saturation of Acid-Alcohol with Potassium Chloroplatinate

1946 A.O.A.C. Collaborative Samples	80% Acid-Alcohol[a] Per Cent K_2O No. of analyses averaged	Av.	Av. difference	95% Acid-Alcohol[b] Per Cent K_2O No. of analyses averaged	Av.	Av. difference
A(0-12-12)						
N.S.[c]	12	13.05	...	4	13.13	..
S.[d]	8	13.22	0.17	6	13.52	0.39
B(0-20-20)						
N.S.	12	20.85	..	12	21.04	..
S.	6	21.16	0.31	6	21.06	0.02
C(0-9-27)						
N.S.	12	26.30	..	8	27.41	..
S.	6	27.59	0.29	7	27.41	0.00
D(8-8-8)						
N.S.	12	8.14	..	10	8.24	..
S.	6	8.40	0.26	7	8.27	0.03
E(4-12-8)						
N.S.	12	8.36	..	12	8.48	..
S.	6	8.66	0.30	6	8.48	0.00
F. S. Royster Guano Co.'s Samples						
R-7[e] (July 1945)						
N.S.	4	10.49	..	4	10.64	..
S.	4	10.94	0.45	4	10.73	0.09
R-3[f] (March 1946)						
N.S.	2	15.61	..	4	15.67	..
S.	4	16.00	0.39	4	15.81	0.14
R-5[g] (May 1946)						
N.S.	4	5.18	..	4	5.25	..
S.	4	5.60	0.42	4	5.33	0.08
R-6[h] (June 1946)						
N.S.	4	12.88	..	4	13.02	..
S.	4	13.25	0.47	4	13.06	0.04
R-7[i] (July 1946)						
N.S.	4	5.33	..	4	5.39	..
S.	4	5.76	0.43	4	5.52	0.13

[a] 200 ml. of 80% alcohol with 20 ml. of HCl.
[b] 200 ml. of 95% alcohol with 20 ml. of HCl.
[c] Acid-alcohol not saturated with potassium chloroplatinate.
[d] Acid-alcohol saturated with potassium chloroplatinate.
[e] 3-9-9 grade, average % K_2O 10.31.
[f] 5-10-5 grade, average % K_2O 5.20.
[g] 3-8-5 grade, average % K_2O 5.34.
[h] 2-12-12 grade, average % K_2O 15.83.
[i] 0-12-12 grade (with borax), average % K_2O 12.71.

Table II. Effect of Replacing Sodium Hydroxide with Sodium Acetate

[1946 A.O.A.C. collaborative sample A (0-12-12)]

	No. of Analyses Averaged	Per Cent K_2O Av.	Av. difference
Sodium acetate 80% alcohol. N.S.[a]	12	12.86	..
Sodium hydroxide 80% alcohol. N.S.	12	13.05	0.19
Sodium acetate 80% alcohol. S.[b]	4	13.06	..
Sodium hydroxide 80% alcohol. S.	8	13.22	0.16
Sodium acetate 95% alcohol. N.S.	3	12.96	..
Sodium hydroxide 95% alcohol. N.S.	4	13.13	0.17

[a] Acid-alcohol not saturated with potassium chloroplatinate.
[b] Acid-alcohol saturated with potassium chloroplatinate.

Experiment C. To test the purity of the potassium chloroplatinate obtained, the weighed salt in each case was reduced for platinum recovery and chloride titration. To facilitate the reduction, the salt in each case was dissolved in hot water, transferred to a new unscratched 250-ml. beaker, and, if necessary, concentrated to a volume of about 75 ml. While boiling, 2 to 5 ml. of 40% formic acid were added and as soon as reduction started a piece of filter paper on a glass rod was used to prevent sticking. As soon as the reduction was complete, the reduced platinum black was filtered on a tared asbestos-padded Gooch crucible, dried at 100° C., ashed in a muffle at 600° C. for about 5 hours, cooled, and weighed. The filtrate from the reduction in each case was collected and made to volume and aliquots were taken for the estimation of the chloride by the Volhard method of titration. The end point of this titration was sharpened by coagulation of the precipitated chloride by shaking with 1 to 2 ml. of nitrobenzene and filtering it off before the final titration adjustment was made. The amounts of platinum and chloride found are compared with the theoretical values for each case in Table III.

RESULTS AND DISCUSSION

The data in Table I show that if the acid-alcohol made from 80% alcohol is saturated with potassium chloroplatinate, higher potash results may be expected. The increases obtained in this study ranged from 0.17% with a 0-12-12 fertilizer to 0.47% with a 0-12-12 fertilizer containing borax. The average increase was 0.35%. Such an increase is indicated by an experiment performed to determine the solubility of potassium chloroplatinate in acid-alcohol made from 80% alcohol; in this experiment potassium chloroplatinate was soluble in acid-alcohol made from 80% alcohol at 25° to 30° C. to the extent of 1.17 grams per liter. This would mean that if the 6 ml. of acid-alcohol became saturated during the 15 minutes in contact with the residue, it would dissolve out the equivalent of 0.14% K_2O based on a 0.25-gram

Table III. Effect of Ethanol Concentration and Saturation of Acid-Alcohol[a] on Purity of Potassium Chloroplatinate

Sample	Platinum		Chloride	
	Theoretical	Found	Theoretical	Found
	Gram	*Gram*	*Gram*	*Gram*
	80% Unsaturated			
A (0-12-12)	0.0682	0.0671	0.0743	0.0740
B (0-20-20)	0.1079	0.1064	0.1177	0.1178
C (0-9-27)	0.1433	0.1428	0.1563	0.1560
D (8-8-8)	0.0422	0.0417	0.0460	0.0460
E (4-12-8)	0.0435	0.0431	0.0474	0.0473
	80% Saturated			
A	0.0706	0.0687	0.0770	0.0767
B	0.1104	0.1085	0.1204	0.1199
C	0.1463	0.1443	0.1595	0.1592
D	0.0452	0.0438	0.0493	0.0492
E	0.0460	0.0443	0.0501	0.0500
	95% Unsaturated			
A	0.0692	0.0673	0.0754	0.0748
B	0.1092	0.1077	0.1192	0.1183
C	0.1462	0.1447	0.1595	0.1585
D	0.0432	0.0421	0.0470	0.0455
E	0.0434	0.0428	0.0477	0.0465
	95% Saturated			
A	0.0686	0.0677	0.0748	0.0745
B	0.1092	0.1088	0.1192	0.1178
C	0.1467	0.1469	0.1595	0.1574
D	0.0433	0.0426	0.0470	0.0473
E	0.0444	0.0435	0.0477	0.0476

[a] Average of determinations in each case.

Table IV. Potash Determinations on Mixed Fertilizer Using 80 and 95% Alcohol

1946 A.O.A.C. Collaborative Samples	No. of Analyses Averaged	Average % K_2O	Average Difference between Alcohols, %
A(0-12-12)			
80%[a]	12	13.05	..
95%[b]	4	13.13	0.08
B(0-20-20)			
80%	12	20.85	..
95%	12	21.04	0.19
C(0-9-27)			
80%	12	27.30	..
95%	8	27.41	0.11
D(8-8-8)			
80%	12	8.14	..
95%	10	8.24	0.10
E(4-12-8)			
80%	12	8.36	..
95%	12	8.48	0.12
F. S. Royster Guano Co.'s Samples			
R-7(3-9-9)			
80%	4	10.49	..
95%	4	10.64	0.15
R-3(2-12-12)			
80%	4	15.61	..
95%	4	15.67	0.08
R-5(5-10-5)			
80%	4	5.18	..
95%	4	5.25	0.07
R-6(0-12-12) with borax			
80%	4	12.88	..
95%	4	13.02	0.14
R-7(3-8-5)			
80%	4	5.33	..
95%	4	5.39	0.06

[a] 80% alcohol by volume. [b] 95% alcohol by volume.

sample. Less than one fifth as much potassium chloroplatinate (0.21 gram per liter) was dissolved by the higher strength acid-alcohol (made from 95% alcohol).

In the case of acid-alcohol made from 95% alcohol saturated with potassium chloroplatinate, Table I shows that, except in two cases where the results were the same, somewhat higher potash results may be expected. This increase ranged from zero with a 4-12-8 and a 0-9-27 fertilizer to 0.39% with a 0-12-12 fertilizer. The average increase was 0.09%. The average increase would be expected to be less with acid-alcohol made from 95% alcohol than with acid-alcohol made from 80% alcohol, because of the greater solubility of potassium chloroplatinate in acid-alcohol made from 80% alcohol.

Table IV provides further confirmation of the findings of Ford and Hughes (*4*) and Mitchell and Ford (*6*) that 95% alcohol gives higher potash values than 80% alcohol. These values ranged from 0.06% with a 3-8-5 fertilizer to 0.19% with a 0-20-20 fertilizer. The average increase was 0.11%.

The use of sodium acetate in place of sodium hydroxide in the official method resulted in somewhat lower potash values (Table II). The results in this limited study under three different sets of conditions showed values ranging from 0.16 to 0.19% lower when sodium acetate was used.

In Table III it is shown that platinum and chloride values found agree well with the theoretical.

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Titration of Fluoride Ion with Aluminum Chloride

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THE titration of fluoride ion with aluminum chloride depends on the formation in nearly neutral solution of the stable complex ion, AlF_6^{---}, the sodium salt of which is only slightly soluble in the presence of an excess of sodium ion or in alcoholic solutions. Published methods propose conductometric titration in alcoholic solutions with aluminum chloride (*5*), titration in aqueous solution with basic aluminum chloride to the phenolphthalein end point (*3*), and titration in neutral (phenolphthalein) aqueous solution to the methyl red end point (*6*). Geyer (*4*), who has reviewed most of the current methods for determining fluoride ion, found that the last-named method gave the best results.

The present work describes the titration of fluoride ion in aqueous solution with aluminum chloride, using Eriochromcyanine R as an internal indicator. This dye was first utilized as a qualitative test for aluminum ion (*2*) and later made the basis of colorimetric procedures (*1, 7, 8, 10*).

PROPERTIES OF ALUMINUM LAKE

Eriochromcyanine R in aqueous solutions forms a red-violet lake with aluminum ion. The formation of the lake is strongly dependent on the pH of the solution and the color of the dye itself in aqueous solution varies with pH. A solution of the dye is yellow-orange at pH 5.4 to 6.0, yellow at a higher pH, and red-orange at a lower pH. The color also varies with the age of the solution, changing from red-orange to yellow after about a week.

A method is described for titrating fluoride ion with aluminum chloride, using Eriochromcyanine R as an indicator. The method was tested by the analysis of pure sodium fluoride which was distilled as hydrofluosilicic acid.

The colorimetric determinations of Millner (*7*, *8*) were done in a buffer of pH 5.4, while Richter (*10*) showed that better results were obtained at a pH of 3.8 and with freshly prepared solutions of the Eriochromcyanine. However for use as an indicator, it is necessary to adjust the pH so that the Eriochromcyanine is yellow before the addition of aluminum ion.

It has also been pointed out by the previous investigators that Eriochromcyanine R is not a specific reagent for aluminum ion but various other metal ions, particularly divalent and trivalent ions, interfere. The reaction is also subject to a salt error. Sulfate ion in particular interferes with the formation of the lake but sodium chloride has very little effect.

Table I. Standardization of Aluminum Chloride Solutions against Sodium Fluoride

(20 ml. of sodium fluoride solution, 1.000 gram of F^- per liter, used for each titration)

Solution 1, $AlCl_3$, Ml.		Solution 2, $AlCl_3$, Ml.	
4.518	4.525		4.349
4.505	4.527		4.350
4.526	4.519		4.350
4.522	4.514		4.352
Mean	4.520	Mean	4.350
Mean dev.	1/1000	Mean dev.	0.2/1000
Max. dev.	5/1000	Max. dev.	1/1000
$AlCl_3$	0.2330 *N*	$AlCl_3$	0.2421 *N*

$AlCl_3$ 0.2319 *N* from analysis for Al.

EXPERIMENTAL

Sodium fluoride was prepared from hydrofluoric acid and sodium acid carbonate in platinum as described by Reynolds and Hill (*9*). Solutions of sodium fluoride containing 1.000 gram of fluoride ion per liter were used as standard solutions. The Eriochromcyanine R was obtained from the Geigy Company, Inc., New York, N. Y.

Standardization of Aluminum Chloride Solutions. Two drops of phenolphthalein were added to 20.00 ml. of standard sodium fluoride solution and the pH was carefully adjusted with split drops of 0.1 *N* sodium hydroxide and 0.1 *N* hydrochloric acid until the pink of the phenolphthalein just disappeared. Then 10 grams of sodium chloride (reagent grade, sulfate-free) and 4 drops of a 0.1% aqueous solution of Eriochromcyanine R were added. The resulting solution should be yellow. The solution was then placed on a hot plate and heated just to boiling and if necessary, the pH of the hot solution again adjusted until the color was yellow. The solution should be saturated with sodium chloride.

The aluminum chloride solution was slowly added from a microburet to the hot solution. The temperature of the solution should be just below boiling, and the slow addition of the aluminum chloride (one drop every 2 or 3 seconds) is important. Near the end point, the addition was still slower with good mixing. Just before the end point, the color of the solution becomes darker with a sharp change to pink at the end point. The end point is not sharp if the titrations are done at temperatures below 85° to 90° C. It proved convenient to use very gently boiling solutions or solutions at temperatures just below boiling, as, if the solutions are boiled vigorously, the lake formed at the end point precipitates. The same results were obtained with both freshly prepared and aged solutions of Eriochromcyanine. The indicator blank was 0.002 to 0.004 ml. for the volumes used in these titrations.

Some typical results for the standardization of two different aluminum chloride solutions are given in Table I. One solution was also analyzed for aluminum by precipitation with 8-hydroxyquinoline, giving results for the normality differing from that determined by the titration of sodium fluoride by 4 parts per 1000. The mean deviation in the aluminum determinations was 2 parts per 1000. In view of this discrepancy, it was deemed desirable always to standardize the aluminum chloride solutions used against pure sodium fluoride. The normality of the second solution was found to decrease by 6 parts per 1000 over a period of 2 months.

Determinations of Sodium Fluoride Distilled as Hydrofluosilicic Acid. Lead, nickel, chromium, carbonate, silicate, sulfide, and sulfate ions when present in appreciable quantities gave high results in the titration and doubtless other divalent and trivalent ions will give similar results (*10*). Therefore, since in most cases it will be necessary to separate fluoride from interfering substances before titration, a series of determinations was made with sodium fluoride in which the fluoride ion was distilled as hydrofluosilicic acid according to the method of Willard and Winter (*11*).

Fifty milliliters of the standard sodium fluoride solution and 20 ml. of 18 *M* sulfuric acid were placed in the distillation flask and 250 ml. of solution were distilled into a volumetric flask. Further portions were distilled and shown to be free of fluoride ion. The presence of larger amounts of fluoride ion often requires the distillation of larger volumes. Different aliquots were titrated as described above, using 2 drops of the Eriochromcyanine solution and 5 grams of sodium chloride for each 10 ml. of the aliquot. The indicator blank was found to be 0.015 ml. for the 50-ml. and 0.03 ml. for the 100-ml. aliquots. The results are summarized in Table II.

While the high results obtained when the distillation was carried out at 145° might arise from sulfuric acid in the distillate, it is believed that the results in Table II do not justify a definite conclusion.

Table II. Determination of Fluoride Ion Distilled as Hydrofluosilicic Acid

[50 ml. of standard sodium fluoride solution (0.1105 gram of NaF) distilled with sulfuric acid and titrated with 0.2421 *N* aluminum chloride. Temperature of distillation 135° ± 5° C. unless otherwise stated. Volume of distillate 250 ml.]

Run No.	$AlCl_3$, Ml.	Aliquots, Ml.		F Found, %
1	2.163	50		45.0
	2.169	50		45.1
2	2.163	50		45.0
	2.164	50		45.0
	2.167	50		45.1
3	2.694	25	(250 ml. of distillate evaporated to 75 ml. and made to 100 ml.)	44.8
	2.710	25		45.1
	2.702	25		45.0
4	2.169	50		45.1
	2.483	50		45.4
	4.356	100		45.3
5	2.178	50	(temperature 145° ± 5°)	45.3
	4.371	100		45.5
			Mean	45.1 ± 0.1
			Theory	45.24

In general, better results have been obtained when the solution is not evaporated after the distillation. High results were usually obtained when the distillates neutralized to phenolphthalein were evaporated in glass to a small volume. Such results were probably caused by dissolved silica.

CONDUCTOMETRIC TITRATIONS

Some work has been done on the conductometric titration of alcoholic solutions of fluoride ion with aluminum chloride as described by Harms and Jander (*5*). Results were consistent to about 10 parts per 1000, which was about the limit of the instrument used. The method is much more tedious than the ti-

tration method described here. Efforts to titrate sodium fluoride conductometrically with thorium nitrate were unsuccessful, as no definite end point was obtained.

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Evaluation of Catalysts for Catalytic Cracking

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A group of physical and chemical analyses is discussed, to be used for the evaluation of catalyst in fluid catalytic cracking units.

CATALYTIC cracking is a relatively new, but very important, process in the field of petroleum refining. Within recent years the fixed-bed catalytic cracking units have been outnumbered by the newer fluid-type process. By means of both processes, enormous quantities of high octane aviation gasoline were produced during World War II. Today these same units are producing high-performance fuels of low lead content from varied types of charging stocks.

For the efficient operation of catalytic cracking units, the refiner must have a knowledge of all the properties of a solid catalyst. Since the catalyst is a fine solid having an amorphous lamellar structure, the majority of catalyst tests have measured the physical rather than the chemical nature of the catalysts. When it is realized the catalyst is a very fine solid similar in appearance to fuller's earth, the purpose in measuring these physical properties can be better appreciated. There are two generally accepted catalysts suitable for use in the fluid cracking process—natural and synthetic. The synthetic catalyst is of a more uniform physical structure and has been refined to contain a minimum of contaminants. Probably three of the most important physical tests of these catalysts are density, volatility, and particle size. Density and volatility are most valuable for inventory and for checking quantity and conformation to specifications.

PHYSICAL PROPERTIES (7)

Densities are usually expressed as pounds per cubic foot and may be determined by four general methods—aerated, freely settled, compacted, and pressure.

A known weight (approximately 100 grams) of catalyst is weighed into a graduated cylinder. The aerated density requires the mixing of the catalyst with air. This is done by placing the palm of the hand over the open end of the graduate and inverting it several times, allowing the catalyst to fall completely from one end of the cylinder to the other. From the volume after aeration and the weight of catalyst, the aerated density is calculated.

Using the same sample, the cylinder is left undisturbed until the volume becomes constant. In general, 15 to 20 minutes are sufficient for establishing this condition. This volume divided by weight of catalyst results in freely settled density.

The graduated cylinder is then tapped by hand on a surface such as the top of the laboratory table approximately 120 times per minute until the volume has become constant. Density calculated from this volume is the compacted density.

The density under pressure may be determined at any pressure desired. Most commonly, this is 5 pounds per square inch (1.4632×10^4 grams per sq. cm.). Approximately 100 grams of catalyst are weighed into a graduated cylinder and allowed to settle freely. The desired pressure is then applied and the volume recorded. Pressure may be applied by several methods; however, a very simple method is to use a piston-type assembly. The rod may be the upright from a ring stand and the piston is easily made from a cork. From the diameter of the cylinder and the weight of the piston assembly, the mass to be applied on the rod is calculated. If the same cylinder is always used, this mass may be used continually, being checked periodically for any change of weight. Typical densities are reported for aeration, freely compacted, and pressure 5 pounds per square inch in Table I.

Table I. Catalyst Densities

	Synthetic	Natural
	Pounds per cubic foot	
Aerated	39.0	49.1
Freely settled	45.2	46.5
Compacted	63.7	55.7
Pressure, 5 pounds per square inch	52.2	54.6

Total volatility, generally used for correction of catalyst weight, is determined by heating the catalyst sample at 1750° F. to a constant weight. This usually requires no more than 30 minutes. The catalyst is weighed into a low-form wide-mouthed crucible and placed in a cold muffle furnace. The temperature is then gradually raised until 1750° F. is attained. By this method of heating the evolution of volatile materials is not rapid enough to spatter the fine catalyst from the crucible. The crucible and catalyst are cooled in a desiccator and reweighed. From the loss in weight the total volatility is calculated:

$$\text{Total volatility} = \frac{\text{loss in weight}}{\text{weight of sample}} \times 100$$

The size of the particles is of eminent importance in evaluating the fluid characteristics of the catalyst. Ordinary sieve analysis is useful to a certain extent but includes only the material retained on a 200-mesh screen. This may represent only a small portion of the total catalyst.

For measurement in the subsieve range, the Roller particle analysis has been found satisfactory. This procedure, based on air elutriation, separates the catalyst containing particles varying from 0–10 microns to greater than 80 microns into fractions, usually 0–10, 10–20, 20–40, 40–80, and 80+ microns.

The actual analysis is comparatively simple in operation. The procedure may be followed by referring to the diagram (Figure 1) of Roller particle analyzer (2).

Trap I is intended to receive any oil or dirt in the air supply; the humidifying jar is charged with a solution of sulfuric acid (40% sulfuric acid plus 60% water by volume) to maintain a relative humidity of 25%, and trap II is to collect acid spray that may be carried over from the humidifier. The paper filter is filled with paper thimbles of the type used for collecting the fractions. These prevent entrance of any foreign particles into the analyzer proper. The flowmeter is equipped with two orifices: 0.067 inch (0.170 cm.) for flow rates up to about 13 liters per minute, and 0.120 inch (0.305 cm.) for greater flow rates. The jet, varying from 0.038 to 0.096 inch in diameter (0.089 to 0.244 cm.), located just inside the U-tube and above the catalyst sample, is so selected as to give a pressure differential on the mercury manometer of approximately 1.5 inches (3.810 cm.). This ensures a fairly constant jet velocity regardless of air rate. The sample (approximately 10 grams) remains in the bottom of the U-tube until it is aerated by air from the jet.

The U-tube, with the jet in one end, is connected to the bottom of the settling chamber at the other end by means of a short rubber coupling. A metal arm guides the motion of the tube. During operation, fiber hammers constantly tap the U-tube, working the catalyst towards the jet. The settling chamber is connected to the collection thimble through a glass gooseneck; rubber couplings are used at all points of junction. The separation of the selected particle size takes place in the settling chamber and is dependent on air velocity, which is controlled by changing settling chambers and maintaining a constant flow rate. Four chambers are available, having diameters of 9, 4.5, 2.5, and 1.125 inches (22.86, 11.430, 5.715, and 2.858 cm.) and providing relative air velocities of 1, 4, 16, and 64 at a constant rate of air flow. The ground tap dispels static electricity generated by friction, and fiber hammers constantly tap the side walls of the chamber to prevent adherence of the particles. The collector thimble is of such material as to allow passage of the air but retain the catalyst.

The instrument is calibrated by making separations and examining these microscopically. A micrometer eyepiece calibrated against a precision micrometer stage enables one to take measurements of the particles with comparative ease. The variable operating conditions are altered until the mean size of the particles as measured is approximately the average of the fraction—that is, the mean size of the particles of the 20- to 40-micron fraction should be 30 microns.

The actual analysis is performed by placing a weighed sample of catalyst in the U-tube, elutriating with air, and collecting the fractions in a clean tared thimble; the settling chamber is changed after each fraction. The per cent of particles occurring in each fraction is calculated as follows:

$$\% = \frac{\text{weight} \times 100}{S}$$

where

% = per cent of sample which occurs in a given fraction
Weight = total weight, in grams, of material collected during separation
S = weight of sample in grams

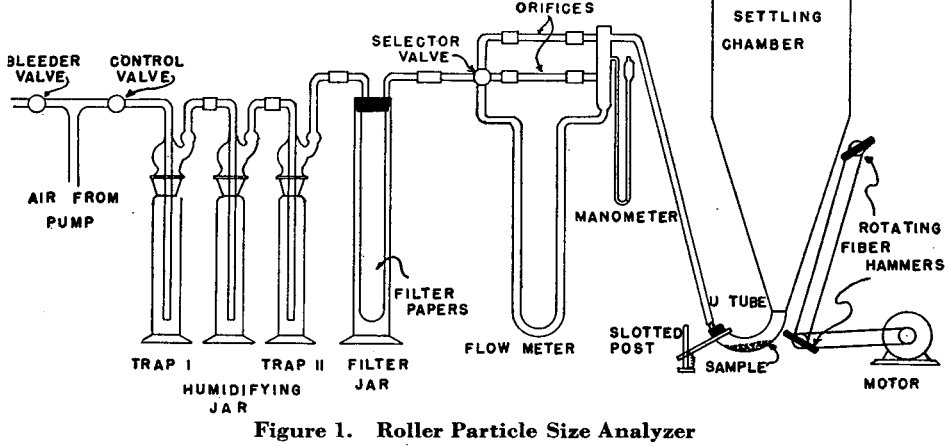


Figure 1. Roller Particle Size Analyzer

Table II. Typical Analysis of New Synthetic and Natural Catalysts

	Synthetic	Natural
Total volatile	6.0	21.0
Alumina, Al_2O_3	10.6	15.7
Sodium, Na_2O	0.05	0.32
Iron, Fe_2O_3	0.05	0.32
Particle size, weight %		
0–10 microns	11	6.3
10–20 microns	12	11.5
20–40 microns	21	19.0
40–80 microns	30	25.2
80+ microns	26	38.0
Sieve analysis, weight %		
+40-mesh	0	0.1
40–80-mesh	0.5	1.9
80–100-mesh	0.2	1.9
100–200-mesh	20.0	26.3
200–325-mesh	46.8	43.6
−325-mesh	32.5	26.2
D + L activity	62	45
Gas-producing factor	0.7	1.0
Carbon-producing factor	1.0	1.3
Aromatic adsorption index	70	27
Estimated surface area	475	185

Table III. Typical Analysis of Regenerated Synthetic and Natural Catalysts

	Synthetic	Natural
Sodium, Na_2O	0.09	0.42
Iron, Fe_2O_3	0.31	1.61
Particle size, weight %		
0–10 microns	4.2	6.4
10–20 microns	11.0	12.3
20–40 microns	17.8	25.8
40–80 microns	22.8	26.7
80+ microns	44.2	28.8
Sieve analysis, weight %		
+40-mesh	0	0.3
40–100-mesh	0.4	4.6
100–200-mesh	12.6	16.7
200–325-mesh	30.0	32.6
−325-mesh	57.0	45.8
D + L activity	28.0	23.5
Gas-producing factor	0.8	2.9
Carbon-producing factor	1.0	3.0
Aromatic adsorption index	16.7	15.5

Sieve analysis is useful if interest is centered in the coarse material.

A weighed sample (approximately 30 grams) is placed in the sieves, which vary from 40- to 325-mesh. After being shaken for 30 minutes on a Ro-Tap shaker, the sieves are removed and the catalyst retained on each is carefully removed and weighed. From this weight the percentage of catalyst retained by each sieve is calculated. The size distribution by both the Roller analyzer and Ro-Tap sieve is shown in Tables II and III.

CHEMICAL PROPERTIES

The composition of the catalyst is determined by chemical analysis (7). Mostly the catalysts are aluminum silicates with varying quantities of other elements. Routinely, only iron, sodium, and aluminum are determined, but some investigations have indicated that natural catalyst contains appreciable quantities of calcium, magnesium, titanium, and other substances (Table IV). The iron and sodium content of the catalyst changes considerably with use (Tables II and III). In some respects the change in iron and sodium contents indicates catalyst aging.

In general, conventional methods of chemical analysis are used. A weighed sample of catalyst is treated in a platinum crucible with hydrofluoric and perchloric acids and heated until a clear solution is formed. (Care must be taken not to allow the volume to become too small, as some insoluble perchlorates may be formed.)

This solution is then made up to volume and aliquoted for analysis of the various elements, not including silica. The R_2O_3 group is precipitated as the hydroxides and a separation between iron and aluminum is made. After such reprecipitations, the precipitate is filtered and ignited to the oxide. Such a procedure is used for the aluminum determination, although others could be used. Iron lends itself readily to reduction and consequent volumetric analysis as well as to colorimetric analysis. The authors have found reduction by diphenylamine hydrochloride, followed by the measurement of the color intensity formed with *o*-phenanthrene, adaptable to routine analysis (*4*). A Beckman quartz spectrometer is used for the color measurement. Sodium is determined by precipitation as the triple salt, sodium zinc uranyl acetate, in an alcoholic solution. The silica must be determined on a separate sample and is sublimed with hydrofluoric acid in the presence of a small amount of sulfuric acid. Since silica represents from 75 to 85% of the sample, 1.5 to 2.0 grams of sample are sufficient. If it is desirable to analyze for other possible constituents, any approved quantitative reaction is satisfactory.

Carbon content of the regenerated catalyst is determined by means of combustion in a stream of oxygen and absorption of the resulting carbon dioxide. The reaction is carried out in a carbon-hydrogen furnace fitted with multiple tubes for control analysis. Recently a volumetric procedure for measuring the carbon dioxide has been introduced. The advantages of this modification are obvious.

It is difficult to interpret the results of chemical analysis with respect to unit operations. The effect of contaminants on the activity of catalytic cracking catalysts has not been well established. However, the effect of small amounts of contaminants is not so serious in this type of catalyst as the poisoning effect observed in either oxidation or hydrogenation catalysts. Of all the possible elements present in either a regenerated or spent catalyst, carbon is of primary interest to the operator, while the others may prove very beneficial to the engineer or the chemist who is looking toward improvements.

ACTIVITY OF CATALYSTS

The exact mechanism of catalysts in cracking may not be known, but it is known that the desirable cracking reactions are accelerated. The extent to which the catalyst can aid the reaction is dependent upon its variable and intangible property known as activity. The manner of measuring this intrinsic property can be perplexing, as no one test, physical or chemical, is in itself sufficient. Several procedures have been offered and may be directly divided into two classifications: those which measure surface area, and those which employ small-scale laboratory cracking units, subjecting the catalyst to conditions which approximate the condition met in the large commercial unit.

SURFACE AREA MEASUREMENTS

There are several advantages and disadvantages involved in surface area measurements. In general, they are comparatively rapid, can be performed without excessive difficulty, require no elaborate special equipment, and are reproducible. A correlation between surface area measurements and activity ratings has been developed.

Three common methods of the surface area procedures are potassium hydroxide adsorption, aromatic adsorption (*6*), and nitrogen adsorption (*8*). All are dependent upon the adsorption of an adsorbate on the surface of the catalyst.

Table IV. *Probable Magnitude of Other Constituents of* Natural Catalyst

Titanium, TiO_2	0.29
Manganese, MnO	0.05
Magnesium, MgO	4.80
Calcium, CaO	3.18
Phosphorus, P_2O_5	0.43
Zirconium, ZrO_2	0.19
Carbonate, CO_3	0.04
Sulfate, SO_4	5.57

In the potassium hydroxide adsorption, the catalyst is ignited in a muffle furnace (1750° F.) to a constant weight to remove the volatiles. Ten grams of the ignited catalyst are weighed into an adsorption vessel and 100 ± 0.3 ml. of 0.5 ± 0.002 *N* potassium hydroxide are added. After thorough mixing, the vessel is placed in a constant-temperature bath (75° F.) for 24 hours. The catalyst is then filtered from the caustic and the filtrate is titrated with a standard hydrochloric acid solution. The final results are expressed as millimoles of potassium hydroxide adsorbed per gram of volatile-free catalyst. This method is easily reproducible but time-consuming, because of which it has been replaced by the aromatic adsorption method in several laboratories.

The aromatic adsorption procedure requires heat-treatment of new catalyst for 2 hours at 850° F. and regenerated catalyst for the same period at 1000° F., the higher temperature being used in the latter case because of the desirability of complete carbon removal. The catalyst (3.5 ± 0.01 grams) is weighed into an adsorption vessel to which are added 5.0 ± 0.1 ml. of a toluene–iso-octane mixture, prepared by mixing on a volume basis 30% toluene and 70% iso-octane. The vessel is shaken for 2 hours at room temperature and the catalyst is then allowed to settle. A portion of the supernatant liquid is removed with a small pipet and the refractive index ($n_D^{25°}$) is determined. From the change in refractive index of the aromatic-paraffinic mixture an index is calculated by the following equation:

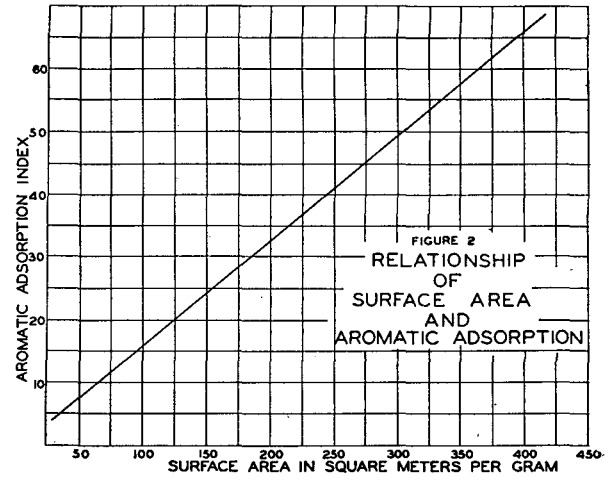
$$\text{A.A.I.} = (n_D^0 - n'_D) \times 10^4$$

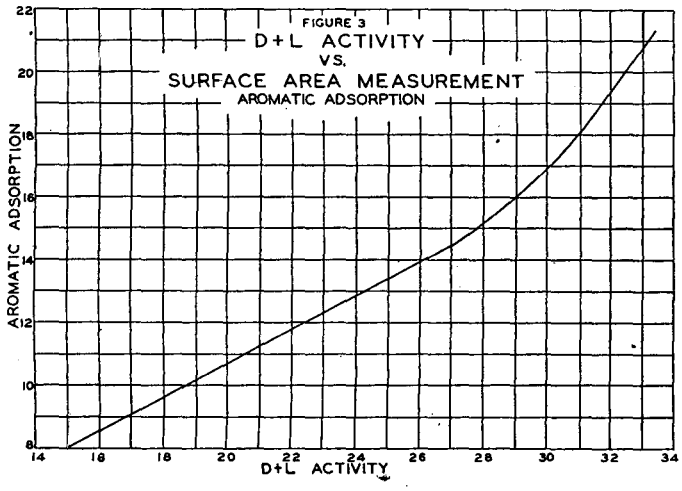
where

A.A.I. = aromatic adsorption index
n_D^0 = refractive index of original toluene–iso-octane mixture
n'_D = refractive index of mixture after contacting with catalyst

This method is in general use in the authors' laboratory and has been correlated with laboratory determination of activity in a Kellogg test unit as shown in Figure 3. These data pertain to synthetic catalyst but present investigations are being extended to include natural catalyst. The aromatic adsorption has also been correlated with surface area (Figure 2); it is a straight-line function of surface area.

Nitrogen adsorption, though used in some laboratories, is not in use in this laboratory at the present time. Briefly, when a gas such as nitrogen is contacted with a degassed adsorbent, in this





case catalyst, at very low temperatures, a portion of the nitrogen is adsorbed on the surface of the adsorbent. At such low temperature (liquid nitrogen), the volume of nitrogen adsorbed on a unit weight of solid is solely dependent on the pressure of the gas. The adsorption isotherm from the volumes at different pressures can be plotted to give the volume of gas required to form a monolayer of adsorbed gas on the surface of the solid. By further theoretical consideration, the surface of the solid may be calculated.

Figure 3 shows the relationship of aromatic adsorption and Kellogg fluidized fixed-bed activity. These data were obtained from a large number of determinations on plant catalysts of varying particle size and contamination. Synthetic catalyst was used in this extensive investigation, which is being extended to include natural catalyst. Figure 2 gives a correlation of aromatic adsorption and surface area. Data have been developed to give the relationship between surface area by nitrogen adsorption and catalyst activity measurements.

Experience with surface area measurement by aromatic adsorption and with Kellogg distillation plus loss (D + L) activity tests has indicated that these properties may be equal in importance to unit operations. However, the aromatic adsorption has not been reproducible enough to obtain the desired accuracy of activity level, nor is it indicative of contamination which would affect the catalyst's selectivity.

DIRECT DETERMINATION

The mechanism by which the catalyst accelerates the more desirable cracking reactions is not fully understood; thus, no one test of its physical or chemical properties is sufficient to describe its catalytic value in a commercial unit. Therefore, small-scale laboratory cracking tests were devised to evaluate the ability of the catalyst to convert gas oil into gasoline.

Two generalized procedures have been used in direct laboratory determinations of activity. The first tests of activity were made to compare catalysts of rather different physical and chemical characteristics for use in catalytic cracking. The test procedures and equipment were simple and permitted a number of activity determinations with a moderate amount of equipment and personnel. The results of these tests were studied and compared with pilot-plant data, until test conditions were found which gave a general correlation with pilot-plant yields.

Other activity tests were devised for a more particular purpose. The fluidized fixed-bed test was designed to test the activity of the fluid cracking catalyst in commercial units. The conditions were arranged to duplicate plant conditions in so far as possible. Certain mechanical features, beyond the scope of a simple laboratory test, include the degree of contact between catalyst and oil vapors, the density of catalyst bed, and the continuous regeneration of catalyst to maintain a low carbon content. As other commercial unit conditions, such as feed stock, are not uniform, a standard gas oil feed stock had to be selected. The results of these tests were also correlated with pilot-plant data.

Since each of the catalytic cracking processes varies chiefly in its mechanical handling of the catalyst, it would appear necessary to approximate the condition of the catalyst in the activity test for that particular process. This is the case in some of the tests described below. The value of interpreting the activity of a plant catalyst in terms of a different stock or a different set of test conditions depends upon the ability of the tester to correlate these results with plant yields and with other activity tests.

Four rather widely accepted direct activity methods are described below. They represent activity tests for catalysts used in the chief catalytic cracking processes.

U.O.P. ACTIVITY TEST (5)

The activity of a cracking catalyst is determined by comparing the total weight per cent conversion of a mid-continent gas oil to gasoline and gas by the unknown catalyst to that produced by a standard catalyst at the same conditions.

The powdered catalyst is poured into the reactor tube, consisting of a preheater and catalyst section of 2-inch I.P.S. stainless steel pipe, which is then placed vertically in an electrically heated block. The standard gas oil is pumped into the top of the reactor tube, is vaporized and heated to 932° F., and passed through the catalyst, and the products resulting from cracking are collected. The quantity of gas is measured by volume and density. The liquid product is distilled according to A.S.T.M. method D86–40. The gasoline fraction is obtained by cutting at 400° F. This is very carefully weighed; the weight per cent of gasoline is calculated. The gas is collected and measured.

The unknown catalyst is tested at a space velocity of 4 volumes of oil per volume of catalyst per hour. The conversion of the gas oil to gasoline is referred to the space velocity of a standard fresh catalyst (100 activity) at the same conversion. The ratio of space velocities necessary to produce the same amount of cracking multiplied by 100 (the activity of the standard catalyst) is known as the U.O.P. activity rating.

HOUDRY CATALYTIC ACTIVITY INDEX (1)

This laboratory method represents a duplication of the Houdry type of plant operation. In contrast to other methods, this test has a 10-minute cracking period.

Procedure. The catalyst tube and system are constructed of glass. The preheater section of the 25-mm. tubing has a volume of 100 cc. and the catalyst section a volume of 200 to 220 cc. The glass tube is handled in an electrically heated pipe-type furnace with a preheater section and a reaction section.

The catalyst sample, 200 cc., is placed in the tube and brought to temperature under nitrogen. The gas oil is fed from a buret through a capillary under adjustable nitrogen pressure. The oil enters through the preheater section and flows down through the catalyst and out through a West condenser into a liquid receiver. Both the condenser and receiver are held at 60° F. The gas is measured and sampled.

The gas oil is charged to the catalyst zone for 10 minutes; then the catalyst is flushed with exactly 900 cc. of nitrogen. The liquid product is now removed for subsequent analysis.

The carbon is then burned off the catalyst at 950° to 975° F. The carbon monoxide, which may be formed along with the carbon dioxide, is converted to the dioxide by passage over copper oxide and the total carbon dioxide determined by adsorption on Ascarite.

The liquid product is carefully distilled in a small 5- to 10-plate column for a 410° F. cut point gasoline. The weight per cent of gasoline is then calculated. The weight per cent of gas and of carbon is also reported for direct comparison with other catalyst.

KELLOGG FLUIDIZED FIXED-BED ACTIVITY TEST (5)

The activity of the powdered catalyst is measured by the amount of gasoline produced from a standard gas oil when the

vaporized oil passes up through the catalyst sample under standard conditions.

Procedure. The catalyst is blown with air to remove the very fine catalyst. This elutriated catalyst is treated for 2 hours at 850° F., if fresh, and for 2 to 3 hours at 1000° F. if regenerated. The reactor (Figure 4) consists of 5 feet of $1^1/_4$ inch pipe, for contacting the catalyst and oil vapors, with an additional 6 inches (15 cm.) of 2-inch pipe to settle catalyst from the vapors.

The powdered catalyst is charged to the reactor and kept in suspension by a stream of nitrogen entering at the bottom of the reactor. The reactor is placed in an electrically heated pipe furnace and heated to 850° F. The temperature of the catalyst is measured by means of a thermocouple located in the center of the catalyst bed.

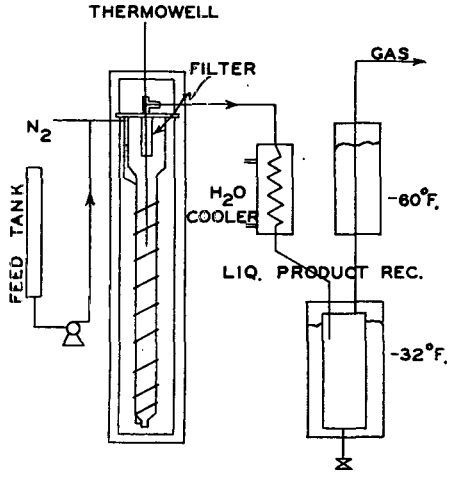


Figure 4. Kellogg Fluidized Fixed-Bed Activity Test

Test Conditions

Catalyst volume, 800 to 1200 cc., 710 grams
Catalyst zone height, 57 inches
Temperature, 850° F.
Space velocity, 0.6 weight of oil/weight of catalyst/hour (500 cc. of oil/hour)
Period length, 2 hours
Feed stock, 35° A.P.I. mid-continent light gas oil

The feed stock is pumped through the preheater coil, small-sized tubing, and the vaporized oil is charged to the reactor at the bottom of the catalyst bed. The stream of nitrogen is cut off during the cracking period, but is used as a purge gas at the end of the test period. Oil vapors pass through the catalyst, are filtered in the settling zone, and pass out at the top of the furnace into the receiving system. The liquid products are cooled and collected at 32° F. and the gases are vented through a trap held at −60° F. to a wet-test meter.

JERSEY D + L ACTIVITY TEST (3)

The Jersey D + L activity test is designed for the determining of catalysts in the form of pellets. A total of 200 cc. of pellets ($^3/_{16} \times {}^3/_{16}$ inch) is charged to each reactor tube. The furnace, containing four reactor tubes, is controlled electrically between 850° and 860° F. The charge stock is an East Texas light gas oil with a 33.8° A.P.I., and boiling between 485° and 700° F.

For 2 hours the gas oil flows down through a preheater section and catalyst bed where a space velocity 0.6 V_o/V_c per hour is maintained. The products of reaction are collected after passing through suitable condensers. The liquid products are subjected to distillation analyses and the noncondensables are measured by passing through a wet-test meter. The carbon deposits on catalysts are determined in the usual manner.

In Table V, a tabular form comparing the test conditions of all four methods is presented. All four methods are similar, with the exception of the short reaction time (10 minutes) in the Houdry catalytic index and the upward flow in the case of the Kellogg fluidized fixed-bed test. In the Jersey D + L and the Houdry catalytic index procedures, the catalyst is pelleted, while the catalyst is in a state of suspension (fluidized) in Kellogg procedure.

DISCUSSION OF ACTIVITY TESTS

It is evident from the general description of the different activity tests that a considerable variation in activity ratings may exist. It is not within the scope of this paper to discuss comparative data compiled from these tests. However, the agreement between the Jersey D + L and Kellogg fluid tests has been found fairly satisfactory for synthetic catalysts of relatively low activity.

In order to make a comparison of methods, the test conditions and methods of handling the catalyst must be studied. The three procedures for preparing the catalyst to be tested depend on the physical method of contacting the oil vapors and the catalyst sample. The Jersey D + L method employs the pelleted catalyst which must be pilled from the powdered catalyst. This method with a fixed bed of uniform pellets has a more reproducible surface area and contact between vapor and catalyst, but it neglects the shape and surface area of the original powdered catalyst.

The Kellogg fluidized fixed-bed test is the upflow type using the powdered catalyst in a partially fluidized state. This more nearly duplicates the condition of the catalyst in the commercial fluid unit. When the catalyst is very fine, it tends to resemble a liquid in its fluid properties; as such, the vapors rise in the form of bubbles instead of flowing through a porous bed. The difference in the efficiency of contact under these conditions is large. To eliminate this difficulty, the Kellogg method employs air elutriation of the catalyst to remove the finer particles. The fine material is so removed in glass apparatus until the catalyst shows proper aeration of activity test velocity conditions. This usually requires the removal of 15 to 35% fines. This procedure may be considered unsatisfactory, since the sample in its entirety is not being subjected to test. However, investigations have indicated that activity is approximately uniform throughout the size ranges. Among the studies of this effect measurements of surface area by aromatic adsorption have shown uniformity of surface in catalysts of different particle size.

The U.O.P. test utilizes a downflow unit with a fixed bed of powdered catalyst. Although the catalyst is in a powdered state, the catalyst bed is dense and channeling and pressure drops do occur. These, of course, are unfavorable to uniform contact and activity rating.

The purpose of preliminary heat-treatment is to remove volatile matter and carbon deposit. New natural catalyst may have volatile matter in the order of 25% when subjected to

Table V. Comparison of Operating Conditions on Laboratory Cracking Procedures

	Jersey D+L	Houdry Catalytic Index	U.O.P. Fluid Test	Kellogg Fluidized Fixed-Bed Test
Catalyst volume	200 cc. of $^3/_{16} \times {}^3/_{16}$ inch pellets	200 cc. of catalyst	25 cc. of catalyst	800–1200 cc. (710 grams) of catalyst
Temperature, ° F.	850–60	830–50	932	850
Space velocity	0.6 V_o/V_c/hour (120 cc. oil/hour)	$^1/_5$ V_o/V_c/hour (5 cc. of oil/min.)	4 V_o/V_c/hour	0.6 weight of oil/weight of catalyst/hour (500 cc. of oil/hour,
Period length	2 hours	10 minutes	2 hours	2 hours
Feed stock	East Texas LGO, 33.8° A.P.I., 485–700	East Texas LGO	31° A.P.I., Mid-cont. LGO, 450–470 I.B.P.	35° A.P.I., Mid-continent LGO
Equipment	4-tube furnace	Glass reaction tube in furnace	4-tube furnace	Reactor, 5 feet of $1^1/_4$ inch pipe with settling zone and filter. External preheater
Flow	Downflow	Downflow	Downflow	Upflow

treatment at 850° F. At this temperature synthetic catalyst is not appreciably deactivated by either heat or steam; though natural catalyst is much more easily deactivated, the temperature 850° F. is much lower than the regenerator temperature of the unit to which the catalyst is subjected. The heat treatment of used catalyst at 1000° F. for 2 or 3 hours will reduce the carbon deposit to less than 0.04%. Removal of carbon is considered permissible since the carbon is a function of the unit rather than the catalyst.

The selection of a standard gas oil feed stock for activity determinations is very necessary to ensure comparable results. It would seem best to select a virgin gas oil fraction, whose paraffinicity would lie in the average of most charging stocks, or which would be similar to that used by others in the same procedure. The initial boiling point should be well above 400° F., and the end point sufficiently low to obtain complete vaporization at the operating temperature designated by the test conditions. It is readily conceivable that difficulties of comparison would arise if changes in gas oil were made.

The test equipment and conditions represent a compromise between duplication of plant operations and laboratory facilities. This compromise is chosen to give the best correlation of plant yields with activity test results. The quantity of catalyst depends largely on the testing apparatus itself, but under given conditions sufficient products must be obtained for subsequent analysis. The precise control of test conditions, such as temperature and gas oil feed rate, is necessary. Separation between the gas and liquid product should be held constant in the receiver system.

The length of the test period must be long enough to produce satisfactory quantity of products and reproducible run conditions, but short enough to avoid the formation of excessive carbon deposits. It appears reasonable to attempt to hold the carbon content to the level in the commercial unit. Investigation has shown that the conversion, or activity, in the Kellogg method decreases rapidly with carbon deposit increase on the catalyst.

The analysis of the liquid product should be as accurate as the test conditions are reproducible. Two methods are used: a modified A.S.T.M. gasoline distillation, or a fractionation using a column with three to ten theoretical plates. Fractionations with a simple apparatus and procedure including measurement by weight would be preferred.

The spent catalyst must be carefully removed and analyzed for total carbon produced. The gas may be measured by volume and density, though some procedures specify analysis for hydrogen and individual hydrocarbons.

The results may be interpreted in terms of productivity or selectivity. The productivity is reported as distillation plus loss (D+L) activity or conversion. The D + L activity is obtained as the per cent evaporated at 400° F. in the distillation of the liquid product. The "conversion" or "gas-oil disappearance" is equal to 100 minus gas oil at 400° F., based on 100% product recovery. This result is a quantitative measure of the ability of a catalyst to crack gas oil under test conditions. This may roughly be considered as the activity of the catalyst.

In addition to gasoline, carbon and dry gas are also produced in the activity test. It has been found that different catalysts produce different amounts of carbon and dry gas at the same gas oil conversion. Factors, known as the carbon producing factor and the gas producing factor, have been used to report the ratios of carbon and dry gas yields to the corresponding amount of carbon and gas produced by new catalyst at the same conversion in the test unit.

New catalyst is assumed to be a standard uncontaminated catalyst with the maximum selectivity for the production of gasoline. Unit catalysts have been found to produce more carbon and dry gas after use. Attempts to correlate those factors with actual pilot-plant yields of carbon and dry gas have been only partially successful. The selectivity of the catalyst in the unit may vary appreciably, as shown by the pilot-plant studies of catalyst which has been in use for the long periods possible in the commercial unit; while surface measurements indicate that the surface area of the catalyst has been reduced, these measurements do not account for the large increase of dry gas and carbon.

Contamination of the catalyst by such active materials as iron may be responsible for this reduction of the selectivity of the catalyst. In general, this has been confirmed in laboratory and pilot-plant tests.

CATALYST ANALYSIS IN OPERATIONS

By means of the various catalyst tests the operator is assisted in determining whether the commercial unit is operating according to specifications. The effect of smooth operation at optimum mechanical conditions will improve the life and performance of the equipment and the yields from the process.

The physical properties of the catalyst are rather critical in the fluid cracking unit. The catalyst is aerated by air, steam, and hydrocarbon vapors to produce catalyst beds of varying densities which permit the circulation of catalyst in the unit. The apparent bulk density of the used catalyst is an indication of the relative amount of aeration gas necessary to reduce the actual phase density. This density is also used to convert the volume of catalyst to corresponding weight of catalyst to calculate catalyst loss. Since the density of the fines is less than that of coarser material, the density is indicative of fine concentrations in the catalyst.

The particle size is important in checking the average size of the fine catalyst particles. The sieve analysis is necessary to determine whether the catalyst contains too much coarse catalyst which may cause aeration and wear on the catalyst lines. The loss of the finer catalyst though the Cottrell precipitator or other means of separation from the flue gases will result in a unit catalyst devoid of fine catalyst. To check the retention of fines in the unit, the catalyst particle size is determined.

The operator controls the carbon content of the catalyst to prevent excessive build-up of carbon which is usually being removed at the maximum capacity of the unit. Thus, it is difficult to maintain smooth operation at maximum capacity unless the carbon level is constant. The presence of carbon on the catalyst reduces its efficiency as a catalyst, so lower levels of carbon contents are sought. If the steam stripping of the spent catalyst is not adequate, high carbon yields may result.

The operation of the regenerator depends on a very well controlled combustion of the carbon deposited on the catalyst in the cracking reaction. By maintaining a steady carbon level it is possible to attain controlled burning. The partical size of the catalyst has a very appreciable effect on the uniformity of the regular bed. Hot spots or uneven temperatures may lead to a number of serious difficulties in maintaining controlled combustion. Result of such upsets in addition to inefficiencies is to produce high temperatures causing rapid deactivation of catalyst.

The effect of these variations in catalyst is very pronounced on yields and quality of gasoline and C_4 gases. Thus it is important to determine whether the catalyst is being used to the best advantage in the unit.

The practical value of low carbon content has been demonstrated. The effect of certain contaminants on catalyst has been shown to be an increase in coke yields and probably dry gas yields. The degree of contamination economically feasible should be ascertained from plant data on catalyst additions and product yields.

The effect of activity is most important. The rate of deactivation depends on the partial pressure of the steam, the temperature, and period of time the catalyst is subjected to these variables. It is desirable to know the rate of deactivation, in order to calculate the cost of maintaining the catalyst activity. Improvement in operating conditions which may contribute to deactivation can cause substantial cost savings in fresh catalyst additions.

At the present time, many research laboratories are concentrating their efforts on improving techniques for measuring the properties of the cracking catalysts. It is believed these funda-

mental investigations will contribute much of practical significance to the present tests for catalytic cracking operations.

CONCLUSIONS

The chemical analysis of the catalyst indicates possible contamination of the catalyst. However, information on the various physical properties of the catalyst is essential to efficient operation of the unit. The catalyst activity can be estimated by surface area tests, such as aromatic adsorption or nitrogen adsorption. Several procedures for direct determination of catalyst activity in laboratory units have been described and discussed.

It is possible that future analyses on cracking catalysts will include a more detailed analysis of the metals present in catalysts. No doubt the present laboratory cracking procedures will be standardized to allow a better interpretation of the results. The use of surface area measurements may become more widely accepted.

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Analysis of Cemented Carbide Compositions

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A procedure for the complete analysis of complex cemented carbide compositions is described. The classical methods for the separation of the elements encountered and the published procedures for the analysis of these compositions leave much to be desired. The method described by the authors is more rapid and is shown to give good agreement on known mixtures. Procedures are also given for the determination of individual elements.

THE analysis of cemented carbide compositions is among the most difficult to be performed in the field of inorganic materials. Very little has been published on the analysis of these compositions and the classical methods of Schoeller (*4*) and others for the separation of tungsten, tantalum, columbium, and titanium are time-consuming and unsatisfactory. Evans and Box (*2*) have published a method which is based on the unavailability of a powdered sample and involves a time-consuming solution treatment as well as several difficult separations. Although many of the elements present in cemented carbides are present in steel as minor constituents, the methods for determining them in steel fail when applied to the quantities present in cemented compositions.

The major constituents of virtually all the compositions marketed at present are tungsten carbide and cobalt. Compositions containing only these constituents present no great problems for the analyst. By far the majority of the compositions also contain titanium carbide, sometimes as much as 30% or more, and may contain tantalum and columbium carbide in addition to or in place of the titanium carbide. Other elements present in small percentages usually as impurities include iron, nickel, molybdenum, vanadium, chromium, free carbon, nitrogen (*3*), oxygen, and sometimes aluminum. In the face of such a complexity, it is worth while for the analyst to have a qualitative spectrographic analysis as a guide, since the scheme can be simplified if certain elements are known to be absent. Such an analysis is always run in this laboratory as a preliminary to the chemical analysis.

The scheme outlined below has been found to be more rapid than any with which the authors are familiar and at the same time to give good agreement on known mixtures.

The accuracy of the various determinations is limited as compared with that to which the analyst is ordinarily accustomed in the analysis of such materials as steel, because of the lack of suitable methods for complete separation of some of the elements. In particular, tantalum, columbium, and titanium, when they occur together, present a very difficult problem.

The procedure for complete analysis is based on solution of a powdered sample in hydrofluoric and nitric acids, precipitation of the tungsten with cinchonine, correction for the impurities in the tungsten precipitate by fusion, and precipitation with cupferron. The total oxides of tantalum, columbium, and titanium are then determined by a cupferron precipitation, and the titanium is determined colorimetrically, the columbium by the use of a Jones reductor, and the tantalum by difference. Minor elements are separated and determined during the course of the analysis. Even this procedure requires a minimum of three working days for a complete analysis.

Since the determination of only individual elements is desired on many occasions, much time can often be saved by the use of procedures for the individual elements instead of the complete analysis scheme.

SAMPLE PREPARATION

Sample preparation is most important with these materials, inasmuch as solution by any means is difficult. In this laboratory all samples are crushed to pass a 200-mesh sieve. To avoid contamination, a mortar with a carbide insert and a carbide-tipped pestle are used, the latter driven by a small riveting hammer. The general arrangement is shown in Figure 1. This equipment has been found entirely satisfactory through three years of use and far more satisfactory than the use of a hand hammer with the same mortar and pestle. The crushing of tips in steel mortars

has been found to introduce as much as 1% of iron contamination.

DETERMINATION OF CARBON

Total carbon is determined by combustion. The 200-mesh samples burn readily at 1800° F. without accelerators. Since the carbon content is high, running as much as 8% or more, no more than an 0.5-gram sample should be taken and ample time, usually 10 minutes, should be used to sweep the tube.

Free carbon is determined as follows: Weigh 1 to 5 grams of the sample into a platinum dish and add 15 ml. of nitric acid (sp. gr. 1.42). Warm the dish gently and add a few drops of hydrofluoric acid (48%) from time to time until solution is complete. Add 5 ml. of phosphoric acid (sp. gr. 1.71) and heat until most of the hydrofluoric acid has been removed. Add 15 ml. of a saturated boric acid solution and warm for a few minutes. Filter on a thin layer of burned asbestos in a perforated platinum boat. Wash thoroughly with hot water and dry in an oven 1 hour at 105° C. Determine the carbon by combustion in the usual manner, correcting for any carbon in the asbestos by a blank run.

DETERMINATION OF TUNGSTEN, TITANIUM, COLUMBIUM TANTALUM, IRON, COBALT, NICKEL (ALUMINUM)

Solutions Required. Cinchonine Solution. Dissolve 5 grams of cinchonine alkaloid crystals in 100 ml. of hydrochloric acid (sp. gr. 1.19).

Cinchonine Wash Solution, 2 ml. of cinchonine solution and 50 ml. of hydrochloric acid (sp. gr. 1.19) per liter.

Cupferron Solution. Dissolve 50 grams of cupferron (nitrosophenyl hydroxylamine–ammonium) in distilled water and dilute to 1 liter. This solution is unstable upon long standing and should be prepared daily.

Ferric Sulfate Solution. Dissolve 100 grams of ferric sulfate in a solution of 150 ml. of phosphoric acid (sp. gr. 1.71), 20 ml. of sulfuric acid (1 to 1), and 850 ml. of water.

Hydrochloric Wash Solution, 50 ml. of hydrochloric acid (sp. gr. 1.19) diluted to 1 liter.

Ammonium Hydroxide Wash, 30 ml. of ammonium hydroxide (sp. gr. 0.9) diluted to 1 liter.

Procedure. Transfer an accurately weighed 0.5000-gram sample (0.2500 gram may be used satisfactorily if only a small sample is available) to a 200-ml. platinum dish and add 10 ml. of hydrofluoric acid (48%) or sufficient to cover the sample. Cover the dish with a platinum lid and place the dish on a steam bath. Add nitric acid (sp. gr. 1.42) dropwise and warm until the sample has completely dissolved. Remove the lid, rinse with distilled water, and continue heating until a low volume is obtained. Add 30 ml. of perchloric acid (70%) and heat the dish at a higher temperature until fumes of perchloric are observed. Cool, add 15 ml. of water, and warm gently with stirring to dissolve the soluble salts. Transfer the contents of the platinum dish to a 400-ml. beaker. Police the platinum dish and add the rinsings to the 400-ml. beaker, add a few drops of ammonium hydroxide (sp. gr. 0.9) to the dish, police, and rinse into the beaker. Add 10 ml. of hydrochloric acid (sp. gr. 1.19) to the platinum dish and also rinse into the beaker. Fume the solution until heavy fumes of perchloric are observed, cool, wash down the lid and sides of the beaker, add 20 ml. of boric acid (2%), and refume. Care must be taken not to drive off all the perchloric acid.

Cool, rinse down the top and sides of the beaker, add 10 ml. of hydrochloric acid (sp. gr. 1.19), 5 ml. of cinchonine solution, and 50 ml. of water, and boil for 15 minutes. Dilute to 300 ml., add paper pulp, and allow the tungstic acid to settle by standing in a warm place for at least 10 hours or overnight.

Filter the tungstic acid, using a No. 40 Whatman filter paper and adding ashless paper pulp in the apex of the filter paper. Reserve the filtrate in a 600-ml. beaker (filtrate I). Wash the precipitate (precipitate A) 10 to 12 times with warm hydrochloric acid (5%) containing 2 ml. of cinchonine per liter of wash. Return precipitate A to the 400-ml. beaker and add 40 ml. of hot hydrochloric acid (1 to 1). Macerate the paper with a glass stirring rod, and add a few drops of nitric acid (sp. gr. 1.42). Add 5 ml. of cinchonine solution, dilute to 300 ml. with distilled water, and continue boiling for 5 minutes. At the end of this period, allow the tungstic acid precipitate to coagulate for 4 to 6 hours. Filter precipitate A, using No. 40 Whatman paper and paper pulp, wash well with warm hydrochloric acid wash, and add the filtrate and washings to the 600-ml. beaker containing filtrate I. Place precipitate A in a weighed platinum crucible, ignite carefully, and retain in a desiccator until later.

Reduce the volume of filtrate I by boiling, and add 10 ml. of nitric acid (sp. gr. 1.42) and 10 ml. of perchloric acid (70%).

Reduce the volume of filtrate I and fume (sufficient perchloric acid is present). After fuming, dilute the solution to 100 ml. with distilled water, add 10 ml. of hydrochloric acid (sp. gr. 1.19) and 5 ml. of cinchonine, and boil for 10 minutes. After 3 or 4 hours' standing, filter the solution, using No. 40 Whatman paper and paper pulp. Wash precipitate B well (10 to 12 times) with hydrochloric acid (5%) containing cinchonine. Retain the filtrate as filtrate II. Carefully ignite precipitate B in the crucible containing the ignited precipitate A, remove the crucible from the heat, and cool. Add 1 ml. of hydrofluoric acid (48%) and a few drops of sulfuric acid (sp. gr. 1.84) to remove any silica that may have been picked up from the beaker, and evaporate to dryness on a sand bath. Heat the crucible at 800° C., to ensure complete volatilization of excess hydrofluoric acid, cool, and weigh. The weight represents impure tungstic oxide and must be corrected, as some titanium, columbium, tantalum, etc., are carried along with the tungstic oxide. (By proper washing of the tungstic acid, cobalt, nickel, and iron are eliminated.)

After checking filtrate II for further tungstic acid, correct the impure tungstic oxide as follows: Fuse the impure tungstic oxide with 6 to 8 grams of C.P. potassium bisulfate at a low heat in the original dish. Cool the melt, add 20 ml. of tartaric acid (50%), and warm the dish on a steam bath. Transfer the contents of the dish when dissolved to a 250-ml. beaker, dilute to 200 ml., and cool to 10° C. Add cupferron solution (5%) with constant stirring until an excess is indicated by the appearance of a white precipitate which disappears rapidly. Filter the precipitated titanium, columbium, and tantalum. Wash with a dilute hydrochloric acid wash containing tartaric acid. Ignite the cupferron precipitate and repeat the purification by addition of 5 ml. of hydrofluoric acid (48%). Reduce the volume to 1 ml. on a steam bath, add 20 ml. of tartaric acid (50%), warm the dish for 5 minutes on a steam bath, transfer the contents of the dish to a 250-ml. beaker containing 30 ml. of saturated boric acid solution, and dilute to 200 ml. Cool to 10° C. and precipitate with cupferron as before. Filter, wash, and ignite the precipitate at a final temperature of 1100° C. This weight (C) represents the titanium, columbium, and tantalum that was coprecipitated with the tungstic acid.

Deduct weight C from the weight of precipitates A + B. The difference represents tungstic oxide plus any molybdenum which is present. Combine the filtrates from the cupferron precipitations and determine molybdenum by precipitating with hydrogen sulfide. Make the filtrates 5% ammoniacal and pass hydrogen sulfide gas through the solution for 30 minutes. Add sulfuric acid (1 to 1) cautiously to the solution and adjust to 2%

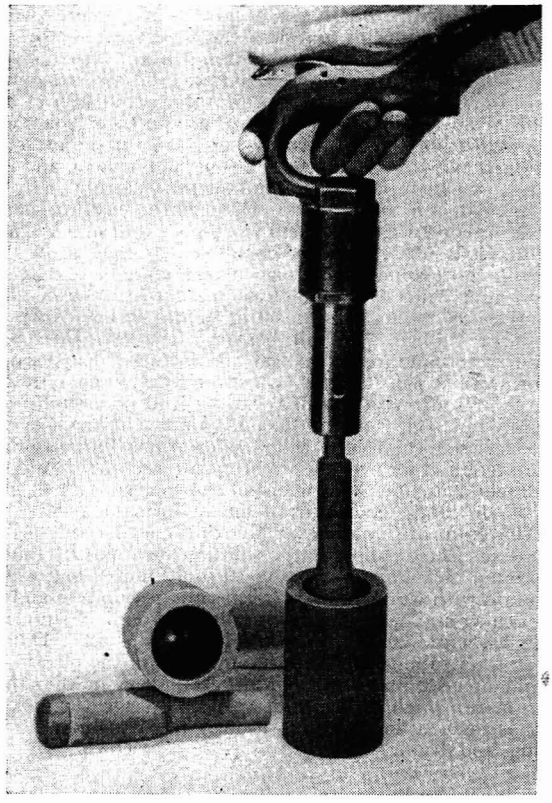

Figure 1. Mortar and Pestle

acidity. Continue gassing for an additional 20 minutes. Warm the solution to just below boiling and keep warm for at least 5 hours. The addition of paper pulp will aid in the settling of the molybdenum sulfide precipitate. Destroy the sulfide with nitric acid (sp. gr. 1.42) and sulfuric acid (sp. gr. 1.84) and determine molybdenum colorimetrically. Convert to MoO_3 and deduct from the impure tungstic oxide (AB). Convert the balance of weight AB to tungsten by multiplying by 0.793. Retain precipitate C.

Fume filtrate II. (Any further tungstic acid precipitate is filtered and added to precipitate AB before correction of the impure tungstic oxide.) Dilute to 200 ml. with distilled water, add 30 ml. of hydrochloric acid (sp. gr. 1.19), and cool to 10° C. Add ashless paper pulp and cupferron solution (5%) until precipitation is complete. Filter, using No. 42 Whatman filter paper with gentle suction. Wash the paper and precipitate at least 15 times with cold hydrochloric acid (10%) containing 20 ml. of cupferron per liter. Retain the filtrate (III). Add the precipitate (D) to the crucible containing precipitate C and ignite carefully at a temperature not over 800° C. Fuse the precipitate with 5 to 10 grams of C.P. potassium carbonate. Leach the cold melt with water and add paper pulp. Cool to room temperature, filter, and wash the precipitate well with dilute potassium carbonate solution. Return the precipitate to a 400-ml. beaker, add 60 ml. of hydrochloric acid (sp. gr. 1.19), and boil 5 minutes. Add 150 ml. of water and cool the solution to 10° C. Precipitate the titanium, columbium, tantalum, and iron with cupferron, filter, wash well with hydrochloric acid wash, and ignite as before raising the temperature finally to 1100° C. The weight of this precipitate (CD) represents the weight of the oxides titanium, columbium, tantalum, and iron.

The separation of the total oxides is more easily carried out if the sample has been previously examined spectrographically. The elimination of any of the elements (titanium, columbium, tantalum, or iron) simplifies the separation of the oxides obtained. If the spectrographic examination has shown tantalum and columbium to be absent or virtually so, the combined oxide weight provides a gravimetric value from which the titanium content is calculated. If the other two elements are present, the color method is used as described below.

Fuse the combined oxides (precipitate CD) with 8 to 10 grams of C.P. potassium pyrosulfate and dissolve the melt in 30 ml. of tartaric acid (50%). Transfer to a 250-ml. beaker containing 2 ml. of sulfuric acid (sp. gr. 1.84), make the solution 2% ammoniacal, and pass hydrogen sulfide through the solution for 20 minutes until the iron is completely precipitated. Filter the iron sulfide after the precipitate has settled, using No. 40 Whatman paper and paper pulp. Wash the precipitate 8 to 10 times with ammonium hydroxide wash containing 5 grams of C.P. ammonium oxalate saturated with hydrogen sulfide. The precipitate (E) is iron sulfide, the filtrate (IV) contains titanium, columbium, and tantalum.

NOTE. The authors have never encountered any difficulty from platinum picked up earlier in the analysis, which, if present in excess, might not be separated sufficiently by the following ammonium hydroxide precipitation and would thus cause high results for iron. According to Cunningham (*1*) this can be overcome by first precipitating with hydrogen sulfide in the acid solution and then proceeding to the hydrogen sulfide precipitation after filtration and washing to remove the platinum and other elements.

Return the iron sulfide (E) to the beaker, add 20 ml. of nitric acid (sp. gr. 1.42) and 10 ml. of sulfuric acid (sp. gr. 1.84), and fume. When all the organic matter has been removed, dilute the contents and make an ammonium hydroxide separation. Filter the iron hydroxide and wash with dilute ammonium hydroxide.

Dissolve the iron hydroxide with hot hydrochloric acid (10%) and determine iron by the Zimmermann-Reinhardt method.

Boil the filtrate (IV) containing titanium, columbium, and tantalum to expel the hydrogen sulfide, add 40 ml. of hydrochloric acid (sp. gr. 1.19), and boil until the volume has been reduced to about 300 ml. Cool the solution to 10° C., precipitate titanium, columbium, and tantalum with cupferron, filter, and wash as previously described. Ignite the precipitate (F) in a weighed platinum crucible, heating finally at 1100° C. Note the weight and use as a check on the iron content. Fuse precipitate F with C.P. potassium pyrosulfate, cool, dissolve the melt by adding 10 ml. of concentrated sulfuric acid, and fume.

Cool the solution and add 50 ml. of the following solution: 10 ml. of concentrated sulfuric acid, 1 gram of C.P. succinic acid and 1 ml. of hydrogen peroxide (30%) per 100 ml. of solution. Transfer to a 100-ml. volumetric flask, using portions of the solution to rinse the beaker. Cool to 20° C. and dilute to the mark, using the above solution. Determine the titanium content colorimetrically by the use of a good photoelectric colorimeter. In this laboratory a Lumetron 402-E (Photovolt Corp.) has been found satisfactory. Transfer the necessary amount to the colorimeter tube and determine the per cent transmittance. Calibrate the colorimeter by means of pure solutions of titanium oxide for the range 0.00003 to 0.0060 gram of titanium per 100 ml. of solution (equivalent to 1.20% titanium on an 0.5-gram sample) using a No. M 465 filter (Photovolt Corp.). For titanium contents of 1.00 to 12.0% calibrate with the No. M 550 filter (Photovolt Corp.). If the per cent transmittance shows the titanium content to be in excess of 12.0%, transfer all the portions to a 250-ml. volumetric flask, using the sulfuric-succinic acid–hydrogen peroxide solution for dilution. Dilute to the mark and determine the per cent transmittance as above. The range is to 30.0% titanium. Should the titanium content exceed 30% the method can be extended by further dilution as above but at the expense of accuracy.

Return all portions used for the titanium determination to a suitable beaker, heat the solution to 60° C., and pass through a Jones reductor having a 30-inch (75-cm.) column of amalgamated zinc.

Amalgamate the zinc by treating 20-mesh zinc of low iron content with a 2% solution of mercuric chloride. Shake or stir the zinc vigorously for 2 minutes, decant, and wash with water. Fill the reductor with amalgamated zinc, wash well with hot sulfuric acid (2.5%), and discard the washings. Place 25 ml. of ferric sulfate solution in a 1000-ml. suction flask and connect to the reductor, making sure the delivery tube is beneath the surface of the liquid. Pass 100 ml. of hot water, followed by 100 ml. of hot (60° C.) sulfuric acid (20%), through the reductor. Pass the solution (also at 60° C.) to be reduced slowly through the reductor, followed by 100 ml. of hot sulfuric acid (20%) containing 1 gram of C.P. succinic acid. Finally pass distilled water through. A minimum of 30 minutes should be taken for the passage of the solution and wash solutions through the reductor. Care should be exercised to prevent the reductor inlet from becoming empty and when not in use the reductor should be filled with distilled water. The reductor must be frequently emptied and recharged with freshly amalgamated zinc.

Cool the solution and titrate with 0.05 *N* potassium permanganate. Calculate the percentage of columbium present. Run a blank solution on the reagents and on the reductor, and deduct the titration obtained from the total volume of the titration of a reduced solution. In the reduction of $Cb_2(SO_4)_5$ to $Cb_2(SO_4)_3$ and $Ti(SO_4)_2$ to $Ti_2(SO_4)_3$ any tantalum that may be present is not affected. The amount of tantalum can be determined by difference when the amount of columbium and titanium is known.

Fume filtrate III, which is obtained from the cupferron precipitation of the titanium, columbium, tantalum, and iron after the addition of 30 ml. of nitric acid (sp. gr. 1.42). Cool (make a sodium hydroxide–sodium peroxide separation if the presence of chromium is noted). Make the solution ammoniacal, add 20 ml. in excess, and plate the cobalt plus nickel electrolytically for 1 hour at 0.5 ampere and 3 volts. Dissolve the cobalt plus nickel from the cathode with nitric acid (sp. gr. 1.42) after a weight has been obtained. Determine the cobalt potentiometrically by the potassium ferricyanide–cobaltous nitrate method or the nickel by potassium cyanide–formaldehyde method as described below.

Dissolve the cobalt plus nickel from the cathode with nitric acid (sp. gr. 1.42) in a 250-ml. beaker. Rinse the cathode with distilled water and remove from the beaker. Evaporate the solution until it is a "sirupy" consistency (volume 1 to 2 ml.). Dilute to 150 ml. with distilled water. Add potassium cyanide cautiously in a well ventilated hood. (Sufficient has been added when a clear solution is obtained. Seven grams of potassium cyanide are required for every gram of cobalt present.) Add 5 ml. of hydrogen peroxide (3%) and boil the solution to half its volume. Cool, dilute, and add 10 ml. of formaldehyde solution. Add 0.05 gram of dry dimethylglyoxime powder (more if high nickel is suspected) and stir the solution vigorously. Filter the precipitated nickel after standing 10 to 12 hours, and wash the precipitate with warm water. Return the precipitate and paper to the beaker and destroy by the addition of 5 ml. of sulfuric acid (sp. gr. 1.84) and 20 ml. of nitric acid (sp. gr. 1.42). Dilute the solution after fuming, boil, and filter. Retain the filtrate, make just ammoniacal, and add 10 ml. of 1% alcoholic dimethylglyoxime (more if high nickel is suspected). Weigh the nickel glyoxime as such after filtering through a fritted-glass crucible, washing, and drying.

Aluminum can be determined on the electrolyte of the cobalt plus nickel. Chromium, vanadium, and molybdenum are usually

present as impurities in very low percentages and are more accurately determined individually on larger samples.

PROCEDURES FOR INDIVIDUAL ELEMENTS

Tungsten. SOLUTIONS REQUIRED. Cinchonine Solution. Five grams of cinchonine alkaloid crystals are dissolved in 100 ml. of hydrochloric acid (sp. gr. 1.19).

Cinchonine Wash, 20 ml. of cinchonine solution plus 50 ml. of hydrochloric acid (sp. gr. 1.19) per liter.

Sodium Hydroxide–Sodium Carbonate Wash, 5 grams of sodium hydroxide and 10 grams of sodium carbonate per liter.

Ammonium Nitrate, 50 grams per liter.

PROCEDURE. Fuse in a nickel crucible with 5 to 7 grams of sodium peroxide 0.25 gram of 325-mesh material. Cool the melt, tap loose from the crucible, and place in a dry 600-ml. beaker. Add 60 ml. of hydrochloric acid (sp. gr. 1.19); a few milliliters of distilled water may be needed to help dissolve the melt. Rinse, police the crucible with hot hydrochloric acid (10%), and add the rinsings to the beaker. When the melt has dissolved, add 5 ml. of cinchonine solution (5%) and boil for 5 minutes. Dilute to 400 ml. and continue boiling for 10 minutes. Remove the beaker from the heat and allow the precipitated tungstic acid to settle. The addition of paper pulp and a warm settling place will hasten the settling.

Filter the tungstic acid after 10 to 12 hours or overnight, using No. 40 Whatman filter paper, with ashless paper pulp in the apex of the funnel. Wash the precipitate 15 to 20 times with cinchonine wash. Return the precipitate and paper after washing to the original beaker and macerate with 50 ml. of hydrochloric acid (1 to 1). Add 5 ml. of cinchonine solution (5%) and a few drops of nitric acid (sp. gr. 1.42) and boil for 10 minutes. Dilute the solution to 300 ml. and allow the tungstic acid to settle as before. After 4 or 5 hours, filter the tungstic acid, using a No. 40 Whatman filter paper and paper pulp. Wash the precipitate 10 to 15 times with cinchonine wash and transfer the precipitate to a weighed platinum dish. Ignite carefully in a muffle furnace at 750° C. Remove from the furnace and when cool add a few drops of hydrofluoric acid (48%) and place the dish on a steam or sand bath. When dry, return the dish to the muffle and reheat to 750° C. Cool and weigh the impure tungstic oxide and correct for impurities.

Fuse the impure tungstic oxide with 6 to 8 grams of C.P. potassium bisulfate at a low heat in the original dish. Cool the melt, add 20 ml. of tartaric acid (50%), and warm the dish on a steam bath. Transfer the contents of the dish when dissolved to a 250-ml. beaker, dilute to 200 ml., and cool to 10° C. Add 60 ml. of cupferron solution (5%) or until the appearance of precipitated excess cupferron and filter the precipitated titanium, columbium, and tantalum. Wash with a dilute hydrochloric acid wash containing tartaric acid. Ignite the cupferron precipitate and repeat the purification by the addition of 5 ml. of hydrofluoric acid (48%). Reduce the volume to 1 ml. on a steam bath, add 20 ml. of tartaric acid (50%), warm the dish for 5 minutes on a steam bath, transfer the contents of the dish to a 250-ml., beaker containing 30 ml. of saturated boric acid solution, and dilute to 200 ml. Cool to 10° C. and add cupferron. Ignite and weigh and deduct this weight from the weight of the impure tungstic oxide. Retain the filtrates and determine molybdenum colorimetrically by the method described below. Destroy the precipitate with nitric (sp. gr. 1.42) and sulfuric acids (sp. gr. 1.84). Dilute and reprecipitate, using ammonium hydroxide (sp. gr. 0.9) and 1 gram of C.P. ammonium carbonate, and boil 5 minutes. Filter the precipitate, using a No. 40 Whatman filter paper, wash with dilute ammonium nitrate solution, and ignite. Deduct the weight of this precipitate from the impure tungstic oxide. Any molybdenum found is converted to molybdenum oxide and likewise deducted.

Molybdenum. SOLUTIONS REQUIRED. Sodium Thiocyanate Solution. Dissolve 25 grams of reagent grade sodium thiocyanate in 500 ml. of distilled water.

Stannous Chloride Solution. Dissolve 125 grams of reagent grade stannous chloride in 100 ml. of hydrochloric acid (sp. gr. 1.19) and add 400 ml. of distilled water.

Ether, regular reagent grade.

PROCEDURE. Transfer a 0.25-gram sample to a clean platinum dish or crucible. Add 5 ml. of hydrofluoric acid (48%), dilute, and add a few drops of nitric acid (sp. gr. 1.42) from a dropping bottle. Cover the dish with a platinum lid and place on a steam bath until solution is complete. Add 10 ml. of sulfuric acid (1 to 1) and heat gently until fumes of sulfuric acid are evolved. Remove from the heat, cool, dilute with 10 to 20 ml. of water, and transfer to a 250-ml. beaker. Add 10 ml. of sodium hydroxide (20%) to the dish, warm to dissolve all the tungstic acid, and add these rinsings to the 250-ml. beaker. Add 1 gram of sodium borate (reagent grade borax) and 10 ml. of citric acid (50%) to the solution, and then sodium hydroxide (20%) until alkaline. Heat the solution to dissolve all the tungstic acid. When the solution is clear, add 10 ml. of citric acid (50%). Cool to room temperature, add 50 ml. of sulfuric acid (1 to 1), and dilute to 250-ml. in a volumetric flask.

Transfer 25 ml. of the solution to a 250-ml. separatory funnel, using a calibrated pipet. Add 10 ml. of ferric sulfate solution and 10 ml. of sodium thiocyanate solution, shake thoroughly, add 10 ml. of stannous chloride solution, and shake thoroughly again. Add 25 ml. of ether and shake thoroughly. Allow the two layers to separate and draw off the acid layer. Add 10 ml. of sodium thiocyanate solution and 5 ml. of stannous chloride solution, shake, and cool using tap water. Draw off the acid layer, and transfer the ether extract to a clean 50-ml. volumetric flask which has been rinsed with ether. Wash the funnel with ether, adding the washings to the flask. Dilute to 50 ml. with ether and determine molybdenum colorimetrically.

Iron (Titanium, Columbium, Tantalum). PROCEDURE. Dissolve a 1-gram sample in a covered platinum dish by addition of hydrofluoric acid (48%) and nitric acid (sp. gr. 1.42). Rinse the cover and the sides of the dish with distilled water and take to dryness on a steam bath. Add 5 ml. of hydrofluoric acid (48%), take to a volume of 1 ml., add 50 ml. of tartaric acid (50%), and continue warming for 10 minutes. Transfer the contents of the dish to a 600-ml. beaker containing 30 ml. of saturated boric acid solution, dilute to 400 ml., and cool to 10° C. Precipitate the iron (titanium, columbium, tantalum) with cupferron solution (5%), wash well with dilute hydrochloric acid (2%), and ignite the precipitate.

Fuse the ignited precipitate with 6 to 8 grams of C.P. potassium pyrosulfate and dissolve the cooled melt by the addition of 50 ml. of tartaric acid solution (50%). Transfer the contents of the dish to 600-ml. beaker, dilute to 400 ml., and separate the iron (titanium, columbium, tantalum) by addition of cupferron. Wash with hydrochloric acid wash (2%). Ignite the precipitate (repeat cupferron separation if tungsten is evident), and fuse with 6 to 8 grams of potassium pyrosulfate. Add 4 grams of C.P. ammonium oxalate crystals to the melt and dissolve by the addition of hot water. Transfer to 250-ml. beaker containing 2 ml. of concentrated sulfuric acid, add an excess of 2% ammonia, and pass hydrogen sulfide through the solution until the iron is completely precipitated. Filter the iron sulfide after the precipitate has settled, using a No. 40 Whatman filter paper and paper pulp. Wash the precipitate 8 to 10 times with ammonium hydroxide wash containing 5 grams of C.P. ammonium oxalate per liter saturated with hydrogen sulfide. Return the precipitate to the beaker, add 20 ml. of nitric acid (sp. gr. 1.42) and 10 ml. of sulfuric acid (sp. gr. 1.84), and fume. When all the organic matter has been removed, dilute the contents and make an ammonium hydroxide separation. Filter the iron hydroxide and wash with ammonium hydroxide (5%). Dissolve the iron hydroxide with dilute hot hydrochloric acid (10%) and determine iron by the Zimmermann-Reinhardt method.

The filtrate can be treated as in the complete analysis scheme for titanium, columbium, and tantalum.

Cobalt. Cobalt can be determined most readily potentiometrically. This method has been found very successful and is most rapid, as an analysis can be obtained in a few minutes.

SOLUTIONS REQUIRED. Buffer Solution. Dissolve 500 grams of C.P. citric acid in 100 ml. of water and 675 ml. of concentrated ammonium hydroxide.

Standard Potassium Ferricyanide Solution. Dissolve 11 grams of the pure salt in water, dilute to 1 liter with cold, freshly distilled water, mix thoroughly, and standardize as follows: Add a 35-ml. portion of the solution (from a calibrated buret) to a 600-ml. beaker; add 100 ml. of ammonium citrate solution (buffe solution) and 80 ml. of ammonium hydroxide (sp. gr. 0.9), dilute to 250 ml., and cool to 15° C. Accurately measure 25 ml. of standard cobalt nitrate solution into a 400-ml. beaker, and dilute to 75 ml. with cold water; then add slowly, with stirring, to the cold ammoniacal ferricyanide solution. Rinse the beaker well with cold water and dilute to 400 ml. Complete the titration of the excess ferricyanide with the standard cobalt nitrate solution as described below. Store the ferricyanide solution in a dark-colored bottle, and standardize at least every two weeks.

Standard Cobaltous Nitrate Solution. Dissolve exactly 10.000 grams of cobaltous nitrate in water and dilute to 1 liter after adjusting to room temperature. Standardize this solution as follows: Transfer 50 ml. of the solution with a pipet to an electrolytic beaker and add 10 ml. of sulfuric acid (1 to 1). Evaporate carefully to heavy fumes of sulfuric acid. Cool, add a few milli-

Table I. Analysis of Known Mixtures

	Mixture 1		Mixture 2		Mixture 3		Mixture 4		Mixture 5	
	% added	% obtained	% added	% obtained	% added	% obtained	% added	% obtained	% added	% obtained
W	77.75	77.46	65.00	65.10	65.12	65.30	73.00	72.94	62.50	62.40
Ta	10.00	10.16	1.30	1.34	6.84	6.77	...	...	3.95	3.73
Cb	...	...	9.27	9.22	11.15	11.09	...	...	2.91	2.99
Ti	...	...	0.06	0.11	1.61	1.58	8.20	8.04	5.29	5.06
Co	6.00	6.12	15.00	14.90	8.78	8.68	10.50	10.45	20.41	20.33
C	6.25	6.39	9.32	9.42	6.46	6.60	8.27	8.24	...	...

liters of water by washing down the sides of the beaker, and again cool. Add 25 ml. of fresh ammonium hydroxide (sp. gr. 0.9) and again cool to room temperature. Electrolyze for 45 minutes at 1.5 amperes, depositing the cobalt on the weighed cathode. Rinse with water and alcohol, dry, cool in a desiccator, and weigh. Make the solution slightly ammoniacal by neutralizing most of the excess ammonia with sulfuric acid (1 to 1) and check for completeness of deposition of cobalt by passing hydrogen sulfide through the solution.

PROCEDURE. Transfer a 1-gram sample to a platinum or gold dish. Add 10 ml. of hydrofluoric acid (48%) and a few drops of nitric acid (sp. gr. 1.42), cover the dish, and place on a steam bath. Rinse the cover and sides of the dish when solution is complete and dilute to 150 ml. Add 100 ml. of buffer solution and 80 ml. of ammonium hydroxide (sp. gr. 0.9) to a 600-ml. beaker. Add sufficient excess (about 5 ml.) of potassium ferricyanide to oxidize all the cobalt that is anticipated in the sample. Pour the cooled acid solution of the sample into the buffer solution with stirring and rinse out the dish with distilled water. Place the beaker on the potentiometric titration apparatus and observe whether sufficient ferricyanide solution has been added. If not, start another sample, as erroneous results will be obtained if an excess of ferricyanide is not present at this point. If sufficient ferricyanide is present, add cobaltous nitrate solution dropwise until the end point is reached. A ratio must be run daily between the ferricyanide solution and the standard cobaltous nitrate solution.

Satisfactory results are obtained using the platinum-calomel electrode system and with a Beckman laboratory pH meter or a Fisher Junior titrimeter. The proper setting of the potentiometer for the end point must first be determined by plotting a curve for the titration of a portion of standard potassium ferricyanide with standard cobaltous nitrate. From this plot the point of maximum inflection is taken as the end point and the dial setting which may be considered the end point is determined. To titrate an unknown solution the dial is set at the above-determined reading. The beaker is placed under the apparatus, the stirrer started, and observation is made as to whether sufficient potassium ferricyanide is present.

Manganese is an interfering element in this method, but is seldom encountered in carbide analysis. If manganese is present, it should be determined by a suitable method. The percentage of manganese times 1.07 is deducted from the cobalt content. The percentage of cobalt is determined from the weight of the sample, amount of ferricyanide used, and the cobaltous nitrate used in the back-titration.

Cobalt plus Nickel. Nickel is sometimes substituted for cobalt or, generally, it is an impurity of the cobalt and must be determined in the complete analysis.

Dissolve a 0.5-gram sample in a covered platinum dish by the addition of hydrofluoric (48%) and nitric acid (sp. gr. 1.42). Add 20 ml. of sulfuric acid (1 to 1) and fume strongly. Cool and transfer the contents of the dish to a 600-ml. beaker containing enough sodium hydroxide solution to maintain alkaline solution. Clean the dish by the addition of a few pellets of sodium hydroxide and rinse contents into the beaker, add 5 ml. of hydrochloric acid (sp. gr. 1.19) to the dish, and also rinse into the beaker. Add 1 gram of sodium peroxide to the alkaline solution and boil for 5 minutes. Dilute the solution to 450 ml. with distilled water, add paper pulp, and let stand for at least 6 hours. Filter the precipitate, using No. 40 Whatman paper, wash the precipitate with sodium hydroxide wash solution (5%), and return the precipitate to the beaker. Destroy the precipitate by the addition of 10 ml. of sulfuric acid (sp. gr. 1.84) and 30 ml. of nitric acid (sp. gr. 1.42).

Test the filtrate to ensure complete precipitation by adding 5 grams of tartaric acid, making just acid with sulfuric acid (1 to 1), and adjusting to 2% ammonium hydroxide. Pass hydrogen sulfide through the solution. Filter any which is being destroyed. Fume the solution, cool, dilute with 100 ml. of water, and make a second precipitation with sodium hydroxide–sodium peroxide as before. Filter and destroy with 10 ml. of sulfuric acid (sp. gr. 1.84), 30 ml. of nitric acid (sp. gr. 1.42), and 2 ml. of perchloric acid (70%). Fume the solution until all the perchloric is driven off, dilute to 50 ml. with water, cool, and make ammoniacal, adding 15 ml. in excess. Plate the cobalt plus nickel electrolytically, using a platinum cathode. The gain in weight represents the amount of cobalt plus nickel present.

If a separation of cobalt and nickel is needed, individual percentages can be obtained by titrating cobalt potentiometrically on a different sample and obtaining the nickel by difference or determining nickel by potassium cyanide method on the "plate" as described in the complete analysis scheme.

Chromium. Chromium is determined by the persulfate oxidation method after solution with nitric (sp. gr. 1.42) and hydrofluoric acids (48%), followed by fuming with sulfuric (sp. gr. 1.84) and phosphoric acids (sp. gr. 1.71).

Vanadium. Vanadium is determined by reduction with ferrous sulfate and titration with potassium permanganate after solution with hydrofluoric acid (48%) and nitric acid (sp. gr. 1.42) and fuming with sulfuric acid (sp. gr. 1.84) and phosphoric acid (sp. gr. 1.71).

RESULTS

No standard samples of these compositions are available and since there are also no recognized standard methods, it was necessary to make up synthetic standards from ingredients of known purity. For this purpose carbides, oxides, and metals of known purity were weighed into dishes to give the mixtures shown in Table I. Only traces of iron, nickel, and molybdenum were present in these mixtures and hence were not determined.

The agreement will be seen to be excellent for analysis of such complex materials, particularly when the wide range of variation of the constituents is taken into account. Such a variation does occur in the compositions presently on the market.

A discussion of accuracy must be included. Since the colorimetric method is relied on for the determination of titanium and the accuracy of this method is 1% of the amount present, it will be seen that the accuracy of determination of 25% titanium is only ±0.25%. When tantalum and columbium are also present the limiting accuracy for the tantalum determination is likewise ±1% of the amount of titanium present because of the determination of tantalum by difference. These are the greatest errors involved in the analysis.

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PETROLEUM SOLVENTS

Correlation of Kauri Butanol Solvency with Gravity and Aniline Point

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A correlation has been developed which relates the A.P.I. gravity, 50% boiling point, and aniline point with kauri butanol solvency values. This relation is expressed mathematically by two equations, one applying to solvents below 50 kauri, the other applying to higher solvency materials.

THE kauri butanol solvency test, originally developed by Kiehl (*4*) and later officially adopted by the Paint and Varnish Superintendents Club of the Philadelphia District (*6*), has been widely used by the industry as an aid in evaluating the solvency power of hydrocarbon mixtures for different applications. Various modifications for standardization of this test procedure have been proposed by other investigators (*1, 2, 3*), but as yet the procedure has not been officially standardized as a uniform test procedure for all laboratories.

Since the kauri butanol solvency test is rather tedious to perform and requires precise laboratory technique, a correlation is desirable to predict the kauri butanol solvency values of petroleum spirits from other easily determined, standardized physical tests. McArdle and Baldeschwieler (*5*) indicated that kauri butanol values can be correlated with A.P.I. gravity, mixed aniline point, and other properties, but did not completely develop or evaluate these relations. The purpose of this paper is to show that kauri butanol solvency can be predicted accurately from physical properties. The correlation which was developed, as shown in Figure 1, relates the A.P.I. gravity test (A.S.T.M. D278–39) and aniline point test (A.S.T.M. D611–46T) with kauri solvency values as determined in this laboratory. The procedure is based on samples having mid-boiling points varying not more than 10° F. (5.5° C.) from 340° F. (171.1° C.). The relation expressed in the graph is represented by the following equation:

$$K = \frac{123.5 - G - 0.22(A)}{1.24} \qquad (1)$$

where K = kauri butanol solvency

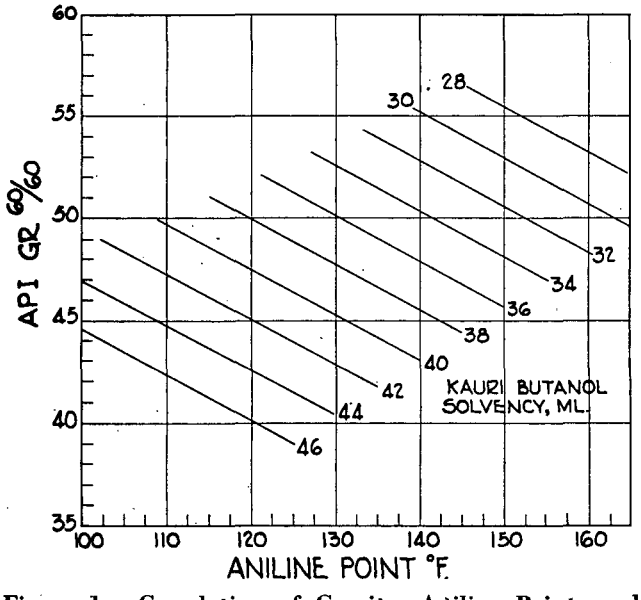

Figure 1. Correlation of Gravity, Aniline Point, and Kauri Butanol Solvency for Petroleum Solvents of 330° to 350° F. Mid-boiling Point

G = A.P.I. gravity at 60° F./60° F., and A = aniline point, ° F.

Deviations were encountered in applying this relation to samples having mid-boiling points (A.S.T.M. D86–46) substantially different from 340° F. The deviation appeared to be proportional to the difference in mid-boiling point. For this reason boiling point correction terms were incorporated into the original equation to extend its range of application. The improved equation is as follows:

$$K = 99.6 - 0.806G - 0.177A + 0.0755\,(340 - B) \qquad (2)$$

where K = kauri butanol solvency
G = A.P.I. gravity at 60° F./60° F., A = aniline point, ° F., and B = mid-boiling point, ° F.

Table I. Accuracy of Correlation for Solvents Having Mid-boiling Points of 340° ± 10° F. and Kauri Values Less Than 50

Sample	A.P.I. Gr./60	Initial, ° F.	50% Boiling Point, ° F.	End Point, ° F.	Aniline Point, ° F.	Kauri Butanol Solvency, Ml. Determined	Kauri Butanol Solvency, Ml. Calculated[a]	Dev., ml.
1	52.8	316	342	388	157.1	30.4	29.1	−1.3
2	53.8	308	345	400	150.3	30.4	29.4	−1.0
3	54.5	307	335	402	148.5	30.5	29.9	−0.6
4	54.1	311	339	396	149.0	30.5	29.8	−0.7
5	51.6	314	345	390	152.6	31.7	30.7	−1.0
6	49.0	308	347	426	140.4	33.8	34.7	+0.9
7	49.9	302	346	406	130.9	34.4	35.8	+1.4
8	49.4	298	345	415	138.2	35.1	34.9	−0.2
9	49.6	300	338	412	136.8	35.4	35.6	+0.2
10	49.0	310	340	398	136.8	35.7	35.9	+0.2
11	48.5	306	349	399	138.0	35.9	35.4	−0.5
12	48.7	298	341	407	153.3	36.0	33.1	−2.9
13	48.3	311	344	398	135.3	36.2	36.4	+0.2
14	49.1	306	335	396	135.3	36.3	36.5	+0.2
15	48.6	308	336	400	134.6	36.5	36.9	+0.4
16	48.4	310	338	408	132.5	37.0	37.3	+0.3
17	48.4	301	336	407	129.6	37.0	38.0	+1.0
18	48.4	308	338	398	130.1	37.0	37.7	+0.7
19	48.2	313	340	388	131.2	37.2	37.5	+0.3
20	47.3	310	342	389	128.7	37.5	38.6	+1.1
21	47.8	308	341	399	131.5	38.0	37.7	−0.3
22	47.9	300	336	386	128.1	38.1	38.6	+0.5
23	47.3	306	333	414	126.7	38.2	39.6	+1.4
24	47.3	316	344	396	127.2	38.2	38.5	+0.3
25	47.1	303	347	412	133.0	38.4	37.6	−0.8
26	47.6	300	338	414	125.0	38.5	39.3	+0.8
27	47.7	308	338	389	129.5	38.6	38.4	−0.2
28	48.1	312	336	387	125.9	38.7	38.9	+0.2
29	47.6	310	333	418	131.9	38.8	38.4	−0.4
30	46.3	310	345	398	123.0	39.2	40.1	+0.9
31	47.3	307	335	401	123.4	40.0	40.0	0.0
32	45.9	310	340	396	118.4	40.8	41.6	+0.8
33	44.8	313	342	408	121.3	41.8	41.9	+0.1
34	46.2	312	336	390	115.7	42.0	42.2	−0.2
35	46.1	300	333	392	115.0	42.1	42.6	+0.5
36	44.0	305	336	392	120.0	42.2	43.2	+1.0
37	46.0	303	331	383	105.1	43.0	44.6	+1.6
38	44.9	324	338	394	113.5	43.1	43.2	+0.1
39	43.1	310	342	418	119.0	43.4	43.7	+0.3
40	43.1	306	337	408	120.9	43.7	43.7	0.0
41	42.4	300	340	414	120.9	43.9	44.0	+0.1
42	46.1	304	333	390	105.0	44.0	44.4	+0.4
43	43.9	304	341	397	113.2	44.1	44.1	0.0
44	42.5	290	331	418	120.0	44.2	44.8	+0.6
45	45.3	303	333	390	106.7	44.3	44.7	+0.4
46	45.2	303	333	382	109.6	44.4	44.3	−0.1
47	41.2	308	342	425	119.6	45.0	45.1	+0.1
48	42.4	314	346	409	112.1	45.1	45.1	0.0
49	41.4	311	345	402	114.2	46.0	45.6	−0.4
50	43.8	309	340	393	99.5	46.4	46.7	+0.3
51	43.7	308	341	396	99.0	46.4	46.8	+0.4
52	43.1	311	336	395	102.0	46.9	47.1	+0.2
53	43.1	300	333	389	102.2	47.5	47.3	−0.2
						Av. deviation		0.55
						Deviation of av.		+0.14

[a] Calculated by Equation 2.

Table II. Accuracy of Correlation for Solvents Having Mid-boiling Point above or below 340 ± 10° F. and Kauri Values Less Than 50

Sample	A.P.I. Gr./60	Initial Boiling Point, ° F.	50% Boiling Point, ° F.	End Point, ° F.	Aniline Point, ° F.	Kauri Butanol Solvency, Ml. Determined	Calculated[a]	Deviation, ml.
1	52.5	349	370	395	152.9	29.5	28.1	−1.4
2	48.8	306	353	429	140.2	34.4	34.5	+0.1
3	48.7	302	353	427	140.9	34.7	34.4	−0.3
4	42.6	361	408	462	140.7	35.4	35.2	−0.2
5	58.8	204	244	328	130.8	36.2	36.3	+0.1
6	66.2	109	193	282	125.2	37.4	35.2	−2.2
7	46.0	335	359	424	130.1	37.7	38.1	+0.4
8	56.1	243	254	297	127.8	37.9	38.3	+0.4
9	56.3	204	241	317	120.2	40.4	40.4	0.0
10	47.9	250	324	406	118.2	42.1	41.3	−0.8
11	56.6	200	210	268	109.4	43.6	44.4	+0.8
12	37.2	336	362	413	124.3	45.3	46.0	+0.7
						Av. deviation		0.6
						Deviation of av.		−0.2

[a] Calculated by Equation 2.

Equation 2 has been applied to a variety of samples to establish its accuracy. Table I shows the accuracy for 53 commercial spirits ranging from approximately 30 to 50 kauri value and having mid-boiling points of 340° ± 10° F. The average deviation for these samples is 0.55 ml., and the deviation of the average is +0.14 ml. Six of this number show deviations greater than one unit, and one sample has a deviation greater than 2.0 ml. of kauri.

Table II shows the accuracy of this correlation for commercial solvents having mid-boiling points which differ from 340° F. by more than 10° F. For this group of samples the average deviation is 0.6 ml., and the deviation of the average −0.2 ml. Two of these samples show deviations greater than 1.0 unit of kauri butanol.

The accuracy of this correlation for a group of miscellaneous samples is shown in Table III. The data given in this table were not obtained in the authors' laboratories, or necessarily by their procedure for kauri solvency. They represent data presented in sales pamphlets and similar literature, and in some cases they may represent product specifications rather than data on individual samples. For such data, as would be expected, the accuracy of the correlation is not so good as shown in Tables I and II. The average deviation for these data is 1.2 ml. and the deviation of the average is +0.27 ml. Twenty of the thirty-six samples show deviations greater than 1.0 ml.; nine have deviations greater than 2.0.

The data presented show the accuracy of the correlation is satisfactory for kauri butanol values up to 50. However, in applying this correlation to samples above this range, abnormal deviations were encountered which increased with increasing kauri butanol value. This indicates a change in the relationship involved and necessitated the development of a new equation, involving the same properties, to be applied in the range above 50. This modified equation is as follows:

$$K = 117.7 - 1.06G - 0.249A + 0.10\,(340 - B) \qquad (3)$$

Data presented in Table IV show the deviations encountered using Equations 2 and 3 for samples having kauri values above 50. Whereas Equation 2 gives almost entirely negative deviations, in some cases as high as 7.0 units, Equation 3 gives random deviations with a maximum of about 2.0 units. The equation is limited to approximately 75 kauri butanol value, since the freezing point of aniline occurs in this solvency range. It may be possible to develop a correlation for higher kauri butanol solvency materials by replacing straight aniline points with mixed aniline point determination. There may be other complicating factors in this range, however, since solvents are encountered that are completely miscible with the kauri butanol solution, indicating infinite solvency. As an example, a solvent rich in polycyclic aromatics was blended with a solvent having a low kauri butanol value. It was found that the kauri butanol values followed a linear relationship up to 80 (75% of the higher solvency component). Above this concentration, a sharp break in the curve occurred and the kauri values approached 100% concentration as an asymptote. It will be extremely difficult for a correlation to predict such behavior as this.

It is recommended that Equation 2 be used for all samples having calculated kauri values below 50 and that Equation 3 be used for samples above 50 kauri and up to the freezing point of aniline.

KAURI BUTANOL SOLVENCY TEST PROCEDURE

Apparatus. A 250-ml. extraction flask (similar to AHT 4955). A 50-ml. buret. An analytical balance. A suitable water bath. A clear glass jar, 11.4 cm. in diameter and 7.6 cm. deep, half filled with distilled water, is convenient.

Reagents. Kauri Butanol Solution. Weigh 400 grams of clean, powdered No. 1 kauri gum into a 3-liter flask, and add with considerable agitation 2000 grams of *n*-butyl alcohol,

Table III. Accuracy of Correlation on Miscellaneous Data Having Kauri Values Less Than 50[a]

Sample	A.P.I. Gr./60	Estimated 50% B.P., ° F.	Aniline Point, ° F.	Kauri Butanol Solvency, Ml. Given	Calculated[b]	Deviation, ml.
1	43.6	445	158.0	29.5	28.3	−1.2
2	51.0	348	154.0	30.0	30.6	+0.6
3	48.5	355	143.6	31.8	34.0	+2.2
4	71.6	184	138.0	31.8	29.2	−1.4
5	46.4	390	147.0	32.0	32.4	+0.4
6	49.0	352	140.0	32.2	34.4	+2.2
7	67.8	192	137.3	32.3	31.8	−0.5
8	55.0	290	141.8	32.6	34.0	+1.4
9	70.5	170	129.0	32.7	32.8	+0.1
10	58.4	247	135.5	33.5	35.6	+2.1
11	48.9	358	139.0	33.5	34.2	+0.7
12	53.5	306	141.8	33.9	34.0	+0.1
13	70.0	166	124.4	34.0	34.3	+0.3
14	43.0	425	142.0	34.5	33.4	−1.1
15	62.9	239	139.3	34.6	31.9	−2.7
16	56.9	260	152.6	34.9	32.8	−2.1
17	55.5	250	138.0	34.9	37.2	+2.3
18	54.9	253	134.0	35.2	38.2	+3.0
19	57.9	245	121.0	35.2	38.7	+3.5
20	59.7	233	126.5	35.8	37.2	+1.4
21	56.4	270	133.0	36.9	35.9	−1.0
22	58.0	261	129.0	37.0	36.0	−1.0
23	69.0	165	126.0	37.0	34.9	−2.1
24	60.5	230	122.9	37.1	37.4	+0.3
25	47.5	349	135.0	37.5	36.7	−0.8
26	46.5	363	129.0	37.8	37.6	−0.2
27	50.4	311	122.9	38.0	39.4	+1.4
28	59.4	225	120.0	38.5	39.2	+0.7
29	54.0	265	122.0	39.0	40.2	+1.2
30	55.4	256	118.4	40.0	40.3	+0.3
31	60.5	207	113.0	41.5	40.9	−0.6
32	59.0	218	112.1	42.8	41.4	−1.4
33	55.9	221	106.0	43.0	44.8	+1.8
34	56.2	211	109.0	45.0	44.8	−0.2
35	50.3	258	92.0	49.0	49.0	0.0
36	38.0	360	98.3	50.0	50.1	+0.1
				Av. deviation		1.2
				Deviation of av.		+0.27

[a] Taken from sales pamphlets and other similar literature.
[b] Calculated by Equation 2.

Table IV. Accuracy of Correlation for Solvents Having Kauri Values above 50

Sample	A.P.I. Gr. 60/60	% B.P., ° F.	Aniline Point, ° F.	Kauri Butanol Solvency, Ml. Experimental	Equation 2 Calculated	Equation 2 Deviation	Equation 3 Calculated	Equation 3 Deviation
1	41.4	342	94.6	49.3	49.6	+0.3	50.2	+0.
2	49.7	256	80.6	55.4	51.5	−3.9	53.3	−2.1
3	41.7	333	83.4	51.5	52.0	+0.5	53.4	+1.9
4	39.9	341	88.2	52.4	52.6	+0.2	53.4	+1.0
5	33.7	420	81.3	55.6	52.2	−3.4	53.8	−1.8
6	50.0	236	77.9	55.7	53.3	−2.4	55.7	0.0
7	31.9	423	66.2	59.6	55.9	−3.7	59.1	−0.5
8	46.8	260	58.6	60.0	57.5	−2.5	61.5	+1.5
9	47.2	235	57.2	63.5	59.4	−4.1	64.0	+0.5
10	30.0	429	52.5	65.4	59.4	−6.0	63.9	−1.5
11	44.3	263	35.6	69.0	63.4	−5.6	69.1	+0.1
12	44.4	232	34.9	72.7	65.8	−6.9	72.7	0.0
13	33.0	355	20.0	75.0	68.4	−6.6	76.3	+1.3
14	28.0	405	20.0	75.0	68.6	−6.4	76.5	+1.5
			Av. deviation			3.8		1.0
			Deviation of av.			−3.6		+0.2

water-free (refined grade, boiling point 117° C.). Fit the flask with a reflux condenser and heat on a steam bath until the kauri is all dissolved. The solution may then be clarified by filtering through a Büchner funnel with the aid of suction. Adjust the filtrate, using a blend of 28% C.P. toluene and 72% *n*-heptane, so that a titration of 41.4 ml. is obtained with the toluene-heptane blend.

Procedure. Weigh 20 ± 0.1 grams of the kauri butanol solution into the 250-ml. flask, and from the buret make small additions of sample with constant agitation of the flask. Maintain the temperature of the kauri butanol solution and sample in the flask at 77° F. (25° C.) ± 2° F. by means of the water bath. Take the end point as the point at which a sufficient cloud has developed in the mixture in the flask to obscure the sharp outlines of 10-point print which has been placed directly beneath the water bath and observed through the liquid. Correct number of milliliters of sample added to the standard temperature of the test by means of the following equation:

Ml. correction = 0.0005 × ml. titration × (77° F. − temperature of sample)

Report the corrected number of milliliters added as the kauri butanol solvency.

Accuracy. Duplicate determinations should agree within 0.5 ml.

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Determination of Ethylacetylene and Vinylacetylene in C_4 Hydrocarbon Gases

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A method is described for the determination of ethylacetylene and vinylacetylene in an over-all C_4 hydrocarbon fraction. Total acetylenes are determined from the acidity produced upon treatment of a sample with 2.5% silver nitrate solution. Catalytic hydrogenation is used to differentiate between ethylacetylene and vinylacetylene after corrections have been made for the hydrogen consumed by the olefins and 1,3-butadiene. Olefins plus 1,3-butadiene are determined by bromine addition and 1,3-butadiene by the use of maleic anhydride. Ethylacetylene and vinylacetylene are determined with an average deviation of 0.8% on the basis of the total sample over a concentration range from 1 to 100%. Methylamine and methylmercaptan (methanethiol) interfere and, if present, must be removed before the determination is made. 1,2-Butadiene also interferes, but no chemical method is available for its determination. The percentage of vinylacetylene will be increased and consequently the ethylacetylene will be decreased by the amount of 1,2-butadiene that is present.

DURING recent years many processes involving the catalytic treatment of hydrocarbon fractions have been studied, and these processes have resulted in the formation of some rather complex mixtures. It became necessary to determine the amount of individual acetylenes in the C_4 hydrocarbon fraction of such a mixture, and the simple methods of low-temperature fractional distillation and catalytic hydrogenation (*4*) were incapable of giving sufficient analytical data. Such a fraction, boiling between −17° and +14° C., could contain ethylacetylene (1-butyne), vinylacetylene (1-buten-3-yne), and diacetylene (1,3-butadiyne) as well as *n*- and isobutane, isobutene, the 2-butenes, 1-butene, 1,3-butadiene, and 1,2-butadiene.

A number of methods have been developed for the determination of acetylene (ethyne). Most of them depend on the formation of a metal acetylide or a complex involving a metal acetylide. However, relatively few of these methods have been applied to the determination of higher acetylenes. Peregud (*7*) used oxidation with iodine pentoxide, absorption in an alkaline solution of mercurous cyanide, and absorption in 80% sulfuric acid as a means for determining acetylene, vinylacetylene, and divinylacetylene in mixtures. No method is described for the determination of individual C_4 α-acetylenes in a mixture.

The most widely used acetylene methods employ Chavastelon's procedure (*2*) in which acetylene reacts with silver nitrate to form silver acetylide and liberates 2 moles of nitric acid for each mole of acetylene. The liberated acid is then titrated as a measure of the acetylene content. Ross and Trumbull (*10*) modified the method somewhat and obtained excellent results on synthetic acetylene-ethylene mixtures. Hillyer and Webber (*3*) applied the same reaction to the determination of total acetylenes in C_4 hydrocarbons. This method is limited to α-acetylenes and will give one mole of nitric acid for each mole of monosubstituted acetylene.

In working out a method for determining the individual acetylenes in a C_4 fraction (−17° to +14° C.), it was found that only ethylacetylene and vinylacetylene need be considered. Diacetylene was found, through numerous attempts to prepare it, to be extremely unstable. This instability was so great that there appeared to be little likelihood of its ever being present in a sample, so it was given no further consideration in the development of the method. The other C_4 acetylene, 2-butyne, boils at 27° and so is not included in the C_4 fraction. This left only the vinylacetylene, which is also unstable, and ethylacetylene to be determined in the admixture with saturates, olefins, and diolefins. If the total acetylene content, the total unsaturation, the diene content, and the mono-olefin content of the sample could be determined, sufficient data would be available for calculating the amount of ethyl- and vinylacetylene by the difference in their unsaturation.

The method finally developed is a systematic procedure in which acetylenes are determined individually over a range of 1 to 100% in admixture with olefins and 1,3-butadiene. Total acetylenes are determined by a modification of the Hillyer and

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Webber (*3*) silver nitrate method, the total unsaturation is measured by the hydrogenation technique described by McMillan *et al.* (*6*), the olefins plus 1,3-butadiene are determined by a modification of the bromine titration method of Stanerson and Levin (*11*), and the 1,3-butadiene is measured by the maleic anhydride method (*12*). If 1,2-butadiene is present, it will interfere with the determination of the individual acetylenes but not of total acetylenes. The C_4 fraction upon which this determination is made should be collected from a distillation with a column at least as efficient as the McMillan modified CNGA column (*5*).

HYDROCARBONS USED

The butane and 1,3-butadiene were purchased from The Matheson Company and had purities of 99.4% as determined by low-temperature fractional distillation and 98+% by specification, respectively.

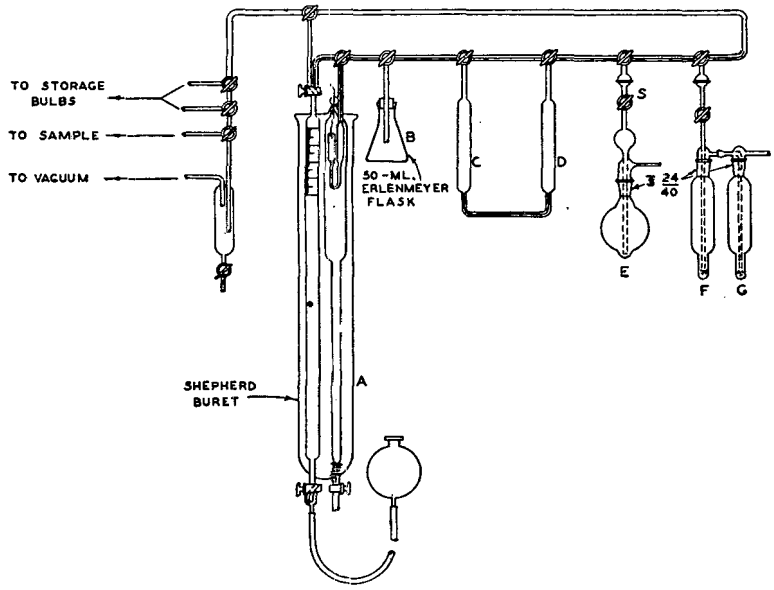

Figure 1. Apparatus for Acetylene Determination

Vinylacetylene was purchased from E. I. du Pont de Nemours and Company, Deepwater Dye Works, Carneys Point, N. J., as a 50% solution in xylene containing 0.1% catechol as inhibitor. This was distilled and tested 98% pure by hydrogenation and reaction with silver nitrate.

The ethylacetylene was prepared by a slight modification of the method of Vaughn *et al.* (*13*) for the preparation of methylacetylene. Ethyl sulfate was reacted with sodium acetylide in liquid ammonia and the resulting gas collected and distilled. By hydrogenation and reaction with silver nitrate, the product tested 99% pure.

A mixture of 2-butenes was prepared by the dehydration of 2-butanol with 60% sulfuric acid (*14*). Distillation yielded a product which tested more than 98% pure by hydrogenation and by bromine addition.

1,2-Butadiene was purchased from Phillips Petroleum Company with a stated purity of 97+%.

REAGENTS AND APPARATUS

Acetylene Determination. Silver Nitrate Solution (2.5% in alcohol). A 10% aqueous solution of silver nitrate is prepared and one part of this stock solution is diluted with 3 parts of neutral formula 30 alcohol or 95% ethanol just prior to using. The alcoholic solution develops appreciable acidity on long standing, but the solution may be used if a correction for the acidity is made.

Mixed Indicator. The indicator is prepared by dissolving 0.1 gram of methyl red powder and 0.05 gram of methylene blue in 100 ml. of 95% ethanol. This is the indicator used by Hillyer and Webber (*3*).

Sodium Hydroxide, 0.02 *N*.

Nitric Acid, 0.02 *N*.

Apparatus. The apparatus used for the determination of acetylenes is shown diagrammatically in Figure 1. The Erlenmeyer flask, *B*, is used only for the determination of olefins by bromine addition which is described below. Scrubbers *C* and *D* are used to remove acidic gases (mercaptans) and basic gases (amines) from samples. Solid potassium bisulfate or oxalic acid is used in *C* and Ascarite is used in *D*.

A detailed sketch of absorber *E* used in the determination of C_4 acetylenes in samples containing from 1 to 100% acetylene is shown in Figure 2. The upper bulb has a volume of approximately 90 ml., and the lower bulb is a modified 250-ml. round-bottomed flask. The absorbers shown in Figure 3 are used only when the concentration of acetylene in the sample is less than 1%.

Olefin Determination. The reagents and apparatus used in the determination of olefins are the same as used by Stanerson and Levin (*11*). However, the apparatus has been incorporated with that used in other phases of the determination of acetylenes (Figure 1).

Unsaturation by Hydrogenation. The reagents and apparatus used for the total unsaturation by hydrogenation are described by McMillan *et al.* (*6*).

Butadiene Determination. Maleic Anhydride. Melting point not less than 52° C.

Diamylamine. Either di-*n*-amylamine (boiling point 198–202° C.) or diisoamylamine (boiling point 188–190° C.) may be used. The use of high-boiling amines was suggested by Robey *et al.* (*9*).

Apparatus. The apparatus used is essentially that described by Tropsch and Mattox (*12*).

EXPERIMENTAL

The experimental work described in this paper is divided into four phases according to the type of measurement being made, and the data obtained are used to calculate the percentages of ethylacetylene and vinylacetylene. The samples were synthetically blended by measuring the pressure of each gas separately in a calibrated pipet and correcting the pressures for compressibility of the gases (*3*). Mercury was used to transfer the gases to a receiver where they were blended. Table I shows the composition of some of these blends which were used in all phases of the work, and the corresponding sample number in each of the tables refers to the same sample. These blends do not necessarily simulate mixtures which would be encountered in present-day refinery samples, but rather were selected to show the effect of the various types of compounds upon the acetylene determination.

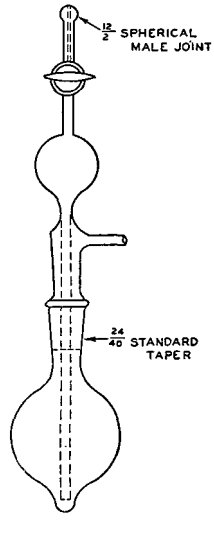

Figure 2. Ross and Trumbull Type of Absorber for Acetylene

The following procedure, which has been previously described (*1*), was used for the determination of total α-acetylenes:

Introduce 100 ml. of alcoholic silver nitrate solution into the lower part of absorber *E*, draw the reagent up to stopcock *S*, and attach the absorber to the manifold. Evacuate the system including the Shepherd buret, *A*, scrubbers *C* and *D*, and manifold to stopcock *S* to a pressure of 1 mm. of mercury or less. Fill this evacuated system with sample from the storage bulbs or the original sample container, and read the mercury level in the buret at atmospheric pressure. If the sample contains moisture, it is passed through a drying tower before being introduced into the apparatus. Force 15 to 90 ml. of sample through the scrubbers and stopcock *S* into the upper bulb of absorber *E*, close *S*, and again read the mercury level in the buret to obtain the volume of sample. The

volume of sample used is dependent upon the acetylene concentration. If more than 15 ml. of C_4 acetylenes are present in the sample used, the silver acetylide will not completely dissolve in the reagent and will interfere with the titration.

Disconnect the absorber and shake it until practically all of the sample is dissolved, taking care that none of the sample is lost from the upper bulb. This is accomplished by holding the lower bulb relatively still as a pivot, while the liquid in the upper bulb is agitated. Draw the sample from the bore of S into the bulb by momentarily opening the stopcock, and then shake the absorber until any acetylene in this gas is reacted. Open the stopcock and allow all the reagent to flow into the bottom of the absorber. Remove the top part, rinse thoroughly with distilled water, and add the rinsings to the solution (total volume 125 to 150 ml.) which is then titrated with 0.02 N sodium hydroxide. The best results are obtained when 6 to 8 drops of indicator are used. The end point is a gray, almost neutral, color just at the disappearance of the pink color of methyl red. If the end point is passed slightly, use 0.02 N nitric acid for back-titration. However, a large excess of alkali (1 ml. or more) will precipitate silver hydroxide, which is difficult to dissolve and will cause high results for the total acetylenes.

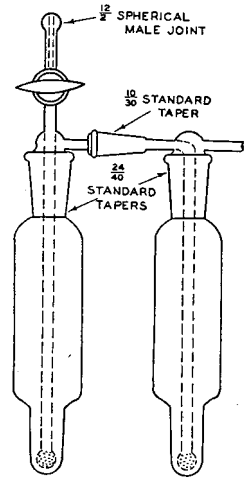

Figure 3. Bubble-Type Absorber for Weak Acetylene Blends

Silver ethylacetylide and silver vinylacetylide are explosive if permitted to become dry; therefore, they must be destroyed promptly. These salts are dissolved in a potassium cyanide solution, and the excess potassium cyanide is destroyed with ferrous sulfate.

Absorbers F and G, which are shown in detail in Figure 3, are used only for samples which contain less than 1% acetylenes. Fifty milliliters of the alcoholic silver nitrate solution are placed in each absorber (this fills the absorber to about one third of its capacity). The sample (4 to 8 liters) is bubbled through the absorbers successively at a rate of about 4 liters per hour. The emergent gas is measured with a wet-test gas meter. No attempt is made to differentiate between ethylacetylene and vinylacetylene in these low concentrations.

The results of the determination of total acetylenes, given in Table II, show an average absolute error of less than 0.2%. The bubble-type absorber (Figure 3) was used in the analysis of samples 6 and 8.

Calculations. Calculate total acetylenes as follows:

$$\text{Volume per cent acetylenes} = \frac{M \times N \times T \times 6235.9}{S \times P \times 1.031}$$

where M = ml. of sodium hydroxide
N = normality of sodium hydroxide solution
T = temperature of sample in degrees Kelvin
S = ml. of sample
P = pressure (mm. of mercury) at which sample was measured

Table I. Composition of Blends

Sample	n-Butane	Vinylacetylene	Ethylacetylene	2-Butene	1,3-Butadiene	1,2-Butadiene
			Volume Per Cent			
1	93.3	....	6.7	..	..	...
2	80.2	....	7.2	5.9	6.7	...
3	74.5	5.4	7.4	5.4	7.3	...
4	74.0	10.1	9.9	..	6.0	...
5	55.3	29.2	11.0	4.5	..	...
6	99.957	0.021	0.022	..	..	...
7	50.6	16.0	8.6	19.4	5.4	...
8	91.7	0.2	0.4	7.7	..	...
9	53.1	0.7	3.3	32.4	8.4	2.1
10	60.2	0.6	7.6	29.0	0.1	2.5
11	48.4	0.6	5.3	30.5	12.7	2.5

Table II. Total Acetylenes by Silver Nitrate Reagent

Sample	Blended: Vinylacetylene	Blended: Ethylacetylene	Acetylene Found	Absolute Error
		Volume Per Cent		
1	....	6.7	6.8	+0.1
2	....	7.2	7.2	0.0
3	5.4	7.4	12.8	0.0
4	10.1	9.9	19.8	−0.2
5	29.2	11.0	40.0	−0.2
6	0.021	0.022	0.045	+0.002
7	16.0	8.6	24.2	−0.4
8	0.2	0.4	0.6	0.0
9	0.7	3.3	3.7	−0.3
11	0.6	5.3	5.7	−0.2

The factor 6235.9 is derived from the following:

$$\frac{22{,}400 \times 760 \times 100}{273 \times 1000} = 6235.9$$

The factor 1.031 corrects for the deviation of C_4 hydrocarbons from the ideal gas law at standard temperature and pressure (*8*).

Total Unsaturation. The differentiation of ethylacetylene and vinylacetylene is based on the difference in unsaturation of the two molecules. McMillan's catalytic hydrogenation method (*6*) is used to determine total unsaturation. The correction given by Robey and Morrell (*8*) for the nonidealistic behavior of C_4 hydrocarbon gases is used with the catalytic hydrogenation method. Table III shows the results of the hydrogenation of blends containing acetylenes along with 2-butene and 1,3-butadiene. The average absolute error is 0.7% with a maximum of 1.3%. The rate of hydrogenation of the acetylenes is somewhat slower than for olefins.

Table III. Unsaturation by Hydrogenation

Sample	Total Unsaturation: Calculated	Total Unsaturation: Found	Absolute Error
	Volume Per Cent		
1	13.4	14.3	+0.9
2	33.7	33.3	−0.4
3	51.0	51.4	+0.4
4	62.1	62.8	+0.7
5	114.1	114.3	+0.2
7	95.4	94.9	−0.5
8	8.1	9.4	+1.3
9	62.1	62.2	+0.1
10	51.2	51.2	0.0
11	73.3	73.4	+0.1

Determination of Olefins. Catalytic hydrogenation measures the unsaturation of the olefins and 1,3-butadiene as well as that of the acetylenes. In order to calculate the total unsaturation of the acetylenes alone, it is necessary to determine the olefins and butadiene by some other method and apply a correction to the results obtained in the hydrogenation. Olefins can be determined rapidly and accurately by the bromine titration method of Stanerson and Levin (*11*). In this procedure an excess of a standard bromine solution is added to the sample and the excess back-titrated after 30 seconds. According to these authors, butadiene interferes in the determination of olefins. However, if the conditions are carefully controlled, the butadiene can be made to react quantitatively as a mono-olefin. The effect of excess bromine on the determination of total unsaturation is shown in Figure 4. Between the limits of 15 and 30 mg. of excess bromine the per cent unsaturation found is within ±0.2% of the theoretical value. The time which was allowed to elapse between the addition of the excess bromine and the addition of potassium iodide was varied from 15 to 50 seconds without any effect on the determination.

Results obtained in the bromination of mixtures of 2-butene and 1,3-butadiene are shown in Table IV. All the samples contained ethylacetylene, and all samples with the exception of

Table IV. Butene and Butadiene by Bromine Titration

Sample	Blended 2-Butene	Blended 1,3-Butadiene[a]	Unsaturation Found	Absolute Error
		Volume Per Cent		
2	5.9	6.7	12.6	0.0
3	5.4	7.3	12.8	+0.1
4	...	6.0	6.1	+0.1
5	4.5	...	4.6	+0.1
7	19.4	5.4	24.4	−0.4
8	7.7	...	7.7	0.0

[a] Butadiene considered as a mono-olefin in calculation of theoretical unsaturation.

No. 2 contained vinylacetylene. The values obtained on bromination show that neither of these acetylenes consumes bromine during the determination.

The apparatus shown in Figure 1 can be used in the determination of olefins by bromination, although it differs somewhat from the apparatus described by Stanerson and Levin. The Shepherd buret is used to measure the sample, which is then condensed and titrated in flask *B* according to the directions given by Stanerson and Levin under Method B. An excess of 15 to 30 mg. of bromine (0.5 to 1.0 ml. of solution) is added to the flask and the flask is allowed to stand 30 seconds to 1 minute before the addition of potassium iodide.

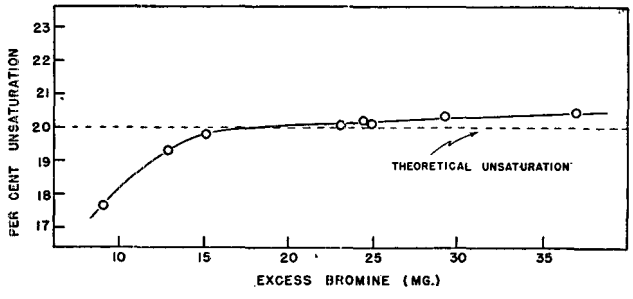

Figure 4. Effect of Excess Bromine on Bromine Addition Number

Sample composition:

***n*-Butane**	**65.3%**
2-Butene	**10.4%**
Vinylacetylene	**5.9%**
Ethylacetylene	**8.8%**
1,3-Butadiene	**9.6%**

Determination of 1,3-Butadiene. The method which is employed for the determination of 1,3-butadiene is essentially that of Tropsch and Mattox (*12*) with modification by Robey *et al.* (*9*). Table V gives results on the determination of 1,3-butadiene which show a mean deviation of 0.5%. These results show that vinylacetylene does not react with maleic anhydride under the conditions of test despite its conjugated double-triple bond system.

Table V. 1,3-Butadiene by Maleic Anhydride

Sample	Butadiene Blended	Butadiene Found	Absolute Error
	Volume Per Cent		
2	6.7	6.2	−0.5
3	7.3	6.8	−0.5
4	6.0	5.6	−0.4
7	5.4	6.1	+0.7
9	8.4	8.5	+0.1
10	0.1	0.1	0.0
11	12.7	12.3	−0.4

Determination of Individual Acetylenes. From the above data ethylacetylene and vinylacetylene are calculated. By means of Equation 1 the total unsaturation by hydrogenation is corrected for the olefins and diolefins present to give unsaturation of the acetylenes alone.

$$A - (B + C) = D \quad (1)$$

where A = volume per cent unsaturation by hydrogenation
B = volume per cent unsaturation by bromine addition (accounts for mono-olefins plus one double bond of diolefin)
C = volume per cent 1,3-butadiene (accounts for the other double bond of 1,3-butadiene)
D = volume per cent unsaturation resulting from acetylenes alone

By simultaneous solution of Equations 2 and 3 the percentages of ethylacetylene and vinylacetylene are calculated.

$$X + Y = E \quad (2)$$

$$2X + 3Y = D \quad (3)$$

where X = volume per cent ethylacetylene
Y = volume per cent vinylacetylene
E = volume per cent total acetylenes
D = volume per cent unsaturation resulting from acetylenes alone

Table VI. Determination of Vinylacetylene and Ethylacetylene

Sample	Vinylacetylene Blended	Vinylacetylene Found	Ethylacetylene Blended	Ethylacetylene Found
		Volume Per Cent		
1	0.0	0.8	6.7	6.0
2	0.0	0.0	7.2	7.2
3	5.4	6.2	7.4	6.5
4	10.1	11.7	9.9	8.1
5	29.2	30.2	11.0	9.8
7	16.0	16.0	8.6	8.2
8	0.2	0.5	0.4	0.1

Table VI shows the percentages of each acetylene blended and found and the deviation of these results from theoretical for each sample. The average error is 0.8%. In addition to the blends shown in this paper, approximately an equal number of other blends of similar composition were analyzed; the mean deviation of the results for the individual acetylenes in all samples was 0.7%.

Interfering Compounds. It is necessary to remove mercaptans and amines from the sample if they are present. The mercaptans will give high results for acetylenes by reacting with the silver nitrate and liberating nitric acid. The amines will cause low results by neutralizing the nitric acid liberated by the acetylenes.

Table VII. Addition of Bromine to 1,2-Butadiene

Run No.	Volume Per Cent 1,2-Butadiene Present	Volume Per Cent 1,2-Butadiene Found[a]
1	97+ (by specification)	100.0
2	97+ (by specification)	97.2
3	97+ (by specification)	99.7
4	97+ (by specification)	97.5
5	97+ (by specification)	101.3
6	16.7	16.4
7	16.7	16.5
8	16.7	16.7
9	16.7	16.7
10	16.7	16.7

[a] Values calculated on basis of one mole of bromine per mole of diene.

No provision has been made for eliminating the interference which will result if 1,2-butadiene is present. However, a limited study has been made of the action of 1,2-butadiene under the conditions of tests used in the determination of the individual acetylenes. 1,2-Butadiene offers no interference in the determination of total acetylenes by reaction with silver nitrate. In the determination of unsaturation by bromine addition, 1,2-butadiene adds bromine to one double bond only, the same as 1,3-butadiene. This is shown by Table VII, where the diene alone and blended with *n*-butane was titrated with bromine solution. The values obtained on the 1,2-butadiene alone agree with the stated purity of 97+% and when the diene was blended with butane agreement was also obtained.

On catalytic hydrogenation 1,2-butadiene quantitatively added 2 moles of hydrogen per mole of the hydrocarbon. This is sub-

Table VIII. Determination of Ethylacetylene and Vinylacetylene in Samples Containing 1,2-Butadiene

Sample	Ethylacetylene Blended	Ethylacetylene Found	Vinylacetylene Blended	Vinylacetylene Found	1,2-Butadiene Blended
			Volume Per Cent		
9	3.3	0.2	0.7	3.5	2.1
10	7.6	3.3	0.6	4.4	2.5
11	5.3	2.1	0.6	3.6	2.5

stantiated in Table III, runs 9, 10, and 11, which contain 1,2-butadiene along with other C_4 hydrocarbons.

Samples of 1,2-butadiene of 97+% purity showed 0.6 and 1.0% absorption in maleic anhydride, whereas 1,3-butadiene is completely absorbed, as indicated in Table V.

No method is available for determining 1,2-butadiene, except those employing spectrographic procedure; hence no correction for its presence can be made in a chemical analysis of this type. The catalytic hydrogenation step will indicate the presence of an extra double bond, which is not accounted for otherwise and will be considered as originating in vinylacetylene. The vinylacetylene result will therefore be high and the ethylacetylene content low by the amount of the 1,2-butadiene present. Table VIII shows this to be approximately so on samples which contain 1,2-butadiene.

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Determination of Cyclopentadiene and Methylcyclopentadiene in Admixtures with Other Hydrocarbons

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A method is described for quantitatively depolymerizing the dimers of cyclopentadiene and methylcyclopentadiene and determining individually the concentrations of the monomers in the resulting mixture. The method is based on the rate of condensation of cyclopentadiene and of methylcyclopentadiene with acetone in an alkaline solution to form the dimethyl fulvenes; and benzaldehyde in an alkaline solution to form the phenyl fulvenes. After neutralization with acetic acid, the intensity of the color produced is measured by means of a spectrophotometer. The concentrations of cyclopentadiene and methylcyclopentadiene are calculated from the extinction coefficients which differ under the conditions of fulvene formation. The determination is not affected by the presence of paraffins, aromatics, naphthenes, mono-olefins, or aliphatic diolefins.

IN THE pyrolysis of hydrocarbons at high temperature, two of the many compounds that are formed are cyclopentadiene and methylcyclopentadiene. These two products in turn dimerize, forming the cyclopentadiene and methylcyclopentadiene dimers, and cross dimerize, forming the codimer. In industrial processing it has been found very difficult to separate these two compounds economically and thus it is desirable to be able to differentiate between the two basic components by chemical analysis. Of the methods mentioned in the literature, none were devised for this purpose nor were they readily adaptable.

Sefton (*3*) devised a method for determining cyclopentadiene, using the heat of reaction with maleic anhydride. He states that his method is not specific for cyclopentadiene, but he expects little interference, as the other dienes present in the same boiling range react more slowly. Methylcyclopentadiene would be expected to react more slowly than the cyclopentadiene, but utilizing this difference in rate of reaction would be complicated by the other dienes present.

Ultraviolet light absorption may offer a basis for a method. Pickett, Paddock, and Sackter (*2*) made a study of the spectrum for cyclopentadiene but have not used it for the determination of this compound. A study of the spectrum of methylcyclopentadiene made by the authors revealed a shift in the absorption curve of this compound as compared with that of cyclopentadiene. However, the use of such a method may be subject to interference from such constituents as aromatics and other conjugated diolefins.

The condensation reaction between cyclopentadiene and aldehydes or ketones forming the highly colored fulvenes as observed by Thiele (*4*) was utilized by Uhrig, Lynch, and Becker (*5*). One

unpublished method investigated involved the reaction of cyclopentadiene with acetone to form the colored compound dimethyl fulvene. Uhrig *et al.* used benzaldehyde in place of the acetone, thus forming the colored compound phenyl fulvene.

As a result of earlier work in which pure methylcyclopentadiene was separated from hydrocarbon mixtures and its properties were determined, it was observed that methylcyclopentadiene reacts more slowly than cyclopentadiene in forming fulvenes with both acetone and benzaldehyde (*1*). The reaction rates of methylcyclopentadiene and cyclopentadiene with acetone are slower than their reactions with benzaldehyde. Table I indicates that the reactions of methylcyclopentadiene and cyclopentadiene with benzaldehyde are complete for both compounds in less than 20 minutes, whereas with acetone neither reaction is complete; however, the cyclopentadiene reaction is considerably more complete than the methylcyclopentadiene reaction. These data suggested that by determining for a mixture of cyclopentadiene and methylcyclopentadiene the optical density of the fulvenes formed with acetone for a 15-minute reaction time and with benzaldehyde for a 20-minute reaction time, the composition of the mixture could be calculated.

The stable form of both cyclopentadiene and methylcyclopentadiene is in the form of the dimers. Therefore, for any analytical method for the determination of the monomers, it is essential that a preliminary step be employed in which the dimers are converted to the monomers. Uhrig *et al.* have proposed such a method involving the destructive distillation of cyclopentadiene. This method is time-consuming and requires certain precautions, and, where two compounds with different boiling points are involved, it becomes more difficult to carry out. It was found that when a hydrocarbon sample containing dimers of cyclopentadiene and methylcyclopentadiene is passed through a tube heated to approximately 340° to 360° C., the dimers will decompose quantitatively, forming the monomers.

REAGENTS

Toluene, C.P. Acetone, technical. Dry ice. Anhydrous sodium sulfate.

Alcoholic potassium hydroxide solution. Dissolve 5 grams of potassium hydroxide in 100 ml. of 95% ethanol.

Acetic acid, 4% solution. Dilute 40 ml. of glacial acetic acid to 1000 ml. with distilled water.

Benzaldehyde, 20% solution. Dilute 20 ml. of C.P. benzaldehyde to 100 ml. with 95% ethanol.

APPARATUS

Depolymerization apparatus as shown in Figure 1.

Beckman spectrophotometer. Constant-temperature bath. Interval timer. Pipets, 1-, 2-, 5-, 10-, 15-, and 20-ml. Volumetric flasks, 50- and 100-ml. Glass-stoppered bottles, 125-ml. Beakers, 50-ml.

PROCEDURE

No preliminary fractionation of the sample is necessary unless it is known that interferences exist which can be removed by this operation. The dimers of cyclopentadiene and methylcyclopentadiene do not form fulvenes; therefore, if these compounds are not all in the monomeric state, a preliminary depolymerization treatment is necessary. If the sample contains both monomers and dimers, they can be determined individually by making the fulvene analysis on both the sample as received and the depolymerized sample.

Depolymerization of Sample. Adjust the power input to the depolymerization apparatus to have the depolymerized sample vapor leave the heating coil at 340° to 360° C. This is accomplished by predetermining the setting of a variable-voltage transformer to give the above temperature of vapors immediately leaving the heating coil as indicated by a test thermocouple inserted within the depolymerization tube. While heating the apparatus, dry the sample with sodium sulfate. From the estimated weight per cent of dimer present, from the following table, determine the dilution of the sample, the volume of diluted sample to depolymerize, and size of volumetric flask receiver for the depolymerized sample to use.

Approximate Weight % of Dimer	Dilution of Sample	Mixture to Depolymerize *Ml.*	Receiver *Ml.*
0.0 to 0.9	None	15	50
0.8 to 2.8	None	5	50
2.6 to 9.0	3/10	5	50
9.0 to 28	1/5	5	100
28 to 90	3/50	5	100

To dilute the sample, place approximately 20 ml. of toluene in the appropriate volumetric flask and weigh. Pipet the correct volume of sample into the flask and reweigh. Record the weight of sample, and dilute to the mark with toluene. Place the outlet tube, extending from the bottom of the depolymerization apparatus, in a second volumetric flask containing approximately 20 ml. of toluene cooled by an acetone–dry ice bath. Transfer the diluted sample into the funnel at the top of the depolymerization apparatus. When the funnel is empty, add 5 ml. of toluene, washing down the sides of the funnel during the addition. After all the toluene has passed through, allow the tube to drain for approximately 1 minute; remove the volumetric flask; allow the flask and the contents to come to room temperature, and dilute to the mark with toluene. Aliquots of this solution are analyzed for cyclopentadiene and methylcyclopentadiene using the following procedure.

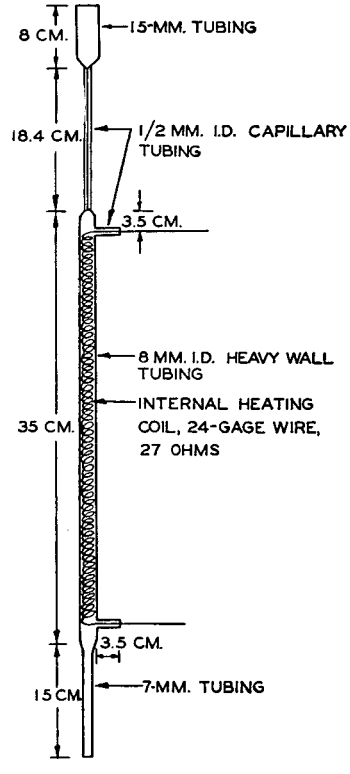

Figure 1. Depolymerization Apparatus

Determination of Cyclopentadiene and Methylcyclopentadiene Monomers. The depolymerized sample should be analyzed as soon as possible to minimize errors from the redimerization of the monomers. It has the proper dilution for the acetone reaction and for the benzaldehyde reaction should be diluted one to five.

In a pair of 125-ml. bottles for the acetone reaction and in another pair of 125-ml. bottles for the benzaldehyde reaction, prepare the following mixtures. In bottle 1 (to be used for reaction)

mix 5 ml. of C.P. acetone and 5 ml. of alcoholic potassium hydroxide. In bottle 2 (to be used for blank) mix 5 ml. of C.P. acetone, 5 ml. of alcoholic potassium hydroxide, and 10 ml. of 4% acetic acid. In bottle 3 (to be used for reaction) mix 5 ml. of 20% benzaldehyde and 5 ml. of alcoholic potassium hydroxide. In bottle 4 (to be used for blank) mix 5 ml. of 20% benzaldehyde, 5 ml. of alcoholic potassium hydroxide, and 10 ml. of 4% acetic acid. Immerse the bottles in the water bath and allow them to come to a bath temperature of 32° C. Add 5 ml. of properly diluted sample to each bottle and swirl the contents without allowing any sample to contact the stopper. After allowing the acetone reaction to proceed for exactly 15 minutes and the benzaldehyde reaction to proceed for exactly 20 minutes, neutralize the contents of the corresponding bottles with 10 ml. of 4% acetic acid. Add 20 ml. of toluene to each bottle, mix thoroughly, and decant the hydrocarbon layers into 50-ml. beakers. Add approximately 1 gram of sodium sulfate to each beaker and cover them with watch glasses. After dehydrating the toluene solution, determine the optical density with the spectrophotometer. Use a wave length of 425 mμ and a slit width of 0.03 mm.

Table I. Specific Extinction Coefficients of Cyclopentadiene and Methylcyclopentadiene Fulvenes as Function of Formation Reaction Time

Reaction Time, Min.	Fulvene	K at 32° C. and 425 mμ[a] Cyclopentadiene	Methylcyclopentadiene
15	Acetone	0.345	0.085
30		0.370	0.140
45		0.403	0.194
60		0.430	0.234
5	Benzaldehyde	0.950	0.732
10		0.930	0.744
20		0.896	0.759
30		0.874	0.759

[a] Units, liters per mole per cm.

Calculations. First calculate the extinction coefficients from the optical densities observed for the two reactions, using the following equation:

$$K = \frac{D}{CL}$$

where

K = extinction coefficient
D = optical density
C = concentration of sample in grams per liter of solution
L = optical path in cm.

Making

K_1 = K acetone reaction
K_2 = K benzaldehyde reaction

The weight per cent of the two components present in the sample may be calculated as follows:

X = weight % of cyclopentadiene = $100\ (k_1K_1 - k_2K_2)$
Y = weight % of methyl cyclopentadiene = $100\ (k_3K_2 - k_4K_1)$

The constants, k_1, k_2, k_3, and k_4 in the above equations must be determined by carrying out the above procedure, using pure cyclopentadiene and methylcyclopentadiene separately, determining the extinction coefficients for the two compounds in both reactions, and substituting these values in the following equations:

$$k_1 = K_dA$$
$$k_2 = K_bA$$
$$k_3 = K_aA$$
$$k_4 = K_cA$$

where

$$A = \frac{1}{K_aK_d - K_bK_c}$$

K_a = extinction coefficient of cyclopentadiene in the acetone reaction
K_b = extinction coefficient of methylcyclopentadiene in the acetone reaction
K_c = extinction coefficient of cyclopentadiene in the benzaldehyde reaction
K_d = extinction coefficient of methylcyclopentadiene in the benzaldehyde reaction

Table II. Determination of Cyclopentadiene and Methylcyclopentadiene in Hydrocarbon Samples

Cyclopentadiene Present, wt. %	Cyclopentadiene Found, wt. %	Methylcyclopentadiene Present, wt. %	Methylcyclopentadiene Found, wt. %
7.7	7.9	10.6	10.4
10.7	11.0	10.4	10.1
16.1	16.1	5.3	5.3
21.1	20.8	0.4	0.4

PRECAUTIONS

Extreme care must be taken to keep acetone out of the reagents used in the benzaldehyde test. Benzaldehyde and acetone react to give the colored compound benzal-acetone which will interfere with the spectrophotometer readings. Separate sets of pipets must be used for the acetone and benzaldehyde reactions.

Uhrig *et al.* reported that the yellow color of phenyl fulvene, the reaction product of benzaldehyde and cyclopentadiene, was stable and did not change with time. Contrary to this, the authors found that the color faded gradually as shown in Table I. Thus in this reaction as well as that using acetone, it is necessary to hold time and temperature constant.

ACCURACY OF METHOD

The results of a series of analyses on synthetic samples containing both compounds in known concentrations are given in Table II. As indicated, this test method has a high degree of accuracy. The widest variation from the actual percentage of either compound is 0.3%. This method has been applied to numerous plant hydrocarbon streams which vary considerably in cyclopentadiene and methylcyclopentadiene content and in admixtures with various types of paraffinic, naphthenic, and aromatic hydrocarbons with satisfactory results. The only type of hydrocarbon compound found to interfere with this test method is indene. However, it would be expected that any other compounds forming fulvenes would interfere, such as higher homologs of indene and other substituted cyclopentadiene compounds with the substitution in the 1 and 2 positions only.

Indene having the same type structure as cyclopentadiene will undergo fulvene condensation; however, its rate of reaction is slow. The rate of reaction with acetone is so low that it does not interfere. With benzaldehyde, the rate of reaction is rapid enough to cause an error in the methylcyclopentadiene content, as calculated in this method, equal to approximately one fourth of the indene content present. Therefore, if more than a small quantity of indene is known to be present, a preliminary fractionation is necessary to remove it.

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(3) Sefton, R., *J. Soc. Chem. Ind.*, **64**, 104 (1945).
(4) Thiele, J., *Ber.*, **33**, 666 (1900).
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RECEIVED July 10, 1947.

Correction. In the report of the Eighth Conference on Applied Spectroscopy [ANAL. CHEM., **19**, 1045 (1947)], the word "Quantometer" appears as a general designation for direct reading instruments. It should have been used only in connection with the instrument manufactured by the Applied Research Laboratories for which it is a trade name.

Measurement of Water in Gases by Electrical Conduction in a Film of Hygroscopic Material

Use of Pressure Changes in Calibration

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The electrical conductivity of a thin film of such a material as phosphoric acid changes over a wide range with changes in the concentration of water in the atmosphere with which it is in contact. By adjusting the pressures of a sample of gas of known and one of unknown composition, they can be made to have the same concentration of water, shown by equal resistances of the detecting film. Apparatus and procedures for determining water vapor under a variety of circumstances are described, and characteristics of the method and sources of error are discussed. The method has the general merits of simplicity of operation, speed, great sensitivity, and wide range. Only small samples are needed, and few substances interfere. The following applications are described: determining water vapor in compressed oxygen, liquid carbon dioxide, and Freon; measuring relative humidity in comparatively inaccessible or small spaces, especially under rapidly changing conditions; determining moisture in powdered solids and the capacity of drying agents; determining the water content of organic liquids and solutions by rapidly measuring its vapor pressure; measuring the permeability of membranes to water; and detecting minute concentrations of combustible gas in air or of oxygen in combustible gas.

THE measurement of water vapor in gases by observing the conductance of thin films of electrolyte has been employed occasionally at the National Bureau of Standards for a variety of purposes during nearly thirty years. The essentials of the method are extremely simple. A thin film of liquid, which may be such a material as phosphoric or sulfuric acid or a solution containing one or more acids, bases, or salts with a binding material such as gelatin or a "high-polymer" plastic, is spread over the surface of a solid insulator between metallic electrodes. The electrolyte tends to reach equilibrium with the water vapor in the atmosphere which surrounds it and to form a solution, the electrical conductance of which is a measure of the water vapor in the atmosphere. We need, in addition, some sort of instrument for measuring or comparing electrical resistances and a means of calibrating the film by comparison with a gas of known moisture content. Polarization makes necessary the use of alternating current for the measurement.

The method was devised initially (*6*) to detect very small concentrations of water vapor in gases entering a catalytic reaction in which water is a poison. The material first tried for the conducting film was a salt, calcium chloride; but it was soon found that the salt became a nonconducting solid at a humidity far higher than that to be detected, and numerous other electrolytes were tried. Among them phosphoric and sulfuric acids were found most useful because they served to detect the smallest concentrations of water vapor. However, films of these materials changed resistance so rapidly that it seemed hardly worth while to calibrate them by comparison with known atmospheres, laboriously prepared.

The method therefore fell into disuse except for qualitative work until Dunmore (*1*, *2*) employed it successfully for much higher humidities in connection with meteorological observations. He used a salt, lithium chloride, as the electrolyte in a plastic film of very high resistivity, but one which held its calibration well. The need for a method of determining rapidly very small quantities of water vapor in aviator's oxygen during the war led to the development of a means of calibrating a sensitive film at the time of its use so quickly and simply that little need remained for a permanent calibration. This at once greatly extended the possible applications of the method, several of which are suggested below.

PRINCIPLE INVOLVED IN CALIBRATION BY ADJUSTMENT OF PRESSURE

As a rough approximation, deviations from which are discussed below, the resistance of a given film is independent of the

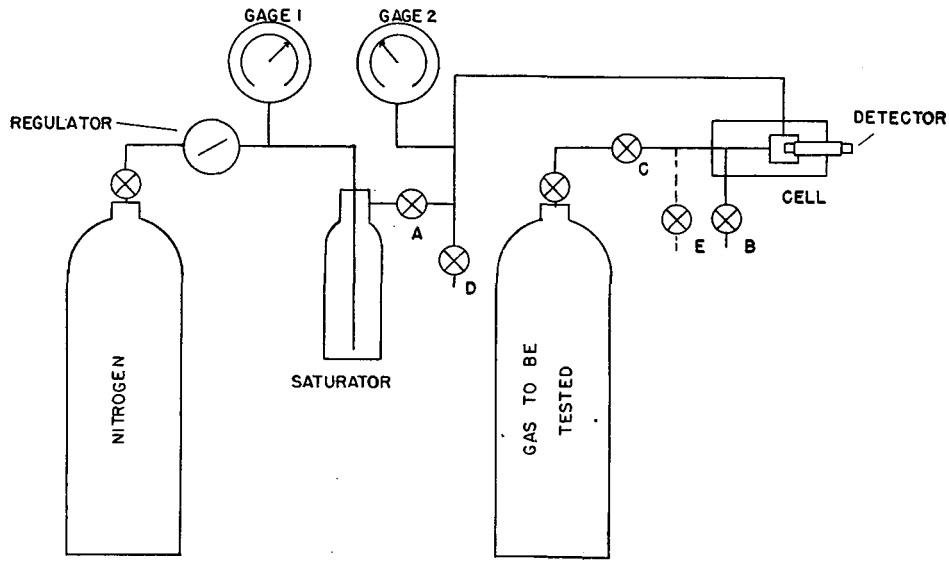

Figure 1. Diagram of Mechanical Connections for Testing Compressed Gas

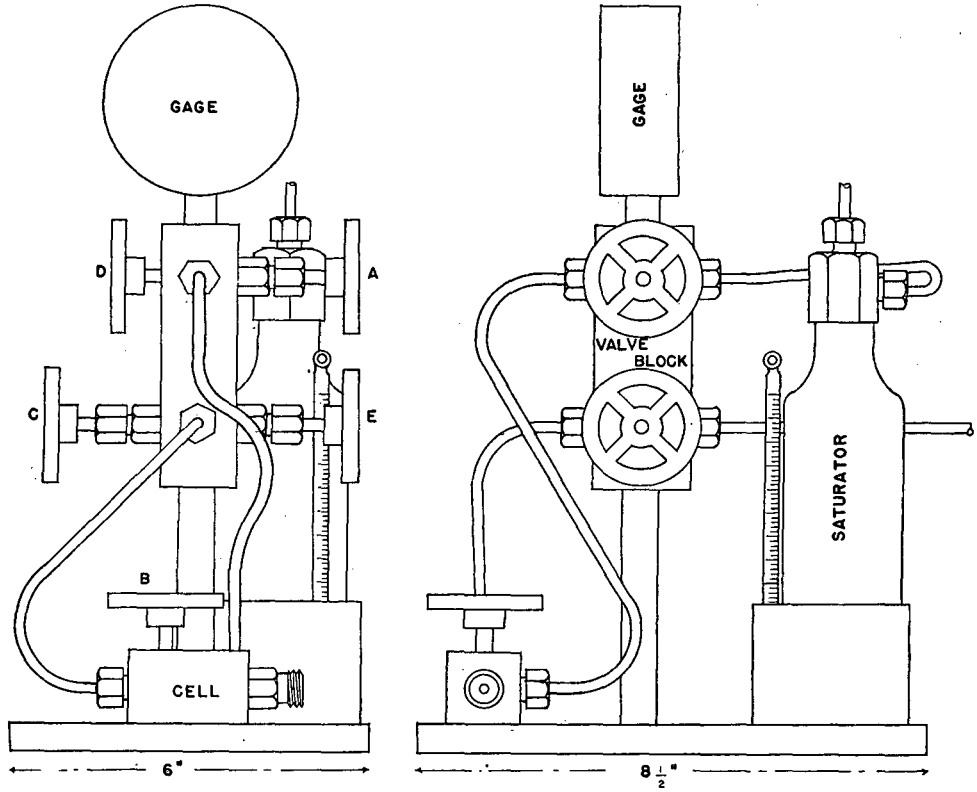

Figure 2. Front and Side Elevations of Portable Instrument

gases other than water vapor with which it is in contact and depends only on the amount of water contained in unit volume. If a sample of gas such as oxygen or air of known water content per unit volume is passed over the film it will assume a certain resistance. If a second sample of gas of unknown water content is then passed over the film, the resistance will usually be different, but it may be restored to its original value by compressing or expanding the second sample until it contains the same quantity of water per unit volume (more exactly, until the water vapor has the same fugacity) as the first sample. When this condition is reached, we note the pressure and readily compute what the water content would be in a unit volume at any other pressure (usually, but not always, 1 atmosphere). If the unknown gas is initially at atmospheric pressure it may be more convenient to change the pressure of the standard gas until the same resistance is produced by both. For brevity, the process of adjusting the pressure of one or both gases to produce the same electrical resistance of the detector will be called "comparing" the gases. In general, four pressures are involved in a comparison:

P_s, the pressure at which the standard gas contains a known concentration of water vapor, S.

P_c, the "comparison pressure" at which the standard gas is "matched" with the electrical resistance produced by the unknown gas at pressure P_x.

P_x, defined by the preceding statement.

P_w, the pressure at which we wish to know the concentration of water in the unknown gas.

The water content, C, of the standard gas at the comparison pressure is

$$C = S\frac{P_c}{P_s} \tag{1}$$

Since we know that the unknown gas has this same water content at the matching pressure P_x, the water content, W, at pressure P_w of the unknown gas is derived from C, just as C was derived from S:

$$W = C\frac{P_w}{P_x} = \frac{SP_cP_w}{P_sP_x} \tag{2}$$

Having determined the value of W, we can obviously use the newly analyzed gas as the standard to determine W_1, the water content of still another unknown gas at P_{w_1} after matching it electrically at pressure P_{x_1} against the new standard at P_w:

$$W_1 = W\frac{P_{w_1}}{P_{x_1}} = S\frac{P_cP_wP_{w_1}}{P_sP_xP_{x_1}} \tag{3}$$

There is obviously no limit to the number of steps of this kind that can be taken, but because some error is involved in each comparison the results soon lose significance.

A gas which contains an approximately known concentration of water, to be used as the first or the only standard, can be obtained easily by saturating compressed air (or other compressed gas that may be available) with water vapor at any convenient pressure and temperature. S then represents the concentration of water vapor in equilibrium with liquid water at the temperature of the measurement, and P_s is the pressure in the saturator. S and W may be expressed in weight per unit volume, relative humidity, or other desired unit, and any unit of pressure may be used, provided it is kept in mind that absolute pressures are involved, not "gage" pressures (above atmospheric).

In the application of the method which has been most extensively made—determining the moisture content of compressed gases—it is convenient to use as the "standard gas" air, oxygen, or nitrogen saturated at about 35 atmospheres pressure and expanded to 1 atmosphere. The water content of the unknown gas is to be determined at 1 atmosphere. Hence, if pressures are expressed in atmospheres, P_c and P_w of Equation 2 are both unity and the equation becomes

$$W = \frac{S}{P_sP_x} \tag{4}$$

in which S is the concentration of water in a vapor space in equilibrium with liquid water.

In the method of use described, the pressure gages are the measuring instruments. We are usually not at all concerned with the actual value of the electrical resistance of the sensitive film, and the electrical instruments are used only to show that two resistances, corresponding to measured pressures, are the same; but in some cases, especially when following changing concentrations of water vapor, it is impracticable to make a separate calibration through the adjustment of pressure for every variation of humidity, and readings of the electrical instruments are recorded and interpreted, usually by interpolation between values determined by pressure readings. The electrical circuit is then truly used as a measuring instrument and not merely as a null-point indicator.

In the foregoing description of principles it was necessary to qualify many of the statements with the words "about," "approximate," etc. The corrections to be made to produce more accurate results and the sources of error are briefly described

below and more completely in a forthcoming research paper of the National Bureau of Standards.

DESCRIPTION OF APPARATUS EMPLOYED

General Arrangement and Procedure. The general method outlined above may be employed with apparatus of great variety. For certain purposes the equipment may be designed for pressures either above or below atmospheric, and many of the parts may be made of glass, metal, or plastic in numerous arrangements. Only the instrument principally used at the National Bureau of Standards and some of its accessories are described here.

The essential electrodes, the separating insulation on which the conducting "film" is spread, and their support will be called collectively the "detector." The electrical equipment used for showing equality of resistance of the "film" under different conditions will be called the "indicator." The "indicator" consists essentially of two parts, the "indicating circuit" involving an adjustable "bridge" of a sort with its power supply and amplifying device and an "indicating instrument" which will be called more briefly the "galvanometer," although its name-plate is more likely to bear the word "microammeter." The other necessary parts of the equipment are a pressure-tight enclosure for the detector called the "cell," a "saturator," two pressure gages, four valves, a cylinder of compressed nitrogen, air, or other gas, and connecting tubing. A high-pressure regulator and a "computer" are desirable but not indispensable.

The preferred arrangement of gas connections is shown diagrammatically in Figure 1.

When used for oxygen testing, the regulator on the nitrogen cylinder is set to deliver gas to the saturator at a pressure of about 500 pounds per square inch as shown by gage 1. The saturated gas is admitted in a slow stream to the cell through valve *A* and, after passing over the detector, is discharged through valve *B*, which is generally left wide open. When the detector has reached equilibrium, the indicating circuit is adjusted so that the galvanometer needle is on-scale and the reading is noted. Valves *A* and *B* are then closed and the gas to be tested is admitted to the cell through valve *C* and discharged through valve *D*. These two valves are manipulated so that with the gas flowing at a moderate rate the galvanometer balances at the reading previously noted. The reading of gage 2 is then recorded. The reading of gage 1 while gas was passing through the saturator is P_s of Equation 4, *and the reading of gage 2 is* P_x.

Nitrogen is indicated as the gas to be saturated because it is usually as available at an oxygen plant, where most of the testing is done, as is oxygen or compressed air, and it does not corrode the steel bottle used as a saturator. Except for the rusting of the saturator, air or oxygen is as satisfactory as nitrogen. If only one cylinder of gas is to be tested, it may first be attached to the saturator to provide the standard gas and then connected as the "gas to be tested." If a high-pressure regulator is not available and gage 1 has a sufficient range, the full pressure of the cylinder may be applied to the saturator.

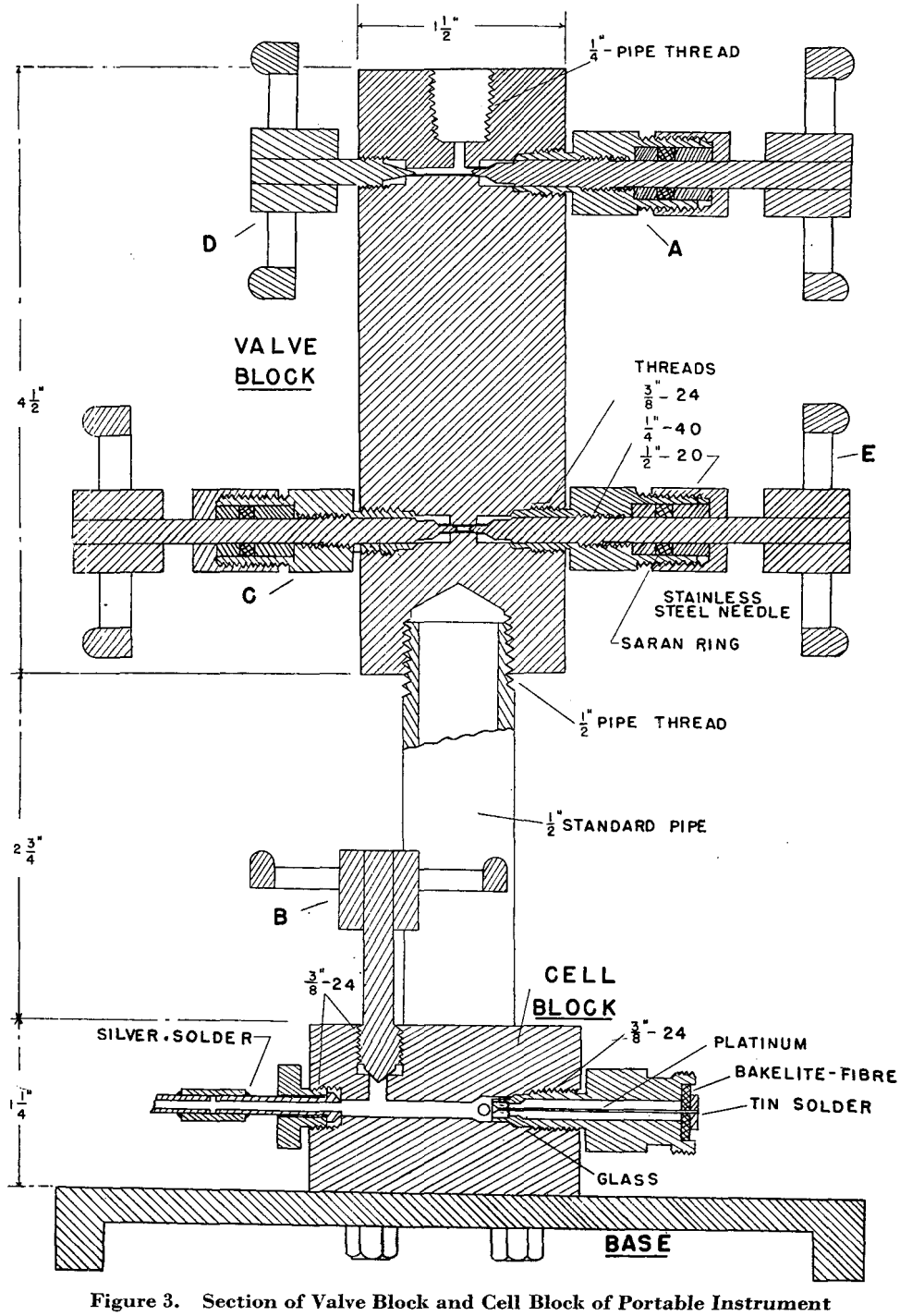

Figure 3. Section of Valve Block and Cell Block of Portable Instrument

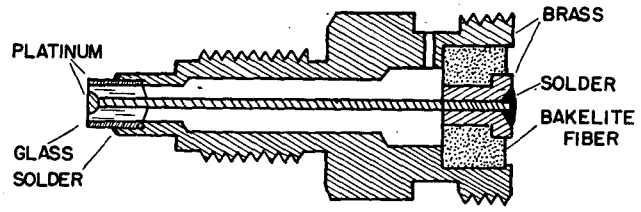

Figure 4. Detail of Detector Most Frequently Used

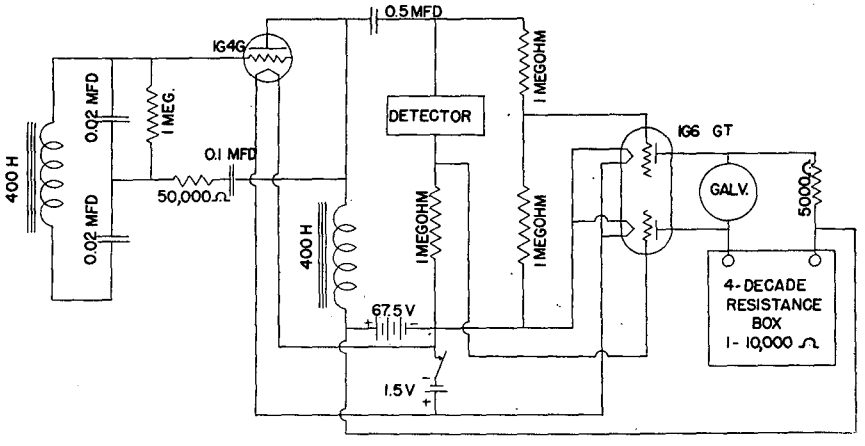

Figure 5. Diagram of Simplified Measuring Circuit

The actual arrangement of apparatus is shown in profile in Figure 2. The valves are lettered as in Figure 1.

A "spare" valve, *E*, controlling entrance to the system at the same point as valve *C*, has been found very convenient for the attachment of a gage more sensitive than gage 2 (0 to 3000 pounds per square inch) or of a "secondary standard," a cylinder of gas drier than can be obtained from the saturator.

Four of the valves are mounted in a single valve block for simplicity of support. Dimensions and further details are shown in cross section in Figure 3. The block is made of heavy metal to conduct heat as readily as possible to the points of expansion of the gas through the principal valves. The cell is connected to the valve block only through considerable lengths of small metal tubing to minimize the effects of expansion on the temperature of the detector. The detector, shown in Figure 4, consists of coaxial glass-insulated platinum electrodes about 1.5 and 3 mm. in diameter in a bushing which can be screwed into the "cell."

F. W. Gross of the bureau's Electrical Instruments Section designed for the authors an indicator in which alternating voltage was supplied from an independent battery-operated oscillator, and the "unbalance voltage" of the bridge was amplified through vacuum tubes. The original circuit has been modified several times, usually in the direction of simplification, by E. C. Creitz and the authors.

The circuit shown in Figure 5 can be used satisfactorily as either a null-point or a measuring instrument. In the first case, the galvanometer needle is merely brought on scale by adjusting the dial-resistance box and further electrical measurements are limited to observing the position of the needle.

The galvanometer is a direct-current instrument which receives alternate pulses in opposite directions from the plates of the twin amplifier. Weston galvanometers, Model 440, and microammeters, Model 801, have been used with equal satisfaction. The galvanometers have a resistance of about 123 ohms and a range of 15 microamperes divided into 60 scale divisions. The microammeters have a range of 50 microamperes with 50 scale divisions. The galvanometers with their thin needles backed by mirrors can be read with greater accuracy, but this is rarely required and the microammeters cost less and are easier to read.

The characteristics of the circuit are shown by the three calibration curves of Figure 6, which, with their corresponding scales, show resistances of the detector and corresponding values of the variable resistance required to

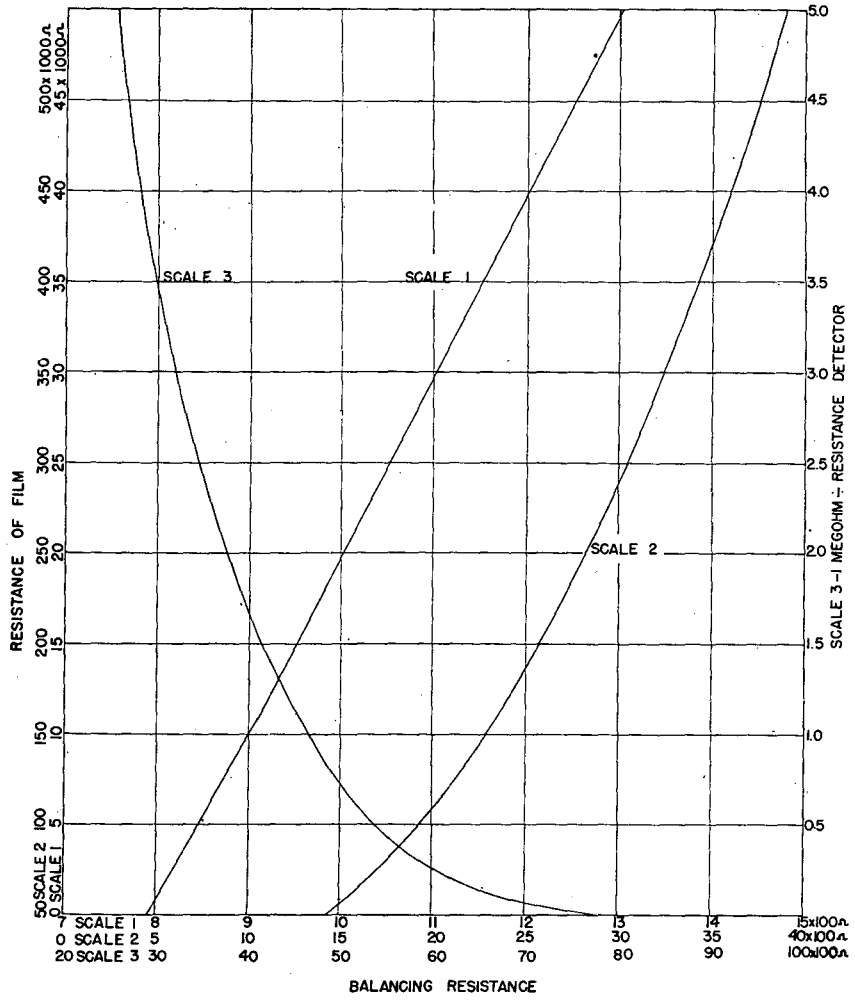

Figure 6. Calibration of Measuring Circuit in Terms of Resistance of Detector

bring the galvanometer to balance. The entire range of possible resistances of the detector from short circuit to open circuit is covered. The higher resistances are plotted on a reciprocal scale. The curves will apply as a definite calibration only to the instrument for which they were drawn.

The amount of current available from the electronic amplifier is never sufficient to damage the galvanometer; hence, at any time any resistance can be connected in the place of the detector with impunity. In view of the very great range of resistances to be encountered and the suddenness with which they sometimes change on going from one atmosphere to another, this is a great advantage.

The Saturator. The saturator pictured in Figure 7 has been generally used. Saturators with more elaborate packing have not worked so well. Saturators more simply packed have worked better. Unfortunately, the first packing of this type worked well, and a large number of other saturators were packed in the same way. More recently the saturator has simply been filled with stream-washed gravel screened to pass a sieve of 5 meshes and be retained by one of 10 meshes per inch. If there are 3 inches (7.5 cm.) of gravel above the water level, no trouble has been encountered with spray from cylinders filled in this way, even when the rate of flow of gas was much greater than necessary. The saturator leaves much to be desired. The gravel has a high heat capacity and with cooling from evaporation at the bottom and changing temperature in the surroundings the actual temperature of saturation is uncertain. For highly accurate results the whole should be placed in a thermostat. What it is hoped will prove to be a better saturator has been designed for use in further study but has not yet actually been employed.

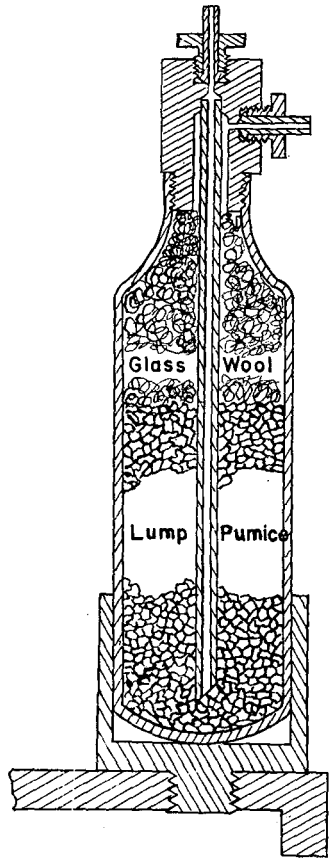

Figure 7. Section of Saturator First Used

In making up the assembly of valves and connections, every precaution must be taken to eliminate places where water can be stored by hygroscopic salts, rust (which is a good adsorbent and acts much like a little silica gel), etc. Soldering flux is particularly bad, and capillary spaces such as screw threads can be troublesome. It is good practice before final assembly of the equipment to wash the parts with a solvent for grease, then to boil them for several hours with several changes of water to remove hygroscopic salts, and finally, to dry the parts in an oven.

The electrolytic film preferred for most purposes is plain phosphoric acid. It is applied in concentrated form by touching the detector with a drop and wiping off the excess with a tuft of cotton. It does not take much experience to apply a film of suitable resistance. One rule of thumb is to moisten the detector and then wipe three times, not too hard, with fresh bits of cotton. For many uses the amount of acid applied may be anywhere within a fifty-fold range and still be satisfactory. The film should be renewed frequently, sometimes after each test. The renewal is hardly more trouble than adding indicator to a solution before a titration. For humidities of less than 5 to 8 micrograms per liter, it is necessary to add sulfuric acid to the phosphoric acid or to use sulfuric acid alone or in a binder such as methyl methacrylate.

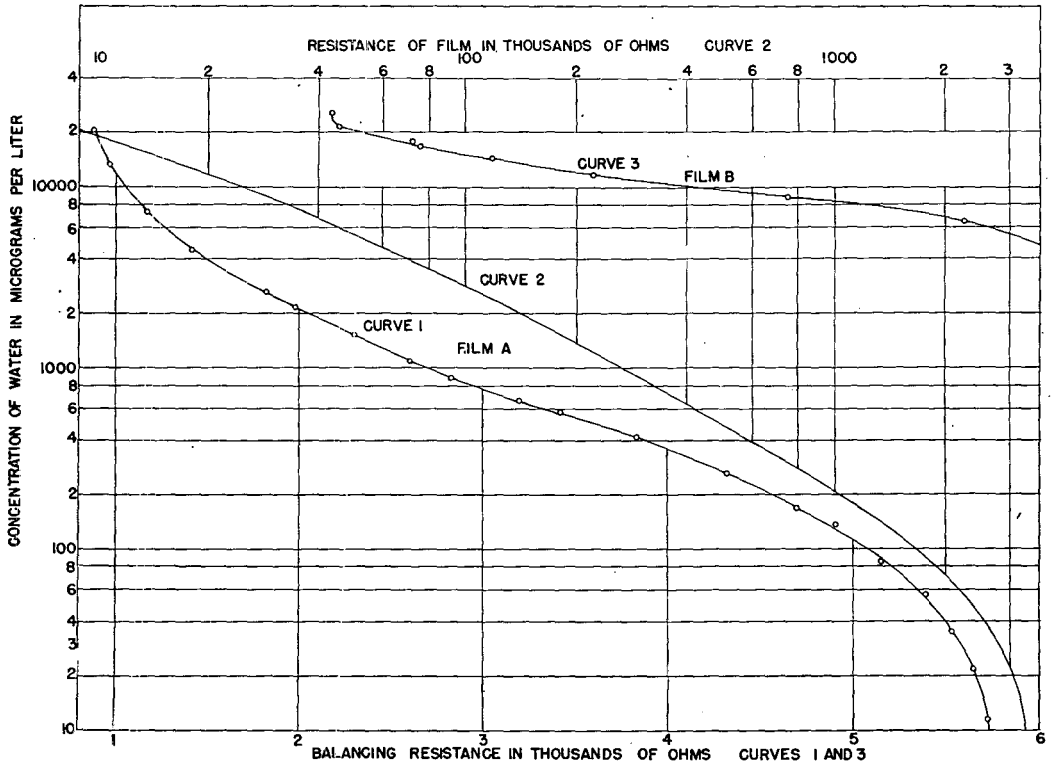

Figure 8. Calibration of Two Conducting Films in Terms of Concentration of Water

The resistance of a single film of phosphoric acid, film A, over almost the whole range of humidities is represented by curve 2 of Figure 8. The concentration of water, in micrograms per liter, is plotted on a logarithmic scale with respect to the "balancing resistance" of the indicating circuit in curve 1. Curve 3 shows similar data for a film B of about 20 times the con-

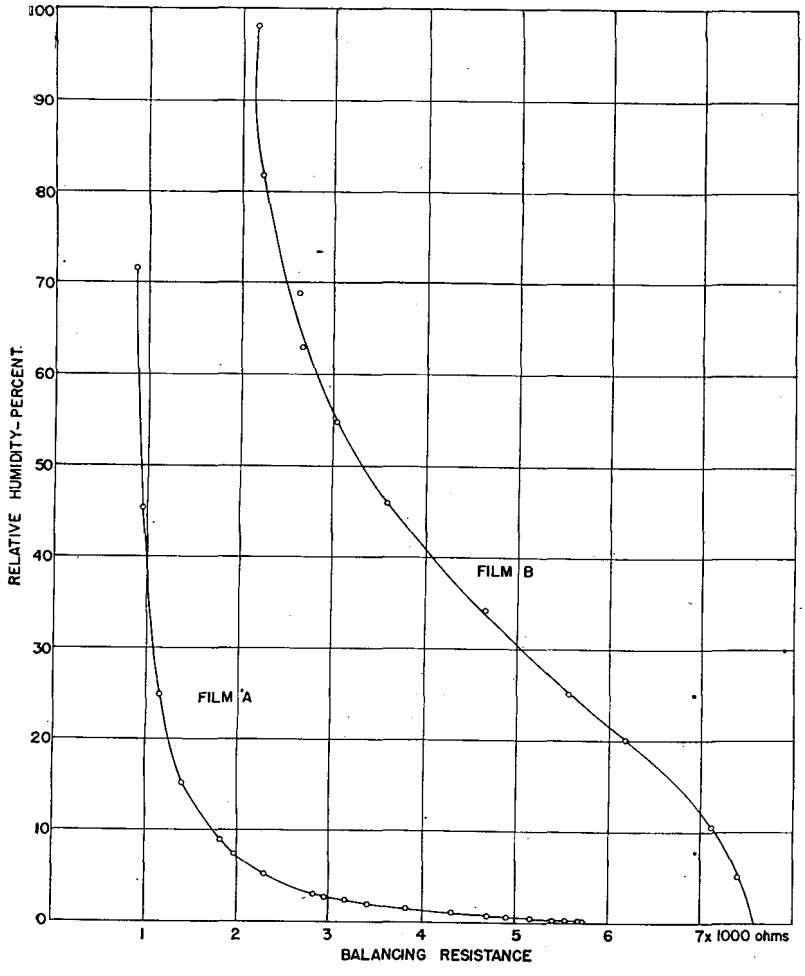

Figure 9. Calibration of Two Conducting Films in Terms of Relative Humidity

ductivity of A. Curves representing instrumental readings with the same films in the ordinary range of atmospheric humidities are shown by Figure 9. Table I shows the approximate resistance of film A and of the balancing resistance at the several measured humidities expressed in several ways.

The sensitivity of the electrical indicator with film A is shown by Figure 10, which is based on the assumption that the balancing resistance could be read to 1 part in 2000 of its magnitude at any point. This corresponds to about 0.8 scale division of the galvanometer. It is apparent at once that the sensitivity so defined approaches about 0.3 microgram per liter or 0.1% of the water present, whichever is greater.

Figure 10 indicates instrumental sensitivity only. It must not be supposed that an absolute accuracy as great as this is usually or ever obtainable. The effects of all other sources of uncertainty remain to be accounted for. Actually, sensitivities, in the lower range of humidities at least, can be considerably increased by using thicker films or by examining gases under pressure, but at present there is usually no object in doing so because the over-all accuracy would not be improved.

The speed with which phosphoric acid films approach equilibrium with the atmosphere in which they are placed is shown for four different films by Figure 11. Data were obtained by alternate exposure of the films to atmospheres containing 1.4 and 0.0114 mg. of water per liter. The abscissa is the change of balancing resistance, which took place in the time represented by the ordinate, expressed as a percentage of the total change which occurred on long exposure. All measurements were made with the drying film. Equilibrium is approached even more rapidly in the opposite direction. Film 1 was several days old and film 2 about 18 hours old; the other films were freshly applied. The tests demonstrated that a film loses its speed of response as well as its sensitivity with age. Of films of the same age the one of highest resistance responds most rapidly.

Corrections and Sources of Error. The principal source of error is without doubt some uncertainty regarding the water content of the gas from the saturator, and this is affected by the condition of the apparatus and the rates of flow employed. To begin with, the regulator rarely controls perfectly the pressure in the saturator. When flow is stopped the pressure builds up a little; when flow is resumed the pressure falls, and this change tends to produce an increase in the water content of the gas as flow is increased. On the other hand, the evaporation of water within the cylinder tends to cool the gas and cause the water content to decrease during the test. If the rate of flow is too high, there may not be time for complete saturation.

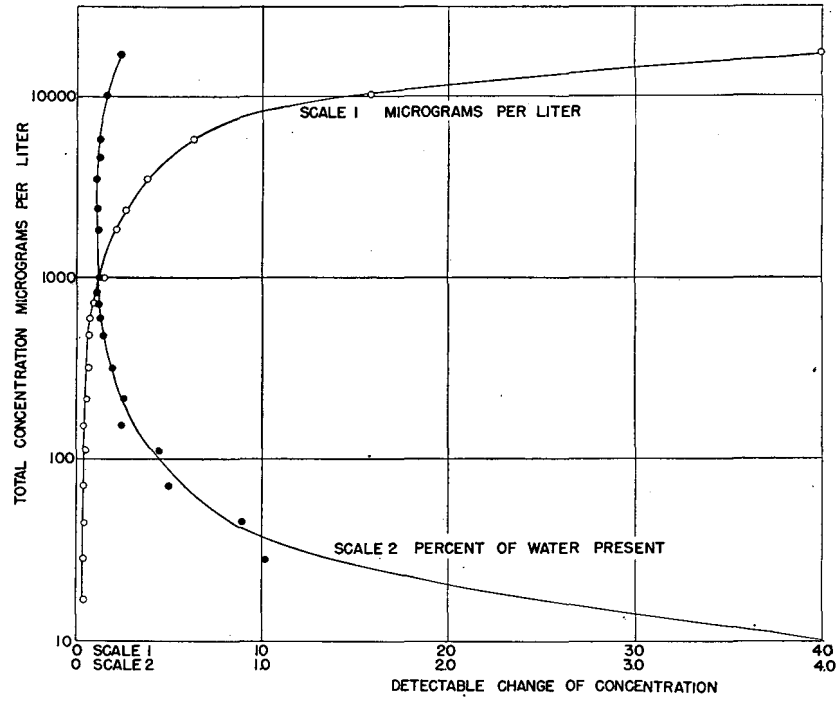

Figure 10. Sensitivity of a Typical Phosphoric Acid Film

Table I. Resistance of a Film of Phosphoric Acid (A) at Various Concentrations of Water Vapor

Balancing Resistance	Resistance of Detector	Concentration of Water			Approximate Dew Point	
			Relative humidity at 83.6° F.	Partial pressure		
Ohms	*Thousands of ohms*	*Micrograms/l.*[a]	*%*	*Mm. Hg*	*° C.*	*° F.*
5730	2870	11.3	0.039	0.011	−74	−101
5664	2700	22.0	0.076	0.021	−53	−63
5541	2390	36.2	0.12	0.034	−49	−56
5540	2050	56.4	0.19	0.055	−45	−47
5167	1600	86.9	0.30	0.084	−41	−42
4913	1280	138	0.48	0.13	−38	−36
4700	1040	171	0.59	0.17	−35	−31
4320	720	63	0.91	0.26	−30	−22
3836	528	411	1.4	0.40	−26.7	−16.2
3420	394	563	1.9	0.55	−23.5	−10.3
3195	337	655	2.3	0.64	−22.0	−7.6
3174	332	655	2.3	0.64	−22.0	−7.6
2955	280	790	2.7	0.77	−20.0	−4.0
2830	253	879	3.0	0.85	−19.0	−2.2
2304	154	1520	5.2	1.48	−13.1	+9.4
1980	106	2170	7.5	2.11	−9.1	15.6
1825	88	2600	9.0	2.53	−7.0	19.4
1420	50	4510	15.6	4.38	−0.5	31.1
1177	37	7220	24.9	7.02	+6.0	42.8
973	17	13200	45.5	12.8	+15.0	59.0
886	8	20800	71.7	20.2	22.3	72.2
790	0	Short circuit				
7814	0	Open circuit				

[a] To obtain parts per million by volume, multiply micrograms per liter by 0.804. To obtain parts per million of air by weight, multiply by 0.62.

Expansion at the valve causes a sharp drop in temperature of the gas with a tendency to precipitate the water as liquid. Fortunately, most of the cooling takes place after the gas passes the narrowest passage in the valve, and any mist that is formed re-evaporates. The massive block is intended to conduct heat rapidly to the valve seat and prevent, as far as practicable without auxiliary heating, the chilling of the inlet to the valve and the condensation of water from the gas before expansion. This is never completely accomplished unless the valve block as a whole is warmer than the saturator, and from time to time a little condensed water comes through the valve and produces a momentary movement of the galvanometer needle toward the "wet" side. In practice these brief deflections of the galvanometer are disregarded. They are comparatively rare, and the amount of water indicated would not affect the reading of the instrument much if it were distributed throughout the gas stream. The slower the flow, the less effect is there from this source of difficulty.

In practice it is commonly assumed that the gas flowing through the cell is at atmospheric pressure. Of course it is not, or it would not flow. Consequently, the detector is exposed to a little higher concentration of water than would otherwise be the case. The gas cooled by expansion may not reach room temperature by the time it arrives at the detector. This affects the reading in two ways; the lower temperature tends to condense more water in the film and thus cause a decrease of resistance, but a film containing a given quantity of water has a high temperature coefficient in the opposite direction. The net effect is still somewhat uncertain, but the needed study of temperature effects has been deferred until a more elaborate set of controls is made available.

The discussion thus far would indicate that accuracy is promoted by making the flow of gas from the saturator very slow. At a very high rate of flow there is danger that liquid water will be carried over from the saturator mechanically and there is even the possibility that a sudden blast of gas over the detector will displace the film (this not infrequently happens with the gas to be tested if valves are manipulated carelessly).

Another factor of importance enters, however. The "dry side" of the instrument is rarely completely dry. Even though the parts of the apparatus are made, dried, and assembled with care, they seem to have the property of sorbing water from moist gas in sufficient quantity to be readily detected and giving it up later to a drier atmosphere. Gages are the worst parts of the apparatus in this respect; valve packings probably next.

This exchange of moisture with surfaces and pockets within the apparatus generally affects the resistance of the detector when there is no flow of gas. A very small flow is affected to some extent; a large flow is not affected appreciably. For this reason we do not want gas from the saturator to flow too slowly; there is also a saving of time in reaching equilibrium if the rate is increased. A rate of 250 ml. per minute from the saturator is probably usually about right. It is not necessary to measure it, however; the observer soon learns to control it satisfactorily

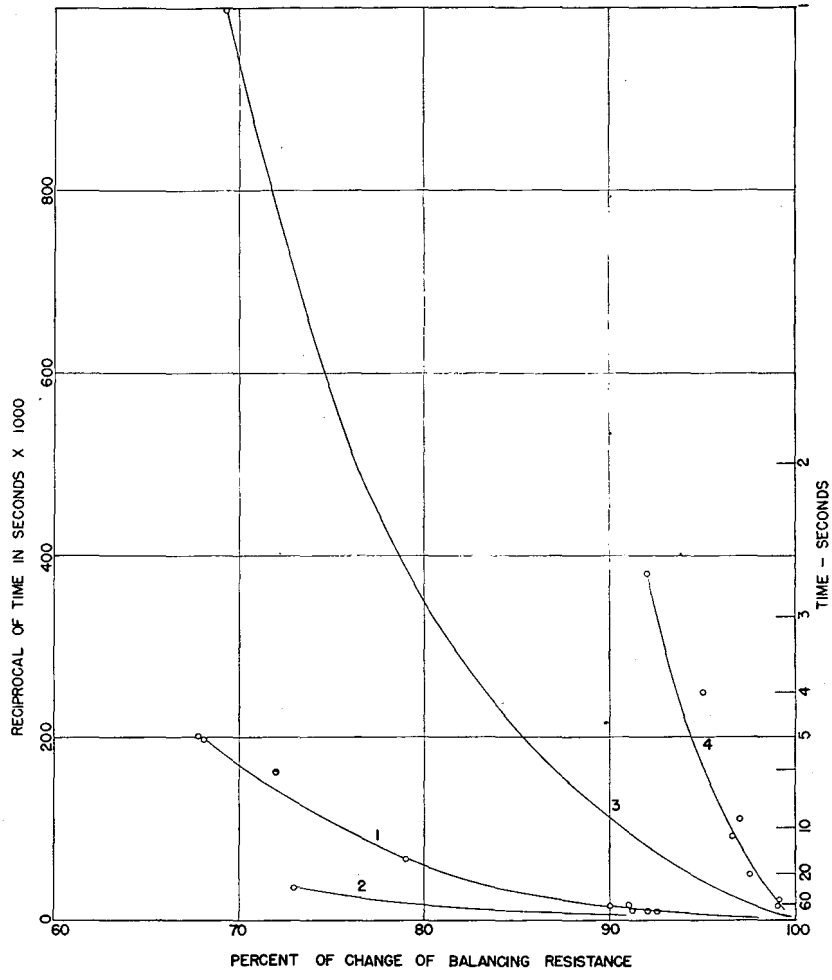

Figure 11. Speed of Approach to Equilibrium of Typical Films

by other means. In a quiet room the escaping gas should be barely audible to a normal ear if the saturating pressure is 500 pounds per square inch, or silent but on the verge of audibility. The stream issuing from the small outlet of valve *B* should not be perceptible to the hand unless the outlet is blocked momentarily with a finger or thumb. The little spurt of gas when the pressure is relieved should be noticeable. Momentarily blocking the flow should also cause the galvanometer to respond decisively and at once. If the apparatus is thoroughly dry, the galvanometer reading should be the same for any rate of flow of gas sufficient to prevent diffusion upstream from the outlet valve and not great enough to build up appreciable pressure in the cell.

Use of Compressed Gas as Standard. Actually it is not practicable to measure the water content of most of the aviators' oxygen now made by direct comparison with gas from a saturator, even if the saturation pressure is 1000 instead of the recommended 500 pounds per square inch. If, for example, gas saturated at 1000 pounds per square inch and 25° C. (77° F.) and expanded to 1 atmosphere matches gas at the usual charging pressure for storage cylinders, 2000 pounds per square inch, the water content of the stored gas is 4 micrograms per liter (after expansion to 1 atmosphere). If the saturation pressure is 500 pounds per square inch, the minimum measurable water content of the stored gas is 7 micrograms per liter. Most of the aviators' oxygen tested at the Bureau of Standards, after the oxygen manufacturers began trying to comply with the specified maximum of 20 micrograms, has contained less than 4 micrograms per liter. To determine the water content actually present in such dry compressed gas, or to measure conveniently the water content below 0.2 or 0.3 mg. per liter of gas not initially under pressure, it is best to use a cylinder of fairly dry compressed gas as a secondary standard. Even for gases within range of direct comparison with the saturator, the cylinder is a convenience because less care is required than in the control of the saturator, and the composition of the standard gas depends less on temperature.

The gas to be used as the secondary standard must be compared frequently with gas from the saturator, for the water content of gas discharged from a cylinder invariably increases as the pressure falls, because the gas in the cylinder is always in near equilibrium with water adsorbed on the walls. This equilibrium is somewhat affected by temperature, but changes in the gas are slow.

Operations Other than Testing Compressed Gases. In most of the numerous possible applications of the method other than testing compressed gases, the gas to be tested is at atmospheric pressure. Instead of the pressure of the unknown gas being varied to obtain a balance corresponding to an observation already made of the standard gas, the first galvanometer setting is made with the unknown gas and the pressure of the standard, whether from saturator or calibrated cylinder, is varied to obtain a balance. The details of the procedure are so like those already given that they probably require no further description. Because we lack the ability to change the pressure of the unknown sample, the range of concentrations that can be measured with a single standard is narrower than in testing compressed gas, and we may need two secondary standards in addition to the saturator, whereas we rarely need more than one in work with compressed gases.

One source of error should be emphasized in connection with miscellaneous uses of the instrument. No rubber whatever can be used in any connection through which a gas to be tested flows. Exposing the gas to contact with any rubber surface is almost equivalent to exposing it to contact with an equal free surface of water.

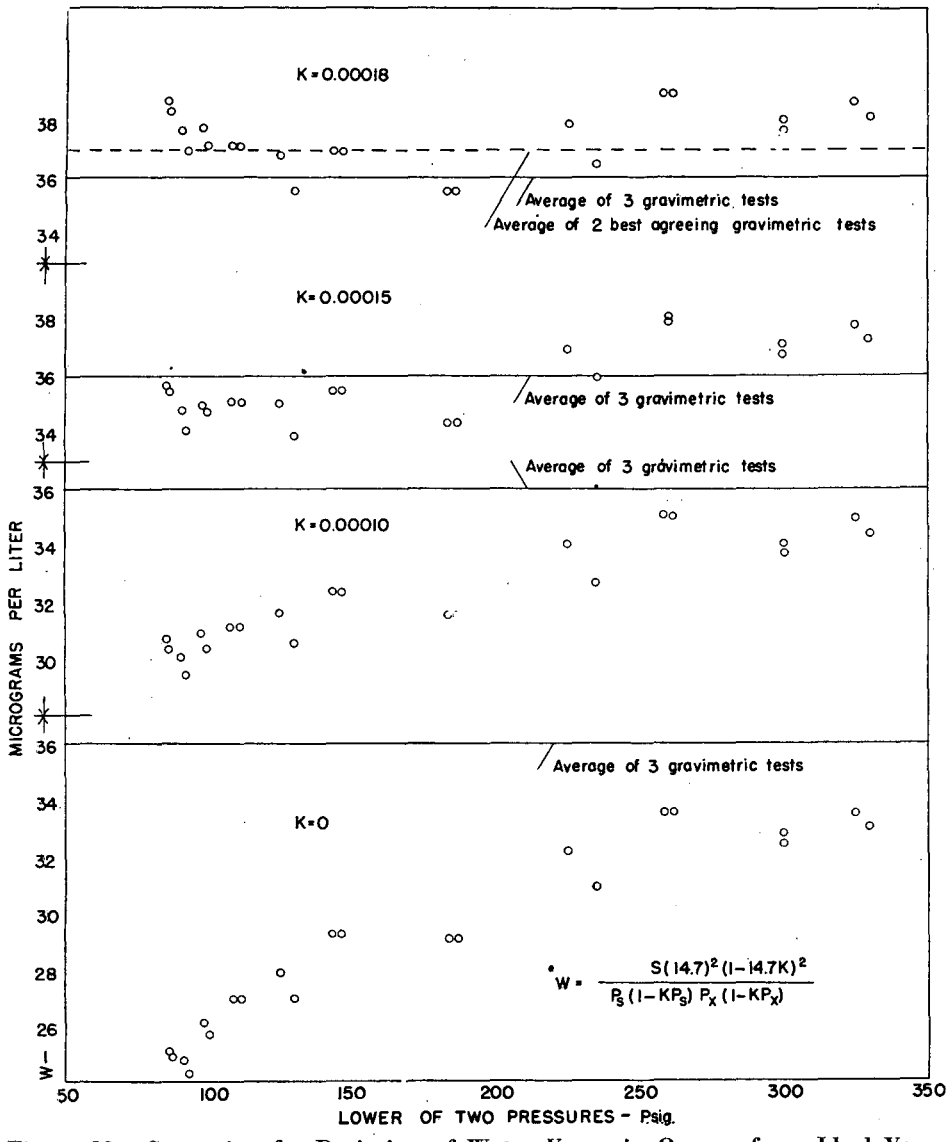

Figure 12. Correction for Deviation of Water Vapor in Oxygen from Ideal Vapor

DEVIATION FROM IDEAL GAS LAWS AND COMPUTATION OF RESULTS

The equations given, (1) to (4), would serve to compute correctly the results of experiments, provided all the gases involved, including water vapor, behaved as ideal gases. Actually the concentration of water in the gas phase in equilibrium with liquid water is always higher than if

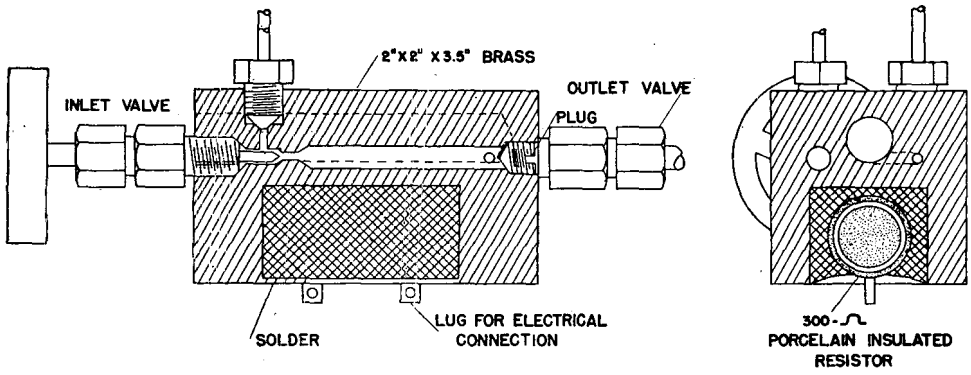

Figure 13. Vaporizer Used for Carbon Dioxide

In testing carbon dioxide with the electrical indicator it was soon found that the cooling effect of expansion through the valves of the oxygen-testing apparatus was too great to permit satisfactory operation. Accordingly an auxiliary heater was constructed which is shown in section in Figure 13. The sample for testing can be drawn either as gas from the top of the cylinder or as liquid from the bottom. (The two methods of sampling should not and do not give the same results except at or above the critical temperature of carbon dioxide, 88° F.)

no other gas were present. The effect has been described and is perhaps best understood as "solubility" of the water vapor in the gas phase, and its magnitude depends on the pressure and chemical composition of the gas. A correction may be made for the effect by replacing Equation 2 with the empirical equation

$$W = \frac{SP_c(1 - kP_c)}{P_s(1 - kP_s)} \times \frac{P_w(1 - kP_w)}{P_x(1 - kP_x)} \qquad (5)$$

and assigning an experimental value to k. For hydrogen and helium the value of k is negligibly small for most purposes. For air, oxygen, and nitrogen, it is about 0.00015 when pressures are expressed in pounds per square inch. For carbon dioxide it is about 0.0009.

Figure 12 shows one set of the experiments on which the correction factor of 0.00015 for air was based. Ordinates show values of W computed by the use of different values of K. Abscissas represent the lower of the two pressures, P_s and P_x. It appears a value of K can be ascertained nearly as well from agreement between tests at different pressures in the saturator as from agreement with gravimetric results.

A computer was designed and is commercially available in metal or transparent plastic, by the use of which all ordinary computations of interest in connection with the method (including relative humidities and dew points under different pressures) can be made in very little time. Without the aid of the computer the consultation of tables, reduction of pressures to absolute, and application of correction factors ordinarily require more time than the observations.

From the data of Wiebe and Gaddy (7), it was computed that if carbon dioxide is compared with air from a saturator the result, computed as though all gases were air, must be multiplied by the factor $\frac{1}{(1 - 0.007\ P_x)}$ in which P_x is the pressure of the carbon dioxide in the comparison. This has been confirmed by experiment. If carbon dioxide is also used in the saturator, the result obtained by computing as though the gases were air is to be multiplied by the factor

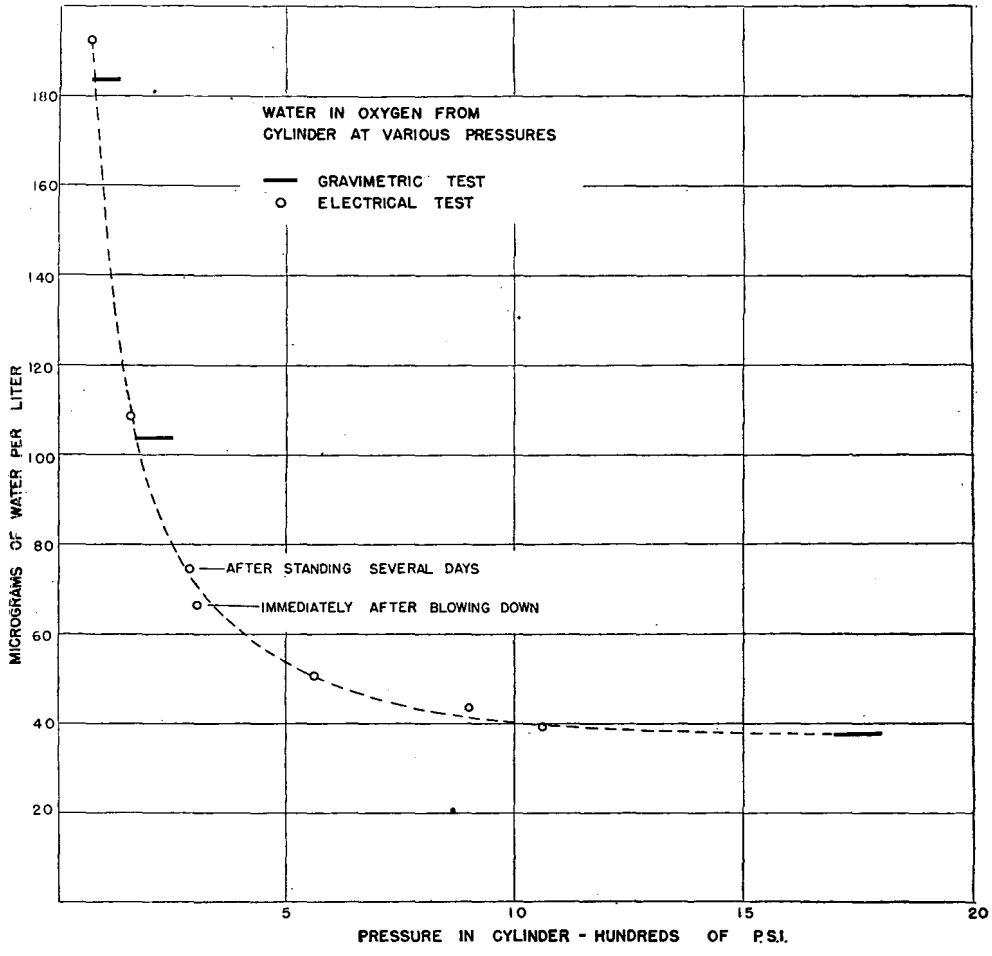

Figure 14. Water Vapor in Gas from a Cylinder of Compressed Oxygen Determined Gravimetrically and Electrically

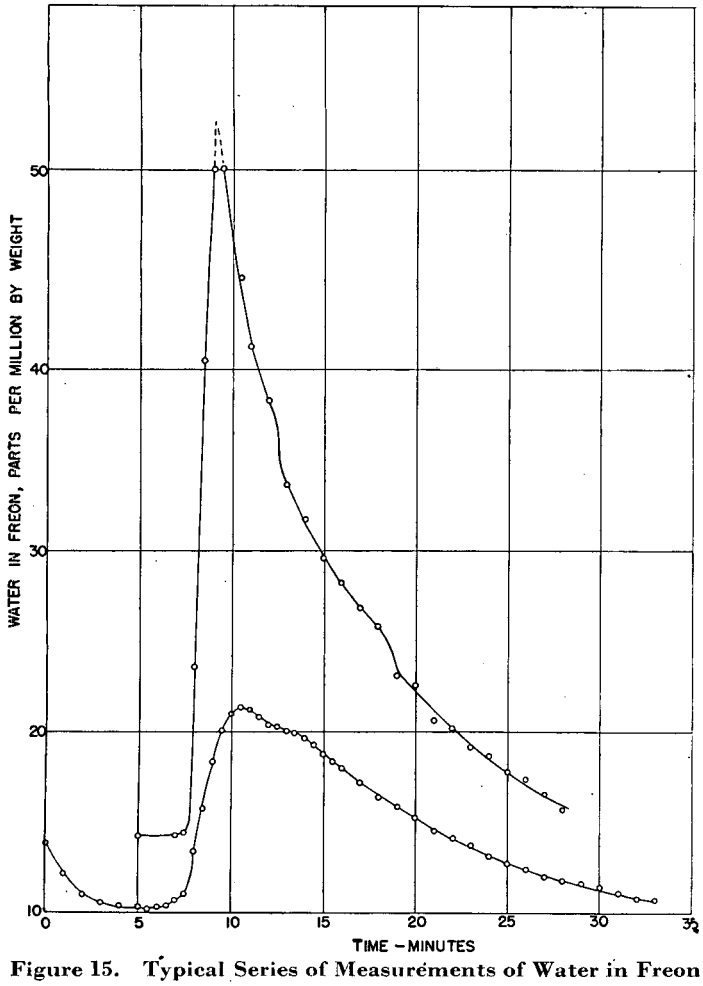

Figure 15. Typical Series of Measurements of Water in Freon

$$\frac{(1 - 0.007P_c)}{(1 - 0.0007P_s)\,(1 - 0.0007P_x)}$$

APPLICATIONS AND RESULTS

Compressed Oxygen. Figure 14 shows the results of seven electrical and three gravimetric tests of the same cylinder of oxygen. The change of water content of the discharged gas as the pressure in the cylinder decreases is typical of many cylinders that have been tested and is attributed to water adsorbed on the cylinder walls, mainly in the scale or rust that is always present to some extent. When the water vapor changes with pressure in this way, the large sample needed for a gravimetric test gives the average of a changing composition. A "spot sample" taken before a gravimetric sample nearly always shows less water, and one taken afterward shows more water than the gravimetric test.

By the use of this instrument it has been found possible for a single observer to test each cylinder for compliance with the specified limit of 0.02 mg. per liter at the rate of 100 cylinders per hour. The cylinders were moved and connected by auxiliary labor. This is more than twice the rate possible with the best of the half dozen frost-point instruments with which the authors are familiar, and twenty or more times as fast as with the worst of them. The testing is much less fatiguing and the results are more positive than with frost-point instruments.

Freon. For the measurement of water in Freon, the same preheater (Figure 13) as for carbon dioxide was used. It was usually convenient to test the Freon at atmospheric pressure or only slightly above, and tests made to determine the effect of deviation from ideality showed no difference from air within the range of pressures covered and within the accuracy of the observations.

The only difficulty encountered in the measurements was from the compressor oil which is in solution in the Freon and came over as a fog which deposited on the detector, screening it from the gas and eventually washing off the phosphoric acid. Even this oil interfered with the tests much less than might have been expected. Apparently the first thin film of oil does not affect greatly the action of the detector.

No determination of water in the Freon was made by an independent method; hence there is nothing with which to compare the electrical measurements. However, the amount of water dissolved in the Freon when the expansion valve froze was always in rough agreement with the published solubility of ice in Freon at the temperature of the experiment.

Figure 15 shows two sets of measurements of water in the liquid Freon in the pipe between the liquid receiver and the silica gel drier of a refrigerating machine following the introduction of small quantities of water into the receiver. The regularity of the curves indicates that changes of 1 part by weight of water per million of Freon are readily followed at intervals of 1 minute or less. The steplike breaks in the descending portions of the curve were sufficiently reproducible in numerous tests to establish their reality, and they were satisfactorily explained by considering the mechanical system involved.

Measurement of Relative Humidity. The electrical method in the form here described can be used to measure relative humidities in meteorology except at the highest values, but it is not better for such a purpose than the simpler instruments in common use. However, it is capable of following changes of relative humidity much more rapidly than any other method known to the authors, it can be applied to stationary atmospheres in small enclosed spaces and affects their moisture content very little, it will measure extremely low humidities, and it does not require the close observation of a dew-point instrument. It has already found some applications in which these characteristics are important and should find others.

Figure 16 shows an arrangement that has been used at the National Bureau of Standards for measuring water in small closed containers without disturbing their atmospheres.

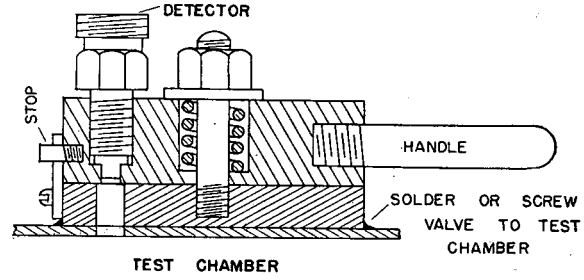

Figure 16. Valve Used to Connect Detector to a Test Chamber

The detector is screwed into a flat disk which forms one half of a rotating slide valve. The other half is another disk through which a hole leads to the container. By rotating the upper disk, the detector is brought to the opening of the container, where it can reach equilibrium with the confined atmosphere; or it can be turned away and the container left sealed. The detector is then unscrewed from its plate and inserted into the cell of a regular instrument and the reading it had when in communication with the test chamber is matched in the usual way. One merit of this arrangement is that with the duplication of only the flat valve, a single detector and measuring apparatus can be used with a number of containers.

A somewhat more elaborate apparatus was designed for another government department and was built and used by it with reported satisfaction (Figure 17). It differs from the previously described arrangement only in the presence of channels in the base plate of the slide valve through which a standard gas can be brought to the detector when the valve has been rotated to the position for "comparison." In other words, the "comparison cell" is built into the valve head. If a very wide range of humidities is expected in the test chamber, an auxiliary screw to tighten the detector support over the comparison cell is supplied as shown. A channel around the port for the standard gas leading to the outside prevents the possibility of high pressure under a large area unseating the valve plate and contaminating the test chamber.

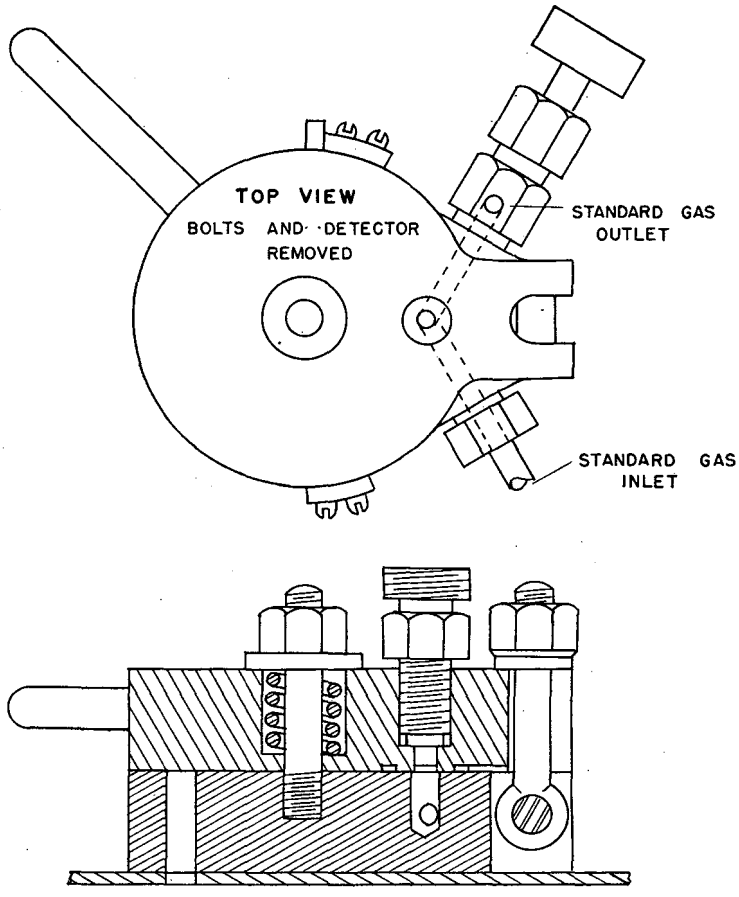

Figure 17. Valve Used to Connect Detector Alternately to Test Chamber and to Built-In Cell for Calibration

Estimating Moisture in Powdered Solids. By passing dry air at a steady rate through a powdered solid and thence through the measuring cell and recording at short intervals of time the electrical resistance of the detector, the amount of water removed from the solid can be estimated. Any desired temperatures may be applied, so long as the water driven off does not condense on the way to the cell. The advantages of the procedure are those of the method in general: use of small sample, speed, sensitivity to very small quantities of water, independence of many (not all) other volatile substances which would be involved in a measurement of loss of weight, and ability to follow the course of the drying operation.

The principal application made of this procedure was in determining the relative dryness of samples of silica gel of a particle size corresponding to about a 30-mesh sieve. The apparatus used is shown in Figure 18. The sample to be tested, usually about 1 gram, was placed in the thin-walled tube in an atmosphere of steam above vigorously boiling water and several minutes were allowed for the solid to reach steam temperature. Then a brisk flow of dry air was started through the solid, and the resistance of the detector observed. The moist air in the connections always caused a momentary sharp drop of resistance of the detector, but a steady resistance was quickly attained and remained almost constant for several minutes, then quickly "broke" to nearly the resistance corresponding to the moisture content of the incoming gas.

Experiment showed that the moisture content of the gas leaving the gel during the period of constancy was nearly independent of the rate of flow, the amount of solid, and the moisture content of the entering gas, which could be either higher or lower than that of outflowing gas. In other words, the greater part of the gel had a characteristic water vapor pressure, and the air entering came to equilibrium with this so rapidly that the system behaved almost as though a plug of air in equilibrium with the sample were pushed along between the initial and final portions of the flow. Different treatments of the gel resulted in products having "vapor pressures" at 100° C. from about 0.1 to 20 mm. of mercury. A few comparisons with gravimetric tests made by drying the gel at much higher temperature showed fairly good correlation.

The need for the test was ended before comparisons could be made between determinations of moisture by weighing and by integrating the product of rate of flow and moisture content of the air passed through the material. The work done on this subject therefore demonstrated merely that observations can be made in a few minutes which will show approximately the condition of such a drying material, once the observer has learned to interpret the results.

An alternative method, which should be better in many cases, especially when the solid is not a good adsorbent and contains a relatively large amount of water, is to shake up the solid with an organic liquid, and to determine the water in the resulting solution by the method described below.

Testing the Capacity of Drying Agents. On a larger scale, the drying capacities of several reagents at normal atmospheric pressure and at 1650 pounds per square inch were measured at various rates of flow by saturating air, passing it through about 2 feet of 0.5-inch iron pipe filled with the drier, measuring the moisture at the outlet at the pressure of experiment, usually in a small flow through a by-pass, and finally measuring the volume of the whole stream with a gas meter at atmospheric pressure.

Figure 19 shows a typical curve, in this case for silica gel previously dried at 165° F. when saturated air is passed into it at about 80° F. (27° C.) at the rate of 20 times the volume of the desiccant per minute. Under these conditions the desiccant dries the air to about 0.1 mg. per liter (a relative humidity of about 0.03%) for approximately 1 hour. At the end of this time the weight of the adsorbed water is about 10% of the weight of liquid water that would fill the space occupied by the desiccant. A point of interest is the interruption of the test after the "break point" of the curve had been reached, and its continuance 1 week later. The purpose of this interruption was to see whether the drying power of the nearly exhausted desiccant would be significantly increased by permitting the water adsorbed by the surface layers of the pieces of solid (screen size, 6 to 16 meshes per inch) to diffuse to the interior of the lumps.

Water Content of Organic Liquids. It is certain that at a definite temperature the water content of a liquid of otherwise

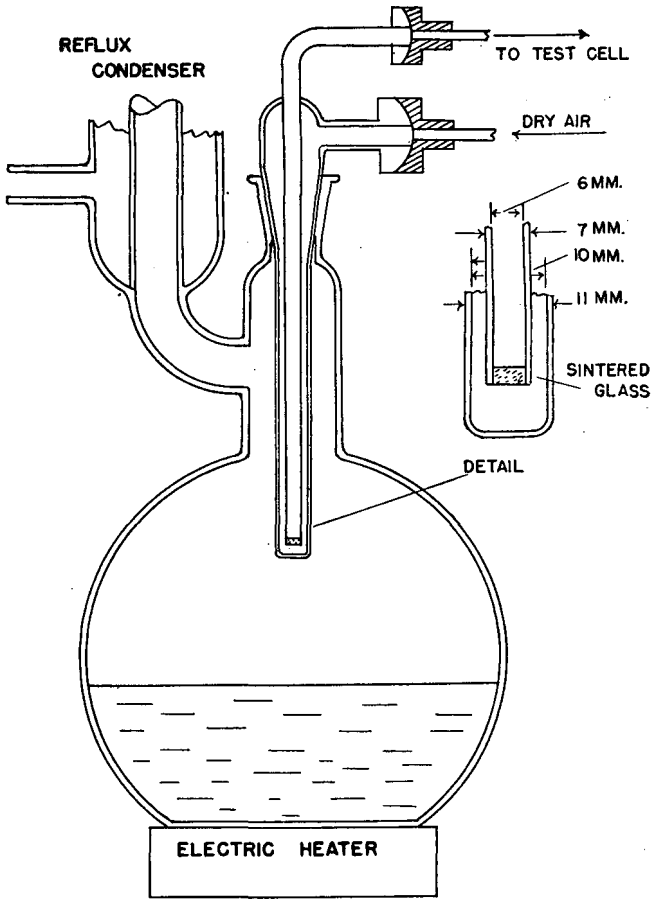

Figure 18. Arrangement Used to Test Moisture Content of Powdered Solids

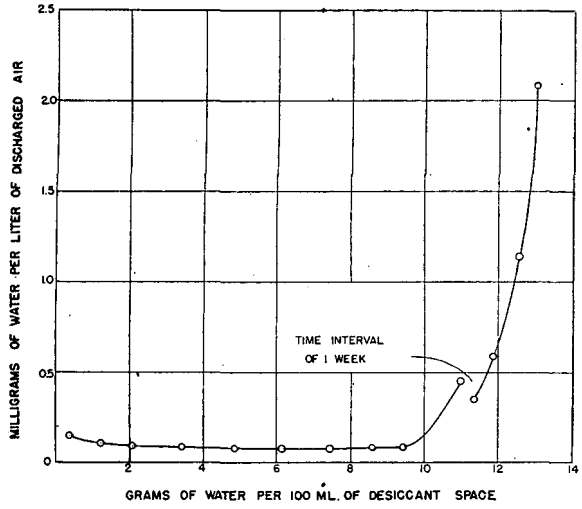

Figure 19. Adsorption of Water by Silica Gel

constant composition will bear a definite relation to the water content of the air with which it will come to equilibrium. If we know from past experience what this relation is and have a means for quickly measuring the moisture content of the air, this can also be used to determine the amount of water in the liquid. With this certainty in view, some experiments were made to find whether it is practicable to determine water in organic liquids by exposing the electrical detector to the atmosphere above them.

The device shown in Figure 20 was constructed for the purpose.

A spring clip was attached to the detector of such form that a glass tube could be quickly attached to cover the detector. This tube had a small opening in the bottom and made a snug but not air-tight fit with the detector plug. When the detector with this attachment is dipped into a bottle of liquid to be tested, the glass cell fills with liquid from well below the surface at a rate which forces air from the cell past the detector under slight positive pressure. The detector is lowered until the detecting surface is only a few millimeters above the liquid surface and left there; or it may be raised once to let the nearly saturated air in the bottle outside the cell sweep it out, then again lowered into place. The resistance of the detector is followed. It changes rapidly at first, but soon reaches practical constancy when the small volume of residual air becomes saturated. Since this volume is almost isolated from the surrounding atmosphere, which is itself fairly near to equilibrium with the liquid, there is very little disturbance by diffusion from the outside. Two or 3 minutes usually suffice to obtain a steady reading, and successive tests are reproducible.

Figure 21 shows results obtained with ethyl ether, the water content of which had been determined by W. Stanley Clabaugh by an independent method. To this ether, measured quantities of water were added. The data obtained are plotted both on a linear scale to show adequately the upper part of the humidity curve and on a logarithmic scale to show the lower part. The method should be capable of measuring with speed and precision very small amounts of water in such a liquid as ether. It can probably be used to determine the water in things that dissolve in ether, such as fats or cellulose derivatives, by testing their solutions.

Alcohol presents complications. In an atmosphere saturated with the vapor of alcohol, believed from other tests to be practically water-free, the detector had a conductivity equal to that in air of about 11% relative humidity. According to recorded data, alcohol in equilibrium with an atmosphere of 11% relative humidity should contain about 2% of water. Small additions of water increase the conductivity of the gas above absolute alcohol by very nearly the amount they would be expected to increase that above 98% alcohol, if the alcohol vapor itself had no effect. The experiments made were of the sketchiest kind. Results are shown in Figure 22, in which are represented the relative humidities of atmospheres in equilibrium with alcohol containing water at 20° and 40° C. (4) and the "apparent relative humidity" of atmospheres above alcohol at 28° C. The open circles representing the observed data have been shifted to the left by 2% where they are shown by the black circles. This entire subject merits further investigation when better facilities, particularly a better saturator, are available. The electrical method will probably be of little use in determining the dryness of otherwise pure alcohol because other quick and easy methods are available, but it gives promise of usefulness in the case of solutions of other things in alcohol which would interfere with the simple determination of water by other methods. It is desirable to express moisture content in terms of relative humidity in this case because this ratio changes relatively little with changing temperature. The method should have the merit of

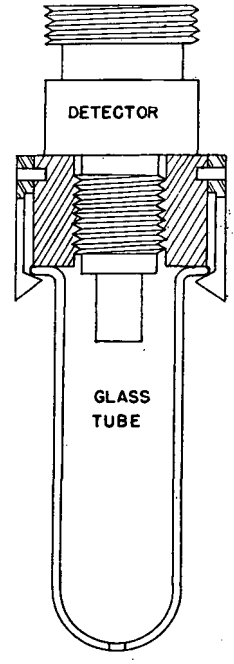

Figure 20. Arrangement Used in Testing Water Vapor in Equilibrium with a Liquid

speed, applicability to small samples, and a fair degree of independence of the presence of other volatile substances, although the alcohols will cause some interference.

If further study of the determination of water in liquids shows the speed and sensitivity expected, it should be possible, as previously suggested, to determine quickly the surface moisture of powdered or granular solids by shaking a measured sample with a suitable liquid and, without removing the solid, submerging the cell used for vapor pressure measurements in the resulting solution. This should be useful for determining surface moisture of molding sand, concrete-making materials, soils, and all sorts of crystalline or powdered materials whose quality or value depends on their moisture content. A similar procedure can probably be used to measure the water in most emulsions.

Permeability of Membranes of Water. The permeability to water vapor of protective films or membranes used in "packaging" materials for shipment and storage is a matter of considerable importance. For a closely related problem, the permeability of balloon fabrics to hydrogen and helium, the Shakespear Permeameter (*3*, *5*) has been extensively used.

In the Permeameter, the fabric or membrane to be tested is clamped between the two halves of a permeability cell, one half of which is suddenly swept out with the gas—e.g., hydrogen—for which permeability is to be determined. The rate at which hydrogen builds up in the other side of the cell is then measured by a physical method, in this case thermal conductivity. A comparison of the time required for the concentration to change between two preselected values is taken as a measure of the permeability. Because of its speed and convenience, the use of the Permeameter has almost superseded in practical use methods which give more direct but more delayed results.

It seemed probable that a similar method of comparing intervals of relative humidity by timing would be applicable to measuring permeabilities to water vapor with the aid of the electrical detector. The arrangement used is shown in Figure 23.

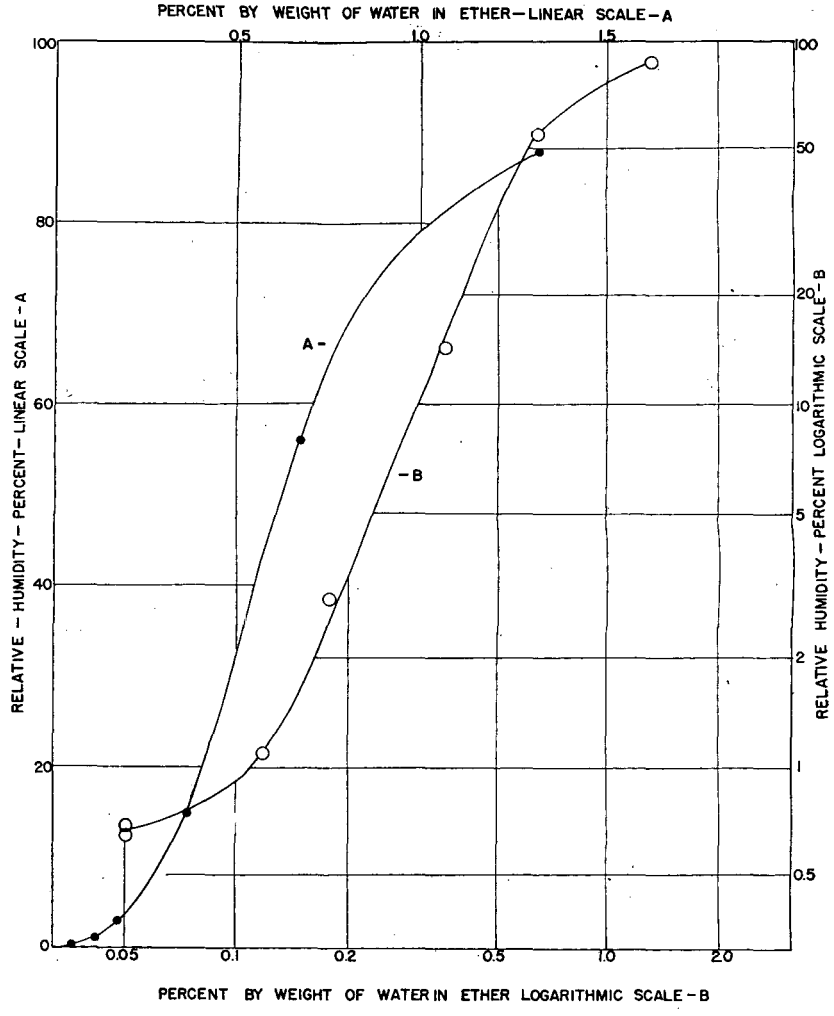

Figure 21. Relative Humidity above Ether

The vapor barrier is clamped over the top of what is, in effect, a dish of water. Above the barrier is a space, arbitrarily chosen as 1 inch, at the top of which is the detector. This space is connected through valves to a supply of dry air and to the outer atmosphere. Before the detector is inserted, its resistance is determined in the usual way at a relative humidity of 25%. It is then inserted in the space above the vapor barrier and the space is swept out with a brisk stream of dried air for 1 minute. Then the valves are closed and the time is recorded until the resistance of the detector indicates a relative humidity in the space of just 25%. The definite duration of sweeping out with dry gas is for the purpose of producing reproducible though arbitrary conditions of the moisture gradient in the membrane itself.

Table II shows the results of testing 15 different membranes by this method. The observations were made by Jean Doyle. Tests in any horizontal row are duplicates on the same piece of membrane and show the agreement between tests that should have given the same result. The tests were only preliminary and were hastily made without temperature control. Probably a more important factor in the variability of re-

Table II. Time Required for 1 Inch of Gas Space above Water Barrier to Reach a Relative Humidity of 25%

Material	Thickness	Test 1	Test 2	Test 3	Test 4	Test 5	Time/ Thickness
	Mm.	*Min. sec.*	*Min. sec.*	*Min. sec.*	*Min. Sec.*	*Min. sec.*	*Min./mm.* $\times 10^2$
Cellulose acetate	0.03	0:46	0:50	0:34	0:32	0:43	0.23
Cellulose acetate	0.13	3:55	5:02	4:47	4:28	5:21	0.36
Cellophane	0.03	0:47	0:50	0:49	0:51	0:34	0.26
Polyvinyl alcohol	0.05	1:39	1:33	1:45	1:50	1:05	0.31
Nylon	0.03	1:45	1:24	1:15	1:15	1:39	0.49
Nylon	0.04	3:40	3:36	3:32	3:38	3:19	0.89
Vinylite plasticizer							
a	0.07	6:47	7:15	7:15	7:40	5:06[a]	0.97
a	0.13	22:40	22:28	30:16	29:30	31:09	2.09
a	0.23	225:34					9.67
b	0.11	16:08	16:14	15:47	16:14	17:12	1.48
c	0.08	18:54	23:47	20:15	23:38	22:30	2.73
d	0.13	30:04	35:43	39:25	42:40	42:20	2.93
e	0.10	12:44	17:01	15:57	17:51	17:51	1.63
e	0.15	81:00					5.40
Saran	0.05	Did not reach 25% saturation in 4 hours.					

[a] Test made after membrane had stood in saturated atmosphere overnight.

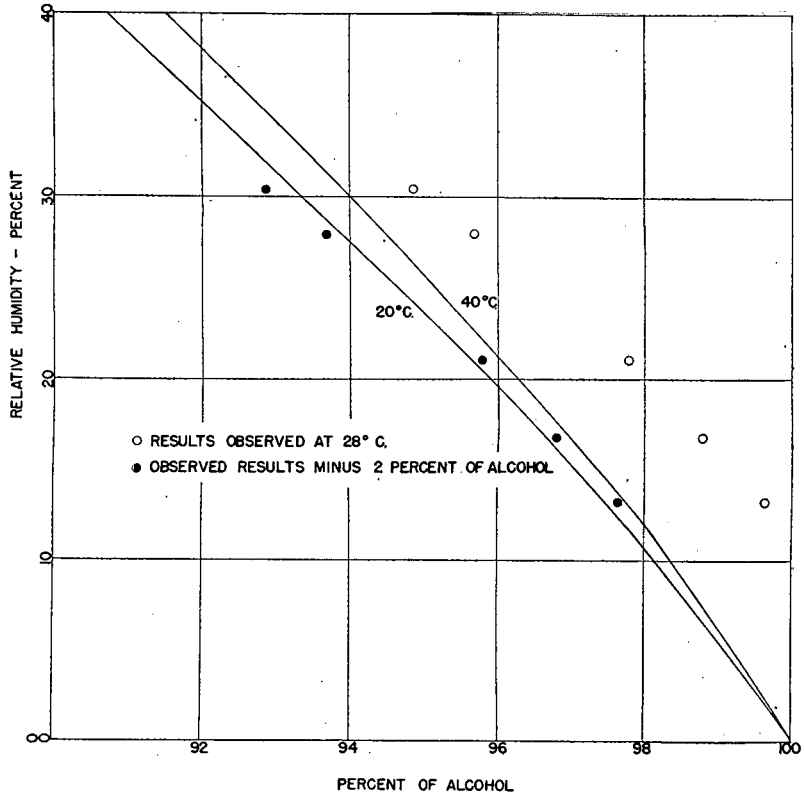

Figure 22. Apparent Relative Humidity above Alcohol

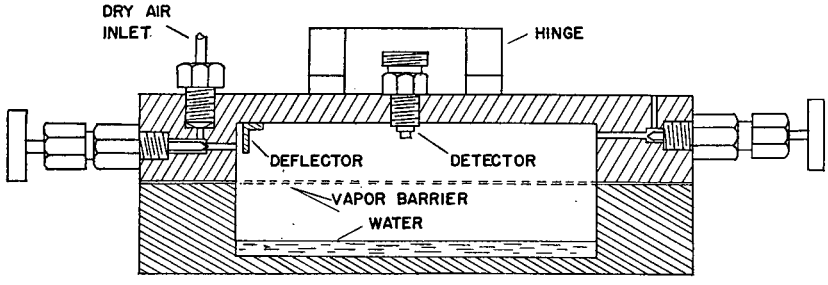

Figure 23. Cell for Testing Permeability of Vapor Barriers

sults is the failure to establish a regular gradient of dissolved moisture through the barrier before beginning the timing. Probably because of this failure, thick films show excessively greater resistance to the passage of moisture than do thin films of the same material. Considering the probability that the method can be greatly improved with a little attention to details, it is apparent that a quick method for getting at least approximate results is available.

One characteristic of the method which may be of value in some cases is the possibility of applying it to very small samples. Although account would have to be taken of the water combined with the phosphoric acid on the detector, it seems entirely possible that a satisfactory test could be made on an area of membrane equal only to that of the end of the detector, a few square millimeters, and that it could be done with nearly the same speed and accuracy as the testing of a large sample.

Gas Detection. One purpose for which the electrical method has been used from time to time since its first description (*6*) is the detection of oxygen in a combustible gas or of a combustible gas in oxygen or air. The method is obvious; the gas is thoroughly dried, then passed over a heated filament or catalyst and thence over a detector. Since all fuel gases except pure carbon monoxide, including the dangerous hydrocarbon gases of mines, contain either free or combined hydrogen, water is formed wherever combustion takes place, and it can be detected and measured if desired, when the amount present is only a minute fraction of that which could cause explosion. The promptness of the reaction suggests its possible use as a leak detector. The sensitivity would be high; if combustion were complete, methane for example, would provide 2 volumes of water vapor per volume of gas and should be detectable without difficulty in a concentration of 0.001% even at atmospheric pressure. Oxygen in hydrogen also gives 2 volumes for 1. In a hydrocarbon it will give less because some of it will go to carbon monoxide, and for this reason the amount of oxygen present may be hard to determine accurately. However, under any conditions of combustion enough water should be formed to make the method a sensitive one for detection.

By using this method for detection with a permeability cell, it should be easy to determine permeabilities to oxygen, to hydrogen, or to many organic compounds with great speed.

ACKNOWLEDGMENT

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The senior author has been unable to learn the whereabouts of Mr. Riley, who served as a civilian at Pearl Harbor during the latter part of the war. The senior author is therefore entirely responsible for the text of the present paper, but most of the observations on which it is based were made by Mr. Riley, who also contributed much of the constructive thought that went into the development of the method.

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Vitamin A and Carotenoids in the Blood Serum of Dairy Cattle

Chemical Methods for Determination

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A comparison is made of the results obtained in the determination of vitamin A and carotenoids by four methods. When cows received large amounts of vitamin A supplements, the results of the vitamin A determination of blood serum were too low if, without a preliminary saponification, a method was employed that utilized carotene precipitation for the removal of interfering substances. Certain components of blood serum in addition to carotene interfered with the determination of vitamin A by the Carr-Price reaction. The interfering substances were susceptible to saponification and to mild oxidation.

THE vitamin A and the carotenoid content of blood are receiving increasing attention in studies of vitamin nutrition in dairy cattle. In previous studies (*18*), differences in the analytical results of the vitamin A content of blood were noted for which there was no suitable explanation. In view of these observations, it seemed possible that a comparative study of various methods of vitamin A and carotenoid analysis might yield information leading to satisfactory interpretation of the differences which had been found. For this investigation four procedures were selected: the Kimble (*11*), which does not involve saponification; the Boyer *et al.* (*2*), both that requiring and that omitting saponification; and the authors', which utilizes saponification before determination of either carotenoids or vitamin A.

METHODS

Blood serum for analysis was obtained by centrifugation of venous blood as soon as possible after clot formation. The serum was stored in tightly closed bottles, in the dark, at 4° C. Most samples were analyzed within 24 hours after collection, and all within 72 hours.

Since artifacts had been observed when absolute ethanol or ethanol containing aldehydes was employed (*18*), and difficulties had been encountered from emulsion formation, the following modifications were made in the procedure of Boyer *et al.* (*2*): 5 ml. of 20% alcoholic potassium hydroxide and 5 ml. of 90% ethanol were used for saponification; a "cold-finger" condenser was placed in the test tube to prevent concentration of the reagents during saponification; and an acidified-alcoholic wash solution (*3*) was used to reduce emulsion formation during extraction of the nonsaponifiable matter.

The authors' procedure is as follows:

Ten milliliters of blood serum are placed in a glass-stoppered centrifuge tube and mixed with 10 ml. of aldehyde-free ethanol, and 20 ml. of diethyl ether are added. The tube is shaken vigorously for 2 minutes and is centrifuged to obtain a clear supernatant solvent layer, which is transferred to a 125-ml. boiling flask. This extraction, followed by centrifugation, is repeated twice using only 10 ml. of ether. The three extracts are combined in the boiling flask and heated gently to remove the ether. Then 8 ml. of potassium hydroxide solution (*3*) and 1 or 2 ml. of distilled water are mixed with the remaining solution. The flask is attached to a condenser, and the extract is saponified by boiling for 20 minutes. The mixture is cooled and transferred to a separatory funnel; 10 ml. of alcohol and 15 to 20 ml. of water are used for rinsing.

For extraction, an adaptation of a two-separatory-funnel procedure (*3*) is used. The saponified mixture is extracted by shaking for 1 minute with 40 ml. of diethyl ether. The lower layer, which separates, is transferred to a second separatory funnel containing 30 ml. of ether and again is extracted. The lower phase, which separates, is discarded. To the first separatory funnel, 80 ml. of distilled water are added and mixed three or four times to wash the ether extract. Upon separation, the water is transferred to the second separatory funnel, gently shaken with the ether extract, and discarded after the phases divide. The ether extracts in each separatory funnel are washed by shaking them in turn with 40 ml. of acidified-alcoholic wash (*3*). Washing is repeated using 25 ml. of the same solution. The ether extracts in the two separatory funnels are combined, 10 ml. of purified Skellysolve B (*9*) are added to reduce the water content, and the solution again is washed with 25 ml. of distilled water. Then the extract is allowed to remain in the separatory funnel for 15 minutes, and the water is drained completely. The ether extract is transferred to an all-glass evaporation assembly, and the solvent is removed under partial vacuum at 60° C. Redistilled Skellysolve F is added as the vacuum is released. The container is cooled, and the solution is transferred to a volumetric flask and diluted to 10 ml. For most samples, 1.0 ml. of this solution is diluted to 10.0 ml. for the determination of carotenoids, and the remaining 9.0 ml. are used for the determination of vitamin A.

When samples of serum are low in vitamin A, such as encountered in newborn calves, 20.0 or 30.0 ml. of serum are extracted.

Hereafter the above procedure is referred to as the authors' and unless otherwise indicated, the Boyer procedures are those developed for blood serum by Boyer *et al.* (*2*).

The same Evelyn photometer was used in the determinations by each method. The procedures for the calibration and the use of the photometer have been described amply (*2*, *3*, *12*).

CAROTENOIDS

Comparative data from the four methods of analysis are presented in Table I. Carotenoid values obtained by the authors' procedure tended to be lower than by the other methods, especially in serums containing large concentrations of yellow pigments. Although the variation in the values often was within experimental error, sometimes the differences in the results of the authors' compared to the Kimble and Boyer procedures were as high as 15%.

There are several possible reasons for the differences. (1) Unlike the authors', the other methods use measured aliquots and involve techniques that allow evaporation of the highly volatile Skellysolve F. Evidence of some concentration in the

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Table I. Results of Four Methods of Analyzing Blood Serum of Dairy Cattle

Sample No.	Carotenoids: Kimble[a]	Carotenoids: Boyer *et al.*[a] Saponification	Carotenoids: Boyer *et al.*[a] Nonsaponification	Carotenoids: Authors'	Vitamin A: Kimble	Vitamin A: Boyer *et al.* Saponification	Vitamin A: Boyer *et al.* Nonsaponification	Vitamin A: Authors
	Micrograms per 100 ml.							
A-1641	156	154	156	148	31.1	30.3	25.0	33.0
J-1510[b]	198	211	195	205	50.6	50.5	28.6	44.8
A-1761	280	279	280	288	35.8	41.6	36.6	42.8
A-1533[b]	299	301	301	295	41.2	43.0	32.9	42.8
H-1682[b]	307	307	302	282	33.3	30.7	28.1	37.7
H-1544[b]	342	347	331	330	34.0	33.5	27.4	37.1
J-1762	406	416	406	424	29.5	36.1	33.8	37.7
A-1545[b]	419	380	419	350	26.2	32.5	27.3	33.2
J-1509[b]	642	605	636	613	42.9	45.7	29.8	42.7
A-1532[b]	675	668	680	610	27.6	31.7	29.3	37.2
H-1225[b]	386	...	400	400	39.8	..	32.3	38.0
A-1681[b]	393	...	400	360	37.3	..	32.0	44.0
G-1463	419	...	419	366	17.8	..	16.9	24.0
H-1571	419	...	413	377	28.2	..	30.8	33.6
A-1382	621	...	615	560	18.5	..	26.0	28.2
G-1221	760	...	793	689	15.0	..	20.8	23.1
H-1250	790	...	785	695	27.6	..	25.3	30.0
G-1361[b]	1220	...	1230	1125	27.6	..	31.5	37.0
J-1410	1285	...	1190	1133	23.4	..	31.2	40.8
G-1381[b]	1664	...	1625	1350	26.5	..	31.2	48.0
G-1310	1853	...	1830	1510	14.3	..	25.0	35.0
G-1355[b]	2110	...	2080	1800	12.9	..	27.5	41.0
J-1332[c]	1	...	...	3.9	5.3	..	..	6.2
J-1435[c]	0	...	...	5.2	9.4	..	..	9.3
G-1597[c]	1	...	...	2.7	6.3	..	..	6.6
H-1781[d]	12	...	...	11.6	11.9	..	..	11.3
H-1824[d]	12	...	...	14.0	24.5	..	..	21.5

H, A, J, G refer to Holstein, Ayrshire, Jersey, and Guernsey breeds, respectively, from which samples were taken.

[a] Original methods designate these values as carotene instead of carotenoids.
[b] Animals receiving vitamin A supplements during prepartal period.
[c] Calves at birth; dams received vitamin A supplements.
[d] Calves at 4 days of age.

latter procedures has been observed, especially in hot weather. (2) The solvents used, Skellysolve F and diethyl ether, may vary in efficiency and/or selectivity in extracting pigments from denatured blood serum. Differences, apparently due to this factor, have been observed with samples of blood serum from some calves. (3) During the saponification and washing of the extracted material, the authors' method may remove or destroy some carotenoid or noncarotenoid substances absorbing light in the 440 mμ region of the spectrum. Such substances would be retained by the methods that do not employ saponification.

The results from replicated samples extracted by the same solvent (Table II) indicate that saponification probably is the major factor in causing the lower carotenoid values obtained by the authors' method. Possibly the extracts containing vitamin A and carotenoids were contaminated with bilirubin which would be removed by the potassium hydroxide solution, as was found in the case of extracts from human plasma (*5*). Palmer (*16*) has pointed out the danger of assuming that all yellow animal pigments are carotenoid in nature. Regardless of whether or not certain pigments may be eliminated in the preparatory treatment for the final vitamin A determination, it is a common practice in routine blood investigations to use the values obtained on the photometer at 440 mμ as a measure of the total carotenoid concentration. Thus the present investigation indicates that variations in the carotenoid content of serum, resulting from the analytical procedure selected, sometimes may be as high as 10 to 15%. Similar decreases in carotenoid concentrations have been observed following the saponification of serum taken from infants (*10*) and from unidentified animals (*4*).

Since a major part of the total carotenoids in the serum of dairy cattle is carotene, the crude carotenoid concentration generally is used as an index of the carotene content (*2*, *11*). If one is interested only in significant changes in the carotenoid levels, the differences in the carotenoid determinations by the various methods ordinarily would not be objectionable. Each method yields carotene values which are satisfactory for most routine studies.

VITAMIN A

In samples of blood serum analyzed by the four methods (Table I), the authors' procedure yielded vitamin A values equal to or higher than those from the other three, except for samples 1509 and 1510, in which the Boyer saponification procedure yielded somewhat higher values. With samples analyzed by only three methods, the values from the authors' procedure were highest except for sample 1225, in which the results by the Kimble method were slightly higher. In the case of most samples of relatively low carotenoid concentration, the results from the Kimble method were higher than those from the Boyer nonsaponification procedure; but in samples with high carotenoid concentrations the values from the latter procedure generally were higher. The results of the vitamin A determinations from the Boyer saponification procedure usually were higher than from the Boyer nonsaponification procedure; sometimes these differences were marked.

To explain the major differences observed in the vitamin A values obtained by the several methods, two factors apparently need to be considered: the effect of the state of combination of vitamin A in the blood serum and the effect of substances inhibiting the development of the blue color by the antimony trichloride reagent. Other factors, such as the effects of analytical procedures and of artifacts, explain some of the other differences (generally smaller) that have been observed.

Table II. Analysis of Blood Serum by Modifications of Kimble Method

Sample No.	Kimble: Carotene, γ/100 ml.	Kimble: $L_{620m\mu}$[a]	Kimble: Vitamin A, γ/100 ml.	Kimble plus Saponification: Carotene, γ/100 ml.	Kimble plus Saponification: $L_{620m\mu}$	Kimble plus Saponification: Vitamin A, γ/100 ml.	Kimble plus Hydrogen Peroxide: Carotene, γ/100 ml.	Kimble plus Hydrogen Peroxide: $L_{620m\mu}$	Kimble plus Hydrogen Peroxide: Vitamin A, γ/100 ml.
G-1856	995	0.220	12.2	827	0.240	30.2	1017	0.244	20.9
G-1857	1290	0.254	5.6	980	0.248	19.5	1277	0.285	17.5
J-1858	672	0.191	23.1	557	0.187	29.7	649	0.198	27.1
J-1859	895	0.225	20.6	737	0.223	29.7	901	0.232	22.9
J-1860	455	0.134	17.3	407	0.136	20.9	455	0.137	18.2
A-1862	1329	0.290	15.2	1215	0.332	38.8	1380	0.310	18.9
A-1863	1185	0.256	12.6	1062	0.277	28.1	1188	0.284	22.0
J-1865	1350	0.286	12.4	1232	0.324	33.2	1360	0.308	19.1

[a] Explanation of $L_{620m\mu}$ may be found in (*11*).

Effect of State of Combination of Vitamin A. The results of Boyer *et al.* (*2*) indicated that vitamin A was present in the blood serum of dairy cattle as either an alcohol or a soluble ester. Their work showed that values from the nonsaponification procedures were 87 to 95% of those found after saponification; consequently, they suggested that the former technique was satisfactory for routine work. By use of a chromatographic method it has been confirmed that normally most of the vitamin A in the blood serum of dairy cattle is in the alcoholic form (*17*). When large vitamin A supplements were given in the ration, the percentage of ester vitamin A in the blood serum increased somewhat, but rarely was over 30% of the total vitamin A. In the removal of carotene in the Boyer nonsaponification procedure, the vitamin A ester

probably was precipitated simultaneously with carotene and did not appear in the final analysis; lower values for vitamin A resulted from this treatment.

Filter papers containing the lipide material precipitated in the Boyer nonsaponification procedure were analyzed for vitamin A by saponification, separation on an alumina chromatograph, and elution of the vitamin with an ethanol–Skellysolve F mixture. In eleven trials with different samples of serum, quantities of vitamin A equivalent to 1.4 to 8.0 micrograms per 100 ml. of serum were recovered. Since tests have shown that complete elution of vitamin A alcohol from the absorbent is difficult to accomplish, the actual losses through precipitation probably exceed the quantities recovered in the above trials. Of the four methods studied, only the Boyer nonsaponification procedure led to low values of vitamin A attributable to precipitation.

Effect of Inhibitors. Large quantities of carotenoids are found in blood when cattle have access to high quality pasture. The reaction of carotenoid pigments with antimony trichloride is believed to interfere seriously with the vitamin A determination (*2*, *19*). However, a comparison of the data of Table I, obtained by the Kimble and the authors' methods, indicates that carotenoids are not primarily responsible for low values for vitamin A which many times are obtained by the former procedure. While there may be a difference of 15% or less in the carotene values, the vitamin A values of the same samples may differ over 100%. In the case of the large differences, the results are always higher by the authors' method. Noncarotene inhibitors of the development of blue color with antimony trichloride apparently are the major cause of discrepancies observed in the vitamin A determination. Similar color inhibitors are believed to be present in human blood serum, since the results were higher after saponification (*1*).

Color inhibitors (*6*, *8*, *14*, *15*) have been encountered in the determination of vitamin A in low-potency cod liver oils. These substances caused the results of the vitamin A determination to be lower if saponification was not employed. Considerable success has been attained in increasing the chromogen in cod-liver oils by mild oxidation (*8*, *15*). The possibility was considered that the color inhibitors in blood serum might be similar to those in cod-liver oil. If this were correct, mild oxidation as well as saponification should overcome the inhibition.

In order to test the foregoing hypothesis, replicate extractions of serum were made by the Kimble procedure. One set of these samples was analyzed in the usual manner; another set was saponified and extracted with Skellysolve F; and a third set was treated with 7 to 10 drops of 30% hydrogen peroxide just prior to the 10-minute shaking for extracting the lipide material from the denatured blood serum. The results of the analysis of these extractions are shown in Table II.

Although, as previously discussed, saponification usually lowered the carotenoid values, the $L_{620\ m\mu}$ frequently was increased by this treatment. On the other hand, carotenoid values obtained following treatment with hydrogen peroxide were practically the same as those from the nonsaponification technique, but the $L_{620\ m\mu}$ often was even higher than after saponification. Calculations of the vitamin A content of samples receiving each of the three treatments show that hydrogen peroxide increased the values above those found by the regular Kimble procedure, but usually did not raise the values to those attained by saponification.

The effect of color inhibitors generally is increased when high carotenoid values are observed (Tables I and II), which suggests that the relative concentration of these inhibitors in the blood serum may vary with carotene concentration. It was not determined whether incomplete oxidation, or other factors, caused the results obtained from peroxide-treated samples to be lower than those of the corresponding saponified samples.

The lower values that are found when the results of the vitamin A determinations by the Boyer nonsaponification procedure are compared with the other procedures (Table I) apparently are not due to color inhibitors but to the state of vitamin A, as previously indicated. Probably inhibitors have no influence in the reaction of the Carr-Price reagent with extracts obtained by the Boyer nonsaponification procedure because these inhibiting substances are lipidelike and are precipitated with the carotene. In the Boyer saponification and the authors' procedures, the inhibitors apparently are removed during the saponification and washing of the extract.

If saponification is not employed and large amounts of color inhibitors are present, the maximum absorption at 620 mμ does not develop within the normal period of about 6 seconds after addition of antimony trichloride, but continues to build up for 1 minute or more. Saponified samples show a small but similar increase in absorption only when carotenoid values are exceptionally high and the vitamin A content is low.

It is possible an analytical procedure might be developed based upon the removal of color inhibitors by oxidation. Although hydrogen peroxide was used in the present work because of convenience, some other oxidizing agent or procedure for adding it may prove more satisfactory, as was the case with cod-liver oil (*15*). Incidentally, the Kimble extraction technique plus saponification is a rapid procedure that deserves consideration as a method for determining vitamin A under a wide range of conditions.

High concentrations of tocopherols are found in blood serum when cattle graze pasture grasses (*13*). Since tocopherols are subject to oxidation, it was thought they might be the color inhibitors in the Carr-Price reaction for vitamin A. However, when natural tocopherols were added to blood serum at a level of 20 times that found in the serum of cattle grazing excellent pasture, no suppression of the development of the blue color with antimony trichloride was observed.

Effect of Other Factors. The data in Table I indicate there are additional differences (usually small) in the results by the various methods that cannot be accounted for by factors previously considered. Some of the differences no doubt arise from the use of the various techniques and solvents employed in individual methods. As in the carotenoid determination, small losses may occur in the extractions and in the washing of precipitates; furthermore, solutions from which aliquots are taken may become concentrated by evaporation.

Another possible source of error is in the application of factors used to correct for the presence of carotenoids (*19*). Since most of the pigment in the blood serum of dairy cattle is carotene, the correction developed for it generally is used. However, if some of the pigment does not react with antimony trichloride, or does so to an appreciably lesser degree than carotene, the correction will be too large if based upon the pigment concentration determined with the photometer at 440 mμ. This source of error would affect the determination by the Kimble method.

In the analysis of low-potency materials, such as blood serum, the effect of artifacts cannot be disregarded. By using aldehyde-free ethanol containing 10 to 15% water for preparing the saponification mixture, the artifact, as found by blank determinations, was held to an average vitamin A equivalence of 1 microgram per 100 ml. of serum. This small error resulting from the artifact was not subtracted from the values recorded in Tables I and II which were obtained with saponified samples. The artifacts apparently result from polymerized aldehydes (*7*). If ordinary commercial absolute ethanol and large concentrations of potassium hydroxide are used in the saponification procedures, the error introduced by artifacts may be the equivalent of 5 to 10 micrograms of vitamin A per 100 ml. of serum.

SUMMARY AND CONCLUSIONS

Blood serum of dairy cattle was analyzed for carotenoids and vitamin A by four chemical methods. Lower carotenoid values

generally resulted from saponification than from nonsaponification of samples. Differences in vitamin A content seemed to be due primarily to the relative amounts of vitamin A alcohol and ester in the serum and to the effect of color inhibitors, which were removed by some methods but not by others.

The Kimble method, the shortest of the four procedures, is suitable for the analysis of the blood serum of calves or of cows if interfering substances are of a relatively low concentration. This condition generally exists when carotenoids are less than 350 micrograms per 100 ml. of serum. Although a saponification procedure increases the time required for analysis, it should be used in the determination of vitamin A in the blood serum of dairy cattle especially when vitamin A ester and/or color inhibitors are likely to be present in significant quantities.

Saponification removes the factors inhibiting the development of the blue color with antimony trichloride which results in low vitamin A values in certain samples of blood serum. At least part of these color inhibitors have been found sensitive to mild oxidation, which may serve as a basis for developing methods for overcoming the interference.

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Analysis of Thorium-Chromium Mixtures

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A method especially suitable for the analysis of thorium-chromium mixtures involves the perchloric acid oxidation of chromium in the presence of thorium, followed by titration with ferrous sulfate and tetrasulfatoceric acid. The thorium is precipitated as the oxalate and determined gravimetrically after removal of the chromium as chromyl chloride.

A SIMPLE and rapid method for analyzing thorium-chromium mixtures was required in connection with a study of the metallurgical properties of thorium-chromium alloys. The literature revealed that very little work has been done on the analysis of such mixtures. Since thorium is unaffected by most of the common oxidizing agents it seemed that chromium might be conveniently determined titrimetrically by a modification of the reversed Penny method (*4*).

Chromic chromium has been oxidized in alkaline solution with hypobromite (*1*, *2*) hypochlorite (*1*), and hydrogen peroxide (*10*). In acid solution, ammonium peroxydisulfate with silver (*5*), lead peroxide (*8*), perchloric acid (*3*, *6*, *12*), potassium bromate (*2*), potassium chlorate (*11*), and potassium permanganate (*1*) have been used. When the use of hydrogen peroxide and sodium peroxide was attempted in alkaline solution, the chromium was apparently oxidized; but though the solutions were boiled several minutes to destroy excess peroxide, the chromium was reduced upon acidification. This is due apparently to the fact that thorium forms a peroxide (*7*) which is not decomposed on boiling and liberates hydrogen peroxide upon acidification. Ammonium peroxydisulfate could not be used because thorium sulfate is insoluble in hot aqueous solutions and thus interferes in the subsequent titration of the chromium. The other oxidizing agents were less satisfactory than perchloric acid. Error in the perchloric acid method due to the loss of chromyl chloride (*3*, *12*) was eliminated by condensing the volatilized chromyl chloride and titrating it along with the bulk of the chromium. This method proved satisfactory and confirms the recent work of Schuldiner and Clardy (*6*).

REAGENTS

Ferroin, $Fe(C_{12}H_8N_2)_3SO_4$. A 0.025 *M* ferroin solution was prepared by dissolving 14.8662 grams of GFS reagent grade 1,10-phenanthroline monohydrate and 6.9505 grams of reagent grade ferrous sulfate heptahydrate in enough water to make 1 liter of solution.

Ferrous Sulfate, $FeSO_4$. A 0.1 *N* ferrous sulfate solution was prepared by dissolving 39.5 grams of reagent grade Mohr's salt and 10 ml. of concentrated reagent grade sulfuric acid in enough water to make 1 liter of solution. This solution was standardized each day against the standard tetrasulfatoceric acid solution using ferroin as the indicator.

Fluosilicic Acid, H_2SiF_6. A 1 to 50 aqueous fluosilicic acid solution was prepared by adding 1 ml. of the concentrated (48%) reagent grade acid to 50 ml. of water.

Hydrogen Chloride, prepared by dripping concentrated reagent grade hydrochloric acid into concentrated reagent grade sulfuric acid.

Hydrogen Peroxide, Merck C.P. grade, 30% H_2O_2.

Nitric Acid, reagent grade. Specific gravity: 1.42; 70% HNO_3
Nitrogen, commercial tank nitrogen.
Oxalic Acid, $H_2C_2O_4.2H_2O$, reagent grade.
Perchloric Acid, $HClO_4$, GFS reagent. Specific gravity: 1.54; 60% $HClO_4$.
Potassium Dichromate, $K_2Cr_2O_7$, reagent grade.

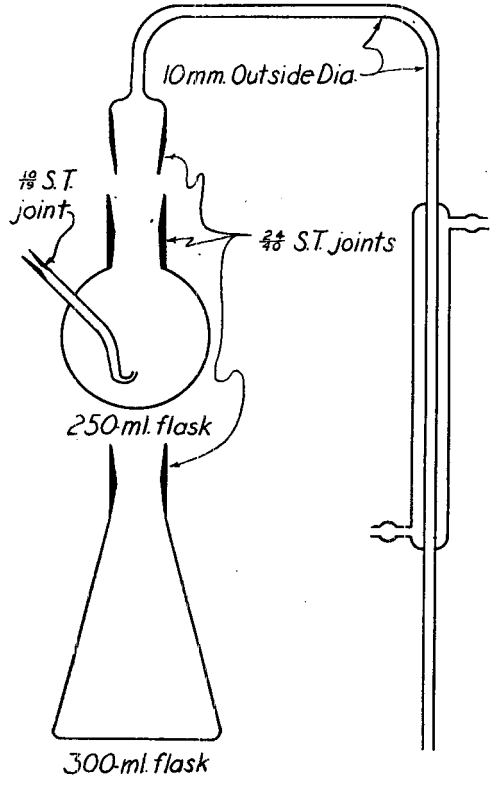

Figure 1. Apparatus

Tetrasulfatoceric Acid, $H_4Ce(SO_4)_4$. A 0.1 *N* tetrasulfatoceric acid solution was prepared by dissolving anhydrous tetrasulfatoceric acid in dilute sulfuric acid, diluting to about 0.1 *N* with water, and filtering through glass wool. This solution was standardized against electrolytic iron, using ferroin as the indicator.
Thorium nitrate, $Th(NO_3)_4.4H_2O$. Lindsay atomic weight–grade thorium nitrate was especially purified and finally recrystallized from reagent grade nitric acid.

APPARATUS

The apparatus used is shown in Figure 1.

Table I. Precipitation of Thorium in Presence of Chromium

Trial	ThO_2 Taken, Gram	Cr Present, Gram	$H_2C_2O_4.2H_2O$ Required[a], Grams,	$H_2C_2O_4.2H_2O$ Present, Grams	ThO_2 Found, Gram	Error, ThO_2, Gram
1	0.2706	1.00	7.5	4.0	0.1287	−0.1419
2	0.2706	0.50	3.9	4.0	0.2616	−0.0090
3	0.2706	0.25	2.1	4.0	0.2706	±0.0000
4	0.2706	1.00	7.5	8.0	0.2707	+0.0001
5	0.2706	1.00	7.5	8.0	0.2704	−0.0002

[a] For both thorium and chromium.

EXPERIMENTAL WORK

Determination of Thorium. The precipitation of thorium as the oxalate in the presence of chromium was studied by mixing known amounts of thorium and chromium solutions and then precipitating the thorium with oxalic acid. Results of these experiments (Table I) show that oxalic acid must be present in sufficient amounts to complex the chromium as $Cr(C_2O_4)_3^{---}$ as well as to react with the thorium, if quantitative precipitation of the thorium is to be obtained.

Table II. Determination of Thorium after Separation of Chromium as Chromyl Chloride

Cr Present, Gram	Th Taken, Gram	Th Found, Gram	Error, Th, Gram
0.077	0.3194	0.3194	±0.0000
0.077	0.3194	0.3192	−0.0002
0.154	0.3194	0.3193	−0.0001
0.154	0.3194	0.3196	+0.0002
0.261	0.1785	0.1783	−0.0002
0.261	0.1843	0.1842	−0.0001
0.261	0.1868	0.1868	±0.0000
0.522	0.2355	0.2355	±0.0000
0.522	0.2296	0.2295	−0.0001

The last three determinations shown in Table I indicate that thorium can be precipitated quantitatively in the presence of as much as 1 gram of chromium; but in every case spectrographic analysis showed that the ignited thorium dioxide was contaminated with a small amount of chromium. In some cases enough chromium was present to be detected visually.

Table III. Determination of Chromium in Presence of Thorium

Th Present, Gram	Cr Taken, Gram	Cr Found, Gram	Error, Cr, Gram
0.042	0.06911	0.06928	+0.00017
0.042	0.06845	0.06842	−0.00003
0.084	0.06918	0.06917	−0.00001
0.084	0.06900	0.06920	+0.00020
0.210	0.07560	0.07550	−0.00010

In order to eliminate this contamination and the necessity of adding large amounts of oxalic acid, the chromium was removed as chromyl chloride prior to the precipitation of the thorium. It is not necessary to remove the chromium in this way if speed is more important than accuracy. Weight burets were used in all the following experiments.

Samples of the standard thorium nitrate solution, containing 200 to 300 mg. of thorium, were weighed into the round-bottomed reaction flask and mixed with varying amounts of a potassium dichromate solution. Three drops of hydrogen peroxide and 30 to 35 ml. of perchloric acid were added to each mixture. A 300-ml. Erlenmeyer flask containing about 150 ml. of water was placed so that the tip of the condenser extended just below the water surface. Nitrogen was bubbled through the apparatus at a rate of 1 to 2 bubbles per second, and the contents of the flask were heated. After oxidation of chromium had begun, hydrogen chloride gas was admitted to the reaction flask and the nitrogen flow was stopped. This procedure was continued until nearly all the chromium had been distilled over as chromyl chloride. The thorium solution in the round-bottomed reaction flask was then transferred to a beaker and evaporated to about 5 ml. to remove the excess perchloric acid. This solution was then diluted to about 300 ml. and heated to boiling temperature. Five milliliters of thick filter pulp and 5 grams of oxalic acid were added, and after digesting for 15 minutes the mixture was cooled and the thorium oxalate filtered, washed, and ignited to the dioxide in platinum crucibles for weighing (*9*). The results of a series of determinations made according to the above procedure are shown in Table II.

Determination of Chromium. The possibility of determining chromium in the presence of thorium was investigated by using the following procedure. [After this work was completed Schuldiner and Clardy (*6*) published a similar method for determining chromium.]

Samples of the standard potassium dichromate solution, containing 70 to 75 mg. of chromium, were weighed into Erlenmeyer reaction flasks and mixed with varying amounts of a thorium nitrate solution. Three drops of hydrogen peroxide and 20 to 25 ml. of perchloric acid were added to each mixture. A 200-ml. Erlenmeyer flask containing about 150 ml. of water was placed so that the tip of the condenser just extended into the water

The contents of the flasks were heated until the chromium was completely oxidized to the hexavalent state, after which the solutions were allowed to cool. In analyzing each sample, the solution containing the volatilized chromium was combined with the main part of the chromium and the mixture boiled 20 minutes to expel any chlorine. After cooling, the chromium was determined by adding excess ferrous sulfate and back-titrating with tetrasulfatoceric acid, using 1 to 2 drops of ferroin as indicator. The results of a series of determinations by this method are shown in Table III.

APPLICATIONS

The procedures described above have been used to advantage in the analysis of thorium-chromium alloys. Separate samples are used for the thorium and chromium determinations.

Determination of Thorium. A sample, containing 200 to 300 mg. of thorium, is weighed into a beaker and dissolved in 10 to 15 ml. of concentrated nitric acid and 5 to 10 drops of the fluosilicic acid solution. The mixture is heated to effect complete solution and then transferred to the round-bottomed reaction flask. Thirty to 35 ml. of perchloric acid are added to the solution and the analysis is completed as described above.

Determination of Chromium. A sample, containing 70 to 75 mg. of chromium, is weighed into a beaker and dissolved in 10 to 15 ml. of concentrated nitric acid and 5 to 10 drops of the fluosilicic acid solution. The mixture is heated to effect complete solution and then transferred to the Erlenmeyer reaction flask. Twenty to 25 ml. of perchloric acid are added to the solution and the analysis is completed as described above.

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Determination of Carboxylic Acid Salts

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The method for determining sodium acetate by igniting to the carbonate and titrating the carbonate has been extended to include other sodium salts as well as potassium, calcium, and barium carboxylic acid salts. The procedure is reproducible to ±0.5%.

THE method previously used to determine carboxylic acid salts was to liberate the acid by adding sulfuric or phosphoric acid (*1*, *3*) and distill the free acid into standard alkali. A method recently devised by Palit (*2*) enables some salts to be titrated directly with acid. The method employs special solvents to accentuate the end point. However, Palit's method is not general for carboxylic acid salts, since usually only potassium and sodium salts are basic enough to be titrated, and some of these give poor end points. Salts of the alkaline earth metals are generally insoluble in the solvent mixtures used, and those which are soluble are too weakly basic to give good end points.

Ignition to sodium carbonate has been used (*1*, *3*) for determining sodium acetate, but no other salts were tried, probably because of the difficulties involved in preparing pure samples. This method has now been extended and found to be applicable to a great variety of carboxylic salts, including salts of sodium, potassium, barium, and calcium. During the experimental work for this paper, no carboxylic salt was found which could not be determined by this method. Only potassium acetate gave difficulty. All indications point to the fact that potassium acetate can be determined by this method; however, it is so deliquescent that no representative sample can be obtained. This salt takes on water so rapidly that accurate weighings cannot be made.

PROCEDURE

A sample containing about 0.010 equivalent of carboxylic acid salt is weighed into a platinum crucible and ignited to a red heat with a Meker-type burner till no particles of carbon are visible. A muffle furnace at 1200° to 1300° F. is more efficient than the burner; however, it is best to char the sample with a burner before putting it in the furnace, since some samples sputter on heating, and others melt and creep badly. The contents of the crucible after ignition should be white or slightly gray. The crucible is allowed to cool and than dropped into a 250-ml. beaker containing 50 ml. of standard 0.5 *N* sulfuric acid. The beaker

Table I. Determination of Carboxylic Acid Salts

	Experimental *Mole*	Theoretical *Mole*	Recovery %
Sodium acetate[a]	0.01285	0.01286	99.9
	0.00996	0.00994	100.2
	0.00995	0.00993	100.4
Sodium benzoate[a]	0.01009	0.01007	100.2
Sodium citrate[a]	0.00367	0.00365	100.4
	0.00323	0.00323	100.0
Sodium succinate[b]	0.00638	0.00642	99.4
Sodium caprylate[c]	0.00601	0.00598	100.5
Sodium palmitate[c]	0.00449	0.00449	100.0
Sodium laurate[c]	0.00544	0.00543	100.2
Sodium caprate[c]	0.00486	0.00491	99.0
Sodium potassium tartrate[a]	0.00742	0.00745	99.6
	0.00994	0.00993	100.1
Potassium succinate[b]	0.00530	0.00528	100.4
Potassium acid phthalate[a]	0.00988	0.00987	99.9
Calcium acetate[a]	0.00724	0.00723	100.2
Calcium gluconate[a]	0.00385	0.00383	100.5
Calcium citrate[a]	0.00289	0.00290	99.7
Calcium stearate[a]	0.00179	0.00180	99.4
	0.00216	0.00217	99.5
Barium acetate[a]	0.01038	0.01036	100.2
	0.00878	0.00879	99.9
Barium tartrate[d]	0.00713	0.00716	99.6

[a] Purchased C.P. chemicals.
[b] Prepared by precipitation from methanol. Alcoholic hydroxide added to methanol solution of acid.
[c] Prepared by adding stoichiometric amount of sodium hydroxide in methanol to alcoholic solution of acid; phenolphthalein was used to indicate end point. Alcohol was then evaporated off and salt dried.
[d] Prepared by adding aqueous barium hydroxide to aqueous solution of tartaric acid.

should be covered with a watch glass to prevent loss of solution during the resulting effervescence.

As soon as the effervescence subsides, the contents of the beaker are boiled for 20 to 30 minutes to expel all carbon dioxide from the solution. The excess acid is then titrated, using 0.5 *N* standard sodium hydroxide with phenolphthalein as indicator in the case of sodium and potassium salts. In the case of barium and calcium salts, it is necessary to use hydrochloric acid and not sulfuric acid, since the barium and calcium sulfates are insoluble and hinder reaction between the carbonate and the acid. In using hydrochloric acid, 50 ml. of standard 0.5 *N* acid and a few drops of methyl red indicator are added to the calcium and barium ignition residue. When the samples are completely dissolved, the excess acid is titrated with standard alkali till the solution is just alkaline, then standard hydrochloric acid is added by buret till just acid. This is to prevent the presence of too much hydrochloric acid which can be lost on boiling. With the contents of the beaker just acid, the mixture is boiled for 20 to 30 minutes, and the excess acid is titrated with standard alkali to the methyl red end point.

The solution must be acidic throughout the period of boiling. If it becomes alkaline as the boiling progresses, the methyl red becomes yellow; then more standard hydrochloric acid should be added.

DISCUSSION

The ignition residue in the case of sodium and potassium salts can be dissolved in water and titrated with standard acid, but the residue is slow to dissolve. It is generally quicker to dissolve the ignition residue in excess acid, boil off the carbon dioxide, and titrate the excess acid. The barium and calcium carbonates are water-insoluble, so that the excess acid method is necessary in those cases.

Sulfuric acid will work with calcium salts, even though the calcium sulfate is insoluble. A period of reaction longer than 0.5 hour is needed, however. Barium salts cannot be determined with sulfuric acid; a coating of barium sulfate forms over the unreacted carbonate and prevents further reduction. Hydrochloric acid, however, gives no trouble with these salts. Methyl red indicator must be used in the case of barium and calcium salts because of the acidity of the barium and calcium chlorides.

Free hydroxides or carbonates have to be determined on an unignited sample to correct the final result. Samples containing more than 10% sodium or potassium hydroxide should not be run by this method, since the free caustic attacks the platinum crucibles. Sulfates and chlorides do not interfere in the analysis.

The simplicity of the method is the main factor contributing to the high reproducibility. Using a sample containing 0.01 equivalent of salt will make possible a reproducibility within ±0.5%. The simplicity enables a technician to run many determinations at one time; the number of determinations is usually limited by the number of platinum crucibles available. One determination run alone seldom requires more than 2 hours; however, four determinations run simultaneously can be done in almost the same length of time as one. Barium and calcium salts usually require a longer period for ignition than do the sodium and potassium salts.

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Potentiometric Determination of Lead

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Determination of lead by potentiometric titration with alkali fluoride in the presence of alkali chloride (or bromide) is proposed. The lead ions are precipitated as lead chlorofluoride (or as lead bromofluoride) and the equivalence point is determined by a drop in the ferric-ferrous oxidation-reduction potential.

A METHOD for the potentiometric determination of calcium by titration with fluoride has been described (*3*). In the present paper the principles of a similar method for the rapid and accurate determination of lead are given. When alkali fluoride is added to a saturated solution of lead chloride or bromide, lead chlorofluoride or lead bromofluoride is precipitated. Both lead chlorofluoride and lead bromofluoride are practically insoluble in the presence of an excess of chloride ions or bromide ions; in fact, the precipitation of fluorides as lead chlorofluoride is the most reliable gravimetric method for their estimation.

If an excess of sodium or potassium chloride is added to a solution containing lead ions, the lead is first partially precipitated as lead chloride; if, then, standard alkali fluoride solution is added with vigorous stirring, the precipitate and the lead chloride still in solution are quantitatively converted into lead chlorofluoride. The equivalence point in the titration, corresponding to the molar ratio Pb:F = 1:1, is marked by the drop in the oxidation-reduction potential of a ferric-ferrous platinum indicator electrode, since ferric ions form a stable complex with fluoride. Whereas in the determination of calcium (*3*) or of magnesium and aluminum (*1*) by a similar method, the titration has to be carried out in the presence of alcohol, the estimation of lead may be carried out in an aqueous solution. In 50% alcoholic solution the potential drop is greater than in aqueous solution, but reaching a constant potential after successive additions of titrant takes too long for most practical purposes. While in the precipitation of calcium fluoride, solubility cannot be decreased by a common ion in the proximity of the equivalence point, the absence of this restriction is a decisive advantage in the case of lead chlorofluoride, which contains a third ion that is not titrated.

Lead ions can also be estimated by adding an excess of an alkali bromide to the aqueous sample solution and titrating with fluoride. In general, however, the lead chlorofluoride method is to be preferred to the lead bromofluoride method, since because of the lower solubility of lead bromide, it takes longer for a constant potential to be established.

EXPERIMENTAL

The potentiometric cell and the methods for standardizing the fluoride solutions are described in a previous paper (*3*). The lead content of lead nitrate solutions was determined gravimetrically as lead chromate and lead sulfate. In the gravimetric determinations the authors followed the procedure described by Treadwell (*2*). The potentials were measured by means of a pH meter of the Cambridge Instrument Co., by which direct measurement of e.m.f. up to a potential difference of 1.4 volts can be carried out with an accuracy of ±1 mv.

Preliminary experiments showed that identical results were obtained where sodium or potassium chloride was added to the sample solution, and whether sodium or potassium fluoride was used as titrant. To 100 ml. of the sample solution 0.04 gram of ferrous chloride containing a small quantity (0.8 mg.) of ferric chloride was added as indicator. The pH of the solution influences the oxidation-reduction potential considerably. The reason for this is that the complex FeF_6^{---} is decomposed by strong acids, and therefore the determination cannot be carried out below pH 3. Generally in these experiments the pH of the sample

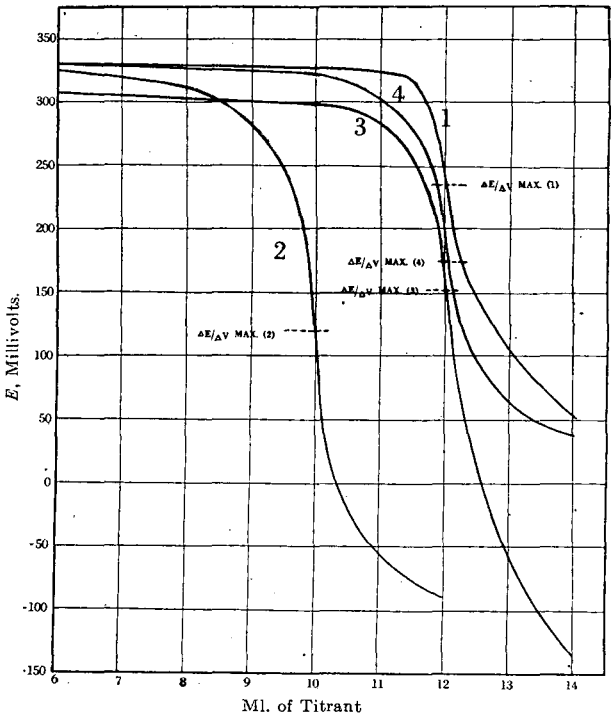

Figure 1. Potentiometric Titration Curves

1. 100 ml. of 0.1 *M* Pb $(NO_3)_2$ + 1.5 grams of NaCl } titrated
3. 100 ml. of 0.1 *M* Pb $(NO_3)_2$ (50% ethyl alcohol solution) + 1.5 grams of NaCl } against 0.833 *M* NaF (A)
4. 100 ml. of 0.1 *M* Pb $(NO_3)_2$ + 3 grams of KBr
2. 100 ml. of 0.1 *M* Pb $(NO_3)_2$ + 1.5 grams of NaCl titrated against 1 *M* KF (B)

Calculated $\Delta E/\Delta V$ maxima at: (1) 12.02 ml.; (2) 10.0 ml.; (3) 12.0 ml.; (4) 12.05 ml.

solution at the beginning of the titration was set at between 4.0 and 4.2. As titrants were used (A) a 0.833 *M* sodium fluoride solution with a pH of 7.25 and (B) a 1 *M* potassium solution with a pH of 9.0.

In Figure 1, potentiometric titrations are compared, with curves 1 and 2 representing titrants A and B, respectively. With the more alkaline potassium fluoride solution the potential drop is steeper, but for practical purposes titrant A is more convenient, since the equilibrium potential is attained more rapidly. Curve 3 (Figure 1) shows the change of potential in 50% (by volume) ethyl alcohol as solvent. In this case, too, the advantage of a greater potential drop is counterbalanced by a slower attainment of the equilibrium potential. Curve 4 shows the change of potential in the event that lead ions are precipitated as lead bromofluoride.

Table I illustrates the influence of the chloride concentration on the change of the potential (with $\Delta E/\Delta V$ values) at various molar ratios of chlorine to lead. At high chloride concentrations the potential course is also influenced by the formation of a labile chloro-complex with ferric ions. The authors found optimum working conditions with the addition of amounts of potassium or sodium chloride corresponding to a molar ratio of ~2.5:Cl:1 Pb. At higher chloride concentrations or at a very small excess of chloride over the molar ratio Cl:Pb = 1:1 the potential change is less pronounced. The accuracy of the lead determination is within the limits of ±0.5% (for concentrations of 0.05 to 0.1 *M* lead). With 0.01 *M* lead nitrate solutions (titrated with 0.1 *M* sodium fluoride) no greater accuracy than ±1.5% could be obtained. At lead concentrations lower than 0.01 *M* the method is not practicable for accurate analytical work.

PROCEDURE

To a dilute lead nitrate solution (0.05 to 0.1 *M*), add 1 gram of potassium chloride (or 0.75 gram of sodium chloride) for each gram of lead in solution, and 0.04 gram of ferrous chloride (containing 0.8 mg. of ferric chloride) for each 100 ml. of solution; then, while stirring vigorously, titrate with standard alkali fluoride. Lead chloride solutions and precipitates of lead chloride (or lead bromide) dispersed in water can be titrated directly against fluoride without addition of alkali chloride (or bromide) to the sample solution. The change of potential is measured by a suitable arrangement, and one should wait until constant potential is reached after each addition of titrant. Titrations are carried out at room temperature and with vigorous stirring. The amount of fluoride added for which $\Delta E/\Delta V$ becomes a maximum is evaluated by graph or calculation. One ml. of a 1 *M* fluoride solution corresponds to 0.2072 gram of lead in the sample solutions.

Table I. Potentiometric Titration of 100 Ml. of 0.1 *M* Lead Nitrate against 0.833 *M* Sodium Fluoride

NaF, ml.	1 Gram of KCl Added (Molar Ratio Cl:Pb = 1.3:1) $\Delta E/\Delta V$ *E*, mv.	2 Grams of KCl Added (Molar Ratio Cl:Pb = 2.6:1) $\Delta E/\Delta V$ *E*, mv.	15 Grams of KCl Added (Molar Ratio Cl:Pb = 20:1) $\Delta E/\Delta V$ *E*, mv.
0	332	330	262
	0.2	0.3	2.8
10.0	300	327	234
	4	2	8
10.5	328	326	230
	6	4	8
11.0	325	324	226
	18	8	12
11.5	316	320	222
	130	110	50
11.7	290	298	212
	150	200	115
11.90	260	258	189
	175	200	125
11.94	253	250	184
	200	275	175
11.98	245	239	177
	250	350	175
12.02	235	225	170
	250	300	175
12.06	225	213	163
	200	275	175
12.10	217	204	156
	155	175	120
12.3	186	169	132
	130	120	160
12.5	160	145	110
	72	98	92
13.0	114	96	64
	42	51	59
14.0	72	45	5

Table II. Precision and Accuracy of Determination of Lead

Test No.	NaF Found, Ml.	Deviation, $\lvert d \rvert$	$d^2 \times 10^2$	Error[a], %
	Sample 1, 100 Ml. of 0.1 *M* $Pb(NO_3)_2$ (Theoretical value, 12.00 ml. of 0.833 *M* NaF)			
1	12.02	+0.01	100	+0.2
2	12.00	−0.01	100	0.0
3	11.98	−0.03	900	−0.2
4	12.02	+0.01	100	+0.2
5	12.00	−0.01	100	0.0
6	12.04	+0.03	900	+0.3
	Av. = 12.01	$\lvert d \rvert_{av.}$ = 0.017	$\sqrt{\Sigma d^2/5}$ = 0.021	
	Sample 2, 100 ml. of 0.0750 *M* $Pb(NO_3)_2$ (Theoretical value, 8.00 Ml. of 0.833 *M* NaF)			
1	8.99	−0.02	400	−0.1
2	9.02	+0.01	100	+0.2
3	9.02	+0.01	100	+0.2
4	9.04	+0.03	900	+0.4
5	8.98	−0.03	900	−0.2
6	9.01	0.00	0.00	+0.1
	Av. = 9.01	$\lvert d \rvert_{av.}$ = 0.0017	$\sqrt{\Sigma d^2/5}$ = 0.022	

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

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

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Determination of Ignition Temperatures of Combustible Liquids and Gases

Modification of the Drop Method Apparatus

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A stainless steel block, heated electrically and containing a 125-cc. Pyrex flask in the center, is substituted for a liquid bath for the determination of the minimum ignition temperatures of liquids and gases by the drop method. The gases are liquefied by means of dry ice or liquid nitrogen before testing. Lower minimum ignition temperatures are obtained in this apparatus than in the liquid baths, by a closer approach to black body conditions. Selected ignition temperatures for 172 compounds are given.

IN CONNECTION with its work for greater safety in mining and industry, the Bureau of Mines determines the explosive properties of various combustible gases, vapors, and liquids as they become commercially important. One phase of the investigation is the determination of the ignition temperatures of liquids. For this purpose, the standard A.S.T.M. test (*1*) was originally employed. In this test, one or more drops of the liquid to be examined were dropped onto the bottom of a 125-cc. Pyrex Erlenmeyer flask suspended in a bath of molten solder or lead heated by a gas burner. In the Bureau of Mines tests, however, antimony and later a mixture of sodium and potassium nitrates were used instead of the solder. To facilitate temperature control, the iron pot was wound with Nichrome wire and the electric heating circuit was operated by means of a temperature controller (*20*).

In accordance with the observations of Mason and Wheeler (*26*), it has been the practice in this laboratory to sweep out the test flask with nitrogen after each trial.

REASONS FOR MODIFICATION OF APPARATUS

One source of annoyance in the use of the liquid bath was the necessity for frequent changes from nitrate bath to lead bath, or vice versa. Neither bath seemed to possess the exact characteristics required for the tests. The possibility of cracking the test flask containing a combustible liquid was a constant source of danger. The molten lead oxidized readily at the surface, and oxidation was augmented by stirring. Time was required for the heat to pass through the silica-protecting tube to the thermocouple junction, and for this reason continuity of temperature between one bath and the other seemed doubtful. Rather than engage in experiments on the baths themselves, it was decided to attempt a modification of the apparatus.

DESCRIPTION OF MODIFIED APPARATUS

In the modified apparatus (Figure 1) a stainless-steel block, *e*, with a stainless-steel lid, *k*, was substituted for the nitrate and lead baths. The steel block weighs about 50 pounds. It was wound with 27 feet of 18-gage Nichrome wire, *b*, encased in a sheath of asbestos tubing. The block was placed on a disk of 85% magnesia insulation, *q*, supported above the table on an iron disk, *r*. Between the metal cylinder, *c*, and the block, *e*, was placed thermal insulation, *p*, consisting of infusorial earth. A 0.375-inch Transite ring, *l*, was placed on top of the lid, *k*, as shown. Over the top of the whole was placed a ring, *s*, consisting of 0.25-inch asbestos board. A smaller ring, concentric with this, was attached to the glass tube, *a*, through which a slow stream of air or oxygen passed into the test flask before a trial test was made. Chromel-Alumel thermocouple *j* passed through a cavity in the block, so that the hot junction was directly under the center of the flask. The 0.25-inch iron pipe was used to protect the thermocouple line from the 110-volt winding. The other ends of the thermocouple were connected to a two-pole, two-throw switch, *h*, so that the thermocouple circuit could be momentarily disconnected from controller *m* and connected to the potentiometer, *i*, for a temperature reading. The cold junction of the thermocouple was buried in an ice bath, *g*, contained in a vacuum bottle. Mirror *f* was sometimes used to observe the results of a test, especially where the flames have little color.

The block was designed for a temperature of 750° C. Since Pyrex test flasks are not suitable at this temperature range, quartz flasks were used.

In carrying out a determination, one or more drops of the liquid to be tested are dropped onto the bottom of the flask, and a stopwatch is started at the same time. If the liquid flashes, the time is noted. This is the "lag" or lag on ignition. The temperature of the bath is then lowered a few degrees and the test repeated. In this manner, a temperature can usually be found, above which the liquid will ignite and below which it will not ignite. After such a temperature is found, the number of drops is varied to determine whether a still lower temperature may be found.

Temperature readings were taken inside the test flasks in the steel bath and in the nitrate bath. The results are shown in Table I.

The steel-block apparatus requires about 2.5 hours to heat from room temperature to 400° C. The bomb can be brought to

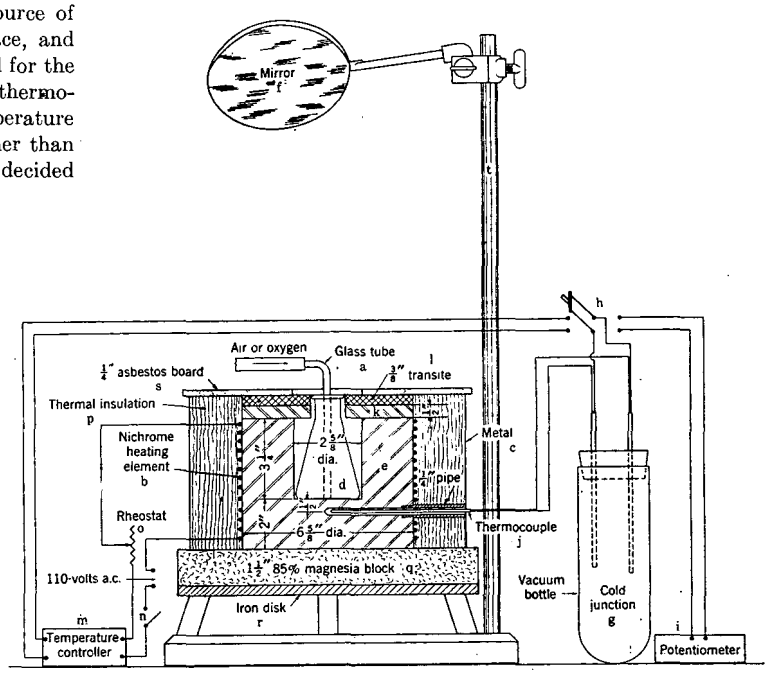

Figure 1. Ignition Temperature Apparatus

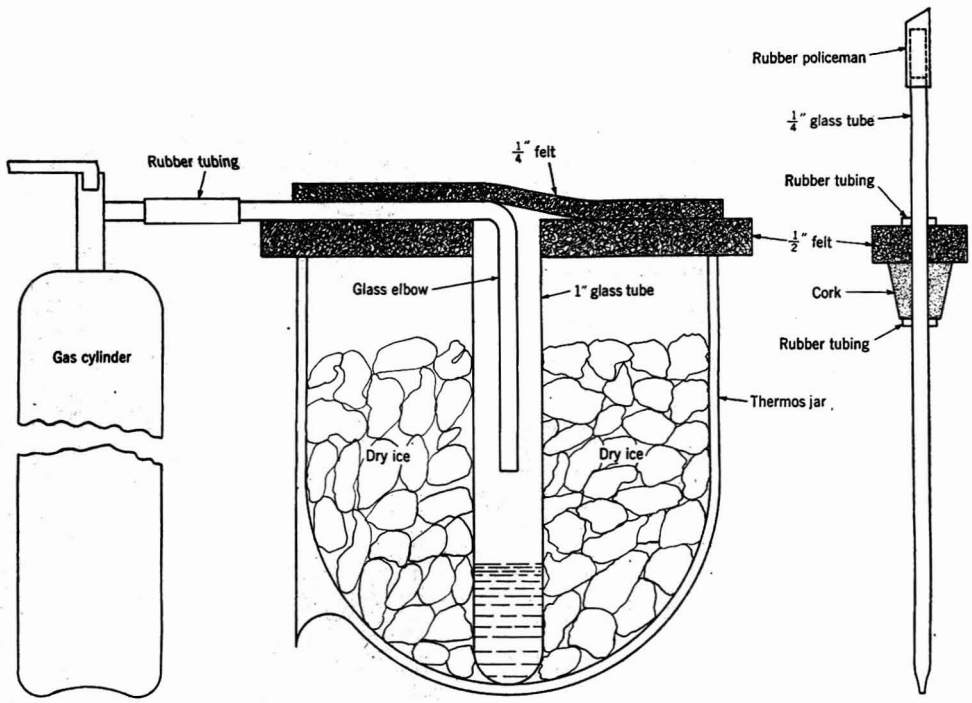

Figure 2. Vacuum Bottle Assembly for Handling Liquefied Gases

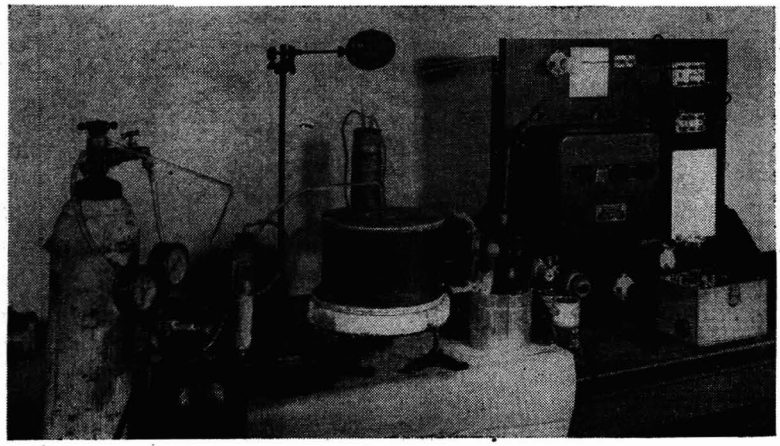

Figure 3. Assembled Apparatus

within a few degrees of any desired temperature at the start of the day's work by setting an electric time switch the night before.

Gases may be liquefied and tested in this apparatus in the same manner as ordinary liquids, except that they must be kept cool enough to remain in the liquid state. Propane and the butanes were condensed out in a bath of dry ice contained in a thermos jar. Ethane was condensed out in liquid nitrogen.

A convenient arrangement for handling gases is shown in Figure 2.

Dry ice is placed around the Pyrex test tube (1 by 8 inches), the open end of which protrudes through a hole in the felt pad. The top of the test tube is covered with another felt pad to exclude moisture. After the tube has become well chilled, gas from the cylinder is admitted slowly through the rubber tube and glass elbow until about 2 inches of liquid are collected. The elbow is then removed, and a pipet containing rings of rubber, cork, and felt is placed in the test tube. After the pipet has cooled, the sample is ready for tests. The pipet must be kept in the tube when not in use, or the expanding vapor will push the liquid out of the pipet before it can be dropped into the test flask.

A photograph of the assembled apparatus is shown in Figure 3.

Gases whose ignition temperatures in oxygen have not been determined because of the violence of the explosions may be liquefied and tested in this apparatus with safety. No flasks have been broken as yet; should shattering occur, the block is strong enough and its construction such that horizontal movement with possible injury to the operator would be prevented.

Table I. Temperature Measurements inside Test Flasks

	Steel Bath	Nitrate Bath
Temperature of bath, ° C.	367	367
Temperature of couple		
Touching bottom of flask, ° C.	367	356
0.125 inch above bottom, ° C.	362	347
1 inch above bottom, ° C.	359	339
1 inch below top, ° C.	319	260

RESULTS OBTAINED WITH STEEL BLOCK

Table II gives the results of several determinations made in the steel block, together with similar results obtained with the nitrate bath.

The ignition temperatures of the compounds tested in the steel block are from 28° to 41° C. lower than in the nitrate bath when air is used, and from 6° to 62° C. lower when oxygen is

Table II. Comparison of Ignition Temperatures Obtained in Steel Bath and in Nitrate Bath

Liquid	Manufacturer	Manufacturer's Designation	Purity	Boiling Point	Nitrate Bath				Steel Block			
					Air		Oxygen		Air		Oxygen	
					Lag	Ignition temp.	Lag	Ignition temp.	Lag	Ignition temp.	Lag	Ignition temp.
			%	° C.	Sec.	° C.	Sec.	° C.	Sec.	° C.	Sec.	° C.
Propane	Phillips	Pure grade	99	−42.5			12	490	6	493	13	468
n-Butane	Phillips	Pure grade	99	− 0.6	5	440	13	300	5	408	28	283
n-Pentane	Eastman	P 2312	..	33–36	4	325	20	270	8	296	40	264
n-Heptane	Eastman	2215	..	98–98.5	12	258	13	248	34	230	54	214
n-Octane	Eastman	1107	..	124–126	13	250	13	246	70	218	107	208
Isobutane	Phillips	Pure grade	99	−12.1	8	490	11	334	14	462	19	319
2,2,4-Trimethylpentane	Eastman	2396	..	98–99	12	474	3	345	20	434	15	283
Ethylbenzene	Eastman	719	..	134–136	7	518	8	488	13	477	14	468

used. From the data of Table I average flask wall temperatures were calculated, and a straight-line relationship between bath temperature and average wall temperature was assumed to hold down to room temperature. To obtain an average wall temperature of 345° C., a nitrate bath temperature of 393° C. is required; however, a steel block temperature of 361° C. produces the same average wall temperature. The wall temperature, *rather than the type of bath, seems to be the controlling* factor. Wall temperatures in the steel block are higher for a given bath temperature because of the closer approach to black body conditions. Longer lags in the steel bath indicate that more of the wall surface is involved in the ignition process.

Table III. Selected Minimum Ignition Temperatures of Gases and Liquids

Substance	Formula	In Air			In Oxygen		
		° C.	° F.	Ref.	° C.	° F.	Ref.
Acetal	$C_6H_{14}O_2$	230	446	(17)	174	345	(17)
Acetaldehyde	C_2H_4O	275	527	(17)	159	318	(17)
Acetic acid	$C_2H_4O_2$	550	1022	(17)	490	914	(17)
Acetic anhydride	$C_4H_6O_3$	392	738	(17)	361	682	(17)
Acetone	C_3H_6O	561	1042	(19)	485	905	(17)
Acetylene	C_2H_2	305	581	(18)	296	565	(18)
Acrolein	C_3H_4O	278	532	(12)	...	...	...
Acrylonitrile	C_3H_3N	481	898	(16)	460	860	(16)
Allyl alcohol	C_3H_6O	378	712	(37)	348	658	(17)
Allyl chloride	C_3H_5Cl	487	909	(17)	404	759	(17)
Ammonia	NH_3	651	1204	(33)	...	..	...
Amyl acetate, *n*	$C_7H_{14}O_2$	399	750	(31)	...	..	...
Amyl acetate, iso	$C_7H_{14}O_2$	379	714	(37)	...	..	...
Amyl alcohol, *n*	$C_5H_{12}O$	427	801	(17)	332	630	(36)
Amyl alcohol, iso	$C_5H_{12}O$	343	650	(31)	...	...	...
Amyl benzene	$C_{11}H_{16}$	...	..	...	255	491	(34)
Amyl chloride	$C_5H_{11}Cl$	259	498	(17)	...	..	...
Amylene	C_5H_{10}	273	524	(22)	...	..	...
Aniline	C_6H_7N	530	986	(13)	...	..	...
Anthracene	$C_{14}H_{10}$	472	882	(39)	...	..	...
Benzaldehyde	C_7H_6O	192	378	(31)	...	...	...
Benzene	C_6H_6	580	1076	(37)	566	1051	(29)
Benzoic acid	$C_7H_6O_2$	573	1064	(17)	556	1033	(17)
Benzyl acetate	$C_9H_{10}O_2$	460	860	(37)	...	..	...
Benzyl alcohol	C_7H_8O	428	802	(37)	373	704	(34)
Benzyl chloride	C_7H_7Cl	627	1161	(27)	...	..	...
Bromobenzene	C_6H_5Br	688	1270	(27)	...	..	...
1,3-Butadiene	C_4H_6	418	784	(17)	335	635	(17)
Butane	C_4H_{10}	408	766	(17)	283	542	(17)
Butyl acetate	$C_6H_{12}O_2$	421	790	(37)	...	..	...
Butyl alcohol	$C_4H_{10}O$	345	653	(37)	328	622	(34)
Butyl alcohol, iso	$C_4H_{10}O$	434	813	(37)	364	687	(36)
Butyl alcohol, *sec*	$C_4H_{10}O$	414	777	(17)	377	711	(17)
Butyl alcohol, *tert*	$C_4H_{10}O$	478	892	(17)	460	860	(17)
Butyl bromide	C_4H_9Br	483	902	(27)	...	..	...
Butyl Carbitol	$C_8H_{18}O_3$	228	442	(9)	...	..	...
Butyl Cellosolve	$C_6H_{14}O_2$	244	471	(9)	...	..	...
Butyl chloride	C_4H_9Cl	460	860	(17)	...	..	...
Butylene	C_4H_8	443	830	(22)	...	..	...
Butyl formate	$C_5H_{10}O_2$	322	612	(17)	308	586	(17)
Butyl propionate	$C_7H_{14}O_2$	426	799	(37)	...	...	...
Butyraldehyde	C_4H_8O	230	446	(17)	206	403	(17)
Butyric acid	$C_4H_8O_2$	552	1026	(27)	...	..	...
Carbon disulfide	CS_2	120	248	(6)	107	225	(6)
Carbon monoxide	CO	609	1128	(3)	588	1090	(3)
Cellosolve	$C_4H_{10}O_2$	238	460	(9)	...	..	...
Cellosolve acetate	$C_6H_{12}O_3$	379	714	(9)	...	..	...
Cetane	$C_{16}H_{34}$	235	455	(35)	...	...	...
2-Chloro-2-methyl-chloride	$C_5H_{11}Cl$	343	650	(17)	318	604	(17)
Creosote	.....	356	673	(9)	...	..	...
Cresol, *o*	C_7H_8O	599	1110	(27)	...	..	...
Cresol, *m*	C_7H_8O	626	1159	(27)	...	..	...
Crotonaldehyde	C_4H_6O	232	450	(22)	...	..	...
Cyanogen	$(CN)_2$	850	1562	(7)	...	...	...
Cyclohexane	C_6H_{12}	...	..	...	296	565	(34)
Cyclopropane	C_3H_6	498	928	(17)	454	849	(17)
Cymene	$C_{10}H_{14}$	466	871	(27)	...	..	...
Decalin	$C_{10}H_{18}$	262	504	(9)	...	..	...
Decane, *n*	$C_{10}H_{22}$	250	482	(25)	...	..	...
Diamyl ether, iso	$C_{10}H_{22}O$	428	802	(27)	...	..	...
1,2-Dichloro-*n*-butane	$C_4H_8Cl_2$	276	529	(17)	250	482	(17)
Dichloroethylene	$C_2H_2Cl_2$	441	826	(17)	...	..	...
Dichloroethyl ether	$C_4H_8OCl_2$	369	696	(9)	...	..	...
Diethanol amine	$C_4H_{11}NO_2$	662	1224	(9)	...	..	...
Diethylene glycol	$C_4H_{10}O_3$	413	776	(37)	...	..	...
Diethyl peroxide	$(C_2H_5O)_2$	189	372	(38)	...	..	...
Dimethylamine	C_2H_7N	402	756	(17)	346	655	(17)
Dimethyl aniline	$C_8H_{11}N$	371	700	(9)	...	...	...
2,3-Dimethylbutane	C_6H_{14}	420	788	(17)	298	568	(17)
Dimethyl ether	C_2H_6O	350	662	(17)	252	486	(17)
2,3-Dimethylhexane	C_8H_{18}	438	820	(35)	...	...	...
Dioxane	$C_4H_8O_2$	266	511	(22)	...	...	...
Dipropyl ether	$C_6H_{14}O$	189	372	(2)	...	...	...
Dipropyl ether, iso	$C_6H_{14}O$	443	830	(9)	...	...	...
Divinyl ether	C_4H_6O	360	680	(14)	...	...	...
Dodecane	$C_{12}H_{26}$	534	993	(27)	...	...	...
Ethane	C_2H_6	472	882	(5)	...	...	...
Ether, diethyl	$C_4H_{10}O$	193	379	(37)	182	360	(23)
Ethyl acetate	C_4H_8O	484	903	(37)	...	...	...
Ethyl alcohol	C_2H_6O	392	738	(10)	...	...	...
Ethylbenzene	C_8H_{10}	477	891	(17)	468	874	(17)
Ethyl bromide	C_2H_5Br	511	952	(33)	...	...	...
2-Ethyl butane	C_6H_{14}	...	...	...	273	524	(34)
Ethyl butyrate	$C_6H_{12}O_2$	463	866	(17)	351	664	(17)
Ethyl chloride	C_2H_5Cl	516	961	(17)	468	874	(17)
Ethylene	C_2H_4	490	914	(23)	485	905	(23)
Ethylene chlorohydrin	C_2H_5OCl	425	797	(17)	400	752	(17)
Ethylene dichloride	C_2H_4Cl	413	776	(9)	...	...	...
Ethylene glycol	$C_2H_6O_2$	413	776	(9)	...	...	...
Ethylene oxide	C_2H_4O	429	804	(9)	...	...	...
Ethyl formate	$C_3H_6O_2$	577	1071	(27)	...	...	...
Ethyl mercaptan	C_2H_5SH	299	570	(15)	261	502	(15)
Ethyl propionate	$C_5H_{10}O_2$	476	889	(17)	440	824	(17)
Furfural	$C_5H_4O_2$	391	736	(17)	...	...	...
Furfuryl alcohol	$C_5H_6O_2$	391	736	(17)	364	687	(17)
Gasoline (regular)	.....	280	536	(33)	...	...	...
Gasoline (73 octane)	.....	299	570	(17)	...	...	...
Gasoline (92 octane)	.....	390	734	(17)	...	...	...
Gasoline (100 octane)	.....	429	804	(17)	...	...	...
Glycerol	$C_3H_8O_3$	393	740	(37)	320	608	(9)
Heptane	C_7H_{16}	230	446	(17)	214	417	(17)
Hexane	C_6H_{14}	248	478	(37)	...	...	...
Hexane, iso	C_6H_{14}	...	..	...	284	543	(34)
Hexyl alcohol	$C_6H_{14}O$	...	...	...	300	572	(34)
Hydrocyanic acid	HCN	538	1000	(9)	...	...	...
Hydrogen	H_2	572	1060	(4)	560	1040	(11)
Hydrogen sulfide	H_2S	292	558	(24)	220	428	(7)
Isododecane	$C_{10}H_{22}$	500	932	(35)	...	...	...
Isophorone	$C_9H_{14}O$	462	864	(17)	322	612	(17)
Isoprene	C_5H_8	440	824	(40)	...	...	...
Kerosene	.....	254	489	(9)	...	...	...
Methane	CH_4	632	1170	(30)	556	1033	(7)
Methyl acetate	$C_3H_6O_2$	502	936	(37)	...	...	...
Methyl alcohol	CH_4O	470	878	(37)	461	862	(17)
Methyl bromide	CH_3Br	537	999	(33)	...	...	...
2-Methylbutane (iso-pentane)	C_5H_{12}	420	788	(17)	294	561	(17)
Methyl butyl ketone	$C_6H_{12}O$	533	992	(22)	...	...	...
Methyl Cellosolve	$C_3H_8O_2$	288	550	(9)	...	...	...
Methyl chloride	CH_3Cl	632	1170	(33)	...	...	...
Methyl cyclohexane	C_7H_{14}	...	...	...	285	545	(34)
Methyl cyclopentane	C_6H_{12}	...	...	...	329	624	(34)
Methylene chloride	CH_2Cl_2	642	1188	(17)	606	1123	(17)
Methyl ethyl ketone	C_4H_8O	514	957	(22)	...	...	...
2-Methyl-3-ethyl-pentane	C_8H_{18}	461	862	(35)	...	...	...
Methyl formate	$C_2H_4O_2$	236	457	(33)	...	...	...
α-Methylnaphthalene	$C_{11}H_{10}$	566	1051	(35)	...	...	...
2-Methylpentane	C_6H_{14}	...	...	...	275	527	(34)
2-Methylpropane (isobutane)	C_4H_{10}	462	864	(17)	319	606	(17)
Methyl propyl ketone	$C_5H_{10}O$	505	934	(22)	...	...	...
Methyl salicylate	$C_8H_8O_3$	454	849	(31)	...	...	...
Monomethylamine	CH_5N	430	806	(17)	400	257	(17)
Naphtha	....	277	531	(9)	...	...	...
Naphthalene	$C_{10}H_8$	587	1089	(20)	560	1040	(20)
Nicotine	$C_{10}H_{14}N_2$	244	471	(21)	235	635	(21)
Nitrobenzene	$C_6H_5NO_2$	482	900	(31)	...	...	...
Nonane	C_9H_{20}	285	545	(25)	...	...	...
Octane	C_8H_{18}	218	424	(17)	208	406	(17)
Ozite A	....	435	815	(17)	...	...	...
Ozite B	....	451	844	(17)	...	...	...
Paraffin	....	245	473	(9)	...	...	...
Paraldehyde	....	242	468	(9)	...	...	...
Pentane	C_5H_{12}	290	554	(17)	258	496	(17)
Petroleum ether	....	329	624	(31)	...	...	...
Phenol	C_6H_6O	715	1319	(9)	500	932	(8)
Pinene	$C_{10}H_{16}$	...	..	...	275	527	(34)
Propane	C_3H_8	493	920	(17)	468	874	(17)
Propyl acetate	$C_5H_{10}O_2$	450	842	(17)	388	730	(17)
Propyl acetate, iso	$C_5H_{10}O_2$	572	1062	(17)	448	838	(17)
Propyl alcohol	C_3H_8O	439	822	(17)	328	622	(36)
Propyl alcohol, iso	C_3H_8O	456	853	(37)	...	...	...
Propyl bromide	C_3H_7Br	490	914	(17)	255	491	(17)
Propyl chloride	C_3H_7Cl	520	968	(17)	...	...	...
Propyl cyclopentane	C_8H_{16}	285	545	(35)	...	...	...
Propylene	C_3H_6	458	1036	(22)	...	...	...
Propylene dichloride	$C_3H_6Cl_2$	557	1035	(22)	...	...	...
Propylene glycol	$C_3H_8O_2$	421	790	(17)	392	558	(17)
Pyridine	C_5H_5N	482	900	(31)	...	...	...
Solvasol	....	276	529	(17)	258	496	(17)
Stearic acid	$C_{18}H_{36}O_2$	395	743	(9)	...	...	...
Styrene	C_8H_8	490	914	(17)	450	842	(17)
Tetrahydrofurfuryl alcohol	$C_5H_{10}O_2$	282	540	(17)	273	524	(17)
Toluene	C_7H_8	552	1026	(37)	516	961	(23)
Toluidine, *o*	C_7H_9N	482	900	(31)	...	...	...
Toluidine, *p*	C_7H_9N	482	900	(9)	...	...	...
Trichloroethylene	C_2HCl_3	463	866	(17)	419	786	(17)
Triethylene glycol	$C_6H_{14}O_4$	371	700	(17)	244	471	(17)
Trimethylbenzene	C_9H_{12}	...	...	...	509	948	(34)
2,2,4-Trimethylpentane	C_8H_{18}	434	813	(17)	283	542	(17)
Trioxane	$C_3H_6O_3$	424	795	(17)	...	...	...
Turpentine	$C_{10}H_{16}$	252	486	(32)	...	...	...
Vinyl acetate	$C_4H_6O_2$	427	801	(9)	...	...	...
Xylene, *o*	C_8H_{10}	496	925	(37)	...	...	...

Longer lags also allow more time for some of the compounds to decompose.

TABLE OF IGNITION TEMPERATURES

Table III gives the ignition temperatures employed by the Bureau of Mines for a number of compounds. Many have been determined by the bureau; the remainder were selected from the results of other investigators. A variety of methods was, of course, used in the different determinations.

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Determination of the Gamma Isomer of Hexachlorocyclohexane

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A method is described for determination of the gamma isomer of hexachlorocyclohexane in the technical product and dust mixtures. The method is based on the dehydrochlorination of two 0.100-gram samples, dissolved in 50.0 ml. of 95% ethyl alcohol, one for 15 minutes and the other for 50 minutes, at 0° C. with 10.0 ml. of 1 *N* ethanolic potassium hydroxide. The per cent chloride difference multiplied by a factor yields the percentage of gamma isomer.

THE insecticidal value of hexachlorocyclohexane is believed to be due to the presence of the gamma isomer of hexachlorocyclohexane (*7*), and in the enforcement of the Agricultural Code of the State of California, pertaining to the labeling and sale of economic poisons, it is necessary to determine the gamma isomer in commercial dust mixtures offered for sale as insecticides.

A search of the literature and written inquiry disclosed that the only workable methods developed at that time were based on infrared absorption (*8*) or bioassay using insects. The infrared absorption method, though accurate under certain conditions, demands the use of the relatively expensive infrared spectrophotometer, and the bioassay method requires the skill of a highly trained entomologist.

EXPERIMENTAL

Hexachlorocyclohexane is dehydrochlorinated by alcoholic sodium or potassium hydroxide, losing three atoms each of hydrogen and chlorine and forming trichlorobenzene (*2*, *9*). The individual isomers have different rates of reaction to dehydrochlorination (*2*), depending on time, temperature, and concentration of reactants. The reaction goes rapidly to completion at elevated temperatures.

Samples of highly refined alpha, beta, gamma, delta, and epsilon isomers of hexachlorocyclohexane were obtained and their melting points determined as shown in Table I. The reaction rates of the individual isomers were determined at various temperatures and concentrations. Reaction rate curves under the best conditions found were plotted (Figure 1). From these data it was deduced that the alpha and delta isomers should be almost completely dehydrochlorinated before the gamma isomer was appreciably dehydrochlorinated, then using a longer period of time the alpha, delta, and gamma isomers should all be dehydrochlorinated. Since the beta isomer is inert under these conditions, and the epsilon isomer content in the technical product is low enough not to interfere seriously, the difference in chloride produced in a definite short and long period of dehydrochlorination should be a function of the gamma isomer content.

Table I. Melting Points of Purified Isomers

Isomer	Melting Point Range, ° C.
Alpha	157.5–158.0
Beta	309 (sublimes)
Gamma	112.0–112.8
Delta	138.0–138.4
Epsilon	218.5–219.3

Duplicate samples containing known percentages of the five isomers were prepared. Portions of the samples weighing 0.100 gram were dissolved in 50.0 ml. of 95% ethyl alcohol, and dehydrochlorinated at 0° C. (as described below) with 10.0 ml. of 1 *N* ethanolic potassium hydroxide for 5, 10, 15, and 20 minutes for the short periods for dehydrochlorination of the alpha and delta isomers, and 30, 40, 50, and 60 minutes as the periods for dehydrochlorination of alpha, delta, and gamma isomers. The reactions were stopped at the required time by the addition of 10 ml. of 1 to 3 nitric acid, and the chloride was determined by the Volhard method. The percentage of chloride formed during the shorter intervals of time was subtracted from the chloride produced during the longer intervals. These chloride values were then plotted against the percentage of gamma isomer in the samples.

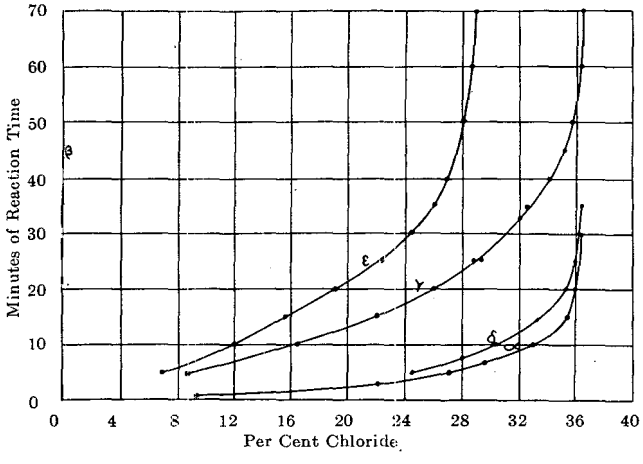

Figure 1. Effect of Time on Dehydrochlorination of Hexachlorocyclohexane Isomers

0.100 gram of isomer in 50.0 ml. of ethyl alcohol at 0° C. with 10.0 ml. of 1 *N* ethanolic potassium hydroxide

The 10-minute period was not long enough to dehydrochlorinate completely mixtures containing over 70% alpha plus delta isomers, while the 40-minute period was too short for a gamma content in excess of 40%. The periods of 15 and 50 minutes seemed to fulfill the requirements, yielding a straight line expressable by the equation:

$$8(\%\text{ chloride in 50 minutes} - \%\text{ chloride in 15 minutes}) - 8.20 = \%\text{ gamma isomer}$$

Two dust mixtures containing known percentages of pure alpha, beta, gamma, and delta isomers of hexachlorocyclohexane were prepared in triplicate with talc as a diluent, only enough mixture being made for each test to eliminate the error of nonuniformity of one large batch. One mixture was extracted with acetone and another with anhydrous ether in a Soxhlet extraction apparatus. After the solvent had been removed, the residues were analyzed for total hexachlorocyclohexane content by dehydrochlorination, by refluxing 0.100 gram of the residues with 10 ml. of 1 *N* ethanolic potassium hydroxide for 20 minutes and determining chloride by the Volhard method, using nitrobenzene to coagulate the silver chloride (*1*). Hexachlorocyclohexane loses 3 molecules of hydrogen chloride when refluxed with ethanolic potassium hydroxide. A weight of the residues equivalent to 0.100 gram of hexachlorocyclohexane was dissolved in 50.0 ml. of 95% alcohol and dehydrochlorinated at 0° C. with 10.0 ml. of 1 *N* ethanolic potassium hydroxide, one sample for 15 minutes and a second sample for 50 minutes. Other portions of the dust mixtures were analyzed for total hexachlorocyclohexane content by dehydrochlorination and the unextracted dusts equivalent to 0.100 gram of hexachlorocyclohexane were refluxed for 20 minutes with 50.0 ml. of 95% alcohol to dissolve the hexachlorocyclohexane. The cooled solutions were then dehydrochlorinated for 15 and 50 minutes at 0° C. Results are shown in Table II.

Table II. Comparison of Methods for Analysis of Dust Mixtures

Sample No.	Gamma Isomer, %	Gamma Isomer Added	Gamma Isomer as Determined, % Acetone extracted residue	Ether extracted residue	Dust sample without extraction
1[a]	In total HCH	12.00	14.52	11.64	11.64
	In prepared sample	0.60	0.73	0.58	0.58
2[b]	In total HCH	20.00	25.56	20.20	21.30
	In prepared sample	0.20	0.26	0.20	0.21
3[c]	In total HCH	10.00	...	...	10.53
	In prepared sample	1.00	...	...	1.05

[a] Dust mixture containing 5% total hexachlorocyclohexane, composed of alpha 70.0%, beta 5.0%, gamma 12.0%, and delta 13.0%, diluted with talc. Finished dust contained 0.60% gamma isomer.
[b] Dust mixture containing 1% total hexachlorocyclohexane, composed of alpha 55.0%, beta 2.0%, gamma 20.0%, and delta 23.0%, diluted with talc. Finished dust contained 0.20% gamma isomer.
[c] Dust mixture containing 10% total hexachlorocyclohexane, composed of alpha 70.0%, beta 3.0%, gamma 10.0%, delta 15.0%, and epsilon 2.0%, diluted with talc containing 0.5% sulfur. Finished dust contained 1.00% gamma isomer.

REAGENTS

Ethyl alcohol, 190-proof, 95% by volume.

Ethanolic potassium hydroxide, 1.000 *N*. Dissolve 57 to 58 grams of C.P. potassium hydroxide pellets in about 950 ml. of 95% ethyl alcohol with the aid of heat, cool, filter into a 1-liter volumetric flask, mix, and standardize against 0.5 *N* hydrochloric acid, using methyl orange indicator. Adjust to 1.000 *N* by the addition of alcohol or alkali.

Nitric acid, 1 to 3, 1 volume of C.P. concentrated nitric acid with 3 volumes of distilled water.

Silver nitrate, 0.1 *N*, containing 16.989 grams of silver nitrate per liter of solution. Standardize by precipitating with a slight excess of dilute hydrochloric acid and weighing as silver chloride.

Ammonium thiocyanate, 0.1 *N*, containing 7.611 grams of ammonium thiocyanate per liter of solution. Standardize against the 0.1 *N* silver nitrate.

Ferric alum indicator, 10%. Dissolve 10 grams of C.P. ferric ammonium sulfate in about 50 ml. of distilled water, filter, decolorize with concentrated nitric acid, and dilute to 100 ml.

Nitrobenzene, purified grade mononitrobenzene.

Anhydrous ethyl ether, reagent grade.

PROCEDURE

The original calibration graph was based on the use of 0.100 gram of 100% pure hexachlorocyclohexane isomer mixtures. The technical product and diluted dust mixtures must first be analyzed to determine their hexachlorocyclohexane content. If the dust mixture is extracted with ether, the thoroughly mixed residue must be analyzed, so that 0.100 gram of total hexachlorocyclohexane is dehydrochlorinated for 15 and 50 minutes at 0° C.

Determination of Total Hexachlorocyclohexane. This may be calculated from total combined chlorine. The lime ignition method of Kimball and Tufts (*4*) is suitable for determination of total chlorine in samples of technical hexachlorocyclohexane.

Those authors have modified the method (*5*) for the analysis of hexachlorocyclohexane by weighing a sample equivalent to approximately 0.15 gram of hexachlorocyclohexane in a 2.5-inch (6.25-cm.) length of ordinary soda straw, crimped at one end. The lower 3 inches of the ignition tube containing the sample in the soda straw are filled with a mixture of hydrated lime containing 15% anhydrous calcium nitrate. The remainder of the tube is filled with lime alone. A blank determination including

a 2.5-inch piece of empty soda straw must be run and the chloride found subtracted from subsequent determinations.

The Parr peroxide bomb (*6*) can be used to determine total chlorine in samples of hexachlorocyclohexane and its mixtures, but it sometimes gives low results. A sample of the technical product in excess of 0.1 gram is difficult to oxidize completely, and low results are obtained. A sample of a dust mixture corresponding to 0.1 gram of total hexachlorocyclohexane can usually be completely oxidized. The total chlorine is determined in the fusion mixture by the Volhard method.

Total hexachlorocyclohexane can be calculated from the total chlorine determination by the formula:

$$\frac{\text{Ml. of 0.1 } N \text{ } AgNO_3 \times 0.4848}{\text{sample weight}} = \% \text{ total hexachlorocyclohexane}$$

Total hexachlorocyclohexane can also be determined quantitatively by dehydrochlorination. When hexachlorocyclohexane is refluxed with ethanolic sodium or potassium hydroxide, 3 molecules of hydrogen chloride are removed, producing trichlorobenzene (*2*).

A 0.1- to 0.2-gram sample of technical hexachlorocyclohexane or an equivalent weight of a dust mixture is refluxed 20 minutes in a 125-ml. ⅌ Erlenmeyer flask with approximately 15 ml. of 1 *N* ethanolic potassium hydroxide. If a large sample weight of a dilute dust is used, sufficient alcohol may be added to cover the sample. After refluxing, the flask is cooled and the inside walls of the flask are washed down with distilled water. The contents are made slightly acid with 1 to 3 nitric acid, using a drop of phenolphthalein solution as an indicator. An excess of 0.1 *N* silver nitrate along with 3 ml. of 10% ferric alum solution and 5 ml. of nitrobenzene is added to the flask. The flask is stoppered and shaken to coagulate the silver chloride (*1*), and the excess silver nitrate is then titrated with 0.1 *N* ammonium thiocyanate. An indicator blank must be applied.

$$\frac{\text{Ml. of 0.1 } N \text{ } AgNO_3 \times 0.9696}{\text{sample weight}} = \% \text{ total hexachlorocyclohexane}$$

Data obtained by the three methods, using purified alpha isomer, are given in Table III. The other four isomers gave similar results.

Determination of Gamma Isomer. Two samples of the technical product, the ether-extracted residue, or the original dust mixture, equivalent to 0.100 gram of total hexachlorocyclohexane are washed into separate 125-ml. ⅌ Erlenmeyer flasks with 50.0 ml. of 95% ethyl alcohol. The flasks are heated under reflux for about 10 minutes to dissolve the hexachlorocyclohexane. When cool, the flasks are stoppered and packed in crushed ice, which covers the lower half of the flask. The flasks, still packed in ice, are placed in a refrigerator for at least 1.5 hours until the contents are cooled to 0° C. This may take 2 hours, as shown by the data in Table IV. A tightly stoppered 250-ml. Erlenmeyer flask containing about 100 ml. of *N* ethanolic potassium hydroxide is packed in crushed ice and also placed in the refrigerator. A 10-ml. volumetric pipet should be placed in the refrigerator to cool at least 30 minutes before it is ready to use.

Table III. Analysis for Total Hexachlorocyclohexane Using Purified Alpha Isomer as Chlorine Standard

Method	Chlorine Found, %	Theory	Hexachlorocyclohexane Calculated from Chlorine, %
Lime ignition	73.19	73.16	100.04
Parr bomb	73.14	73.16	99.97
Dehydrochlorination at reflux temperature	36.52	36.58	99.84

Table IV. Time Necessary to Cool 50 Ml. of Alcohol Packed in Crushed Ice[a]

Time, Minutes	Alcohol Temperature, ° C.
0	27.0
5	9.2
35	0.7
45	0.5
60	0.4
90	0.2
120	0.0

[a] Alcohol contained in a 125-ml. ⅌ Erlenmeyer flask with cork stopper.

Using the cold 10-ml. volumetric pipet, exactly 10.00-ml. portions of the 1 *N* ethanolic potassium hydroxide are withdrawn from the 0° C. temperature storage flask and transferred to each of the cold flasks containing the hexachlorocyclohexane solution. The time of addition to each flask is carefully noted. The contents of the flasks are mixed by rotating the flasks. In exactly 15 minutes 10 ml. of 1 to 3 nitric acid are added to one of the flasks and the flask is rotated to mix the contents. In exactly 50 minutes the reaction in the second flask is stopped by the addition of 10 ml. of 1 to 3 nitric acid. The flasks are removed from the ice bath and an excess of 0.1 *N* silver nitrate (10.00 ml. to the 15-minute flask and 15.00 ml. to the 50-minute flask), 2 ml. of 10% ferric alum solution, and 5 ml. of nitrobenzene are added to the flasks and the flasks are stoppered and shaken. The excess silver nitrate is titrated with 0.1 *N* ammonium thiocyanate.

It is imperative that the end-point color be the same in both the 15-minute and 50-minute reaction flasks. The volume of 0.1 *N* silver nitrate used during the 15-minute reaction period is subtracted from the volume used during the 50-minute period; no indicator blank correction is necessary. This difference in volumes multiplied by 0.3546 and divided by 0.1-gram sample weight gives the per cent chloride difference between the two reaction periods. The per cent chloride difference, on multiplying by 8 and subtracting 8.20 from the product, gives the percentage of gamma isomer in total hexachlorocyclohexane. This percentage of gamma isomer multiplied by the percentage of total hexachlorocyclohexane in the sample yields the percentage of gamma isomer in the original sample.

Extraction of Dust Mixtures. Most dust samples, containing as low as 0.5% gamma isomer content, can be dehydrochlorinated at 15 and 50 minutes without extracting the hexachlorocyclohexane with ether. Some commercial samples are rather highly colored, owing to a yellow or brown diluent. The color makes the end point so uncertain that an extraction with anhydrous ether in a Soxhlet extraction apparatus is necessary. The proper size of sample to be extracted depends on the percentage of total hexachlorocyclohexane. A residue weight of 0.5 to 1.0 gram will give enough sample for duplicate analyses. An extraction period of 16 hours has been found sufficient for most samples, but the extraction thimble should be checked after this period of extraction for the presence of hexachlorocyclohexane by allowing the thimble to dry; if the odor of hexachlorocyclohexane is not apparent the extraction is considered completed. Complete mixing of the dry ether extract is necessary because the alpha and beta isomers crystallize out before the ether is completely evaporated.

The anhydrous ether must be removed from extracted hexachlorocyclohexane in the Soxhlet extraction flask at a low temperature; otherwise some of the isomers of hexachlorocyclohexane will be removed by sublimation. The method found best was to place the extraction flask on a steam bath and run a stream of air into the flask. This facilitates the removal of the ether and keeps the temperature down. As the temperature should not be allowed to go above the boiling point of ether, the last of the ether should be removed with the flask off the steam bath.

EXAMPLE. A commercial dust was analyzed for total hexachlorocyclohexane by refluxing 1.000 gram of the material with approximately 15 ml. of 1 *N* ethanolic potassium hydroxide. After the inside of the flask had been cooled and washed down with water and acidified with nitric acid, 10.00 ml. of 0.1 *N* silver nitrate were added. The excess silver nitrate required 5.90 ml. of 0.1 *N* ammonium thiocyanate for the back-titration. An indicator blank of 0.10 ml. of 0.1 *N* ammonium thiocyanate (Table V), for this volume of solution was subtracted from the volume of 0.1 *N* ammonium thiocyanate solution, giving a final volume of 5.80 ml. of 0.1 *N* ammonium thiocyanate solution.

$10.00 - 5.80 = 4.20$ ml. of 0.1 *N* silver nitrate solution used

$$\frac{4.20 \times 0.9696}{1.0} = 4.07\% \text{ total hexachlorocyclohexane in material}$$

$\frac{100 \times 0.1}{4.07}$ = 2.457 grams of original material equivalent to 0.1 gram of total hexachlorocyclohexane

Two 2.457-gram portions of the material were dissolved in 50 ml. of 95% ethyl alcohol and cooled to 0° C. One portion was dehydrochlorinated at 0° C. for 15 minutes with 10.00 ml. of 1 *N* ethanolic potassium hydroxide, the other for 50 minutes. The 15-minute period required 10.00 − 2.42 = 7.58 ml. of 0.1 *N* silver nitrate. The 50-minute period portion required 15.00 − 6.18 = 8.82 ml. of 0.1 *N* silver nitrate.

8.82 − 7.58 = 1.24 ml. of 0.1 *N* silver nitrate difference

$\frac{1.24 \times 0.3546}{0.1}$ = 4.40% chloride difference

(4.40 × 8) − 8.20 = 27.00% gamma isomer in hexachlorocyclohexane

4.07 × 0.27 = 1.10% gamma isomer in original sample

4.07 − 1.10 = 2.97% other isomers of hexachlorocyclohexane in original sample

DISCUSSION

The accurate determination of total hexachlorocyclohexane from the total chlorine content of technical hexachlorocyclohexane and its mixtures is a difficult task because a very small error in determining the total chlorine content will cause a rather large error when calculated to hexachlorocyclohexane.

Table V. Typical Indicator Blank Data

Solution Volume, Ml.	Excess 0.1 *N* NH_4SCN, Ml.
50	0.00
100	0.10
200	0.15
300	0.22

A common source of error in the Volhard method for chlorine is the amount of standardized ammonium thiocyanate solution necessary to impart a visible color to the solution being titrated after all excess silver has been precipitated. This volume of solution constitutes an indicator blank, and varies with the volume of solution being titrated and the shade of color desired by the chemist for the end point. The Research Analytical Laboratory of the Hooker Electrochemical Company (*5*) has developed a procedure for use in control work which increases the accuracy of the Volhard method by applying an indicator blank. That laboratory determines the indicator blank by titrating 1.00 ml. of 0.1 *N* silver nitrate with 0.1 *N* ammonium thiocyanate in the same volume as used in the chloride titration. The indicator blank is not directly proportional to the volume and should be determined for different volumes of solution, as shown in Table V. The indicator blank may be added to the volume of silver nitrate or subtracted from the volume of thiocyanate solution. Failure to apply an indicator blank can cause a 2 to 3% error in the determination of total hexachlorocyclohexane in the technical product.

This investigation was almost completed before the existence of a fifth isomer, epsilon, was announced (*3*). The effect of the epsilon isomer on the method was demonstrated by analyzing mixtures containing known percentages of all five of the obtainable isomers of hexachlorocyclohexane (Table VI).

The presence of free chloride in hexachlorocyclohexane and its products should be checked in the following manner:

A 0.1- to 1.0-gram sample is refluxed with 25 ml. of 95% alcohol for 10 minutes, cooled, and acidified with a few milliliters of 1 to 3 nitric acid. An excess of 0.1 *N* silver nitrate, 5.00 ml., is added along with ferric alum solution and nitrobenzene. After shaking, the excess silver nitrate is titrated with 0.1 *N* ammonium thiocyanate. Any silver nitrate used must be subtracted from the volume used when determining total hexachlorocyclohexane, keeping the proper volume to weight ratio.

Table VI. Analysis of Mixtures Containing Known Percentages of Pure Isomers of Hexachlorocyclohexane for Gamma Isomer

Per Cent of Pure Isomers in Mixture					Gamma Isomer Found, %	Recovery, %
Alpha	Beta	Delta	Epsilon	Gamma		
75.0	5.0	15.0	...	5.0	5.40	108.0
80.0	5.0	10.0	...	5.0	5.96	119.2
72.0	10.0	10.0	3.0	5.0	6.20	124.0
70.0	5.0	15.0	...	10.0	9.84	98.4
75.0	5.0	10.0	...	10.0	9.40	94.0
70.0	3.0	15.0	2.0	10.0	11.64	116.4
65.0	5.0	15.0	...	15.0	15.88	105.9
55.0	5.0	20.0	...	20.0	20.20	101.0
55.0	3.5	20.0	1.5	20.0	23.00	115.0
55.0	3.5	20.0	1.5	20.0	22.60	113.0
50.0	15.0	5.0	...	30.0	31.48	105.0
50.0	14.0	5.0	1.0	30.0	29.56	98.5
50.0	5.0	10.0	...	35.0	34.36	98.2
20.0	5.0	35.0	...	40.0	40.04	100.1
15.0	10.0	30.0	...	45.0	44.60	99.1
5.0	5.0	40.0	...	50.0	49.96	99.9
5.0	4.5	40.0	0.5	50.0	49.64	99.3
2.2	2.8	25.0	...	70.0	68.27	97.5
1.5	2.0	16.5	...	80.0	85.40	106.8
..	..	..	...	100.0	92.96	93.0
					Av.	104.6

Most samples contain no free chloride, but one sample of commercial hexachlorocyclohexane was found to contain 1.06% free chloride.

No chloride blank or indicator blank need be applied to the time differential determinations of the gamma isomer, as the sample weights are the same and their effect is canceled.

It is imperative that exactly the same sample weight be taken for the 15-minute and 50-minute dehydrochlorination reactions.

Anhydrous ether is the best solvent for extracting dust mixtures. Ordinary solvent ether can be used, but the last traces of alcohol are difficult to remove. Hexachlorocyclohexane is very soluble in acetone, but changes apparently take place during the evaporation of the solvent, giving high results for the gamma isomer, as shown in Table II.

The accuracy of the method falls down on samples containing more than 70% gamma isomer.

The method as written is not applicable to mixtures containing DDT, DDD, chlorinated camphene, chlordan, or other insecti-

Table VII. Determination of Gamma Isomer

Sample No.	Per Cent Gamma Isomer Found		
	By infrared analysis[a]	By dehydrochlorination	
1	12.8	13.32	
		13.08	
		12.76	
		Av.	13.05
2	13.7	13.88	
		14.52	
		14.52	
		Av.	14.31

[a] Reported by Kimball and Tufts.

Table VIII. Analysis of Commercial Hexachlorocyclohexane Dust Samples

	Guaranteed on Label		Found by Analysis	
	Gamma isomer, %	Other isomers, %	Gamma isomer, %	Other isomers, %
1	6.0	..	6.83	40.20
2	4.0	..	4.29	24.32
3	5.7	..	6.42	43.69
4	5.0	45.0	5.35	45.50
5	1.0	..	1.13	5.98
6	0.5	..	0.52	3.06
7	1.0	..	1.33	3.84
8	6.0	21.3	6.85	22.24
9	1.0	3.5	1.06	3.53
10	1.0	7.3	1.08	6.38
11	1.0	2.5	1.10	2.97
12[a]	1.0	7.0	1.34	7.09

[a] Sample contained small amount of sulfur, possibly contamination from unclean mixer.

cides containing labile chlorine. Controlled dehydrochlorination might possibly be used in developing methods for the analysis of these complex insecticides in the presence of one another. Work is being continued along this line of investigation.

The presence of sulfur, whether part of a formula or contamination, in a hexachlorocyclohexane dust causes some difficulty in the analysis for the gamma isomer. The sulfur is converted to sulfide during the dehydrochlorination reaction at 0° C., and when silver nitrate is added to the acidified solution a precipitate of silver sulfide is formed.

This was overcome by adding a large enough excess of 0.1 *N* silver nitrate solution to the 15- and 50-minute reaction flasks, following dehydrochlorination at 0° C., and acidification with nitric acid, to precipitate completely both sulfide and chloride. The flasks were then placed on a hot plate and most of the alcohol was boiled off, 2 ml. of concentrated nitric acid were added to each flask, and the silver sulfide was decomposed by continued boiling. After cooling, the excess silver nitrate was titrated in the regular way and the gamma isomer per cent calculated as described. Sample 3, Table II, shows the results obtained on a dust containing sulfur.

The average accuracy obtained on commercial samples should be in the neighborhood of 5%, though greater accuracy has been obtained. The method tends to give high results for the gamma isomer, as indicated in Tables VI and VII.

Some typical results obtained in analysis of commercial dust mixtures are presented in Table VIII.

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ANTHOCYANIN PIGMENTS

Colorimetric Determination in Strawberries and Strawberry Products

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The amount of red anthocyanin pigment in strawberry products can be quantitatively determined by measuring the light absorption in extracts made therefrom at 500 mμ and at pH 3.40 and 2.00. The measurement consists of subtracting the optical density at 500 mμ of an anthocyanin solution at pH 3.4 from its optical density at pH 2.0, at known concentration. The increase in color intensity under such conditions is proportional to the concentration of anthocyanin in the solution. A solution of Congo red is suggested as a standard of color intensity. Examples illustrate applicability of the method, which may be used for objective comparison of the red color in different samples of strawberries and in strawberry products of different origin, and to follow color deterioration in the product after manufacture.

IN CONNECTION with work in this laboratory on the changes of strawberry preserves during storage, a quantitative method for the determination of the red anthocyanin pigments of strawberries was desired.

During the storage of strawberry products at temperatures above 0° C., two main types of nonenzymatic color reactions occur: the red anthocyanin color is lost and secondary brown pigments develop. None of the existing methods has been found satisfactory for the quantitative determination of the actual loss of red pigment. Usually data are obtained with the Lovibond-type colorimeter (*1*, *9*), which give an indication of the degree of color deterioration in the juice when the ratio of red to yellow light absorption is calculated. Yet these measurements are not strictly quantitative or even directly related to the loss of anthocyanin. Attempts to separate the anthocyanin quantitatively from other colored materials present in the juice by chromatographic adsorption and various solvents were unsuccessful.

The pH of the medium strongly affects the light absorption of anthocyanin (*3*, *8*). For instance, when the pH of fresh strawberry juice is lowered from 3.5 to 2.0 the absorption at 500 mμ, expressed as optical density, is more than doubled. Figure 1 shows the effect of decreasing pH on the absorption at 500 mμ of pure anthocyanin pigment at constant concentration. (The anthocyanin used in these experiments was isolated in crystalline form from Dresden strawberries. Work is now in progress on the characterization of this pigment.) Further experimentation showed that this absorption change can be used for the quantitative determination of anthocyanin in strawberries and strawberry products.

Anthocyanins are amphoteric substances which form oxonium salts with mineral and organic acids. It is highly probable that in neutral or nearly neutral solutions the pigment exists in the free state (*5*) and upon acidification the equilibrium between the color base and the oxonium salt is shifted, resulting in a molecule of higher resonance and therefore exhibiting greater light absorption.

METHOD OF MEASUREMENT IN STRAWBERRY PRODUCTS

When the pH of a solution containing anthocyanins is lowered, the light absorption in the visible range increases. Under the experimental conditions used, this increase is proportional to the concentration of anthocyanin. The readings are taken at 500 mμ, since this is the highest peak of absorption in the visible range and therefore maximum sensitivity is obtained at this wave length. Furthermore, the absorption peaks of ex-

tracts of more than 300 varieties and seedlings of strawberries (*6*) were all found to be at this wave length. Since Schou (*7*) has shown that the absorption peaks of the natural anthocyanidins are at different wave lengths, it seems safe to assume that the anthocyanins in different species and varieties of strawberries are similar. At the concentrations and pH range used all solutions follow Beer's law. Since this shows that the optical density

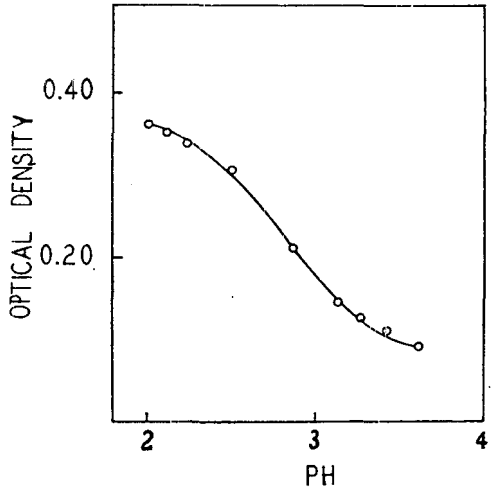

Figure 1. Effect of pH on Absorption of Strawberry Anthocyanin Chloride at Constant Concentration (1.4 Mg. %) and as Measured at 500 mμ

is proportional to the concentration of anthocyanin at a given pH, one can conclude that the absorption increase obtained on lowering the pH is also proportional to the concentration of anthocyanin. Working with purified anthocyanin solutions, the authors found this relationship to hold true in all concentrations tested (Figure 2). A pH change between 3.4 and 2.0, with purified anthocyanin, affects only the intensity of absorption and, as shown in Figure 3, the position of the peak with respect to wave length is unchanged.

The measurement consists of subtracting the optical density at 500 mμ of an anthocyanin solution at pH 3.4 from its optical density at pH 2.0, at known concentration. To facilitate the use of various colorimeters and spectrophotometers this reading is expressed as milligram per cent of Congo red which may be used conveniently as a standard. In Table I the optical density data are also given as milligram per cent of anthocyanin as well as of Congo red. However, it is the authors' opinion that the general applications of this method do not warrant the use of pure anthocyanin as a standard nor do they feel that much can be gained by expressing the results in milligram per cent of anthocyanin.

PROCEDURE

This procedure is applicable to fresh and stored strawberries, strawberry juice, and strawberry preserves.

Preparation of Material. Eighty grams of the sample are homogenized in a Waring Blendor for 0.5 minute with 100 ml. of Sorensen's citrate–hydrochloric acid buffer of pH 3.40. This mixture is then filtered through sharkskin filter paper, or centrifuged and filtered a second time through Whatman No. 2 filter paper. This is solution A, dilution factor 2.25. This step is unnecessary when preparing strawberry juice for analysis.

At times it is difficult to obtain optically clear solutions from fresh strawberries. Adding a pinch (about 25 mg.) of Pectinol 10M (obtainable from the Rohm and Haas Co., Philadelphia, Pa.) at the time of mixing in the Blendor followed by filtration through the sharkskin paper will give clear solutions. Freezing the berries solid for several hours will also eliminate the difficulties in obtaining solutions suitable for colorimetric measurements.

A known volume of solution A is diluted with the above buffer to an extent to give an optical density within the optimum range of the instrument used. If the pH of this solution is not 3.40 ± 0.05, another sample should be prepared; in the dilution small quantities of sodium citrate or citric acid should be used to give the desired final pH value. A Beckman pH meter with glass electrode has been used throughout these investigations. The dilution factor is noted for this solution B.

To a known volume of solution A sufficient dilute hydrochloric acid of such concentration as to produce a final pH of 2.00 ± 0.05 is added. The dilution should again be adjusted to give a reading at 500 mμ in the most sensitive range. This is solution C. It should be allowed to stand for an hour before the readings are taken in order to allow full color development.

Preparation of Color Standard. For a standard of color intensity Congo red (Congo Red Special, obtained from the National Aniline Division, Allied Chemical and Dye Corporation) is dissolved in 0.01 *N* sodium carbonate to give a 20 mg. % solution. The calibration curve is obtained by diluting this solution with 0.01 *N* sodium carbonate and plotting the optical density against concentration.

Measurement and Calculations. All measurements are made at 500 mμ. The per cent transmission is determined for solutions B and C, and expressed as optical density, $\log_{10} I_0/I$. In solutions where the dilution factors of B and C are not the same, the optical density readings should be equalized with respect to dilution. On subtracting the equalized optical density reading of solution B from the optical density reading of solution C the net reading is obtained. This net reading is converted to milligram per cent of Congo red equivalents, using the calibration curve; on multiplying by the total dilution factor the milligram per cent of Congo red equivalent of the original sample is obtained. The color intensity of a solution containing 0.825 mg. of Congo Red Special in 0.01 *N* sodium carbonate equals the increase in absorption which occurs when the pH of a purified strawberry anthocyanin chloride solution containing 1.0 mg. % pigment is changed from pH 3.40 to 2.00. Thus the Congo red values multiplied by 1.2 will give the anthocyanin equivalent of the observed absorption.

The data in this paper were obtained with a Beckman D-U quartz spectrophotometer using 1-cm. Corex cells. With such instruments as the Lumetron and the Coleman spectrophotometer results roughly within 10% of the Beckman spectropho-

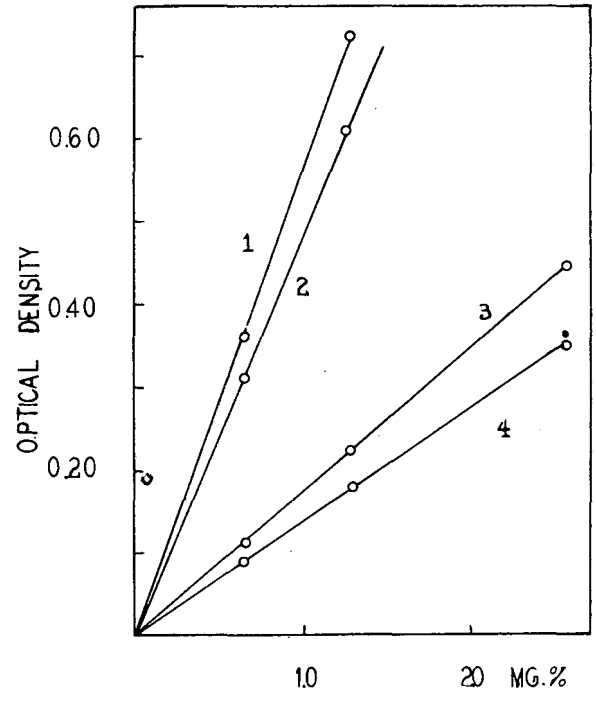

Figure 2. Effects of Concentration and pH on Absorption of Strawberry Anthocyanin Chloride at 500 mμ

1. pH 2.00. 2. pH 2.50. 3. pH 3.42. 4. pH 3.62

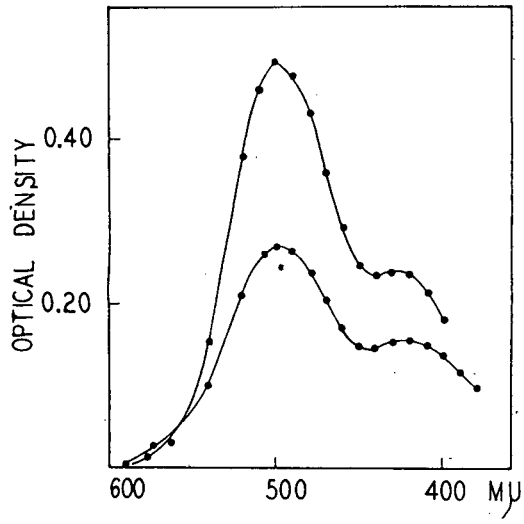

Figure 3. Absorption Curves of Strawberry Anthocyanin Chloride

pH 3.40 (1.98 mg. %) lower curve, pH 2.00 (0.84 mg. %) upper curve

tometer readings might be obtained. (Further work on this comparison of various instruments is now in progress.)

ACCURACY OF DETERMINATION

To study the accuracy of the method recovery experiments were conducted. Anthocyanin chloride dissolved in Sorensen's citrate–hydrochloric acid buffer was added to strawberry preserve extracts prepared as solution A. Heated preserves (14 weeks at 38° C.) were chosen for these experiments since in these samples the anthocyanin content is very low and the brown pigment content considerably higher than in preserves stored at 0° C. They are therefore well suited for studying the effects of brown pigments on the anthocyanin determination. The anthocyanin was diluted to the same volume as that added to the preserves and the determination made as outlined in the procedure, dilution factor 4.5. The results are given in Table I.

For the seven determinations an average deviation of 7.1% from a theoretical recovery was found. The experimental errors caused by pipetting, reproducibility of colorimetric readings, etc., vary from 2.2 to 3.1% for each series of determinations. Since operations entailing these errors are repeated several times during the determination, an average deviation of 7.1% is not excessively high. On taking samples of 20, 40, and 80 grams from the same (homogenized) strawberry preserve and diluting them all to a total volume of 360 cc., the Congo red color equivalents were 2.6, 2.8, and 2.7 mg. %, respectively, indicating the reliability of the method of extraction. It is clear from these data that the change in pH has no appreciable effect on the absorption at 500 mμ of the brown color developed during storage in strawberry preserves. Furthermore, these results indicate the absence of such interfering factors as co-pigments or effects attributable to other components of strawberry preserves.

FACTORS AFFECTING METHOD OF MEASUREMENT

Although the solutions should be optically clear, filter aids such as Celite Super-Cel must not be used, as these materials adsorb some of the pigment and produce changes in the pH of the solution. The method cannot be used in any products which contain alcohol, such as strawberry wines, since different solvents produce great changes in the absorption curves of the anthocyanin—for example, there is a shift from 500 to 520 mμ when strawberry anthocyanin is dissolved in 95% ethanol instead of water. Care must be taken to exclude heavy metals from contaminating the solutions to be analyzed. Iron in concentrations as low as 2 p.p.m. produces "discolorations" in strawberries at room temperature (*2*). The authors are not prepared as yet to state the usefulness of the method for products containing other fruits in addition to strawberries.

According to Fear and Nierenstein (*4*), measurements of anthocyanin solutions must be standardized with respect to pH, temperature, and time of contact with reagents. A temperature range of 18° to 34° C. was found to have no effect on the light absorption of the solutions used in these experiments. When the solutions are stored at 0° C., they are stable for at

Table I. Recovery of Anthocyanin Chloride Added to Strawberry Preserves

Sample	Optical Density At pH 3.40	Optical Density At pH 2.00	Difference	Congo Red Equivalent × Dilution Factor, Mg. %	Net Reading (Added Anthocyanin Chloride)	Congo Red Equivalent of Net Reading, Mg. %	Recovery, %
Anthocyanin chloride, 4 determinations	0.045 ± 0.001	0.175 ± 0.0004	0.130	1.24	...	..	...
Strawberry preserves stored 14 weeks at 38° C., 7 determinations	0.218 ± 0.007	0.240 ± 0.006	0.022	0.21	...	..	...
Strawberry preserves stored 14 weeks at 38° C., plus anthocyanin chloride, 7 determinations	0.277 ± 0.006	0.421 ± 0.009	0.145	1.38	0.126	1.18	95 ± 4.4

Table II. Anthocyanin Concentration in Strawberries and Strawberry Products

Sample	Optical Density At pH 3.40	Optical Density At pH 2.00	Optical Density Difference	Dilution Factor	Congo Red Equivalent Observed, mg. %	Congo Red Equivalent Original sample, mg. %	Anthocyanin Chloride, Mg. %	Loss in Anthocyanin, %
Frozen strawberries								
Dresden	0.234	0.772	0.538	20.25	1.140	23.1	27.9	..
Clermont	0.170	0.490	0.320	30.00	0.676	20.3	24.6	..
Pathfinder	0.149	0.482	0.333	30.00	0.702	21.1	25.5	..
Brightmore	0.200	0.586	0.386	30.00	0.815	24.5	29.6	..
Preserves								
1	0.350	0.894	0.544	9.00	1.150	10.4	12.5	..
2	0.448	0.950	0.502	4.50	1.060	4.8	5.8	..
3	0.538	1.075	0.537	2.50	1.135	2.8	3.4	..
Preserve 3								
Stored 6 weeks at 15° C.	0.272	0.530	0.258	4.50	0.545	2.5	3.0	12
Stored 21 weeks at 15° C.	0.233	0.380	0.147	4.50	0.318	1.4	1.7	50
Stored 31 weeks at 15° C.	0.236	0.348	0.112	4.50	0.240	1.1	1.3	62
Stored 1 week at 38° C.	0.490	0.940	0.450	2.50	0.950	2.4	2.9	15
Stored 3 weeks at 38° C.	0.450	0.720	0.270	2.50	0.570	1.4	1.7	50
Stored 4 weeks at 38° C.	0.408	0.620	0.212	2.50	0.450	1.0	1.2	65
Stored 8 weeks at 38° C.	0.358	0.438	0.080	2.50	0.170	0.4	0.5	85
Stored 14 weeks at 38° C.	0.217	0.240	0.023	4.50	0.049	0.2	0.2	94

least 24 hours. In the preserves tested the pigment concentration in the fruit was the same as in the surrounding jelly.

Some examples of the application of the method are shown in Table II. The total pigment contents of the four varieties of strawberries (measured in frozen samples stored at −18° C. for 6 months) were rather similar. Strawberry preserve sample 1 was unusually high in pigment content, the color intensity being about what one would expect from the results on frozen fruit, after allowing for the effects of dilution by other components of the preserve and for some color loss during manufacture. Preserve 3 was obtained from the same manufacturer as No. 1, and showed only about 27% as much red anthocyanin as No. 1.

The color difference was obvious upon visual inspection of the preserves. Sample 2 was purchased in March on the open market. Preserve 3 when stored at 15° and 38° C. showed rapid loss of pigment, especially at the higher temperature.

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Determination of Safrole in the Oil of Ocotea cymbarum

A Cryoscopic Method

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A cryoscopic method employing congealing temperatures has been developed for the determination of safrole in the oil of *Ocotea cymbarum* of commerce. A graph is included, by means of which the safrole content of the oil as determined by the mercuric chloride method, is correlated with the congealing temperature.

SAFROLE is of considerable technical importance as a flavoring material and as a raw material for the preparation of piperonal, and recently it has come into use as a starting material for the synthesis of insecticidally active materials (*7*). Prior to the recent war, Japanese camphor oil was the only available material from which safrole could be obtained in commercial quantities. It was a fortunate coincidence that a new source was made available in Brazil by the steam distillation of the oil of *Ocotea cymbarum* (*2*).

Since safrole is the only valuable constituent of the oil of *Ocotea cymbarum*, a simple and quick method for its determination was desired. A cryoscopic method appeared to be most suitable. However, for this purpose it was necessary to obtain correlation of physical constants, congealing temperature, and concentration. To determine the concentration of safrole in samples of the oil of *Ocotea cymbarum* the addition compound of safrole and mercuric chloride (*1*, *5*) yielding hydroxychloromercuri dihydrosafrole was used. The methods described in the literature (*3*, *4*) were modified as described below, to minimize the errors due to transfer and solubility of the hydroxychloromercuri dihydrosafrole in water, and thereby give more readily reproducible results. The method outlined by Huzita and Nakahara (*3*) was modified as follows:

The reaction is carried out in one vessel to avoid a troublesome transfer. The reaction is allowed to proceed in a homogeneous solution for 30 minutes, using mercuric acetate solution. Under the conditions of homogeneity the reaction readily proceeds to completion. Conversion to the chloride is then effected. Allowance is made for the solubility of hydroxychloromercuri dihydrosafrole in water at 0° C. by determining the solubility of the material at that temperature and applying a correction factor. By these means the error in general is reduced from ±1.5 to ±0.7% and readily reproducible results are obtained.

Safrole "drainings" were prepared by freezing a sample of the oil of *Ocotea cymbarum*. The congealed fraction was used as a source of safrole, which was subjected to further purification. The noncongealed fraction was taken as safrole drainings. Samples of safrole drainings, oil of *Ocotea cymbarum*, and safrole, the latter purified by freezing, were doubly distilled and center sections were taken as standards for analysis. Congealing points on each were taken, and repeated if necessary until checks within 0.1° C. were obtained. Each sample was then analyzed by the mercuric chloride method. Summarized in Table I are these data, with additional data taken to round out the information.

Table I. Properties of Analytical Standards

Sample	Congealing Point, ° C.	Safrole Content Weight %, Mercury Analysis	n_D^{20}	Specific Gravity, 25° C.
Safrole drainings	2.4	69.1 {69.2 / 69.0}	1.5299	1.0541
Oil of *Ocotea cymbarum*	8.8	91.9 {91.7 / 92.1}	1.5352	1.0843
Safrole	11.0	99.5 {99.4 / 99.7}	1.5382	1.0987

A plot of weight per cent of safrole versus the congealing points was prepared; the points in Table I fell on a straight line. To ensure conformity and check the linearity of the plot, samples differing in safrole content by approximately 1 weight %, in the range 85 to 95%, were prepared from mixtures of the safrole drainings and safrole mentioned above and their congealing points were determined. When plotted, these points fell on the straight line plotted using the standards. All the values fell within

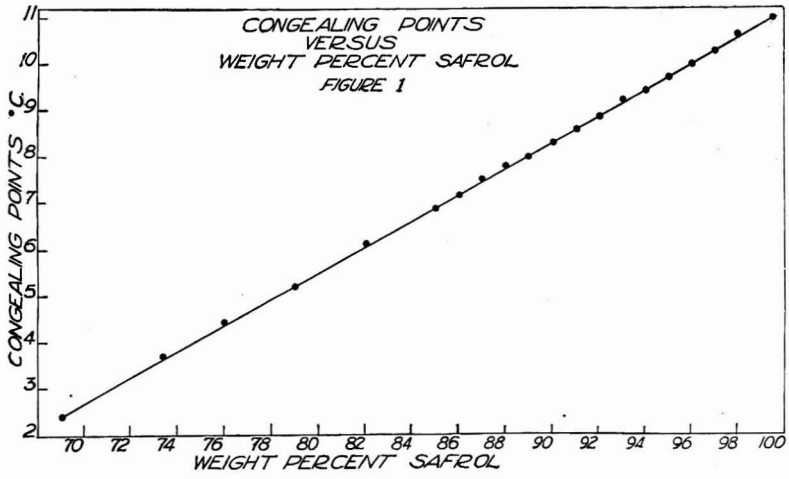

Table II. Congealing Points of Samples Varying in Safrole Content

Weight % Safrole	Congealing Point, ° C.	Weight % Safrole	Congealing Point, ° C.
69.1	2.4	90	8.3
73.3	3.7	91	8.6
76	4.4	92	8.8
79	5.2	93	9.2
82	6.1	94	9.4
85	6.9	95	9.7
86	7.2	96	10.0
87	7.5	97	10.3
88	7.8	98	10.6
89	8.0	99.5	11.0

Table III. Comparative Analyses of Oil of *Ocotea cymbarum* Samples

Crude Oil of *Ocotea cymbarum*	Congealing Point, ° C.	% Safrole from Graph	% Safrole, Mercury Analysis	% Deviation
A	8.7	91.4	92.1 {92.0, 92.2}	−0.7
B	7.2	86.0	85.4 {85.7, 85.1}	+0.6
C	8.1	89.3	88.6 {88.7, 88.4}	+0.7

0.1° C., the limit of accuracy of the experimental method used. Similar results were obtained with samples of 73, 76, 79, and 82 weight % safrole, thereby covering the range 69 to 99.5% safrole content stepwise. The data obtained are given in Table II.

A plot of the data contained in Table II is given in Figure 1.

There is a practical limitation in extending the congealing point analysis much below 0° C. due to difficulty in reproducing readings to 0.1° C. The method can be used in such cases if a known amount of analyzed safrole is added to raise the point above 0° C. The mercuric chloride method can also be used to advantage in such cases.

The congealing points of several samples of crude oil of *Ocotea cymbarum* were determined and from the graph in Figure 1 the safrole content was estimated. Each sample was then analyzed by the mercuric chloride method for safrole content. A comparison of the results obtained is given in Table III.

A sample of 60.0% safrole by weight, the remainder cymene, prepared from the 99.5% safrole standard, was analyzed by the mercuric chloride method to check its validity. The safrole content found in duplicate analyses was 60.2 and 60.6%, averaging 60.4%, a deviation of +0.4% in this instance.

ANALYTICAL PROCEDURES FOR SAFROLE DETERMINATION

Weigh, by difference, to the nearest mg., 0.5 to 0.7 gram of safrole or safrole-containing material, into a 800-ml. beaker. Add about 7 ml. of distilled acetone and stir the mixture with a thermometer (keep the thermometer in the same beaker henceforth). Add dropwise, while stirring, 6 ml. of 35% mercuric acetate reagent solution [35 grams of $Hg(OCOCH_3)_2$ in a 100-ml. volumetric flask. Make up to mark with distilled water after adding 5 ml. of glacial acetic acid to stabilize the solution]. Stir the mixture, and let it stand for 20 to 30 minutes. Add 400 ml. of distilled water followed by 4 ml. of 32% (saturated) reagent sodium chloride solution. Heat the solution while stirring with the thermometer until the thermometer reads 98° to 100° C. Filter the solution hot through a fluted filter paper into a 1-liter beaker. Wash the filter paper thoroughly with four to six 50-ml. portions of hot water; rinse the beaker each time, allowing each wash to drain before adding the next.

Insert the thermometer in the beaker, cover with a watch glass, and chill to 0° C.; do not allow to stand overnight, because of the formation of ice. Chill the Gooch crucible and flask to be used for filtration. Filter the solution by suction as near as possible to 0° C. Wash the beaker and precipitate with three 35-ml. portions of distilled water at 0° C., and air-dry by suction while the Gooch crucible is covered with filter paper. If oil of *Ocotea cymbarum* or safrole drainings are used, wash the precipitate three times with 35-ml. portions of pure, dry, low boiling (30° to 60°) petroleum ether. Measure the final volume of the aqueous filtrate for the calculation of the correction factor. Dry the crucible, covered with a watch glass or filter paper, in a vacuum desiccator over sulfuric acid and potassium hydroxide in separate beakers, and weigh.

$$\% \text{ safrole} = \frac{(\text{weight of ppt.} + \text{correction}) \times 0.3904 \times 100}{\text{weight of safrole sample}}$$

$$\text{Correction} = \text{ml. of filtrate} \times 0.00021$$

Solubility of Hydroxychloromercuri Dihydrosafrole at 0° C. Weigh out about 2 grams, to the nearest mg., of purified (recrystallized from water) hydroxychloromercuri dihydrosafrole and add to a 1-liter beaker followed by 700 ml. of distilled water. Heat the solution to near boiling while stirring. Cover the beaker and chill to 0° C. Chill the Gooch filter assembly, filter the precipitate, dry the Gooch crucible in a vacuum desiccator over sulfuric acid and potassium hydroxide in separate beakers, and weigh. Measure the volume of the filtrate. From the weight difference and volume of filtrate calculate the solubility of hydroxychloromercuri dihydrosafrole in water at 0° C. Duplicate series of determinations gave the values 0.00021, 0.00023; 0.00021, 0.00023 gram per ml. at 0° C. The value 0.00021 was taken as the more probable at 0° C.

Congealing Temperatures (*6*). Place about 10 cc. of the liquid to be tested in a dry test tube about 20 mm. in internal diameter, and cool in water or other suitable medium, the temperature of which is about 5° C. below the supposed congealing point of the liquid. Then promptly suspend the test tube through a stopper, or by some other suitable arrangement, to at least three fourths of its length in a larger test tube or narrow bottle, and gently stir the liquid with a standardized thermometer until it begins to solidify. Congealing may frequently be induced by rubbing the inner walls of the test tube with the thermometer. Discontinue the stirring, and note the rise in temperature every 5 to 10 seconds. The highest temperature remaining constant for about 1 minute is the congealing temperature. A repeat determination should check to 0.1° C.

ACKNOWLEDGMENT

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Adiabatic Calorimeter

For Specific Heat Determinations over the Temperature Range 25° to 300° C.

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Hercules Powder Company, Wilmington 99, Del.

An adiabatic calorimeter for the measurement of the specific heat of solids and liquids over the temperature range 25° to 300° C. has been constructed. This instrument was calibrated using vitreous silica as standard substance. Results on a series of rosin esters are reported, which show a precision of about ±0.5%

NEED has frequently arisen for specific heat data on solids and liquids for use in thermochemical calculations and in engineering design. Such data having an accuracy of 1% were required over various ranges between room temperature and 300° C.

The fact that the calorimeter was to be used primarily for rosin and its derivatives imposed serious restrictions in the choice of materials of construction and of the design. The vessel must withstand a pressure of several atmospheres, due largely to compression of the air in the vapor space, although in certain cases

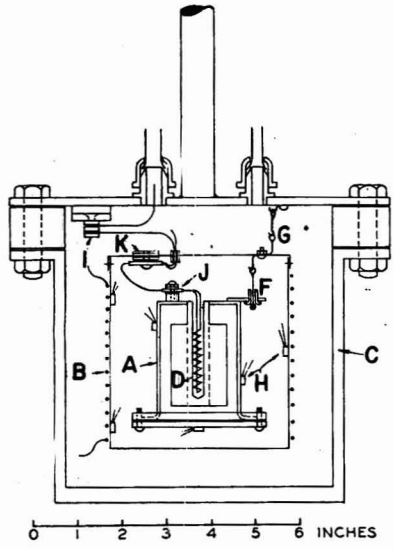

Figure 1. Schematic Diagram of Calorimeter

the vapor pressure of the sample may be appreciable at higher temperatures. The accuracy should be 1% even with materials of low thermal conductivity, necessitating an adiabatic-type instrument. In addition, the calorimeter must be resistant to corrosion by the materials studied, reasonably rugged, and easy to clean and charge. These requirements indicated that the calorimeter vessel itself must be made of or at least be plated with a noble metal.

No calorimeter filling these requirements was commercially available and a survey of the recent literature disclosed little in the way of calorimetric studies in this particular temperature range, although many investigations have been carried out at lower and higher temperatures. The "dropping" calorimeter of Southard (*6*) has been used extensively for specific heat measurements at high temperatures but is not suited to measurements at or near room temperature. The Dewar flask types of calorimeter used for studies of heats of solution, dilution, wetting of solids, etc. (*1, 4*), are not adapted to measurements at higher temperatures where the vapor pressure of the sample may be appreciable. Sturtevant (*7*) has designed an adiabatic calorimeter for the measurement of heats of solution and of mutarotation of sugars. A number of the constructional features of his instrument served as a basis for the design of the present calorimeter.

DETAILS OF CONSTRUCTION

The apparatus shown in Figures 1 and 2 basically consists of a sterling silver calorimeter bomb, *A*, suspended in a silver shield can, *B*, which is in turn hung from the lid of the main brass can, *C*. The whole assembly is placed in a constant-temperature oil bath and evacuated. By employing solid construction of sterling silver for the calorimeter bomb, a reasonable compromise with strength, economy, and durability was achieved.

In the center of the calorimeter is a heavy well, *D*, containing the heating element. The well, extending approximately nine tenths of the length of the bomb, has an inside diameter of 0.25 inch. Twelve fins, $^1/_{16}$ inch thick and 2 inches (5 cm.) long, radiate from this well. No point inside this bomb is more than 1 cm. away from a silver surface continuous with the heating well. The mouth of the can was turned out and machined flat in order to seal against the lid with a lead ring gasket. The inside

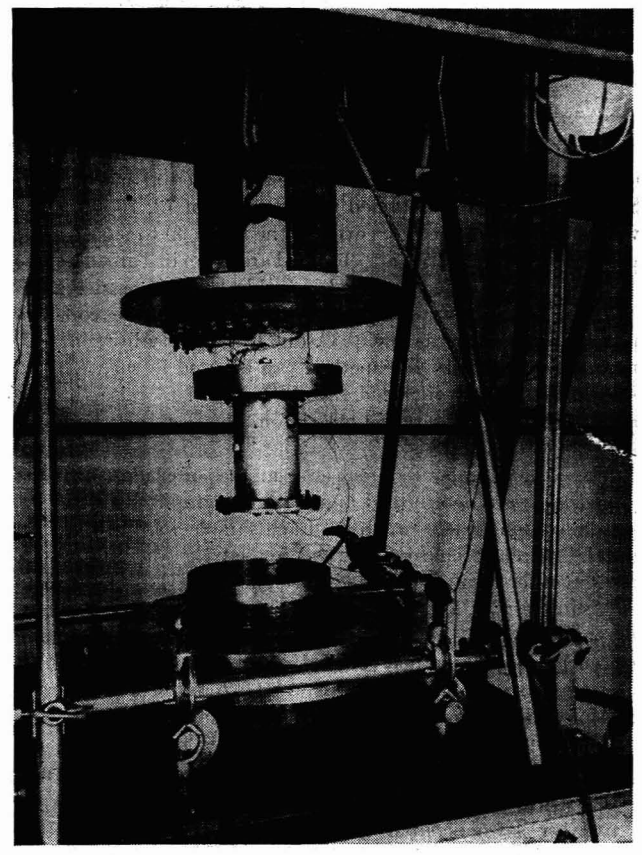

Figure 2. Photograph of Calorimeter

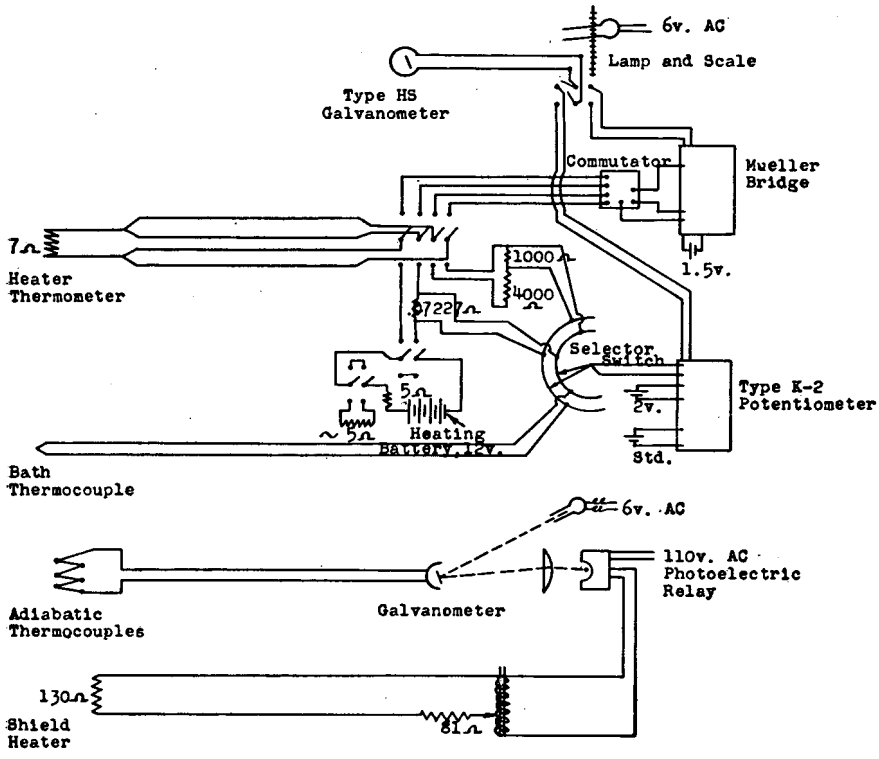

Figure 3. Wiring Diagram

diameter of the calorimeter is 2 inches, the wall thickness $^1/_{16}$ inch, and the total capacity about 100 ml. On top of the calorimeter is soldered a small silver block, *J*, to serve as a "thermal binding post." Three short arms extend from the top of the calorimeter to support the glass-insulated wire hooks by which it is suspended (one shown at *F*). Fully equipped, the calorimeter vessel weighs 654 grams.

The adiabatic shield is a sterling silver can, 4 inches in diameter and 4.5 inches high, which opens at the top with a friction cap lid made secure with pins and slots. The lid of this can supports the calorimeter and is itself hung from the lid of the brass can with three steel hooks, *G*. The heating wires for the shield, 30-gage Nichrome encased in woven glass insulation, are wrapped around the outside of the shield and held in place with Bakelite varnish.

The adiabaticity is controlled by copper-advance thermocouples, three junctions each on the shield and calorimeter (two shown at *H*). The individual thermocouples are insulated with Bakelite varnish and placed in the center of small clips which have the shape of half a cylinder. The free space in these clips is packed tightly with aluminum foil, which ensures good thermal contact. The thermocouple leads are carried out through the lid of the shield and connected in series, couples from vessel and shield alternately, at the insulated binding post block, *I*, mounted on the lid to the main can. The two terminal copper leads for the thermel are connected to wires going out of the can directly to a Leeds & Northrup wall-type galvanometer (Catalog No. 2239-C, sensitivity 1.1μ volts per mm. at 1 meter). A photoelectric relay controls the current to the shield heater. In order to maintain control, it was necessary to use a large (4-inch) condensing lens focused on the photocell. The controlling line is a strip of paper along one edge of the lens. With this arrangement, the shield is heated when the light spot is anywhere on the lens. The relative temperatures of the calorimeter and shield may be changed by adjustment of the rest point of the galvanometer. Movement of the light spot across the lens represents a relative change of about 1.5° C. between the shield and calorimeter. During normal operation the adiabatic control is within 0.1° C. The complete wiring diagram is shown in Figure 3.

A combination heater–resistance thermometer is located in the well in the calorimeter. This is a coil of B. and S. No. 38 platinum wire wound noninductively on a mica cross 2 inches long. Thermal contact with the well is made by packing it tightly with powdered magnesia. The top portion of the well is packed with asbestos. Two lead wires for the heater coil, B. and S. No. 22 platinum, extend from the well to two silver disks at the "thermal binding post," *J*, a distance of about 1 inch. These disks are clamped to the binding post block through washers insulated electrically with mica. The purpose of this device is to keep the temperature of the heater leads close to the calorimeter temperature. From the other side of the disks two B. and S. No. 20 copper wires, about 2 inches long, connect to two other and larger silver disks at *K*, the thermal binding posts on the shield lid. At the other side of each disk, two B. and S. No. 26 copper wires extend to the binding posts on the main can, *I*. Thus the four-lead system begins at the shield binding post. Everything inside the shield is part of the resistance thermometer. The two "thermal binding posts" serve to keep the gradient across the lead wires between the calorimeter and shield negligible, whether it be due to the high temperature of the coil during the heating period or to the temperature difference between the bath and the calorimeter. The initial and final calorimeter temperatures are calculated from the resistance of the thermometer as measured with a Leeds & Northrup Type G-1 Mueller bridge. The calibration is described below.

The heating wattage for the calorimeter is measured with a Leeds & Northrup Type K-2 potentiometer—the current by the potential developed across a 0.07227-ohm series resistor and the potential as divided by two Leeds & Northrup precision resistors, 1000 and 4000 ohms. The series resistor is made of B. and S. No. 14 Chromel wire and kept in a jar of oil at room temperature (25° to 30° C.). Its resistance was determined at 27° C. with the Mueller bridge. The voltage divider was checked with the K-2 potentiometer for division of 1.5 volts, the factor being 5.0005. Time was measured on a large electric wall clock with a sweep second hand. Since the heating periods extend over 10 to 15 minutes, measurements to ± 0.5 second have an accuracy of 0.1%. This is the limiting error in the energy measurements.

CALIBRATION

The specific heat of an unknown material is calculated from the observed temperature rise of the calorimeter vessel and its contents when a measured amount of electrical energy is supplied to the bomb. It was necessary, therefore, to determine the temperature equation for the resistance heater–thermometer and also the heat capacity of the empty bomb. The resistance heater–thermometer was calibrated in terms of a platinum resistance thermometer, certified by the National Bureau of Standards, using a thermocouple made of No. 30 B. and S. copper and advance wire, having a 0° C. reference junction, as a secondary standard. It was found that the temperature-resistance relationship followed the equation

$$t = -233.504 + 36.508r + 0.62202r^2 - 0.00972r^3 \qquad (1)$$

where t is the temperature in degrees Centigrade and r is the resistance in ohms. For the usual heating range of 8° C. errors in Δt due to the use of this equation are in no case greater than 0.4%.

The heat capacity of the calorimeter was determined with the calorimeter empty and loaded with vitreous silica (Figure 4). The values obtained by heating the empty calorimeter were used only for comparison, however, since they did not agree with those obtained with the calorimeter charged with substances of known specific heat. Sturtevant (*7*) and White (*8*) have noted that empty calorimeters cannot be calibrated directly. The errors in this method are probably due to unusual temperature

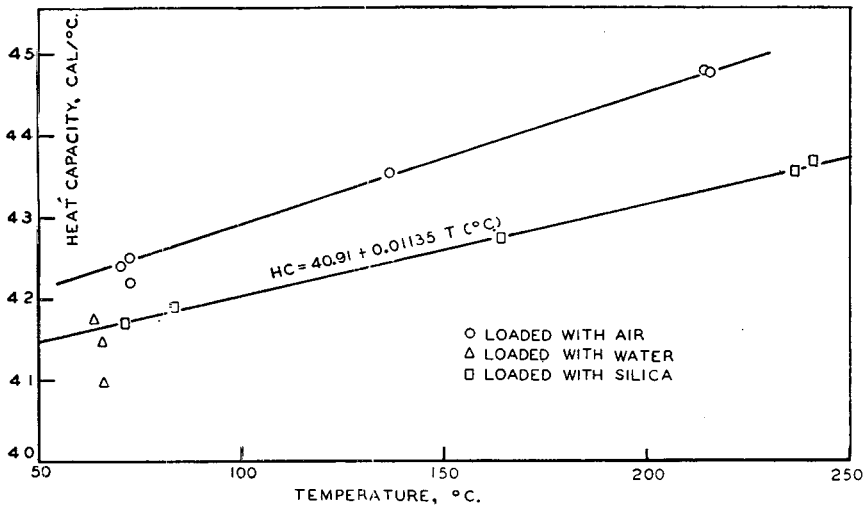

Figure 4. Heat Capacity of Empty Calorimeter

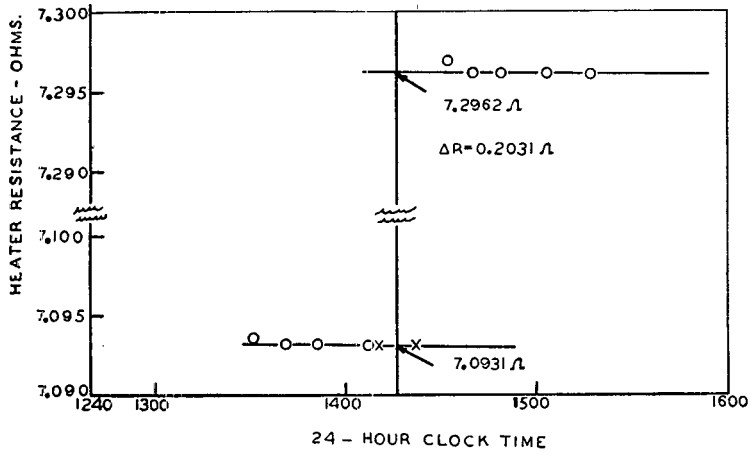

Figure 5. Resistance-Time Curve for Sample Determination

gradients in the vessel and abnormally short heating periods. Vitreous silica made from crushed Vitreosil (Corning Glass Company) rods was used as the calibrating standard. White's data for the specific heat of vitreous silica as reported in the International Critical Tables (*2*) were used. The values for the heat capacity of the calorimeter obtained using this calibrating substance followed the equation

$$\text{Heat capacity} = 40.91 + 0.01135t \ (^\circ \text{C.}) \qquad (2)$$

Silica was a very suitable calibrating substance, since both the total and the rate of energy input were approximately the same in calibration as in the determination of the heat capacity of the materials to be studied. As an additional check, the heat capacity of the calorimeter was determined when loaded with water. The specific heat of water was taken from the International Critical Tables (*3*). As shown in Figure 4, two of the three determinations are well within 0.5% of the curve based on silica. No assignable cause was found for the low point. In the calculation of the specific heat of unknown materials, the values for the heat capacity of the calorimeter based on the silica data were used, since they were obtained using approximately the same heating conditions. If determinations requiring greatly different heating conditions are to be made, it is planned to recalibrate the calorimeter under these new conditions, employing a standard substance having thermal properties similar to the unknown. No evidence of significant systematic errors was found on varying the temperature range between 6° and 12° C. or on reducing the weight of the charge by 30%.

EXPERIMENTAL

One determination of the specific heat of Abalyn (methyl ester of rosin) is given below in detail to describe the experimental procedures. The specific heat of this material was determined between 50° and 200° C.

The calorimeter was loaded with 73.3 grams of Lot HL-17 Abalyn, sealed, and assembled. The whole apparatus was lowered into the oil bath, which was regulated at 52° C. After evacuation of the can to about 0.1 mm. of mercury, the calorimeter was warmed to a temperature about 0.5° C. warmer than the bath. Under these conditions the adiabatic shield operates with less than 1 watt of power.

Readings of the heater resistance were taken about every 10 minutes for 45 minutes (see Figure 5). When equilibrium was established, the adiabatic control circuit was quickly displaced to maintain the shield about 0.1° C. warmer than the calorimeter, and the heating period begun immediately. This empirical adjustment was determined by experience to keep the thermal binding posts on the shield lid and calorimeter at the same temperature when the calorimeter is 8° C. hotter than the bath.

During the heating period (12 minutes ±0.5 second), readings corresponding to the current and potential were taken at intervals of 1 minute. The values of current and potential changed less than 1% during the heating period. The adiabatic control was automatic throughout the run. Measurements of the heater resistance were resumed 10 minutes after the end of the heating period and were continued for an hour.

The initial and final heater resistances were determined from Figure 5 by the method described by Ostwald-Luther (*5*). These data, and the corresponding temperatures calculated by Equation 1, are:

Initial resistance 7.0931 Ω ≈ 53.277° C.
Final resistance 7.2962 Ω ≈ 62.204° C.
Change 0.2031 Ω ≈ 8.927° C.

The average potential reading was 1.2535 volts. Since the voltage divider factor is 5.000, the true heating voltage was 6.2675 volts. The average current reading was 0.04405 volt developed across a 0.07227 Ω series resistor; hence the total current was 0.04405/0.07227 or 0.6095 ampere. The current loss to the 5000-ohm voltage divider = 6.2675/5000 = 0.0013 ampere. Hence the heating current is 0.6082 ampere for a 12-minute heating period.

Table I. Specific Heats

Substance	Range, °C.	*A*	*B*	*C*
Abalyn[a] (methyl ester of rosin)	50–200	0.385	0.00079	.....
Hercolyn[a] (hydrogenated methyl ester of rosin)	50–150	0.418	0.00014	0.0000032
Staybelite[a] Ester 10 (glycerol ester of hydrogenated rosin)	50–150	0.397	0.00052	0.0000017
Flexalyn[a] C (glycol ester of rosin)	50–150	0.384	0.00084	.....
Pentalyn[a] A (pentaerythritol ester of rosin)	50–250	0.368	0.00094	−0.00000040

[a] Registered U. S. Patent Office by Hercules Powder Co.

$$\text{Kilocalories} = \frac{6.2675 \times 0.6082 \times 12 \times 0.8600}{60} = 0.6557$$

Total heat capacity = 655.7/8.927 = 73.45 cal. per ° C.
Heat capacity of calorimeter (Equation 2) = 41.57 cal. per ° C.
Heat capacity of contents = 31.88 cal. per ° C.

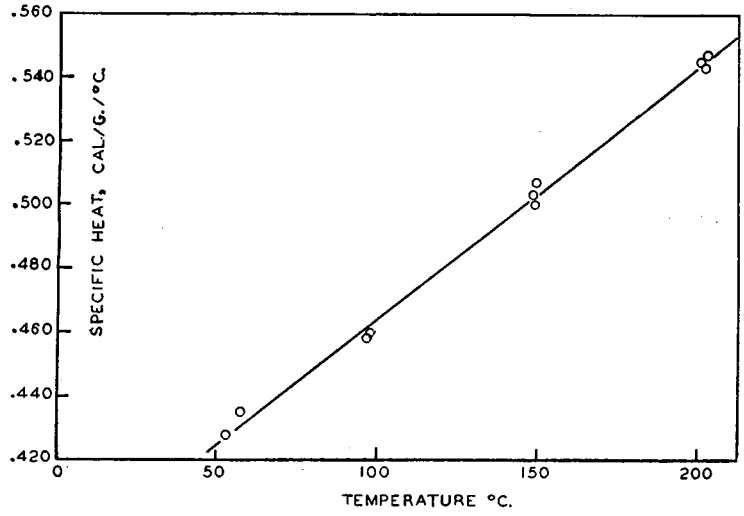

Figure 6. Specific Heat of Abalyn as a Function of Temperature

Specific heat of Abalyn at 57.8° C. (mid-temperature of heating range) = 31.88/73.3 = 0.435 cal. per gram per ° C.

The complete temperature–specific heat curve of Abalyn is shown in Figure 6.

The equations for the specific heats of several resinous materials are given in Table I. For each substance, at least two determinations at each temperature were made at 50° C. intervals over the range indicated. The results for the particular samples studied are given below, where the specific heat (cal./gram/° C.) equals $A + Bt(° C.) + Ct^2$:

CONCLUSION

An adiabatic calorimeter of moderate accuracy (1%) for the determination of the specific heats of solids and liquids over the temperature range 25° to 300° C. has been constructed and calibrated. It has been used to measure the specific heats of a number of rosin esters.

ACKNOWLEDGMENT

The writers wish to express their thanks for the many helpful suggestions made by W. H. Markwood, Jr., of this laboratory.

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Colorimetric Determination of Traces of Gold

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Trace quantities of gold can be isolated by precipitation with stannous chloride, with tellurium as collector, and determined colorimetrically or photometrically with *p*-diethylaminobenzylidenerhodanine as reagent. As little as 0.1 p.p.m. can be determined when a 1-gram sample is taken. Large amounts of iron, copper, lead, and arsenic do not interfere.

THE method for gold described here is intermediate in absolute sensitivity between the usual fire assay method and the highly sensitive method used by Haber and his associates (*2*, *3*) to determine gold in sea and river water. The limit of the fire assay method may be set at 1 or 2 micrograms, the limit of precision of the ordinary microchemical balance, although usually the weighing is made only to the nearest 5 or 10 micrograms. Haber's method, which is based on the microscopical measurement of the diameter of the gold bead, permits the detection of 0.001 microgram of gold. The colorimetric procedure can be used to detect 0.1 microgram of gold in 5 ml. of solution if the cross-sectional area of the tube is 1 sq. cm. The method of isolation used in conjunction with the colorimetric determination allows at least a 1-gram sample to be taken, so that 0.1 p.p.m. of gold can generally be detected.

The absolute sensitivity of the colorimetric method is approximately the same as that of the spectrographic method, which has been used by various workers in recent years to determine minute quantities of gold after concentration by the fire assay procedure. Scobie (*7*) was able to determine as little as 15 p.p.m. of gold in a 100-mg. silver bead with an average deviation of about 5%; this corresponds to the determination of 1.5 micrograms of gold with an average deviation of less than 0.1 microgram. Seath and Beamish (*8*) could detect 10 p.p.m. of gold in a 10-mg. silver bead, or 0.1 microgram, spectrographically. Since the fire assay technique also can be applied for the concentration of gold prior to its colorimetric determination, it seems that the relative sensitivity of the spectrographic and colorimetric procedures is much the same. Spectrography has the advantage of speed and perhaps accuracy; colorimetry has the advantage of apparative simplicity.

ISOLATION OF GOLD

Many procedures have been described for the isolation of gold in the wet way. These all involve the use of a collector such as mercury, mercurous chloride, or other mercury compound, which is usually precipitated in the sample solution by the addition of a strong reducing agent such as stannous chloride, zinc, or magnesium. In the present work, elemental tellurium formed by the reduction of quadrivalent tellurium by stannous chloride was found to be a very satisfactory gathering agent. Pollard (*5*) made use of tellurium as collector in a volumetric method for gold. However, he used sulfur dioxide for the reduction, a reagent which is less suitable than stannous chloride when iron and other reducible substances are present in the sample. Tellurium has been used with good results in the isolation of palladium (*6*, p. 355)

and it was to be expected that it would function equally well for gold.

Tellurium is especially suitable in the colorimetric method because it does not have to be removed before the final determination. Moreover, it is so effective that only a small amount need be used (0.2 mg. in 50 to 100 ml.). The latter point is a factor of importance because foreign substances may be carried down to a greater or less extent by a collector and possibly lead to difficulties in the final colorimetric determination. This danger is obviated or at least greatly reduced if the amount of collector used is so small that the amount of contamination is negligible. As little as 0.2 or 0.3 microgram of gold can be isolated and satisfactorily determined in the presence of 0.5 gram of iron, copper, lead, and arsenic. Silver is coprecipitated with tellurium and if present in sufficient quantity is finally filtered off as silver chloride.

COLORIMETRIC AND PHOTOMETRIC DETERMINATION

p-Diethylaminobenzylidenerhodanine was chosen as the most suitable reagent for the determination of minimal quantities of gold. This reagent (actually the methyl compound) was used by Holzer and Feigl for the detection of gold. Merejkovsky (*4*) applied it in the determination of gold in biological material; his procedure is different from that described below. Other possible gold reagents are organic compounds which are oxidized to strongly colored products by auric gold. *o*-Tolidine (*1*) and other compounds (*6*, p. 255) have been used in this way and are capable of great sensitivity, but, generally speaking, are less specific than the rhodanine reagent. These reagents have not been investigated in the present work, but doubtless they can be used to determine gold after its isolation by the general procedure described below.

When an alcoholic solution of diethylaminobenzylidenerhodanine is added to a weakly acidic auric gold solution, a very slightly soluble red-violet product is formed, which remains in colloidal dispersion for a long time if the gold solution is dilute. The reagent itself has a pale yellow color in acid medium. The nature of the colored product has not been definitely established, but by analogy with the slightly soluble compounds that the reagent gives with silver and cuprous salts it may be supposed that the precipitate is at least partly composed of the rhodanine complex of aurous gold. This conclusion seems to be borne out by the ratio in which the rhodanine reacts with auric gold; slightly more than 1 mole of reagent reacts with 1 mole of trivalent gold. Strong oxidizing agents such as free bromine and chlorine in sufficient concentration can give a reaction similar to that of gold; a slightly soluble red-violet product is formed. This oxidation product of the reagent is soluble in carbon tetrachloride, in contrast to the gold precipitate which is virtually insoluble. The gold precipitate is soluble in chloroform to a considerable extent, less so in alcohol.

Ferric iron produces a brownish coloration with the rhodanine reagent. Since there is a slight possibility that a minute amount of iron may be carried down with the tellurium precipitate, a small quantity of sodium fluoride is added to the final solution to prevent the possibility of error from this source. The amount of fluoride used is sufficient to prevent the reaction of at least 0.1 mg. of ferric oxide, an amount which will not be present even if tellurium is precipitated from a solution containing as much as 0.5 gram of ferric iron.

The acidity of the solution in which the reaction is carried out is the most important factor in the rhodanine colorimetric method. The sensitivity decreases as the mineral acid concentration is increased. A solution of specified acidity is obtained by adding an accurately measured volume of dilute hydrochloric acid to the residue produced by evaporating the aqua regia solution of the tellurium precipitate containing the coprecipitated gold. In the evaporation care must be taken to prevent the thermal decomposition of chloroauric acid. It has been considered advisable to moisten the first evaporation residue with a minute amount of aqua regia and allow this to evaporate at room temperature.

The precision of the photometric determination of gold, without previous separation, was investigated at two acidities—0.075 and 0.12 *M* (calculated) hydrochloric acid solution—in the presence of 0.013 *M* sodium fluoride. In each case the concentration of the rhodanine reagent was 0.0033%.

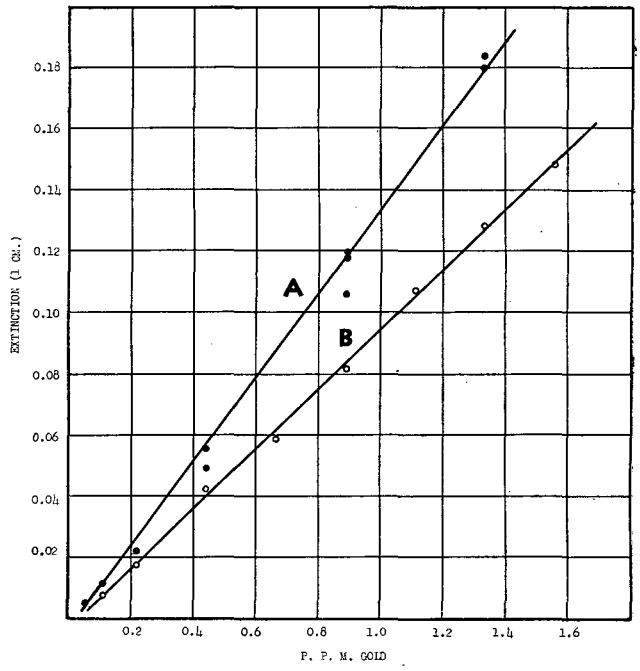

Figure 1. Concentration-Extinction Curves of Gold–*p*-Diethylaminobenzylidenerhodanine Suspensions

Green filter, Cenco No. 2. *A*. In 0.075 *M* hydrochloric acid. *B*. In 0.12 *M* hydrochloric acid

The experiments were carried out by transferring from 1 to 7 micrograms of gold as chloroauric acid to small beakers, and evaporating to dryness after addition of 2 ml. of aqua regia and a few milliliters of water together with 0.2 mg. of tellurium as the tetrachloride. The residue was moistened with 0.01 ml. of aqua regia and, after the latter had been allowed to evaporate at room temperature, was dissolved in 0.20 ml. (or 0.30 ml.) of 2.0 *M* hydrochloric acid. The solution was transferred with water to a 5-ml. glass-stoppered tube, and 0.25 ml. of 1% sodium fluoride solution was added, followed by water to make the volume about 4 ml. After mixing, 0.30 ml. of 0.05% alcoholic diethylaminobenzylidenerhodanine was added, and the contents of the tube were mixed by inverting three times, and finally diluted to the mark at 4.5 ml. The transmittancy of the solution was measured after 10 minutes in a 1-cm. cell of a photoelectric photometer with a green filter (Cenco No. 2). The photometer used allowed extinction values to be obtained with a reproducibility of approximately 0.001. The amount of gold was found by reference to a standard curve (Figure 1) which had been constructed by finding the extinctions of gold suspensions prepared as described, except that the evaporation was not made and tellurium was not added, but known amounts of chloroauric acid with the proper concentration of acid were treated directly with the rhodanine reagent.

Table I indicates that the reproducibility is better at the higher acidity, no doubt because the slower formation of the gold precipitate renders the exact conditions of mixing of less importance. Moreover, substantially the same results are obtained whether or not the gold solution is evaporated with aqua regia or tellurium is present. The standard curve can therefore be established by taking known amounts of gold directly, omitting the evaporation with aqua regia. Although the reproducibility of the color is fairly satisfactory at 0.12 *M* acidity, it is probably not equal

Table I. Precision of Rhodanine Method for Gold without Previous Separation

Gold Taken	Gold Found 0.075 *M* HCl	0.12 *M* HCl
γ	γ	γ
1	1.05	...
2	1.6, 1.9, 2.35	2.05
2.5	2.55	...
4	...	3.9, 3.8
5	4.5, 4.8	4.9
6	5.7	5.85
7	...	7.2

Table II. Photometric Determination of Gold after Coprecipitation with Tellurium

Gold Taken	Gold Found 0.075 *M* HCl	0.12 *M* HCl
γ	γ	γ
0.5	...	0.6
1.0	0.9	0.95
2.0	2.05, 1.75	1.95
2.5[a]	...	2.55
2.5[b]	...	2.4
3.0	2.9	2.85
4.0	...	3.9
5.0	4.7	5.0
7.0	7.75	...
8.0	...	8.3

[a] 1.1 mg. of Ag present.
[b] 500 mg. of ferric iron (as sulfate) present.

to that which could be obtained if the colored product were soluble.

The full color intensity of the suspensions is attained in 1 or 2 minutes (more rapidly at the lower than at the higher acidity), after which it decreases. The rate of fading of the color is illustrated by the following data obtained for a 1.1 p.p.m. gold suspension in 0.12 *M* hydrochloric acid solution in the presence of fluoride (extinction *vs.* time in minutes after mixing): 3 minutes, 0.113; 5, 0.112; 12, 0.107; 18, 0.104; 25, 0.101; 30, 0.100. It is clear that the extinction reading must be made a definite time after the addition of the rhodanine reagent. In the preliminary investigation of the rhodanine method (*6*, p. 252), the optical density of the suspensions was found to increase slowly after mixing, and to reach a more or less constant value after about 15 minutes. The conditions in the earlier experiments were not the same as here, since fluoride was absent and the rhodanine concentration was lower.

The concentration-extinction curve is a straight line up to at least 2 p.p.m. of gold (beyond which the investigation was not carried), but it does not pass through the origin (extinction of the blank solution subtracted). The photometric procedure can be used to determine as little as 0.5 microgram of gold in a final volume of 4 or 5 ml. with a 1-cm. cell. Below this amount visual comparison is applied. In both 0.075 and 0.12 *M* acid medium, 0.1 microgram of gold gives a color distinctly different from the blank under the conditions of the Procedure below. The limit of detectability may be taken equal to 0.05 microgram of gold. An acidity of 0.12 *M* is recommended for general use, but when the quantity of gold present is likely to be close to 0.1 microgram the lower acidity of 0.075 *M* is to be preferred because of the slightly greater sensitivity.

DETERMINATION OF GOLD AFTER ISOLATION

The results obtained in the photometric determination of gold at two acidities after coprecipitation with tellurium are given in Table II. The precipitations were made in a volume of approximately 50 ml. according to the directions given below. Again the precision is better at 0.12 *M* acidity than at 0.075 *M*. At the higher acidity the average error is 3% in the range 1 to 8 micrograms of gold. The standard curve from which these results were derived was set up by direct use of a standard gold solution without the addition of tellurium or evaporation with aqua regia. As much as a week elapsed between the time the curve was established and some of the determinations were run.

Table III contains the results of the visual determination of 0.2 to 0.5 microgram of gold after coprecipitation with tellurium. The acidity of the final solution was 0.075 *M*. The effect of silver, iron, copper, lead, and arsenic was chiefly tested with these small quantities of gold, since any disturbance would be more pronounced under these conditions. The concentration of silver in a saturated silver chloride solution under the conditions of the determination is too small to give a color. Fifty micrograms of mercury as mercuric chloride gave no color. Twenty micrograms of thallium evaporated with aqua regia likewise were without effect. However, palladium reacts even more sensitively than gold with the rhodanine reagent (*6*, p. 354). Small quantities of palladium, up to 3 micrograms in a final volume of 5 ml., can be made harmless with dimethylglyoxime. The acidified sample solution (see Procedure) is treated with 0.05 ml. of 1% alcoholic dimethylglyoxime solution, allowed to stand 10 minutes, and then treated with rhodanine reagent. Under these conditions no coloration is produced by 3 micrograms of palladium. The gold reaction is not affected by dimethylglyoxime. A determination of 0.5 microgram of gold in the presence of 3 micrograms of palladium gave the value 0.5 microgram when dimethylglyoxime was added.

Platinum (IV) in small amounts has little effect (*6*, p. 253). Small quantities (mostly 1 to 2 mg.) of molybdenum, titanium, tungsten, uranium, vanadium, zirconium, bismuth, and germanium were carried through the procedure but yielded no color (a precipitate of tungstic acid in the final solution was removed by filtration).

Table III. Determination of Gold with Diethylaminobenzylidenerhodanine by Visual Comparison after Coprecipitation with Tellurium

Addition	Gold Taken	Gold Found
	γ	γ
None	0	0.0
	0.3	0.4
0.2 mg. Ag	0	0.0
0.5 mg. Ag	0.5	0.5
0.5 gram Fe (as ferric sulfate)	0	0.0
	0.2	0.2
	0.3	0.3
	0.5	0.5
0.5 gram Fe (as ferric sulfate), 0.005 mg. Ag	0.5	0.55
0.5 gram Fe (as ferric sulfate), 0.02 mg. Ag	0.2	0.2
0.5 gram Fe (as ferric sulfate), 0.2 mg. Ag	0.2	0.25
0.5 gram Cu (as cupric sulfate)	0	0.0
	0.3	0.25
0.6 gram Pb (as nitrate)[a]	0	0.0
	0.3	0.35
0.5 gram As_2O_3, 0.05 gram Sb (III)[b]	0.3	0.25

[a] Total volume ca. 90 ml. Some lead chloride precipitated; dissolved by washing tellurium precipitate with 25 ml. of hot 1 to 4 HCl.
[b] Volume 70 ml. at time of precipitation.

Special Apparatus. Flat-bottomed glass-stoppered tubes, of capacity slightly greater than 5 ml., with approximate dimensions 1.2 × 8 cm. They should be marked for a volume of 4.5 or 5 ml.

Apparatus for suction filtration consists of a small wide-mouthed bell jar (which can be made by cutting an ordinary 250-ml. wide-mouthed bottle about 10 cm. from the top and grinding the cut edge smooth) resting on a plate of ground glass. It is fitted with a two-hole rubber stopper provided with a small funnel in which the filter crucible is placed. A rubber ring which can be made from a slice of a rubber stopper is used to make an air-tight connection between crucible and funnel. The ring should be of such size that it fits some distance above the bottom of the crucible to prevent contact between rubber and solution.

The filter photometer or spectrophotometer should permit measurements with not more than 4 or 5 ml. of solution. Extinction measurements should be reproducible to 0.001.

Special Solutions. *p*-Diethylaminobenzylidenerhodanine, 0.05

gram in 100 ml. of absolute ethyl alcohol. The solid dissolves slowly. The solution is stable.

Stannous chloride, 20 grams of the dihydrate in 100 ml. of 2 *N* hydrochloric acid, prepared fresh at reasonable intervals. Any insoluble material should be removed by filtration.

Tellurium tetrachloride, 1 mg. of tellurium per ml. Treat 100 mg. of precipitated tellurium with 1 or 2 ml. of nitric acid and evaporate to dryness. Add 1 ml. of hydrochloric acid and again evaporate to dryness. Dissolve the residue in 10 ml. of concentrated hydrochloric acid and dilute to 100 ml. with water.

Sodium fluoride, 1 gram in 100 ml. of water.

Standard gold solution, 0.001% gold as chloroauric acid in 0.10 *M* hydrochloric acid. This solution is conveniently obtained by diluting a 0.010% gold stock solution in 1.0 *M* hydrochloric acid with water.

Procedure. The sample solution (0.1 to 10 microgram of gold) may conveniently have a volume of 50 ml. It should not contain strong oxidizing agents such as nitric acid.

Add enough hydrochloric acid to make its concentration 2.5 *N*, and 0.2 ml. of tellurium solution. Mix, and add 5 ml. of stannous chloride solution or more as required to reduce iron and copper and produce a brown colloidal precipitate of tellurium, followed by an excess of 3 to 5 ml. Heat to boiling and keep near the boiling point for 0.5 hour or until the precipitate is well coagulated. Collect the precipitate in a small porous porcelain filter crucible (7 ml.). Wash the precipitation beaker and the crucible with five portions of 1 to 4 hydrochloric acid of 5 ml. each. Wash carefully to remove all iron and other foreign substances.

Add 1 ml. of aqua regia (1 volume of nitric acid to 3 volumes of hydrochloric acid) to the precipitation beaker, moisten the walls with the aid of a stirring rod, heat almost to boiling, and pour the solution into the crucible. By the use of a stirring rod bring the acid into contact with the tellurium on the walls of the crucible, and when all or most of the precipitate has been dissolved draw the solution through the crucible, catching the liquid directly in a 20-ml. Pyrex beaker. Add 1 ml. more of aqua regia to the beaker and repeat the operation as described to complete the solution of any remaining tellurium. Then wash the beaker and crucible with two portions of water of a few milliliters each. Evaporate the solution to dryness on the steam bath, avoiding prolonged heating of the dry residue. Allow the beaker to cool and add 0.01 ml. of aqua regia. By means of a stirring rod moisten the bottom and lower sides of the beaker with the drop of acid, so that all the residue is wetted. Set the beaker aside to permit the acid to evaporate at room temperature. (Conveniently the beaker is allowed to stand overnight under a large inverted beaker to protect from dust.)

Prepare standards containing 0, 0.2, and 0.4 microgram of gold by transferring the proper amount of standard gold solution to the glass-stoppered tubes, adding 0.30 ml. of 2.0 *M* hydrochloric acid and water (redistilled) to make the volume almost 4 ml., followed by 0.25 ml. of sodium fluoride solution, and mixing. (It would be more correct in principle to prepare the standards by evaporating to dryness after the addition of aqua regia and tellurium and further treating in the same manner as the sample solution, but this is believed to be an unnecessary refinement.)

Determination of Gold. When the tellurium residue is entirely dry, add exactly 0.30 ml. of 2.0 *M* hydrochloric acid to the beaker and bring into contact with all of the solid by the use of a stirring rod. Add 1 ml. of water and stir. If the solution is clear, transfer it to a tube and rinse the beaker carefully with small portions of redistilled water to make the total volume in the tube 3.5 ml. If the solution is turbid (silver chloride), filter through a small porous porcelain filter crucible, catching the filtrate directly in a tube, and wash with small portions of water to give a total volume of 3.5 ml. (or 4 ml., if the final volume is to be 5 ml.).

Add 0.25 ml. of sodium fluoride solution to the sample and standard tubes and mix by inversion. Now add 0.30 ml. of rhodanine reagent to each tube and mix at once by inverting three times. Bring the volume of each solution to the mark (4.5 or 5 ml.) with water and again mix by inverting three times. In a few minutes the colors will have reached their full intensity and, if the sample is less strongly colored than the 0.4 microgram standard, find the gold content by visual comparison, examining the tubes axially against a white background. If the gold content of the sample falls between two standards, a more exact comparison can be made by mixing the two standards in a small beaker, dividing the mixture between the two tubes, and again comparing.

If more than 0.4 microgram of gold is present in the sample solution, transfer the latter to a dry absorption cell, and obtain the transmittancy with a green filter exactly 10 minutes (or other fixed time) after the addition of the rhodanine reagent. To establish the standard curve take 0, 0.5, 1.0, 2.5, 5, 7.5, and 10 micrograms of gold, add enough 2.0 *M* hydrochloric acid to make the total volume equal to 0.30 ml. (bear in mind that the standard gold solution is 0.10 *M* in hydrochloric acid), treat with sodium fluoride and rhodanine reagent as described, and dilute to volume. A plot of extinction versus concentration should give a straight line.

The absorption cell should be cleaned with dilute hydrochloric acid after each reading to dissolve any precipitate that may have been deposited on the walls.

DETERMINATION OF GOLD IN BIOLOGICAL MATERIAL

The general method above has been applied to the determination of gold in plant material after ashing by ignition. Destruction of all carbon is a necessity. Any colloidal carbon remaining is carried down by the tellurium precipitate and may give a colored final solution. Addition of nitric acid to the ash, followed by evaporation and ignition, has been adopted as an effective way of destroying carbon.

The recovery of gold was tested by adding 0.2, 0.3, and 0.5 microgram to 1.5-gram samples of the ash of Lombardy poplar (*Populus nigra* var. *italica*) leaves and carrying through the procedure described below, making the final determination by visual comparison in 0.075 *M* hydrochloric acid medium. Good recoveries were obtained (Table IV).

Table IV. Recovery of Gold from Ash of Lombardy Poplar Leaves

Gold Present, P.P.M.			Gold Found, P.P.M.
Original	Added	Total	
0.10[a]	0.13	0.23	0.27
0.10	0.20	0.30	0.30
0.10	0.33	0.43	0.45

[a] Average of 0.13 and 0.08 p.p.m.

Procedure. Ash the sample in a porcelain dish at low redness (not higher than 500° C.) in the customary manner. Take enough material to yield several grams of ash. Burn off as much as possible of the carbon. Transfer from 1 to 2 grams of ash to a small porcelain dish or a 20-ml. porcelain crucible (for an expected gold content of 0.2 microgram or more, a 1-gram sample is sufficient). Add a few milliliters of water followed by 2 ml. of concentrated nitric acid (for 1 gram of sample) added in small portions; keep the vessel covered with a watch glass. Evaporate to dryness on the steam bath or low-temperature hot plate, gradually heat to low redness, and keep at that temperature for about 15 minutes or until brown fumes cease to come off.

Add 5 ml. of 1 to 1 hydrochloric acid to the residue and evaporate to dryness. Add another 5-ml. portion of dilute hydrochloric acid and evaporate to dryness again to destroy any remaining nitrate. Take up the residue in a mixture of 5 ml. of concentrated hydrochloric acid, 5 ml. of water, and 2 ml. of saturated bromine water. Heat almost to boiling while stirring at intervals and filter through a sintered-glass crucible. Wash with 10 ml. of 1 to 1 hydrochloric acid and a few portions of water.

Transfer the filtrate and washings to a 100-ml. beaker, dilute to 50 ml., and add 0.2 ml. of tellurium solution followed by 5 ml. or more as required of stannous chloride solution. Then continue as in the general procedure described above.

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Pressure Regulator for Use in Microdetermination of Carbon and Hydrogen

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A new pressure regulator for use in the microdetermination of carbon and hydrogen is described which is believed to have distinct advantages over the Pregl type.

ALTHOUGH the Pregl (*5*) type of regulator is used generally in the microdetermination of carbon and hydrogen, it has certain disadvantages. The prongs which hold the attachable inner tube in place are subjected to the corrosive action of the solution used and the life of the regulator is greatly shortened. Likewise, there is no attached scale to aid in making the settings. Substitutes (*1–4, 6, 7*) for the Pregl regulator have been offered but none has received wide acceptance. The pressure regulator described here has proved excellent over a number of years (in approximately five years' use by M. F. Furter at the Federal Institute of Technology in Zurich and at F. Hoffmann-La Roche & Company, Ltd., Basle, Switzerland, and in six years' use of five units by Al Steyermark in these laboratories). It has an attached scale and contains no metal parts that are subject to attack by acid or alkali. The rubber connecting tube is the only part that needs replacing after several years of use.

APPARATUS

The apparatus consists of two essential parts: the pressure regulator proper and a leveling bulb for obtaining the desired height, connected by means of rubber tubing. Where only oxygen is used one unit is required, while setups using oxygen and air require duplicates, as shown in Figure 1. The two regulators are connected by means of a T- or Y-tube, which in turn is connected to the bubble counter of the combustion train. Five per cent solution of sodium hydroxide is used in the regulators.

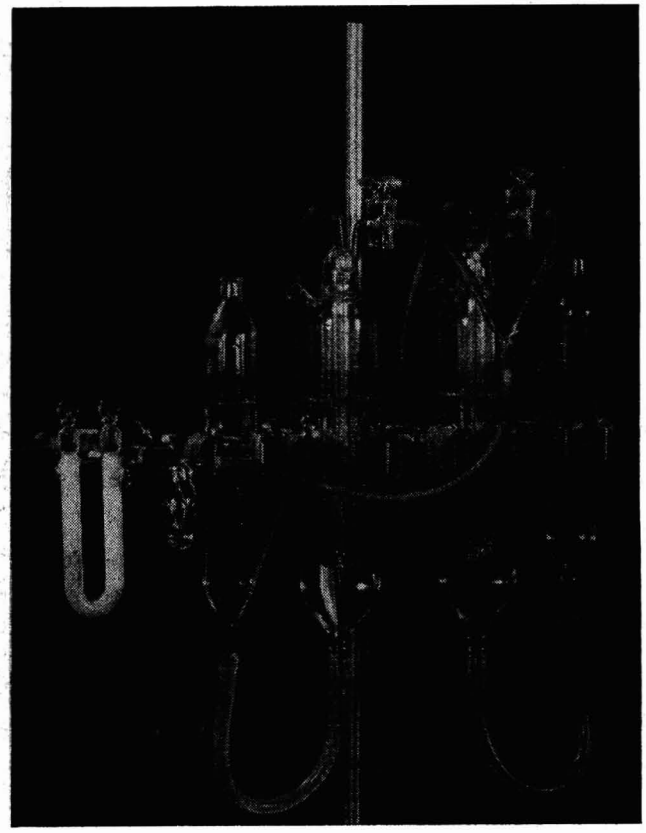

Figure 1. Pressure Regulator

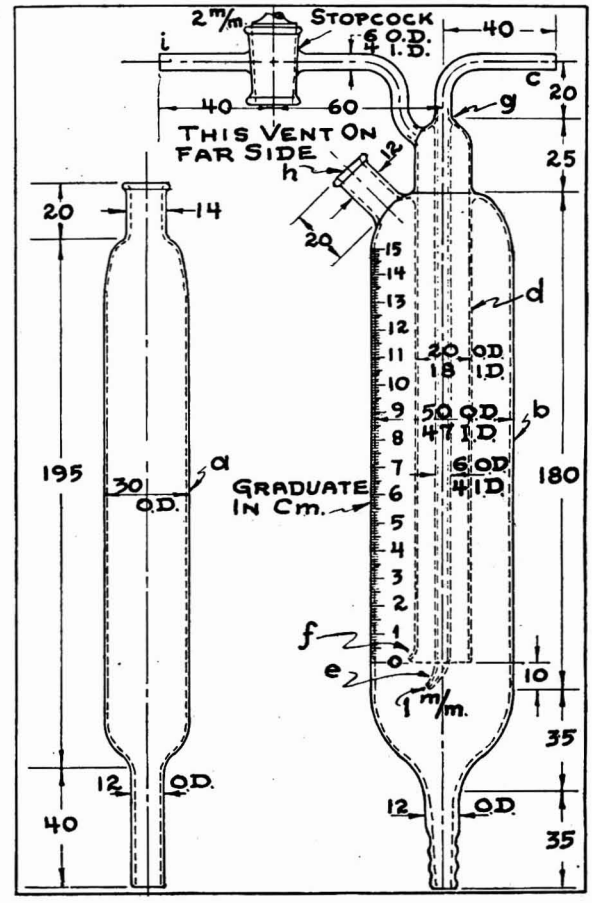

Figure 2. Diagram of Unit

Figure 2 shows the details of construction of the unit. *a* is the leveling bulb and *b* the regulator proper. *c* is the inlet tube which is connected to the source of oxygen or air. The gas passes vertically down through it, coming out at outlet *e* and displacing the solution between the vertical part of *c* and the jacket, *d*. When the space between *c* and *d* is completely filled, the excess gas overflows at *f* and passes up through the solution and out into the air through *h*. The position of *e* should be such that the gas bubbles strike the notch, *f*. (If, on testing a regulator, it is found that the outlet has been improperly placed, the condition may be corrected by applying the flame of a small blast lamp at point *g*. When the glass has softened slightly at *g*, that section of the tube between *g* and *e* is allowed to fall into place by gravity.)

The height at which the solution stands in *b* is shown on the

graduated scale, this also being the pressure head maintained in *d*. The gas under the desired pressure passes out through the stopcock and tube *i* to the bubble counter and the combustion tube.

ACKNOWLEDGMENT

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MICROEFFUSIOMETRY

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An apparatus is described for determining the molecular weight of 0.5 cc. of permanent gas or 0.5 mg. of volatile liquid. The apparatus is easy to construct and operate, and no microweighings are involved. A single determination requires about 15 minutes, and an average error of less than 2% is found with single-component samples. The method has wide applicability for permanent gases and condensable vapors. Organic liquids with boiling points up to 170° C. may be used. Within experimental error, a strict adherence to Graham's law is found in practically all cases. The apparatus is shown to meet the essential criterion for the application of Graham's law, and it is indicated that previous failures to secure satisfactory results with pinhole orifices in glass were caused by failure to meet this criterion.

THE identification of traces of gas unabsorbed in gas analysis systems, and of small amounts of volatile organic liquids which are occasionally isolated, presents some difficulty. A method providing rapid approximate data for the molecular weights of these specimens would yield a worth-while clue to their qualitative nature.

Unfortunately, such a method is not always available. Infrared and mass-spectrographic determinations are excellent, provided the requisite equipment is at hand. The Edwards gas density balance (*5*), particularly in its microadaptations, requires some skill in its construction and operation, and it is not well suited for use with materials of relatively low volatility. Microadaptations of the Victor Meyer and Dumas methods are well known, but they necessitate an accurate microweighing and a generally refined technique, and they cannot be used for determinations with permanent gases.

A micromethod based on the measurement of relative rates of effusion and the use of Graham's law appears to present many advantages. It is unquestionably rapid and can be made simple as far as apparatus and technique are concerned, particularly since no microweighings are involved. Furthermore, there is reason to believe that a low-pressure (micro) effusiometer may function more satisfactorily than the conventional high-pressure (macro) apparatus, other things being equal.

A very considerable number of modifications of the ordinary Bunsen-Schilling type effusiometer have been described, but most of them require 100 to 200 cc. of noncondensable gas. Neither these nor a macromethod recommended for the study of condensable vapors (*7*) seem well suited to microadaptation. An excellent semimicroeffusiometer has been described by Kahle (*10*), but about 30 cc. of sample at a pressure of approximately one-third atmosphere are required. Perhaps the only true microdesigns of simple effusiometers are those of Knudsen (*14*), which require a very delicate quartz suspension gage; and that of Debierne (*2*), which requires an accurately calibrated McLeod gage and is thus obviously unsuited for work with condensable vapors.

A design for a microeffusiometer combining the properties of simplicity, accuracy, and wide applicability has therefore been sought. It should operate with small volumes and at low pressures, in the interests of economy of material. Low pressure is further desirable in the interests of accuracy, and in order that the method may be applied successfully to materials of low vapor pressure. For the measurement of these low pressures a McLeod gage will not serve if the method is to be applied to condensable vapors, and most of the other low-pressure gages are unsuitable either because, like the Pirani gage, they are not absolute gages, or, like the Knudsen gage, they are fragile and expensive. A horizontal-form Huygens micromanometer (*15*), in a form modified for this work, was chosen as the most likely possibility.

The construction of an orifice suitable for use in a microeffusiometer has probably been the main obstacle to progress along these lines. Very fine orifices in extremely thin platinum foil can be prepared (*13*), but the process is not unattended by difficulties. The use of punctured collodion films (*17*) did not seem promising if organic materials were to be studied. An obvious possibility, however, would be a pinhole produced by a spark discharge through a thin glass membrane. Such an orifice should be small, inexpensive, and easy to fabricate and to build into the apparatus. Despite previous reports indicating their unsuitability (*3*, *7*), such orifices have proved satisfactory in practice.

APPARATUS

A microeffusiometer meeting the specifications outlined above is shown in Figure 1. Other dispositions are possible and have been used successfully, but the one shown seems to be the most generally satisfactory.

M represents the body of the micromanometer, made from 24-mm. tubing with an over-all height of 6 to 7 cm. The manometer is filled to the level shown with distilled mercury. The space above the left branch of *M* communicates directly with orifice *O* and, through stopcock *S*, with the sampling system and the pumps. The bore of stopcock *S* should be at least 2 mm. in diameter and preferably somewhat larger. The right branch of the manometer terminates in a length of heavy-walled capillary tubing of the following specifications: Sections *B* and *D* are 3-cm. lengths of 2-mm. capillary; sections *C* and *E* are 2-cm. lengths of 0.5-mm. capillary; and section *F* is a 6-cm. length of 2-mm. capillary, terminating in bulb *G*, which has a volume of

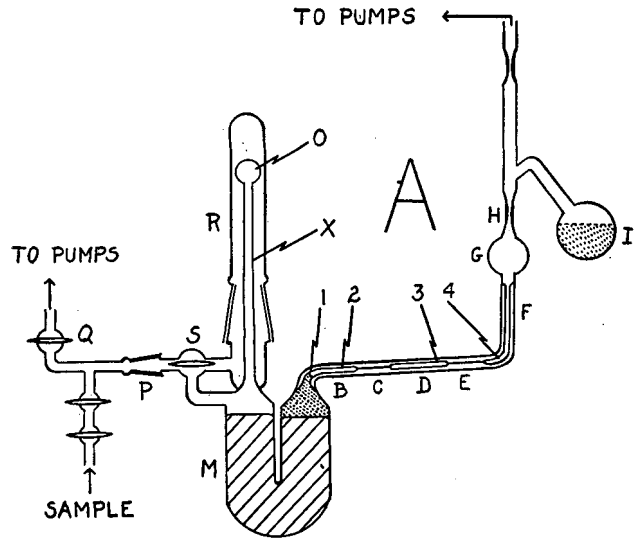

Figure 1. Diagram of Microeffusiometer

3 to 5 cc. The sections of capillary tubing should be united with smooth, tapered seals, and section *BCDE* should be very slightly inclined to the horizontal, as indicated in the diagram. Bulb *G* communicates through constriction *H* with the reservoir of auxiliary manometer fluid, *I*, and with the pumps.

Orifice *O* is prepared by blowing a thin-walled bulb (0.01 to 0.02 mm. in thickness), of diameter about 12 mm., at the end of a length of 6-mm. tubing. A grounded copper wire is inserted in the tubing so that its free end extends into the bulb. The point of a Tesla coil leak tester is then moved around the outside of the bulb while the voltage of the discharge is gradually increased until a spark strikes through the weakest part of the bulb. The orifice so prepared is sealed into the apparatus at point *X*, and the equipment is finally assembled as shown.

To prepare the apparatus for use, *S* is turned so that both *R* and *M* are connected with the pumps, and connection is also established between the pumps and region *GHI*. The pumps are started cautiously, and continued in operation until the system is well evacuated. The auxiliary manometer fluid (Tetralin was used in most of this work) is then distilled from *I* into the right branch of the manometer, until the Tetralin level is close to point 1 (see diagram). Several determinations of the effusion time of the selected standard material are then made, by a method described below. An effusion time of 6 to 8 minutes is satisfactory. If the observed time is much longer than this, a little of the Tetralin should be removed from the manometer; if much shorter, a little more Tetralin should be added. When, by these manipulations, a satisfactory effusion time has been secured, constriction *H* is sealed shut and the apparatus is ready for use.

PROCEDURE

Standardization is the first step in using this equipment. The apparatus described was intended for use with permanent gases, and nitrogen, which is readily obtainable in pure condition and whose molecular weight is close to the middle of the most important range of molecular weights (2 to 50), was chosen as the standard.

With stopcock *Q* closed, and *S* turned to connect *P* and *M*, a small amount (ca. 0.5 cc.) of dry nitrogen is introduced into the system. The double stopcock "doser" shown in the diagram is useful for this purpose. The pressure in the system rises upon the introduction of the sample, and the Tetralin meniscus should reach a position in the neighborhood of point 4. Stopcock *S* is then turned to connect *R* and *P*, and simultaneously *Q* is opened. The pressure in *R* drops rapidly to a low value, and effusion through orifice *O* ensues. As the pressure over the left branch of *M* decreases the Tetralin meniscus retreats down the side arm. It passes fairly rapidly through section *E* and then springs out into section *D*, owing to the reduced effect of capillarity in the larger tube. As the meniscus passes point 3 a stopwatch is set in motion. Effusion continues and the meniscus enters section *C* after a considerable pause, traverses *C* rather slowly, and emerges with a sudden rush into the larger diameter tubing of section *B*. The instant the meniscus passes point 2 the stopwatch is stopped and the time for effusion noted. After a brief pumping the procedure is repeated until concordant results for the standard's effusion time are secured.

In making a determination with an unknown the same procedure is followed, the sample being introduced in place of the standard. The molecular weight of the unknown is then determined, using Graham's law, from the observed times of effusion and the known molecular weight of the standard:

$$M_{\text{unk.}} = \frac{t_{\text{unk.}}^2}{t_{\text{stand.}}^2} M_{\text{stand.}}$$

For most accurate work the standardization should be repeated after running the unknown, but once the apparatus has come to equilibrium it appears to hold its standardization well, so that restandardization need be performed only intermittently. Bulb *G* appears to have a beneficial effect in stabilizing the standardization, perhaps by minimizing pressure fluctuations in the closed arm of the manometer. Condensation of droplets of the auxiliary manometer fluid in or around *G* was prevented by placing a 7-watt light bulb next to *G*.

If for no other reason, the standardization should be repeated from time to time to provide assurance that the orifice has not been partially plugged. Although plugging occurs infrequently, a sharply increased effusion time for the standard usually indicates a plug. Under such conditions the orifice can almost always be restored to its pristine condition by simply introducing a small amount of nitrogen into *R* while *M* is evacuated, and then applying the leak tester to the outside of *R*. The discharge in *R* tends to travel into the lower pressure region in *M*, and passes through the orifice, which may be seen as a sharp white point in the discharge. The discharge and the reverse flow of gas have been successful in every case in dislodging the obstruction in the orifice.

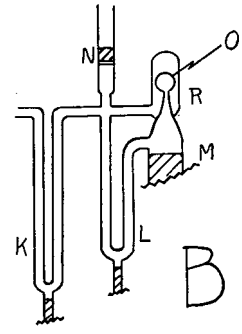

Figure 2

Since extension of this method to volatile organic compounds seemed desirable, a slightly modified apparatus has been constructed in which all greased joints have been eliminated to prevent any aberrations due to solution of the organic vapors in the grease.

The modified part of the apparatus is indicated in Figure 2. Here mercury cutoffs replace the stopcock, and the orifice is permanently sealed in place. To make a determination the apparatus is first evacuated, and then the mercury level is raised to shut tube *K*. A small amount of the (liquid) sample is introduced into the effusiometer by touching the tip of a capillary pipet containing the sample against the surface of the fine porosity fritted disk in *N*, which is sealed against the atmosphere by a shallow pool of mercury (*16*). When enough material to raise the pressure to the desired value has been introduced, the pipet is withdrawn and the mercury is raised (to a fixed point) to seal cutoff *L* and lowered to free tube *K*. The rest of the procedure is then precisely like that described above.

In the calibration of this apparatus, intended for use with organic vapors, nitrogen is not entirely satisfactory. If the nitrogen effusion time is sufficiently long to be measured with accuracy, the times of efflux for the heavier vapors will be inconveniently lengthy. Furthermore, it is generally desirable to calibrate the equipment with a material similar to the unknowns to be run (*4*). Benzene is readily obtainable in pure form

Table I. Permanent Gases

Sample	Molecular Weight Found	Molecular Weight Theoretical	% Error
Hydrogen	2.04	2.016	+1.2
Helium	4.17	4.00	+4.25
Methane	16.05	16.04	+0.1
Carbon monoxide	28.0	28.0	0.0
Oxygen	32.35	32.0	+1.1
Argon	40.0	39.94	+0.1
Carbon dioxide	44.3	44.0	+0.7
		Av.	1.0

and its molecular weight lies close to the middle of the useful range of the equipment. It was, therefore, chosen as a suitable standard.

RESULTS

Table I presents the results obtained when a series of permanent gases was studied with apparatus *A* (Figure 1), standardized with nitrogen. Each determination listed represents the average of from two to five trials. Tank gases of good quality were used throughout, except in the case of carbon monoxide, which was prepared by the dehydration of formic acid with phosphoric acid. With the possible exception of the helium determination, the results seem satisfactory.

Table II presents the results obtained when a series of organic compounds was studied with apparatus *B* (Figure 2), standardized with benzene. It is believed that the abnormally high results for the alcohols may be due to adsorption effects. Water, when studied by the same general technique, showed an entirely analogous deviation. The other results appear to be satisfactory.

Table II. Condensable Vapors

Sample	Molecular Weight Found	Molecular Weight Theoretical	% Error
Methyl alcohol	33.5	32.0	+4.7
Ethyl alcohol	47.5	46.1	+3.0
Acetone	59.1	58.1	+1.7
Ethyl ether	74.6	74.1	+0.7
Ethyl acetate	86.2	88.1	−2.2
Toluene	91.2	92.1	−1.0
o-Xylene	106.0	106.1	+0.1
Chloroform	120.0	119.4	+0.5
Mesitylene	116.5	120.1	−3.0
Carbon tetrachloride	152.0	153.8	−1.2
Bromobenzene	160.0	157.0	+1.9
s-tetrachloroethane	171.5	167.8	+2.2
		Av.	1.85

Table III presents the results obtained when a series of determinate mixtures of hydrogen and carbon monoxide was analyzed with apparatus *A* (Figure 1), standardized with nitrogen. It was expected that the results could not be very precise, and this expectation has been confirmed.

DISCUSSION

On the basis of kinetic theory it appears that Graham's law must apply exactly to rarefied gases (*4, 13*). The results given above show, within experimental error, a fairly good adherence. To determine whether or not Graham's law applies exactly under the operating conditions, a closer study of the experimental parameters is indicated.

The volume of the high-pressure side of the orifice was usually about 10 cc. While the pressures in this region have varied somewhat in the different assemblies tested, they have generally amounted to ca. 1.8 mm. at the beginning of the run and 0.7 mm. at its conclusion. Thus the mean operating pressure in the high-pressure region was ca. 1.25 mm. The pressure on the low-pressure side of the orifice was not measured accurately but can hardly exceed 0.001 mm. Therefore the median pressure in the apparatus was ca. 0.6 mm.

The thickness of the orifice membrane was variable, but generally amounted to ca. 0.01 mm. This thickness was measured by taking a fragment of the membrane from the bulb, in the neighborhood of the orifice, and determining its area roughly by placing it on coordinate paper. The fragment was then weighed, and from the weight, area, and density of the glass the thickness was estimated. As a check the thickness was also determined by focusing a microscope on the upper surface of the membrane, in the neighborhood of the orifice, and then on the under surface. The vertical movement of the microscope barrel, as read from the appropriate scale, gives a fair estimate of the thickness of the membrane. The results of these two methods when applied to the same membrane, agreed reasonably well.

With the data given above the effective area of the orifice may be estimated by using the well-known formula for the number of collisions of gaseous molecules with the walls of the container, assuming that every molecule "striking" the orifice area passes out of the high-pressure region. This assumption is admissible if the mean free path of the molecules is significantly greater than the orifice diameter and the membrane thickness, and is justified by the results of the calculation.

The collision formula may be written in the form:

$$-dN = \frac{N\bar{c}A}{4v}\,dt$$

where N represents the total number of molecules present in a high-pressure region of volume v, $-dN$ represents the number of molecules "striking" orifice area A in time dt, and $\bar{c}$ represents the average molecular velocity.

Integrating over the period of the run, and using subscripts 1 and 2 to denote conditions at the beginning and end of the run, respectively, we find:

$$\ln \frac{N_1}{N_2} = \frac{\bar{c}A}{4v}\,(t_2 - t_1)$$

Making the appropriate numerical substitutions, and basing the calculation on nitrogen, with an average effusion time of 420 seconds, we find that orifice area A is 1.8×10^{-6} sq. cm., from which, assuming that the orifice displays a circular aperture, the diameter is found to be about 0.015 mm. While this is not proposed as a precise estimate of the orifice dimensions, it must at least be correct in order of magnitude.

If the average mean free path of a gaseous molecule under normal temperature and pressure conditions is taken as 2×10^{-5} cm. (*9*), then at room temperature and the median working pressure of 0.6 mm. the mean free path is approximately 0.28 mm. Thus the mean free path is substantially greater than the diameter of the orifice and the thickness of the orifice membrane, and the assumption on which the above calculation was predicated appears to be justified.

Table III. Mixtures of Hydrogen and Carbon Monoxide

No.	Molecular Weight Found	Molecular Weight Theoretical	Per Cent Hydrogen Found	Per Cent Hydrogen Theoretical	Deviation in Hydrogen Percentages
1	26.7	25.4	5.0	10.0	−5
2	23.7	22.4	16.5	21.5	−5
3	20.1	19.1	30.4	34.2	−3.8
4	16.7	16.0	43.5	46.2	−2.7
5	14.2	13.7	53.2	55.0	−1.8
6	9.83	10.3	69.9	68.1	+1.8
7	6.75	7.95	81.8	77.2	+4.6
8	4.38	5.57	90.8	86.4	+4.4
9	2.70	3.35	97.3	94.8	+2.5
			Average % error on basis of 100%		3.5

Knudsen has shown (*13*) that the essential criterion for ideal molecular effusion following Graham's law is that the mean free path be equal to or greater than ten times the orifice diameter. With a mean free path (at the median pressure) of ca. 0.28 mm. and an effective orifice diameter of ca. 0.015 mm. our experi-

mental conditions appear to meet the essential criterion for ideal molecular effusion satisfactorily.

Since the mean free path–orifice diameter ratio does not exceed the critical value by a wide margin, deviations from Graham's law might be expected to materialize in trials run at slightly higher pressures. This prediction is verified by the results of some preliminary experiments made at higher pressures. With an initial pressure of 20 mm. the following values were found: hydrogen 2.5; helium 5.6; methane 14.8; carbon dioxide 40. These results indicate that the flow has acquired a hydrodynamic character and is strongly affected by viscosity, etc. At 7-mm. pressure the deviations from Graham's law were substantially reduced: hydrogen 2.17; helium 4.5; methane 15.9. On further lowering the pressure to 2 mm. satisfactory results were secured, although the abnormally large error in helium, which showed the worst deviation of the gases tested at higher pressures, suggests that even at the lowest pressure used there may have been some slight hydrodynamic character to the flow.

A condition often given as essential for the application of Graham's law is that the membrane thickness be much less than the orifice diameter. While this is a serious consideration in high-pressure effusiometers, Knudsen (*12*) has shown that the relative rates of flow of rarefied gases through long thin capillary tubes obeys Graham's law precisely, provided that the mean free paths of the gases are ten or more times greater than the capillary diameter. Therefore the fact that the orifice diameter and the membrane thickness were roughly equivalent in the present work need occasion no concern. Actually, satisfactory orifices have been prepared in much thinner bulbs, but the thinner membranes sometimes were ruptured when, through misadventure, a large pressure differential existed across the orifice.

Inasmuch as this instrument has been shown to satisfy the essential theoretical condition for the application of Graham's law, and since the results show a fairly strict adherence to the law, the reasons for previous failures to secure satisfactory results when pinhole orifices in glass were used to study effusion at pressures varying from several hundred millimeters to 1 atmosphere (*3*, *7*) should be examined. The explanation given in both cases was that the "orifice" actually consisted of a number of cracks so extremely fine that predominantly viscous flow occurred, but this explanation can hardly be correct.

Christiansen's experiments on gas flow between plane ground-glass prisms (*1*) indicate that effusion at atmospheric pressure follows Graham's law only if the opening is excessively minute. These experiments showed that Graham's law applied accurately only when the separation was reduced to 0.00015 mm. or less—i.e., molecular effusion occurred only when the plate separation was reduced to the same order of magnitude as the mean free path at atmospheric pressure. Thus previous experiments with pinhole orifices have failed not because the openings were too fine, but because they were too coarse. Indeed, since the limiting width at 1 atmosphere deduced from Christiansen's work is only one quarter the wave length of sodium *D* light, any cracks visible under an ordinary microscope (Donnan) are obviously too coarse.

Microscopic examination of some of the orifices prepared for this work showed them to be real holes, with sharply defined edges, and a shape that was sometimes circular and sometimes of a more irregular pattern. A very few radial cracks were observed in some cases, no cracks at all in others—contrary to previous reports (*3*). Perhaps by using very thin-walled bulbs and a moving electrode and only gradually increasing the voltage of the discharge, so that penetration can occur at the weakest point in the membrane, the extent of generalized shattering may be minimized.

The orifices prepared for this work always seemed to have the same order of magnitude and, in any case, there is an auto-compensatory device that tends to maintain a satisfactory ratio between the mean free path and the orifice diameter, provided that the volume on the high-pressure side of the orifice and the time of efflux of the standard are maintained constant. For example, if the hole is abnormally large, the desired time of efflux can be maintained only by working in a lower pressure range. However, the mean free path is increased by the diminution in pressure, so that the condition for ideal effusion is still maintained.

The reason for the relative failure of the method as applied to mixtures seems apparent. It is well known that a separation of the components of a mixture occurs during molecular effusion (*2*). If the whole gas sample could be allowed to effuse, no error need result, but in practice such a procedure is not feasible. In the present case a portion of the sample enriched in the lighter component is lost at the beginning of the run, and a portion enriched in the heavier component remains behind at the end of the run. Since these effects work in opposite directions, and tend to make the middle fraction, for which the effusion time is measured, more or less representative of the original sample, trials with hydrogen–carbon monoxide mixtures were undertaken to ascertain the extent of the compensatory mechanism. From Table III it is obvious that exact compensation did not obtain over a wide range of composition, but that the deviation from the norm appears to vary in a systematic way. Consequently this method cannot be recommended for use with mixtures unless a calibration curve is used and care is taken to standardize the relative amounts of sample discarded at the beginning and end of the run. Further work on this point is in progress.

CONCLUSION

The apparatus described is simple to construct and operate. The glass orifices are sturdy under large pressure differentials. The importance of a shape factor, which complicates the construction of satisfactory orifices for high-pressure effusiometers (*6*, *11*), is negligible in low-pressure apparatus. No plugging of the orifice due to condensation of sparingly volatile materials in the orifice need be anticipated in a system operating at low pressures, although it is sometimes a source of error in apparatus of conventional design (*11*). Plugging in apparatus of conventional design is a not infrequent occurrence and is remedied only with difficulty, but since there is no stream flow through or toward the orifice in the low-pressure apparatus, there is no great tendency to carry particles to a position where they can obstruct the opening. When plugging has occurred it has always been eliminated simply by reversing the direction of the gas flow and using a leak tester.

The Huygens horizontal micromanometer requires only 1.5 pounds of mercury, and the gas sample comes in contact only with the mercury, so that solubility errors (*6*) are avoided. The best auxiliary manometer fluid tested was Tetralin, but any oil of low density, viscosity, and vapor pressure should serve adequately. The modified design of the horizontal side arm produces a sharp movement of the oil meniscus (a distance of about 1 cm. is traversed in a fraction of a second) at each of the timing points. Because of this large movement parallax errors in reading the meniscus at the timing points, a significant factor in apparatus of conventional type (*8*), are virtually eliminated.

No temperature shielding has been provided for this equipment. The rate of effusion, as measured by pressure drop in the high-pressure region, varies only as the square root of the absolute temperature. Thus a change of 6° C. around room temperature produces an alteration of the effusion time of but 1%. Occasional restandardization provides an adequate check on this factor.

The accuracy of the method described appears to be somewhat better than 2% when applied to single-component permanent gases or condensable vapors. The method is not recommended for mixtures. The time for a single determination, after the

apparatus has been standardized, should not exceed 15 minutes. Requirements as to quantity of sample are about 0.5 cc. at normal temperature and pressure for permanent gases and about 0.5 mg. for volatile liquids—i.e., roughly 0.5% of the requirements of conventional equipment. Further decrease in the amount of material required, without any apparent compromise of accuracy, should be obtainable by working at still lower pressures. Condensable samples can be recovered easily by inserting a small liquid air trap between the effusiometer and the pump. The presence of quantities of nonvolatile impurities in the liquid samples does not affect the result, because in this method, unlike most microdeterminations of molecular weight, no weighings are involved.

In applicability, it appears that any material, exerting a vapor pressure of at least 2 mm. at room temperature, which does not react with and is not powerfully adsorbed on glass or mercury, may be tested by this method. With regard to organic compounds, mesitylene (boiling point 165° C.) was run successfully, while cymene (boiling point 175° C.) barely failed to develop sufficient pressure in the apparatus. Therefore it appears that organic liquids with boiling points under ca. 170° C. can be treated by this method.

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Photoelectric Balance Indicator

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A relatively simple and inexpensive photoelectric assembly may be applied to the average analytical balance in such a manner as to give a sensitive indication of the equilibrium position. The device serves either to extend the usable sensitivity of a balance, to improve its readability, or both. The arrangement was applied with particular success to an ordinary analytical balance, which was being used for work on a semimicro scale. The idea can be extended to cover a variety of types of balances.

THE arrangement described involves a photoelectric indicator, the purpose of which is to facilitate the reading of the rest point, to give sensitive weighings directly, or both. A precedent for this application is to be found in the much more elaborate electronic recording balance of Müller and Garman (*5*).

The present arrangement, in its simplest form, involves placing behind the indicating pointer of the balance a photocell which is connected to a suitable meter. To the balance pointer is affixed an opaque screen of some lightweight material which is of such a size and so located as partially to interrupt illumination to the cell. An illumination unit, placed in front of this screen and directed toward the cell, completes the requirements. Changes in the equilibrium position of the balance beam assembly—i.e., changes in weight or alteration in rest point—will be reflected in changes in the amount of illumination reaching the photocell. The resulting alteration in the cell's electrical output may be read conveniently and accurately from the attached meter. The proper design of such a device increases the usable sensitivity of any balance manyfold and contributes greatly to the ease of reading sensitive types of balances.

There are numerous situations in which one would like to make the maximum use of the capabilities of an analytical balance of ordinary design. This problem is usually approached in the manner described by Benedetti-Pichler (*2*) and Niederl and Niederl (*8*), who employ the standard analytical balance for quantitative work on the micro scale. This procedure involves, among other things, setting the balance sensitivity as high as is practical and reading the deflections of the freely swinging beam. Such an expedient is practical and rather widely useful. However, the process of making repeated weighings by this method is somewhat tedious and a serious source of eyestrain. The photoelectric reading device described herein was first improvised with this specific application in mind, but may be applied to almost any type of balance. A detailed description of a simple application of the idea is given, followed by only the briefest outline of some of the more promising extensions of the theme.

A PHOTOELECTRIC SEMIMICROBALANCE

In the initial application of the device one of the lowest priced ($55) analytical balances on the market was used. Despite its low cost, the instrument, a product of one of the more reliable domestic balance manufacturers, proved to be of excellent quality. When fitted with a 5-mg. rider (used only on whole-milligram divisions) and a reading lens before the pointer scale, and with the sensitivity adjusted to the maximum usable value, the balance fulfilled every need of a semimicro instrument. The sensitivity under a load of 10 grams (per pan) was 0.0106 mg. per deflection unit and the average reproducibility of readings was ±2.11 deflection units. This leads to an average precision for a single weighing of ±0.022 mg. Much useful work was achieved with the balance in this condition, the single complaint being the appreciable tedium and fatigue borne by the user. The rectification of this difficulty was sought in the design of a magnetically damped and photoelectrically indicating, null-reading instrument. Properly applied, damping should lead to no decrease in the sensitivity of a balance and it adds greatly to

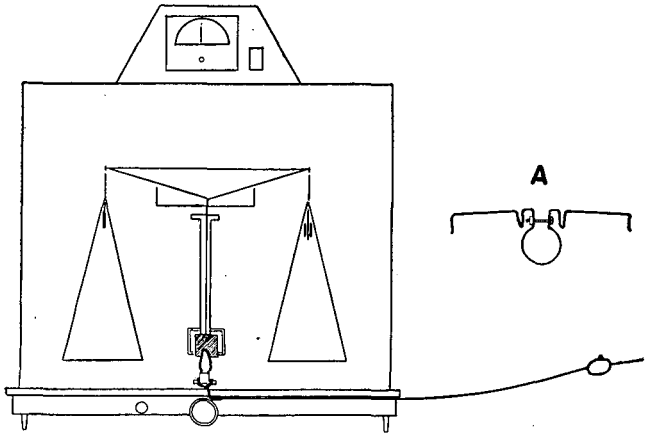

Figure 1. General View of Assembly

the ease of reading. It is not difficult to devise a sufficiently stable photoelectric device to yield a much more sensitive measure (on a meter scale) of a given beam displacement than is afforded by the visual observation of the pointer position.

The simplest photosensitive element is the barrier-layer type of photocell, the output of which is directly readable on a meter without the complication of electronic amplification. A fairly rugged indicator may be employed, such as the pointer style galvanometer or a low-range microammeter. A number of considerations led first to the use of twin photocells in opposition (mounted on either side of the balance support column) versus a zero-center microammeter. The foremost consideration, admittedly, was the fact that a pair of matched barrier-layer cells and a suitable 20-0-20 microammeter were at hand. Aside from this, however, the opposed-cell and zero-center meter combination seemed the more natural approach with the magnetically damped, dead-stop type of reading which was desired. Further, the location of one cell on either side of the central balance column fitted the geometry of the balance in the best manner. Alternatively, either one or two cells might have been located at the end(s) of the balance beam, or a single cell could be accommodated in front of the column by bending the pointer outward.

The general features of layout are evident in Figure 1.

The barrier-layer photocells used (G.E. catalog 88 × 565) were rectangular, measuring 6 cm. ($2\ ^{5}/_{16}$ inches) high by 2.9 cm. (1.125 inches) wide and only 1.3 cm. (0.5 inch) deep. The effective photosensitive surface is 3.8 cm. (1.5 inches) by 1.9 cm. (0.75 inch). They were mounted with the longer axis in the vertical position. This is obviously the position which will give the maximum change in photocurrent for a given horizontal displacement of the light shield. The cells are mounted on either side of, and with their edges set slightly behind, the central column. This is most conveniently done by means of two long strips of thin sheet brass 1 cm. (0.375 inch) wide. These partially encircle the central column and are clamped behind it with a small bolt, nut, and lock-washer. The extended ends of these strips are bent to form a spring clamp for the cells on either side of the column *A*, Figure 1. Two such clamps, one each for the tops and the bottoms of the cells, should suffice.

The light screen was made from a 3.2 × 4.5 cm. (1.25 × 1.75 inch) piece of 28-gage sheet aluminum. The back side and edges of the shield were painted a dull black, while the metallic surface was left on the front face. For mounting, a deep scratch was made down the center of one side and parallel with a longer axis. The pointer was laid in this groove and permanently attached with a few drops of Duco cement. The shield must be positioned, so as to be parallel with the plane of the beam and at such a height along the pointer as to cover the maximum area of the photocells when the unit is assembled with the beam arrest freed. On most balances the pointer scale would partially block the light path. This scale may usually be removed by simply taking out two small setscrews holding it to the base of the central pillar. The permanent attachment of the light shield to the pointer will alter the previous sensitivity of the balance by lowering the center of gravity of the entire beam assembly. The sensitivity should, therefore, be adjusted to the desired level only after this portion of the construction has been completed.

The lamp, shown uncovered in Figure 1, is a small, cone-shaped, 115-volt, 7-watt type (G.E. type C-7) mounted in a miniature candelabra base. In use, it is enclosed in a small blackened box of such a size that a suitable lens may be mounted in the side facing the cells; the size of the box will be dependent upon the particular lens chosen. In general, the focal length of the lens should be short and the size of the box small if it is to be accommodated inside the front door of the balance. The lamp wiring may be brought out under a small V-notch cut in the center of the front door and thence led to one side of the balance under the front edge of the base plate. A line cord switch installed within easy reach of the balance is convenient.

A 4.5-inch rectangular, zero-center microammeter calibrated to 20 microamperes on either side of zero was used on the author's instrument. The scale is marked in 0.5-microampere divisions and readings to $^{1}/_{5}$ division are easily estimated. A 0.25-inch Masonite panel was fitted over the glass and inside the wood frame on the top of the balance case. This serves the double purpose of preventing too strong overhead illumination from affecting the photocells and of furnishing a base on which the meter panel may be mounted. This panel is also of Masonite and may be of whatever size is required for mounting the available meter plus an on-off toggle switch for the meter circuit. The panel is mounted on the base with two small right-angle brackets, far enough back to allow easy clearance for the front sliding door past both the meter face and the switch handle. A damping condenser may also be employed. If this is of the usual type, it will be furnished with a mounting strap or bracket by which it may be mounted on the base plate behind the meter panel.

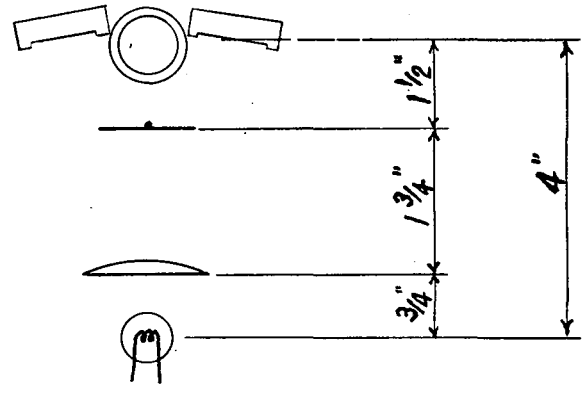

Figure 2. Optical Diagram

The optical diagram shown in Figure 2 will clarify some details of the disposition of the various components. The lens used was a single convex lens from an old flashlight case. It was about 38 mm. in diameter and had a focal length of approximately 5 cm. (2 inches). The exact geometry of the layout must depend upon the balance used.

The electrical circuits of Figure 3 are self-explanatory except as regards the condenser. The application of a low-voltage, high-capacity, electrolytic condenser across the meter terminals will contribute greatly to the facility with which the meter can be read by absorbing minor fluctuations. This furnishes another example of the utility of the principle of condenser damping which has been applied so successfully in the field of polarographic work (*4*). A 1000-microfarad, 6-working-volt condenser connected as indicated makes a vast improvement, particularly if one wishes to average the extremes of two small meter readings rather than waiting for a truly "dead-stop" reading. The most effective capacitance is best determined by trial within the approximate range of 500 to 3000 microfarads. Any value within this range, however, will usually result in marked improvement.

For use as a semimicrobalance, the sensitivity adjustment (sliding weight on the pointer) is now set to the highest value which is found by trial to give consistently reproducible weigh-

ings. After making any such adjustment, it is desirable to allow at least one full day to elapse prior to the final calibration. External illumination should, for obvious reasons, be limited to that which is just necessary for convenient manipulations. Before a series of readings is taken, both the lamp and photocell circuits should be allowed at least a 5-minute warmup period to reach stable conditions. In practice, the compromise of taking readings after the deflections had decreased to 0.5 microampere was adopted as a short cut. The average of two extremity readings (each to 0.1 microampere) was then taken as the rest point. A calibration chart of microamperes versus milligrams should be carefully prepared to cover the usable range of the meter. Since this calibration will not, in general, be linear, as many points as can be obtained should be included. It is advisable to spot-check the calibration periodically to be assured of its constancy.

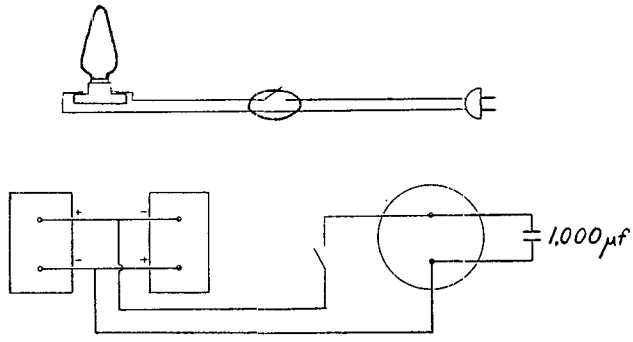

Figure 3. Electrical Circuits

Operating under these general precepts, the author's balance showed a sensitivity with a load of 10 grams (per pan) of 0.00194 mg. per 0.1 microampere and an average reading reproducibility of ±0.434 microampere. An average precision for a single weighing of ±0.0084 mg. was therefore achieved along with a considerable improvement in the ease of weighing and a one-third decrease in the time required per weighing.

POSSIBLE VARIATIONS

The reader who wishes more electronics background is referred to the excellent source book of Müller *et al.* (*6*). Similarly, for details concerning the construction and operation of the several types of microbalances mentioned, he can only be referred to the references cited in the specific case.

Relative to more sensitive circuits, up to a certain point stronger illumination, or more sensitive galvanometers, or both, would suffice. The inherent stability of the barrier-layer type of cell is probably sufficient to justify some such extension, but not a great deal. A bridge circuit in which a variable resistance is altered to reach a null instrument reading might have some advantages. The reading in this instance would be taken from the dial plate of the variable resistor. A more stable sensitivity might be achieved by employing the photoemissive type of cell in conjunction with electronic amplification of any desired degree. In this instance one could again take readings from a calibrated resistor dial, but employ as a null instrument a tuning indicator ("magic eye") type of tube instead of the zero-center meter.

Sensitivity without stability is useless, however, and one would find in each of the above cases that he has another factor to contend with. An increased sensitivity in the measuring circuit will magnify any existing instability in the light source. It is much simpler to design a stable measuring circuit of high sensitivity than to devise a light source of sufficiently constant intensity to justify this sensitivity. Some of the conventional designs of "constant-voltage" supplies, however, would decrease this limitation to the extent of justifying much more sensitive circuits than the very simple one which has been described. The simple expedient of using a lower-voltage lamp with storage battery operation will, of course, give marked improvement over line-voltage operation. Operation of most lamps at slightly lower than their rated voltage may enhance the stability to some degree. In addition, any circuit employing twin photocells in balance (and operating from the same source of illumination) will enjoy appreciably greater stability than a single-cell unit. This effect will be the more marked, of course, the more nearly the output characteristics of the two cells are matched.

The application of photocells to various types of micro- and ultramicrobalances presents some interesting possibilities.

The simple Salvioni balance (*1*, *3*) was tested with a single barrier-layer cell mounted about 38 mm. (1.5 inches) behind the flexing fiber, and with a 38 mm. (1.5 inches) × 19 mm. (0.75 inch) light shield of very thin aluminum foil attached to the fiber as near to the weighing pan as possible. The 7-watt bulb and lens were used as before, with the bulb about 7 cm. (2.75 inches) from the shield. A 4.5-inch, 0- to 50-microampere meter was used with 1000-microfarad condenser damping. The balance used was of a relatively coarse type, having a range of 50 mg. readable only to 0.5 mg. With the photoindicator incorporated, a readability of 0.02 mg. was attained. The same idea could advantageously be incorporated in a balance of the Nernst type (*7*) with few modifications.

Finally, one might speculate as to the adaptability of the idea to the "project-type" of balance, the constructional details of which have been sketched by Seaborg (*9*). Here, the adaptation could be made by employing two sheets of very thin aluminum foil as light screens, one to be located near either end of the cross beam. The index fiber is, of course, omitted. It would be desirable from the standpoint of greater stability to replace the twin light sources by a single source split with appropriate mirrors into two beams. The balancing would proceed as in the original construction, except that the zero point would be approached on a meter rather than by the visual matching of the projected ends of the index fiber. It is possible that with a sensitive zero-center galvanometer, a reasonably constant light source, and a sufficiently large reading disk, the sensitivity of this instrument might be much improved. Condenser damping of the meter would likely prove to be a *sine qua non* in this application.

SUMMARY

A serviceable photoelectric reading device has been applied in the direction of increasing the sensitivity of balances ranging from semimicro to ultramicro in character. The improved readability attending the use of a properly designed device of this nature recommends its more general application, even to analytical balances intended for no more than ordinary purposes. Some few of the many possible variations in the design and application of the principle have been indicated.

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Identification of Free Silica in Dusts and Fumes

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A method applicable to the electron (or light) microscope is described for distinguishing siliceous from nonsiliceous particles by treatment of specimens with hydrofluoric acid vapor. A method is described for sampling dusts and fumes directly on nitrocellulose film by electrostatic deposition.

THE electron microscope is a very useful tool in the investigation of finely divided solids. Used in conjunction with the light microscope and other means, it is possible to extend the measurement of size distribution to include particles of about 50 Å. (0.005 micron). Much additional information is also revealed with respect to particle shape.

Special techniques of specimen preparation are required for investigation by electron microscopy and a survey of these techniques, which includes a discussion of the relative advantages and defects of the various methods recommended, has been reported (*2*). The present paper describes techniques that have been applied in the investigation of certain specific siliceous dusts and fumes, which may be of general interest, by indicating methods involving chemical reaction for increasing the information revealed by the electron micrographs.

While most dusts are composed of particles of irregular shape and size, fumes collected above electric furnaces used in smelting mixtures of alumina and silica, with or without other materials such as iron and titanium oxides, are composed of particles predominantly spherical in shape. Most of these particles are too small to be visible with the light microscope. Because the silica particles are not crystalline but amorphous (fused silica glass), the customary use of quantitative x-ray spectrography to estimate the proportion of free silica is not applicable. There is also no difference in shape or appearance which is sufficient to distinguish silica particles from silicate or alumina particles. Tests have shown that such silica particles may be clearly distinguished from the others by their volatility in the presence of hydrofluoric acid gas. It is believed that the same method may be used to identify quartz particles and distinguish them from other particles in other dusts, such as those collected in mines, foundries, etc.

PREPARATION OF SPECIMENS

Most examinations of this nature are preceded by a determination of particle size distribution. In general, the methods mentioned (*2*) are applicable for this purpose, but if the material contains a water-soluble component, methods involving dispersion in water are precluded if this component has any significance. In some cases a water-soluble component, in particular the alkalies, destroys the film if spread on water, by producing discontinuous or lacy membranes. If the nature of the material is unknown, the safest preparation method starting from collected material (as distinguished from air borne) is probably by casting the dispersion in a resin solution on glass. If water-soluble components are present, the method of Schaefer and Harker may be used to transfer the film to the specimen screen (*1*). If the film is stripped under water, the casts occupied by the water-soluble particles prior to the stripping operation remain and may be taken into account in statistical appraisals.

Perhaps the least objectionable method of specimen preparation for particle size determinations for air borne dusts and fumes is electrostatic deposition directly on blank film. Nitrocellulose films produced by spreading a collodion solution on water by the usual technique can be supported on strips of 100- or 200-mesh screen in sizes up to about 12.5 cm. (5 inches) square. The supported films can be constrained to fit the inner surface of a miniature Cottrell precipitator. Deposition in this manner may be fairly uniform, giving easy control of the thickness of deposit. Specimens may be cut from different positions along the length of the precipitator to show variations in the amount deposited and particle size distribution.

The technique for distinguishing between the components in the specific silica-bearing fumes mentioned requires that the

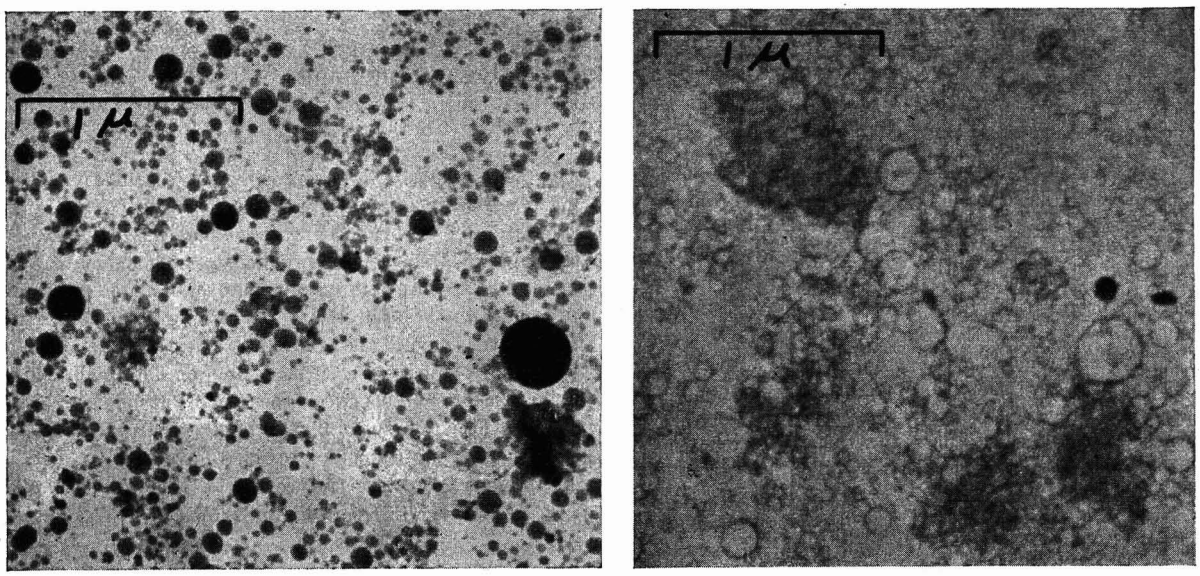

Figure 1. Silica Fumes

Left. In nitrocellulose. Right. After treatment with HF vapor for one minute

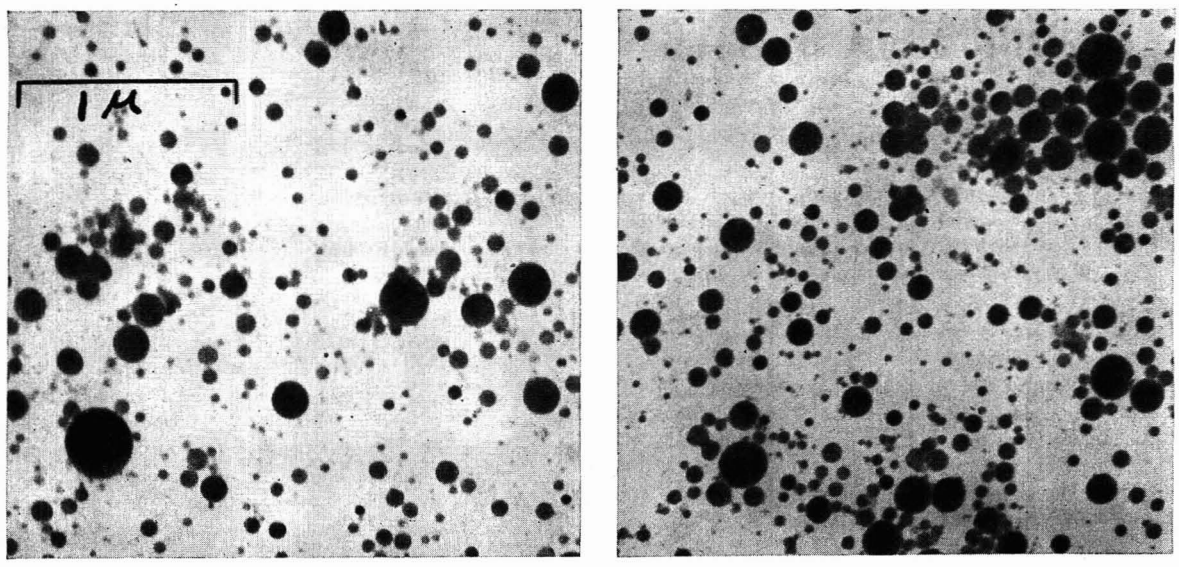

Figure 2. Aluminum Oxide Fumes

Left. In nitrocellulose. Right. After treatment with HF vapor for 5 minutes

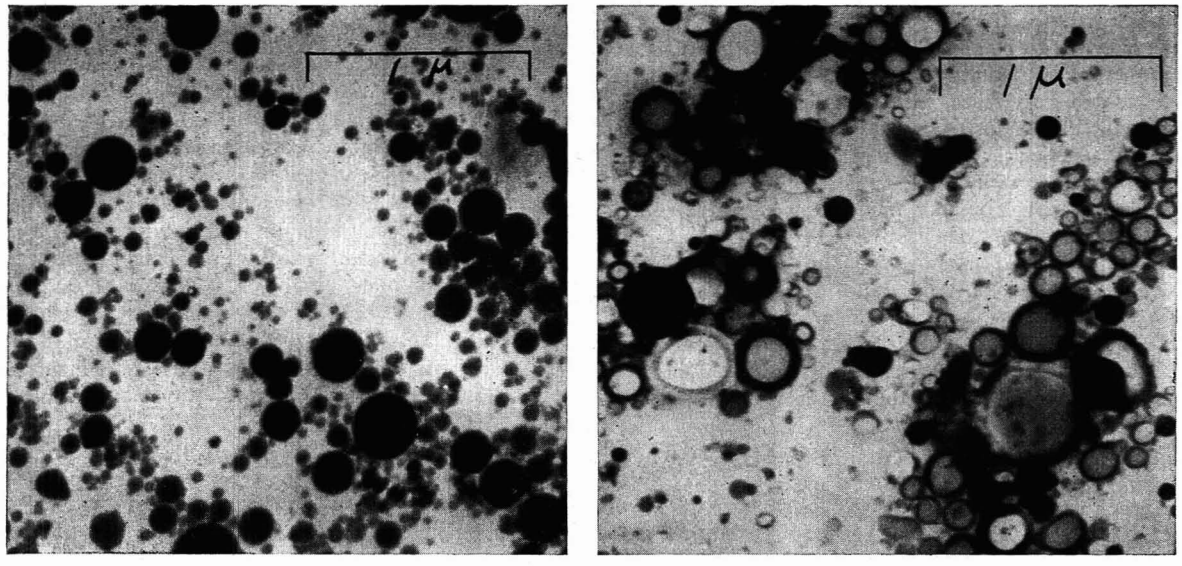

Figure 3. Furnace Fumes from Smelting Alumina Containing Silica

Left. In nitrocellulose. Right. After treatment with HF vapor for 5 minutes

material be dispersed in the resin film rather than on its surface. The sample may be dispersed in the resin solution (Formvar or Parlodion), spread on water or glass, whichever provides a continuous film. The film is stripped and exposed to hydrofluoric acid vapor above concentrated hydrofluoric acid (48%) at room temperature. Although the resin film completely surrounds the particles, the film is so thin that many vapors readily permeate through it. The hydrogen fluoride vapor diffuses into the film, and reacts with the silica particles which are vaporized as silicon tetrafluoride and disappear from the film. Their shape and size are, however, indicated by the fossils or casts which they leave in the film. Silicates are indicated by incomplete vaporization of the material in the casts and partial or complete conversion to fluorides may be observed by the appearance of crystalline forms within the casts. The alumina spheres show no significant change.

By standardizing on a fixed distance between the specimen and the surface of the acid, it is possible to control the time to indicate various stages in the progress of the volatilization which may be of significance in appraising the activity of the fume. The time required for vaporizing fume particles between 0.02 and 0.4 micron is short, but prolonged treatments are not detrimental. Exposure of the specimen to air of high relative humidity just prior to the hydrofluoric acid vapor treatment accelerates the volatilization of the silica and reduces any tendency for the formation of obscuring surface films of fluosilicic acid. Upon fixing the distance between the specimen and the acid surface at 4 cm., fume produced by sparking a vertical carbon electrode against metallurgical silicon was completely vaporized within one minute. The appearance of these specimens both before and after the vaporization (Figure 1) identifies this spherical fume as silica. Aluminum oxide fume produced by sparking two aluminum electrodes shows no significant alteration in particle size or shape after the vaporization treatment for a 5-minute period and in some cases for as long as 60 hours (Figure 2).

This retention of the spherical form may be considered a distinguishing feature between the alumina and silica fumes.

Fumes occurring above electric furnaces producing fused alumina from impure source materials containing silica may contain some crystalline forms but are predominantly spherical in form. When subjected to the vaporization treatment with hydrofluoric acid, many casts show only partial removal of the spherical particles (Figure 3). These particles may be silicates or co-condensations of the two major components.

Further distinctions may be possible by submitting the specimens to electron diffraction.

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Colorimetric Microdetermination of Formic Acid Based on Reduction to Formaldehyde

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A colorimetric method for determination of 0.25 to 15 micrograms of formic acid in 0.5 ml. of solution is based on reduction to formaldehyde by means of magnesium with subsequent measurement of the formaldehyde by means of chromotropic acid. For determinations in blood, formic acid is first separated from interfering substances by quantitative vacuum microdistillation at a low temperature. In application to mixtures of formic acid and formaldehyde, the formaldehyde is first removed by reaction with phenylhydrazine.

METHODS for detection and estimation of formic acid have been based principally either on oxidation of formic acid by mercuric chloride or on reduction by magnesium. The sensitivity of measurement by means of mercuric chloride in a colorimetric procedure is sufficient for determination of quantities of formic acid as small as 5 to 30 micrograms, but greater sensitivity by this method does not appear readily attainable (*6*). The single quantitative procedure which has been described, based on reduction of formic acid by magnesium and measurement of the resultant formaldehyde, has hitherto been found satisfactory only in the range of 40 to 1000 micrograms (*1*). However, this reduction method has theoretical potentialities for application to smaller quantities in view of the relatively high sensitivity of the procedures available for colorimetric determination of formaldehyde.

To increase the sensitivity of formic acid measurement, especially for toxicologic and microbiologic applications, factors influencing the reduction of formic acid to formaldehyde have been investigated further and it has been found possible to utilize magnesium reduction in conjunction with colorimetric determination of formaldehyde by means of chromotropic acid to measure 0.25 to 15 micrograms of formic acid in 0.5-ml. samples with an average error of 0.13 microgram for single analyses. For analysis of samples such as blood which contain protein and carbohydrate interfering substances, the formic acid may be separated by low-temperature vacuum distillation (*5*). For measurement of formic acid in samples containing formaldehyde, reaction with phenylhydrazine may be utilized for preliminary removal of the formaldehyde.

REAGENTS

Chromotropic Acid Reagent. To a solution of 0.6 gram of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid, Eastman Kodak Co., pract.) in 20 ml. of water are added 180 ml. of concentrated sulfuric acid.

Magnesium Ribbon. Strips 10 cm. long and 3 mm. wide, weighing approximately 80 mg., are rolled into coils 1 cm. in diameter. The supply of ribbon should be protected from atmospheric attack in a desiccator containing sodium hydroxide.

PROCEDURES

Solutions of formic acid which are free from interfering substances are analyzed by adding a 0.5-ml. sample containing not more than 15 micrograms of formic acid to an 80-mg. coil of magnesium ribbon in a test tube immersed in an ice bath. A total of 0.5 ml. of concentrated hydrochloric acid is then added in ten separate portions of 0.05 ml. each at intervals of not less than one minute. The tube is removed from the bath a minute after the last addition of hydrochloric acid and 1.5 ml. of chromotropic acid reagent are added. The mixture is heated on a boiling water bath for 30 minutes with precautions against absorption of water vapor and uneven illumination, as described by MacFadyen (*7*). The mixture is then centrifuged clear of white precipitate and the color of the supernatant fluid is measured photoelectrically, using a filter with peak transmission at 570 mμ. The relationship between colorimeter reading and quantity of formic acid is established by measuring the color produced by a series of standards of 0 to 15 micrograms of formic acid in 0.5 ml. of 0.01 *N* hydrochloric acid solution submitted to the procedure already described. The relationship between log galvanometer reading and amount of formic acid is linear in the range of 0 to 10 micrograms.

Samples for analysis which may contain carbonates should be acidified to approximately pH 2 by addition of hydrochloric acid before submission to the magnesium reduction procedure.

For measurement of formic acid in blood, protein is removed by mixing 0.5 to 1 ml. of blood with 2 volumes of a solution containing 5% sulfosalicylic acid in 0.25 *M* sulfuric acid. The mixture is centrifuged and the formic acid is separated from carbohydrates by low-temperature vacuum distillation of the supernatant fluid in a previously described apparatus (*5*). This apparatus employs a closed system; the distillate condenses at the temperature of dry ice and distillation of milliliter samples proceeds to dryness in approximately 2 hours without heating. The distillate is submitted to analysis by the procedure described for pure solutions. In calculation of the concentration in the original blood, correction should be made for the change in volume resulting from removal of nonvolatile substances. For average rabbit blood, the mixture of blood and sulfosalicylic acid solutions contain 93% by volume volatile materials.

When formaldehyde is present in the sample to be analyzed for formic acid, the formaldehyde may be removed preliminarily or the amount may be measured and correction made for the color produced by it in the analysis for formic acid. Formaldehyde is readily removed from blood samples by adding phenylhydrazine to the supernatant fluid from the mixture of blood with sul-

fosalicylic and sulfuric acid before distillation in the proportions of 5 to 10 mg. of phenylhydrazine hydrochloride per milliliter of supernatant fluid. For concentrations up to 10 micrograms of formaldehyde per ml., an interval of 5 minutes is allowed for the reaction with phenylhydrazine to take place at room temperature before the mixture is frozen for distillation.

EXPERIMENTAL

The use of magnesium and hydrochloric acid in the manner described in the present procedure was found more favorable for the reduction of formic acid to formaldehyde than the use of several other metals, acids, or conditions of reaction which were investigated. With 5 to 50 mg. of sodium, lithium, calcium, aluminum, or zinc in conjunction with 4 to 12 *N* hydrochloric acid at room temperature no formaldehyde production was detectable from 20 micrograms of formic acid. Magnesium amalgam was considerably less effective than magnesium itself. Addition of platinum black did not increase formaldehyde production.

Investigation of the effectiveness of various acids in combination with magnesium, when approximately 80 mg. of magnesium were employed with 50 micrograms of formic acid in 1 ml. of acid at room temperature, showed that with 1 to 1 dilutions of concentrated sulfuric, metaphosphoric, or orthophosphoric, or saturated solutions of sulfurous or boric acids there was no appreciable formaldehyde production. With aminoacetic, lactic, oxalic, maleic, and sulfanilic acids there was much interfering discoloration. With acetic, monochloroacetic, trichloroacetic, citric, and sulfosalicylic acids, formaldehyde production from formic acid was detectable, but there was also considerable color in blanks without formic acid. With propionic and sulfamic acids, formaldehyde was produced with little interference, but somewhat less efficiently than with hydrochloric acid.

In formic acid reduction by means of magnesium and hydrochloric acid, the manner of mixing and the temperature at which the reduction is carried out influence the efficiency of the process. On the other hand, moderate variation in the total amounts of magnesium and hydrochloric acid employed is possible without markedly influencing the yield of formaldehyde. Addition of 0.5 ml. of hydrochloric acid in ten equal portions at various intervals shorter than a minute resulted in definitely diminished yield of formaldehyde, while approximately constant yield resulted when intervals of from 1 to 3 minutes were employed. Similarly, if 0.5 ml. of hydrochloric acid was added in fewer portions than ten, even though with intervals greater than a minute, less color resulted, while addition in twenty portions gave the same yield as ten. When the reduction was carried out in an ice bath at 0° C. in the manner recommended in the present procedure, a better yield was obtained than in baths at −20°, −10°, 25°, or 100° C. It is noteworthy that slow addition of acid and employment of an ice bath in the reduction of formic acid by magnesium was previously recommended by Droller (*1*), but his stated purpose was the prevention of separation of the fuchsin which he employed for formaldehyde measurement, rather than the improvement of formaldehyde yield.

The quantity of magnesium recommended in the present procedure is based on a compromise between yield of formaldehyde and quantity of precipitate formed with the chromotropic acid reagent. In the reduction of 5 micrograms of formic acid, formaldehyde production is increased as the amount of magnesium ribbon is increased at the rate of approximately 10% per cm. from 7 to 11 cm. However, above 10 cm. the amount of precipitate becomes excessive for direct application of the chromotropic acid. Attempts to increase sensitivity by employing larger quantities of magnesium and hydrochloric acid with subsequent separation of the formaldehyde by distillation were unsuccessful because of difficulties in distilling the concentrated magnesium chloride solutions.

Some limitation of the yield of formaldehyde from formic acid is imposed by loss of formaldehyde through reduction by magnesium and hydrochloric acid. An average loss of 15% occurred when solutions of 1 to 5 micrograms of formaldehyde per ml. were submitted to the procedure described for formic acid reduction.

The reduction of carbon dioxide to formaldehyde by magnesium, as noted by Fenton (*3*), was found to occur under the conditions of the present analytical procedure to a slight extent, indicated by production of a color equivalent to 5.2 micrograms of formic acid per ml. when 1 *N* sodium carbonate was submitted to this procedure. Interference from carbon dioxide was satisfactorily eliminated by preliminary acidification of standards and experimental samples as previously described. Protection of the magnesium ribbon from atmospheric attack was also helpful in obtaining constant results.

Separation of formic acid from interfering substances of blood by means of a procedure (*1*) employing successive treatments with metaphosphoric acid, copper sulfate, and calcium hydroxide was investigated to determine its suitability for use in conjunction with the magnesium reduction and chromotropic acid reactions, but was found unsatisfactory. When normal rabbit blood and blood containing an additional 10 micrograms of formic acid per ml. were submitted to this procedure for removal of protein and carbohydrate and were then treated with magnesium, hydrochloric acid, and chromotropic acid, turbid brown solutions were obtained which were indistinguishable and unsuitable for colorimetry.

The separation of formic acid from blood by low-temperature vacuum distillation, which is recommended both in the present procedure and in a previously described procedure for determining formic acid by means of mercuric chloride (*6*), gave satisfactory recoveries of formic acid and eliminated nonvolatile interfering substances as well as carbon dioxide. Blank values of 1.4 to 8.4, averaging 5.2, micrograms of formic acid per ml., were obtained for seven normal rabbit bloods. When 10 and 100 micrograms of formic acid per ml. were added to blood, 100.5 and 102.6%, respectively, were recovered.

The treatment with phenylhydrazine which is recommended to eliminate small amounts of formaldehyde from samples to be analyzed for formic acid was found not to interfere with recoveries of formic acid, and formaldehyde in concentrations up to 10 micrograms per ml. was completely removed by this procedure. Up to 200 micrograms of formaldehyde per ml. could be removed if the phenylhydrazine mixture was heated for 5 minutes in a boiling water bath, but under these conditions there was a moderate increase in the blank for formic acid, possibly due to some formation of formic acid.

Colorimetric determination on the 1.5-ml. volumes of color solution yielded by the present analytical procedure was satisfactory when a Cenco Photelometer was used, in which the lamp filament was turned horizontally and a piece of rubber stopper was placed in the cuvette compartment to raise the cuvette into appropriate position in the beam. Suitable spectral transmittance was obtained with a combination filter consisting of Jena VG-3 (2 mm.), Corning 9780 (2.56 mm.), and Cenco No. 2 (2 mm.) filters.

DISCUSSION

The present procedure for measurement of formic acid provides advantages in increased convenience, sensitivity, and specificity over previous methods utilizing either mercuric chloride or magnesium. The use of chromotropic acid to measure formaldehyde in this procedure eliminates the uncertainty in color development inherent in the single previous quantitative magnesium method which employed fuchsin–sulfurous acid and required accurate titration of the magnesium by hydrochloric acid (*1*). Use of chromotropic acid also eliminates the wait of 10 to 24 hours recommended for stabilization and clarification

of solutions for colorimetry in the procedure employing fuchsin–sulfurous acid.

The sensitivity of determination of formic acid by the method described here, while superior to that of previous methods and probably adequate for many purposes, yet is somewhat less than the sensitivity which would be attained if the formic acid were completely converted to formaldehyde. At present a net yield of approximately 29% of theoretical is obtained, corresponding to a total yield of 34% with a coincident loss of 15% of the formaldehyde formed. It would appear that if a larger proportion of magnesium could be conveniently utilized or conditions for more efficient reduction of formic acid with sparing of the formaldehyde were devised, the sensitivity might be increased slightly more than threefold.

The specificity of the chromotropic acid reagent for formaldehyde which has been demonstrated by Eegriwe (*2*) and MacFadyen (*7*) indicates a corresponding high degree of specificity for the determination of formic acid by the present procedure, since few substances other than formic acid yield formaldehyde on reduction by magnesium (*4*). Among possible interfering substances is carbonic acid, which can be reduced to formaldehyde by magnesium, but is readily eliminated by preliminary acidification of solutions to be tested. Interference by acetic acid or acetaldehyde would occur only at high concentrations of these substances (*4*, *7*). Preformed formaldehyde would interfere at low concentrations, but is readily removed by means already described. Labile compounds or polymers of formaldehyde presumably would also interfere if not similarly removed.

ACKNOWLEDGMENT

The author wishes to acknowledge the valuable technical assistance of Myra Rolston.

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NOTES ON ANALYTICAL PROCEDURES . . .

Quantitative Volumetric Analysis of Carbon-Bonded Halogen with Sodium Naphthalene

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QUANTITATIVE organic analysis for halogen by the sodium-in-liquid-ammonia method (*2*) is somewhat limited because of the sparing solubility of many compounds in liquid ammonia at its boiling point. It has, however, suggested the possibility of using a solution of sodium naphthalene in an appropriate oxygenated solvent (*1*) as a more convenient analytical reagent. Choice of solvent is rather broad and includes ethylene glycol dimethyl ether, ethylene glycol diethyl ether, dioxane, and methyl isopropyl ether. Since many of these solvents are relatively high boiling, solubility limitation would be much less restrictive than for liquid ammonia.

The volumetric procedure was chosen as the most rapid means of exploring the possibilities of this reagent. The appropriate gravimetric procedure is an obvious variation of the method described.

EXPERIMENTAL

Preparation of Sodium Naphthalene. The solutions of sodium naphthalene in ethylene glycol dimethyl or diethyl ether were prepared according to the directions of Scott (*1*) and were used at approximately 0.5 molar. They were stored in and dispensed from an automatic buret and solutions of sodium naphthalene were transferred from flasks to buret under an atmosphere of dry nitrogen.

Purification of Reagents and Samples. The ethylene glycol dimethyl and diethyl ethers were obtained from the Carbide and Carbon Chemicals Corporation and purified by refluxing over sodium for 3 hours, followed by fractional distillation.

Samples of solid compounds for analysis were purified to maximum melting point by recrystallization. Liquids were fractionally distilled and that fraction of the distillate boiling within the range reported for the pure compound was employed for analysis.

Analytical Procedure. Liquid samples were weighed in thin-walled, sealed glass bulbs and placed in a separatory funnel from which air was displaced by dry nitrogen, and 10 to 20 ml. (an excess) of the sodium naphthalene reagent were added. The separatory funnel was stoppered and shaken vigorously to break the bulb (as indicated by an abrupt temperature rise), and shaking was continued for 2 to 3 minutes longer. The formation of sodium halide is probably instantaneous. Excess reagent was destroyed and the sodium halide was dissolved and separated by adding two to three consecutive portions of water up to a total of approximately 100 ml. The combined aqueous layers were acidulated with nitric acid and titrated potentiometrically with 0.1 *N* silver nitrate solution, using a silver-plated platinum wire and a saturated calomel electrode with an ammonium nitrate–agar gel bridge.

Solid samples were introduced directly into the separatory funnel and 5 ml. of toluene were added to dissolve the samples to facilitate reaction. The procedure was not otherwise altered.

Table I. Analyses.

Compound	Milliequivalents of Halogen, Calculated	Milliequivalents of Halogen, Found	% Error
Ethyl bromide	4.484	4.505	+0.49
	4.594	4.543	−1.11
	4.543	4.594	+1.11
Tetrachloroethylene	4.790	4.810	+0.41
	5.070	5.031	−0.77
	4.841	4.817	−0.49
Carbon tetrachloride	5.210	5.179	−0.59
Bromobenzene	4.319	4.323	+0.09
	5.065	5.042	−0.45
p-Dichlorobenzene	5.020	5.014	−0.12
	4.862	4.867	+0.10
p-Chloroaniline		Very low	
p-Bromo-*N*,*N*-dimethylaniline	4.384	4.410	+0.59
	5.040	5.071	+0.61
β-Bromonaphthalene	5.140	5.105	−0.69
	5.154	5.110	−0.85

DISCUSSION

It was not the purpose either to establish the ultimate precision of this method, or to discover all limitations, but only to demonstrate its applicability to a considerable class of organic compounds with limits of precision which are usually acceptable. It is, of course, to be expected that any compound containing

active hydrogen will probably form an insoluble sodium salt and therefore not give a quantitative yield of sodium halide. This was the case with *p*-chloroaniline, whereas *p*-bromodimethylaniline reacted quantitatively. The nitro group also interferes in aromatic as well as in aliphatic compounds. Hexabromobenzene and 2,2-difluoroheptane do not react at all. This method appears to have broad applications, but in any particular instance it will obviously be necessary to consider possible complications. Since rigorous purification of the substances chosen for analysis was not attempted, it appears likely that precision was limited by sample purity rather than by a nonquantitative liberation of sodium halide.

Potentiometric procedure was employed in this investigation because it offered a means of following the course of the titrations, a requirement which was considered advisable in the study of a new analytical method. The authors believe, however, that this method may be replaced by a more common procedure such as the Volhard or Mohr methods of titration. They hope to extend the investigation at a later time.

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Determination of Radioactive Carbon in Solid Samples

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THE precipitation of radiocarbon (C^{14}) as an insoluble carbonate and the measurement of the activity of the precipitate with a thin mica end-window Geiger counter or an electroscope are generally the most rapid and convenient methods for determining the relative radioactivity of materials containing this isotope. The efficiency of counting obtained with solid samples external to the counter is appreciably less than that with counters (*4*) or ionization chambers (*1*) filled with radioactive carbon dioxide, but the convenience of use of solid samples will, in most cases, outweigh this disadvantage.

The method of collecting a precipitate of barium carbonate described below is easy of application and yields reproducible results in the determination of the actvitiy of both thin and thick precipitates. It also furnishes a gravimetric analysis of the total carbon in the sample when no "carrier" carbonate is added in the preparation of the precipitate. It is probable that this method could be employed in studies using radiosulfur (S^{35}) or radiocalcium (Ca^{45}) by precipitating the former as the sulfate or benzidine salt (*2*) and the latter as the oxalate.

A brass Büchner-type funnel, constructed as shown in Figure 1, *a*, *b*, *e*, has been found suitable for use with a counter whose window diameter is 1.125 inches (2.8 cm.). Suction is applied to the funnel by setting it on the rim of a glass funnel arranged as a part of a conventional suction filtration apparatus. The rim of the glass funnel is ground flat and with an outer diameter equal to that of the brass funnel. The brass funnel is used to support two layers of filter paper, the first of which (Figure 1, *d*) is a circle of qualitative paper cut to fit the inner diameter of the funnel. A Lucite cylinder 1 inch (2.5 cm.) in diameter is used to press a sheet of retentive filter paper (Schleicher and Schüll No. 589) into the funnel and, using a sharp knife, the excess paper is cut off flush with the rim (Figure 1, *c*). Strong suction is applied to the funnel and the paper is wetted with water. By pressure exerted with a small cylindrical vial the paper is closely adapted to the funnel. While the paper is still wet, its cut edge is attached to the rim of the funnel by carefully applying a small amount of molten paraffin around the rim with a finely tipped brush. The funnel and paper are washed successively with acetone and ether. Air is drawn through the filter by suction until the paper is dry and it is weighed.

Barium carbonate is precipitated by the dropwise addition of an excess of 10% barium chloride to a solution of sodium carbonate containing the radioisotope. The precipitate is collected on the filter as a uniformly thick layer by transferring small portions to the funnel and allowing the mother liquor to be drawn through the filter before the next portion is transferred. (If only the relative or specific activities of the carbon in two or more solutions are to be determined or if an analysis for total carbonate is not to be obtained, quantitative precipitation and collection of the carbonate are not required.) Gentle intermittent suction is employed until the filter paper is covered with a layer of precipitate, after which the suction is increased to 7 cm. of mercury. Precipitates prepared from solutions containing a large excess of sodium hydroxide are likely, during transfer of the precipitate from a beaker, to be covered with a film of relatively inactive barium carbonate. This formation of barium carbonate from atmospheric carbon dioxide can be prevented effectively by carrying out the precipitation in a centrifuge tube. After centrifugation of the stoppered tube, the mother liquor is decanted and the precipitate washed once by centrifugation with carbon dioxide–free water, after which the precipitate can be handled without danger of contamination. The precipitate and funnel are washed in order with water, acetone, and ether and dried to constant weight by drawing air through the filter for about 15 minutes. Cracks which appear in thick precipitates are removed by smoothing the surface with the bottom of a cylindrical vial. The filter assembly is then placed at reproducible position beneath a thin window counter and the activity determined.

The radioactivity data used in construction of the curve shown in Figure 2 were obtained with a counter whose window thickness was about 4 mg. per sq. cm. The rim of the funnel was about 2 mm. below the window. All counts were corrected for counter and scaler performance by reference to counts of a permanent uranium standard. The "thick" sample counts shown in Figure 2 were about 3100 counts per minute. The accuracy of the procedure as a method for gravimetric analysis for carbonate was demonstrated by analyses of a standard solution of sodium carbonate from which theory demanded a yield of 150 mg. of barium carbonate. The results of four analyses were 100.2 ± 0.4% of the theoretical yield.

Libby (*3*) has derived empirical equations which describe the internal absorption of beta-rays by soft beta-ray emitting solids. The authors' observations (Figure 2) are in excellent agreement with the deduction made by Libby that, for radioactive carbon,

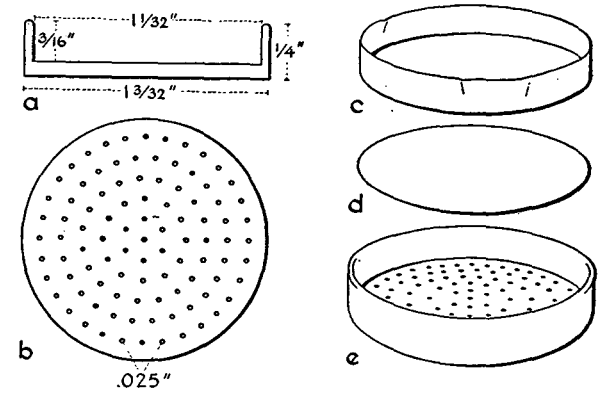

Figure 1. Büchner-Type Funnel for Collecting Barium Carbonate Containing Radioactive Carbon

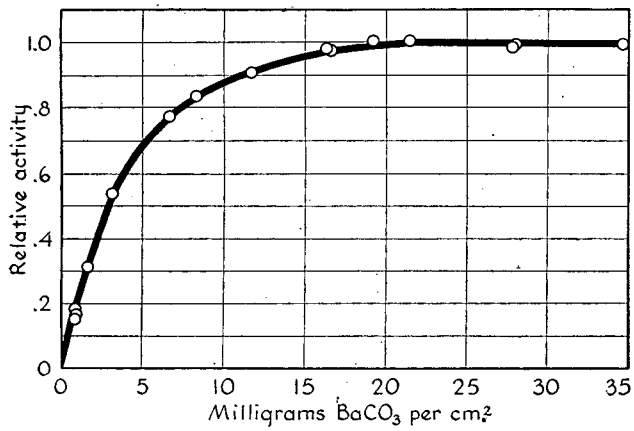

Figure 2. Relative Activity of Various Thicknesses of Barium Carbonate of Uniform Specific Activity

the "saturation thickness"—i.e., that thickness of sample which absorbs completely all beta rays produced in layers of greater depth—is 20 mg. per sq. cm. Their results are also in good agreement with the data reported by Reid (*5*) and with the results of Yankwich, Rollefson, and Norris (*6*), who present data on the absorption of beta-radiation of radiocarbon by barium carbonate.

With precipitates weighing 20 mg. per sq. cm. or more the total relative radioactivity of a carbonate containing solution is calculated as follows:

$$A = \frac{V_1}{V_2} \times \frac{W}{20} \times C$$

where A is the activity in V_1 volumes of carbonate solution, V_2 is the volume of the aliquot of V_1 used in the preparation of the precipitate, W is the weight of the precipitate in milligrams per square centimeter, and C is the counts per minute corrected for resolving time losses and background.

When a precipitate thinner than 20 mg. per sq. cm. is counted, the activity can be referred directly to a standard prepared with an identical thickness of precipitate, or the method of Reid (*5*) whereby a thin sample count is calculated to thick sample activity can be employed.

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Determination of Silver with Ascorbic Acid

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A RECENT paper (*1*) showed that gold may be determined with accuracy by reduction of gold chloride with ascorbic acid. This same reagent is effective for the reduction of silver.

$$2AgNO_3 + C_6H_8O_6 \longrightarrow 2Ag + C_6H_6O_6 + 2HNO_3$$

Table I. Determination of Silver

Silver Added *Gram*	Silver Found *Gram*	Difference *Gram*
0.1376	0.1376	0.0000
0.1063	0.1061	−0.0002
0.0908	0.0909	+0.0001
0.0753	0.0752	−0.0001
0.0695	0.0697	+0.0002
0.0501	0.0501	0.0000
0.0436	0.0435	−0.0001
0.0351	0.0349	−0.0002
0.0168	0.0169	+0.0001
0.0113	0.0112	−0.0001

Table II. Precipitation of Silver from Solutions Containing Other Ions

Silver Added *Gram*	Other Metal Added	*Gram*	Silver Found *Gram*	Difference *Gram*
0.0497	Pb^{++}	0.0325	0.0496	−0.0001
0.0229		0.0162	0.0230	+0.0001
0.0450	Cu^{++}	0.0050	0.0452	+0.0002
0.0284		0.0031	0.0284	0.0000
0.0768		0.0154	0.0767	−0.0001
0.0887		0.0100	0.0886	−0.0001
0.0794	Bi^{+++}	0.0300	0.0794	0.0000
0.0403		0.0150	0.0404	+0.0001
0.0772	Cd^{++}	0.0299	0.0772	0.0000
0.0365		0.0149	0.0364	−0.0001
0.0761	Ni^{++}	0.0315	0.0763	+0.0002
0.0395		0.0157	0.0396	+0.0001
0.0768	Zn^{++}	0.0103	0.0770	+0.0002
0.0948	$Cu^{++} + Zn^{++}$	0.0451 Cu 0.0112 Zn	0.0949	+0.0001

As a result of the investigation of this reaction a new method was developed for the determination of silver, by precipitation with ascorbic acid.

Solutions. Nitric acid, 6 *N*. Ascorbic acid, 2 grams per 100 ml. of solution. Standard silver solutions, made by dissolving weighed portions of pure silver (Schering *pro Analysi*) in 6 *N* nitric acid, removing the acid by evaporation, and diluting the residue to 20 ml. with distilled water.

Copper and nickel solutions, made by dissolving weighed portions of pure electrolytic copper and pure nickel wire in 10 ml. of 6 *N* nitric acid and diluting to 100 ml. with distilled water.

Solutions of lead, bismuth, cadmium, and zinc were made by dissolving a suitable pure salt or pure oxide in water or dilute nitric acid and diluting to 100 ml. Their exact strength was determined by the usual analytical methods.

Procedure. Weigh out 0.1 gram or less of silver into a 100-ml. beaker and add 5 ml. of 6 *N* nitric acid. Heat gently until solution is complete and then evaporate almost to dryness over a steam bath. Dilute to 20 ml. with distilled water, heat the solution to 90° to 100° C., and slowly add 10 ml. of the freshly prepared ascorbic acid reagent. Continue the heating for 15 minutes and promptly filter the precipitate by a porcelain filter crucible. Wash the precipitate with hot water and ignite. Results obtained are given in Table I.

Tests upon the effect of added amounts of lead, copper, bismuth, cadmium, nickel, and zinc show (Table II) that there is no interference.

The proposed method has been applied to the analysis of silver-copper alloys. A U. S. silver coin (one dime, 1929) was found to contain 89.95% silver. The certified figures for this alloy are 90% silver and 10% copper. A Greek silver coin (50λ. K.Π.1901) was found to contain 83.51% silver. The certified figures for this alloy are 83.5% silver and 16.5% copper.

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Use of Tributyl Phosphate for Extracting Organic Acids from Aqueous Solution

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THE authors have found that *n*-tributyl phosphate is a decidedly more effective agent for extracting certain organic acids from aqueous solution than ethyl ether (*1*), isopropyl ether (*3*), benzene (*2*), toluene (*2*), or chloroform (*2*), which are commonly used. The eighteen organic acids thus far studied show a wide range of extraction.

REAGENTS AND APPARATUS

The concentration of the various acids was determined to four significant figures by titrating 20-ml. pipetted portions with carbonate-free standard sodium hydroxide, using phenolphthalein indicator. Glass-stoppered separatory funnels (60 ml.) with the stems cut off 1 cm. below the stopcock were used for the extractions. Vaseline served as lubricant to prevent leakage. An International centrifuge (size 1, type SB) was used to produce complete phase separation.

PROCEDURE

Twenty milliliters of the organic acid were pipetted into the separatory funnel, followed by a 10-ml. pipetted volume, of tributyl phosphate. The mixture was shaken vigorously for 1 minute to effect extraction and then centrifuged for 3 minutes at 500 r.p.m. The aqueous layer (lower) was then quantitatively transferred to a 100-ml. Erlenmeyer flask and titrated with 0.1 or 0.5 *N* standard sodium hydroxide to determine the residual acid.

Standardization of the organic acid and the extractions were done the same day to avoid possible error due to air oxidation, bacterial action, or volatilization. Blanks were deducted for the trace of free acid in the phosphoric ester. All work was done at 25° ± 2° C.

Table I. Results of Single Extractions Using One Volume of Ester to Two Volumes of Aqueous Acid

Acid	Concn., *N*	Extracted, % (±0.2)	$\frac{C_{ester}}{C_{water}}$
Formic	0.10	59.2	2.90
Acetic	3.8	41.2	1.40
	1.2	48.1	1.85
	0.60	51.6	2.13
	0.30	53.7	2.31
	0.10	53.9	2.34
Propionic	0.08	80.7	8.36
n-Butyric	0.50	91.9	22.7
	0.11	93.1	27.0
n-Valeric	0.10	97.8	88.9
Isovaleric	0.10	97.5	78.0
Oxalic	0.25	62.5	3.33
Malonic	0.11	68.7	4.40
Succinic	0.11	74.0	5.69
Malic	0.11	38.7	1.26
Maleic	0.10	64.1	3.57
Tartaric	0.49	21.2	0.54
	0.10	22.4	0.58
Chloroacetic	0.53	86.4	12.7
	0.10	87.5	14.0
Glycolic	0.50	20.4	0.51
	0.10	21.6	0.55
Lactic	0.48	40.0	1.33
	0.11	40.7	1.37
Citric	0.10	50.0	2.00
Gluconic	0.10	4.0	0.083
Mandelic	0.05	93.8	30.3
(NaOH)	(0.10)	(0.0)	....

VALIDITY OF ANALYTICAL PROCEDURE

After the ester and water phases are separated, the acid in the ester phase can be quantitatively converted to salt by adding aqueous sodium hydroxide and shaking. In several different determinations the total acid found by titrating the two separated phases was in excellent agreement with the total acid taken. This indicates that the ester is not hydrolyzed under the experimental conditions.

DISCUSSION

The decrease of extraction with increased concentration (as shown for six acids) would be anticipated for the ternary systems. The distribution ratio is sufficiently constant, however, to indicate that the ester is not an associating solvent for such organic acids. Furthermore, triple extraction of 0.10 *N* succinic acid showed a total of 98.9% extraction compared to 98.2% calculated, assuming a constant ratio. Since *n*-tributyl phosphate is essentially insoluble in water (0.6% by volume) while water is about 7.5% soluble in the ester at 25° C., a calculated volume of water was added after each extraction to maintain constant aqueous volume.

The relation between extraction and the structure of the organic acid is rather marked and consistent.

The extraction increases with the length of the carbon chain for both monobasic (except formic) and dibasic acids, as shown by the two series: acetic-propionic-butyric-valeric-oxalic and malonic-succinic.

The monobasic acids are extracted more than dibasic acids containing the same number of carbon atoms. Here oxalic acid is the exception.

Hydroxyl groups strongly depress extraction as shown by comparing acetic-glycolic, propionic-lactic, and succinic-malic-tartaric, and by noting the effect of five hydroxyl groups on gluconic acid.

Chloro and phenyl groups strongly increase extraction, as shown by acetic-chloroacetic and glycolic-mandelic.

The double bond has a depressing effect, as shown by succinic-maleic.

Sulfuric acid is 1.0% extracted at concentrations of 0.10, 0.50, 1.0, and 2.0 *N*. Hydrochloric acid, however, shows a marked increase with increased concentration—for example, with 0.10, 0.49, 1.0, and 1.9 *N* acid, the per cent extracted is 0.8, 0.8, 1.8, and 4.2, respectively. Nitric acid showed pronounced extraction, ranging from 14.4% with 0.10 *N* to 31.6% with 2.0 *N* acid.

A study of the separation of organic and inorganic acids by this extraction method is in progress.

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Standardization of Microchemical Apparatus

A Committee for the Standardization of Microchemical Apparatus has been appointed by the Division of Analytical and Micro Chemistry of the American Chemical Society under the chairmanship of Al Steyermark, Hofmann-LaRoche, Inc., Nutley, N. J. The committee has begun its meetings, and is desirous of getting in contact with other committees throughout the world which deal with standardization of apparatus, methods, etc., with a view to possible cooperation.

Manifold for Disposal of Fumes Given Off during Macro-Kjeldahl Digestive Process

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THE disposal of fumes arising during the digestive process in the macro-Kjeldahl method for total nitrogen presents difficulties when facilities for exhaustion of fumes into the air are nonexistent. A manifold that can be operated in an open laboratory, described here, achieves fume disposal through solution in water.

The idea of disposing of the fumes originating during the Kjeldahl digestive process through solution in water is used in the manifolds designed by Sy (*3*), Merkle (*2*), and Hastings, Fred, and Peterson (*1*) for macro-Kjeldahl digestions. This principle is likewise employed by almost all semimicro and micro-Kjeldahl procedures where glass manifolds operate in open laboratories. With the exception of the Merkle (*2*) manifold, however, which depends on the pressures developed during digestion to force the fumes into water, such manifolds usually employ filter pumps or modifications thereof to draw off the fumes prior to solution.

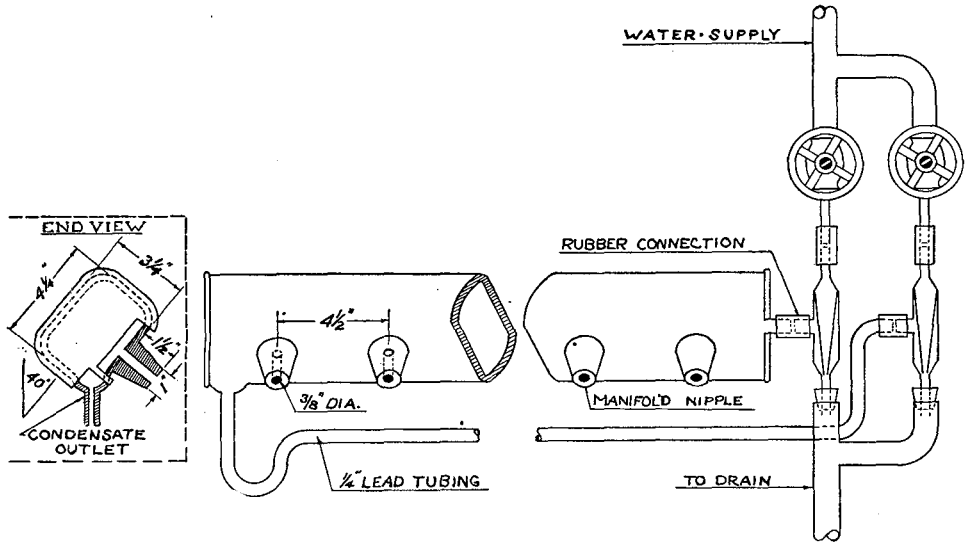

Figure 1. Diagram of Manifold

Four-inch lead pipe was used for the main portion of the manifold illustrated in Figure 1. This was hammered into a rectangular shape (see end view Figure 1) to facilitate subsequent casting operations. A cloth was tied over one end of the pipe, after which the pipe was packed with clean dry sand. Twelve nipples were cast at approximately 11.5-cm. (4.5-inch) intervals on the flat portion of the pipe by pouring molten lead into inverted 25-ml. Caldwell crucibles. A casting technique that resulted in perfect casts at all times consisted in centering the crucible at the desired spot on the manifold and sticking it in place with a ball of plastic clay. A low metal rim (9 cm. in diameter) was then set over the crucible and pushed into the clay matrix surrounding the crucible. Dry sand was poured into the metal rim surrounding the crucible almost to the top of the crucible. The metal rim and sand were merely safety measures to prevent damage to the manifold by spattering of molten lead.

Clean molten lead was then poured into the crucibles. After it had solidified, more lead was added if necessary to take care of any shrinkage at the top of the cast. After the casts had cooled, the crucibles, etc., were removed. An approximately 9-mm. (0.375-inch) hole was drilled through the center of each nipple, the cloth removed, the sand emptied out, and a condensate well hammered out (end view Figure 1), and lead end plates and two approximately 6-mm. (0.25-inch) lead tubing outlets were welded onto the manifold with a low acetylene flame.

In setting up the manifold for operation a slight tilt away from the pumps was given the manifold support, which consisted of a wooden board covered with sheet lead, to assure rapid drainage of all condensates, which are continuously and automatically removed during the digestion process. The manifold rests on the support so that the nipples tip downward (end view Figure 1). This eliminates virtually all out-of-flask drip. Two glass filter pumps were connected to the manifold outlets. The pump attached to the condensate outlet will, under ordinary water pressures, operate the manifold.

The manifold illustrated in Figure 1 is more rugged and has greater capacity than the glass manifold designed by Sy (*3*). The junction of the Kjeldahl flask with the manifold is not tight or rigid as in manifolds previously mentioned (*1–3*). Merkle (*2*) objected to the manifold described by Sy (*3*), because the partial vacuum created by the operation of the filter pump resulted in frothing and an increase in time required for digestion. With the loose-fitting nipple junctions, partial vacuums within the digestion flasks are not produced. No frothing or tendency of spatterings to collect in the neck of the digestion flask or increase in time required for complete digestion has ever been observed with soils or plant materials.

Soils and other materials which contain large amounts of inert solids usually bump strongly during the latter stages of the digestive process. It is conceivable, that rigid manifold–Kjeldahl flask junctions might loosen and permit sulfur dioxide fumes to escape into the open laboratory. Flask motion induced by bumping does not interfere with the operation of the manifold described. The strong inward flow of air around the nipples in the neck of the flask prevents the escape of sulfur dioxide fumes into the open laboratory. Moreover, the loose-fitting nipple junction facilitates turning the flasks during the initial stages of digestion and their removal without the necessity of handling acid-covered stoppers, where rigid junctions are employed.

This manifold has been in use since 1937. The only maintenance required during this period has been occasional replacement of the rubber connections.

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RECEIVED September 14, 1945. Contribution from the Soils Division. Published with the approval of the Director of North Dakota Agricultural Experiment Station.

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Seventh Congress on Spectrography

The seventh congress on spectrography, under the auspices of the Groupement pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Métallurgiques, was held January 21 to 23, 1947, at the Laboratoire Central de l'Armement, 1 Place Saint-Thomas d'Aquin, Paris, France. The report of the congress, in a 280-page paper-bound book, is divided into three sections: an account of the meetings, the technical papers, and illustrations.

CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology

THIS is the first in a series of monthly summaries of crystallographic data to be presented as a public service activity by Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill. This project, under the direction of W. C. McCrone, will present structures from the field of industrially important or common compounds. The purpose of this project is to increase the number of dependable crystal structures, especially of organic compounds, available in the literature. It is hoped that in time these efforts will increase the use of crystallographic methods, both microscopic and x-ray, in research and analysis.

The structures included will be chosen from those determined in the Armour Research Foundation laboratory and those submitted as a part of this project by cooperating laboratories. As announced in the February 16, 1948, issue of *Chemical and Engineering News*, page 472, any laboratory or individual may submit crystallographic data to Armour.

It is, therefore, necessary to set up mechanisms at once to ensure: (1) a continuing supply of crystal data; and (2) a reliable system for checking the data. This requires responsibility both with respect to quantity and quality of the data published. Further details are outlined below.

DATA SUBMITTED

Any carefully determined data, however fragmentary, may be submitted. In general, only those compounds of interest and importance to research and analysis will be completed, checked, and published. Data may be submitted as photostats of notebook pages or in any other form representing little effort. However, any additional material such as well-formed crystals (either for single crystal x-ray work or optical crystallography), crystal drawings, or photomicrographs will be appreciated. The names of all persons contributing different portions of the data should be included, so that acknowledgment can be made. In general, the over-all description will be credited to the laboratories submitting and checking the work and the data itself to the individuals who performed the work. This is desirable because the different portions will, in general, have been determined by different individuals. An outline of the final description is as follows:

I. **Introduction.** Covers crystallization procedure, solubilities, and preparation of crystals used for the work.
II. **Crystal Morphology.** Crystal system, form and habit, axial ratios, and interfacial angles.
III. **X-Ray Data.** Space group, cell dimensions, formula weights per cell, formula weight, density, and principal lines.
IV. **Optical Properties.** Refractive indices, optic axial angles, dispersion, optic axial plane, acute bisectrix, sign of double refraction, and molecular refraction.
V. **Thermal Data.** Behavior before, during, and after crystallization from the melt on a microscope slide.

Any original work included under the above classification may be submitted to Armour.

CHECKING FACILITIES

All the data submitted will be checked in either the Armour Research Foundation laboratory or some outside laboratory. Any laboratory in a position to check crystallographic data under any of the above classifications should write to W. C. McCrone, furnishing all details. Willingness to check any portion of the above outline will be very helpful.

One of the important preliminary steps that had to be taken before launching this project was to choose a set of conventions to be used in describing crystallographic properties. Such a set was drawn up based partly on the literature and partly on a meeting held at the invitation of Armour to a number of crystallographers attending the 1947 fall meeting of the AMERICAN CHEMICAL SOCIETY in New York. This tentative set of conventions was then submitted for criticism to the entire membership of the Crystallographic Society and the American Society for X-Ray and Electron Diffraction. As a result, nearly 100 outstanding crystallographers (eight European crystallographers) representing many diverse backgrounds have sent detailed comments, criticisms, and suggestions. It is, perhaps, unfortunate that these letters cannot be published in their entirety, as they represent the ideas and opinions of some of the best crystallographers in this country and Europe.

These letters show a wide variation in practice on almost every point under discussion. This has made the problem of setting up uniform conventions very difficult, since each crystallographer has good reasons for his point of view. The conventions, shown below, were chosen after careful consideration of these letters and are believed to be the best compromise possible; they will be used for the publication of data by the Armour Research Foundation.

Most of the conventions chosen agree with established usage. In every case an effort has been made to choose nomenclature that will be readily understood by all crystallographers, whether their background is x-ray diffraction, chemistry, or mineralogy. Although every effort has been made to eliminate any cause for criticism of this project in any of its aspects, comments or suggestions are most welcome.

In all cases not specifically covered below, the conventions used will be those published by Donnay (*4*) of Johns Hopkins University or by the Committee of the Division of Analytical and Micro Chemistry (*10*) (C. W. Mason, Chairman; W. M. D. Bryant, Mary L. Willard, E. F. Williams).

CONVENTIONS USED IN CRYSTAL DESCRIPTIONS

Axial Ratios. $a:b:c$ — 0.61:1:1.10.

Bisectrices. If not written out, the acute and obtuse bisectrices will be designated as Bx_a and Bx_o, respectively.

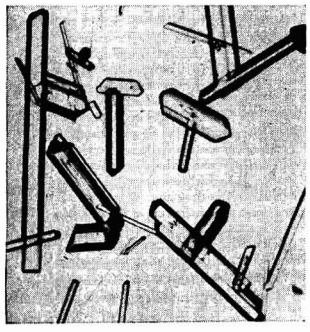
Beta Angle. The beta crystallographic angle will always be expressed as the obtuse angle, in keeping with existing x-ray crystallographic conventions. In the definition of extinction angles the apparently redundant word "obtuse" will be retained to avoid confusion. Thus, for a monoclinic crystal: the view normal to (010) shows oblique extinction; $X\Lambda c = 11°$ in obtuse beta. Acute beta need not be used, because the extinction can always be expressed as an angle smaller than 45° by picking the vibration direction and crystallographic axis to give the smallest angle. Occasionally, the term "acute" may be necessary in the interest of brevity. There is, for example, no other simple way of defining the location of an optic axial plane that is perpendicular to (010) and in the acute angle beta.

Crystallographic Axes. *a*, *b*, and *c* (lower case italics) will be used. The choice of *a*, *b* and *c* is based on the dimensions of the unit cell with $c<a<b$. This is, of course, true only for orthorhombic and triclinic crystals, since monoclinic crystals are defined on the basis of symmetry with *b* normal to the plane of symmetry. However, even in this case, the convention $c<a$ will be used. In no case will the choice of crystallographic axes be based on crystal habit. In the absence of x-ray data the axial ratios should be calculated from interfacial angles. The crystal will then be set up so that $c<a<b$, except as noted above for monoclinic crystals where $c<a$ with *b* having any possible value. This procedure will give

results identical with those obtained from x-ray data except when the crystals under morphological study show a secondary form, such as {210} to the exclusion of the primary {110}, and then only when $110\Lambda1\bar{1}0<90°$ and $210\Lambda2\bar{1}0>90°$, so that the a and b axes could be reversed. This, of course, would occur only in the very rare case where the {210} or similar secondary face crystallizes to the exclusion of {110} or the corresponding primary face.

Dispersion. $v > r$ or $r > v$ will be used.

Interfacial Angle. $hkl\Lambda h'k'l' = \theta°$. Microscopists use the true angle (dihedral angle) between the faces almost exclusively; mineralogists and x-ray crystallographers use the polar angles. Angles between face normals (polar angles) will be used unless otherwise designated by parenthetical phrases such as "(true)" or "(dihedral)."



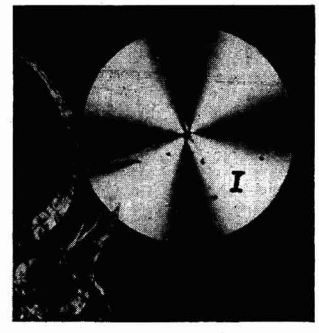


Figure 1 (*left*). Crystals of *p,p'*-DDT from Thymol at 80° C.
Figure 2 (*right*). Dendritic Crystals of *p,p'*-DDT (I and II) from the Melt

Miller Indices. Unenclosed Miller indices will be used on drawings; to indicate a plane direction as, for example, OAP = 010; and to express interfacial angles—e.g., $110\Lambda1\bar{1}0 = 99°$. In descriptions, parentheses around the indices indicate a single face, braces indicate a form, and square brackets a zone axis. Lower case italics will not be used as face designations.

Optic Axial Angle. According to long established usage, $2E$ signifies the optic axial angle in air; $2V$ the corresponding angle in the crystal; and $2H$ the corresponding angle in an immersion medium having a refractive index of 1.515; optic axial angles at different indices may be designated thus: $2H_{1.656}$. The variations, $2V_\alpha$, and $2E_\gamma$, are occasionally used to advantage. Care should be observed to indicate the wave length at which observations were made.

Optic Axial Plane. There is normally no difficulty in expressing the location of the optic axial plane—e.g., OAP = 010. When the optic axial plane is normal to 010, the orientation must be expressed in the same manner as the extinction angle (see Beta Angle).

Pleochroism. This can be expressed qualitatively in the form: X = yellow; Y = orange; Z = red. In tables: X (yellow); Y (orange); Z (red) may be used. In the very rare case of very high dispersion—e.g., crossed axial plane dispersion—it will be necessary to specify that X, Y, and Z are chosen as they exist at some definite wave length, as their position varies with wave length.

Polymorphism. Precedent favors use of alpha, beta, gamma, etc., or I, II, III, etc. The former have the disadvantage of conflicting with accepted designations for geometrical isomers, optical isomers, position isomers, tautomers, and other extraneous forms. The Roman numerals will be used henceforth, therefore, with the added usage that I indicates the stable polymorph at room temperature. Other polymorphic forms will be designated as II, III, etc., in order of their apparent stability. In general, an unstable modification (II, III, IV, etc.) can be stable either above or below room temperature and, unless the transition temperature is given, the stability range will not be known.

Profile Angles. The microscopist and petrographer often use a so-called profile or terminal angle which is usually the projection of an interfacial angle on a plane parallel to a common face, and occasionally is an interfacial angle. It should be noted, as for example: $110\Lambda1\bar{1}0$ (projection on 001) = 109°.

Refractive Indices. The refractive indices of a uniaxial crystal will be expressed as ϵ (parallel to c); and ω (perpendicular to c). For biaxial crystals α will signify the lowest refractive index; β, the intermediate refractive index; and γ, the highest refractive index. Prime values will be used to indicate intermediate indices.

Sign of Double Refraction. The following expressions are all used: "optically positive," "double refraction, positive," "uniaxial positive."

Vibration Directions. The terms X, Y, and Z will be used to express the vibration directions corresponding to the lowest, intermediate, and highest refractive indices, respectively.

DDT

The form to be used for the individual descriptions is shown below for two solid phases—*p,p'*-DDT (I), and *p,p'*-DDT (II). The data are presented under the following headings: Crystal Morphology, X-Ray Diffraction, Optical Properties, and Thermal Data. The latter is included because of the successful use of thermal data in several laboratories for quick identification, purity determination, checking existence of polymorphs, and determination of optical properties. The existence of *p,p'*-DDT (II) became evident during investigation of the thermal properties of DDT, and has, thus far, been obtained only by fusion methods.

The most complete description of these techniques is covered in a mimeographed German edition by Kofler (*9*) an English translation of which will be available about the end of 1948. Since these methods require relatively simple microscopic equipment and only short training, the data are included below.

I (A). Crystallographic Properties of *p,p'*-DDT, Form I (2,2-bis-*p*-chlorophenyl-1,1,1-trichloroethane).

The DDT used was purified from a commercial sample by the procedure of Cristol, Hayes, and Haller (*2*). The crystals used for crystallographic examination were obtained by slow cooling of aqueous ethanol solutions. DDT can be recrystallized with substantially the same habit (Figure 1) from a variety of organic solvents (carbon tetrachloride, chloroform, benzene, acetone, ethanol, etc.) (*7*). Large crystals suitable for single crystal x-ray determination can be grown by slow crystallization from ethanol. *p,p'*-DDT exists in two different polymorphic forms; modification I is stable at room temperature, and modification II is unstable at all temperatures from the melting point down to at least 0° C., where the rate of transformation falls to zero. The transformation could not be reversed even in 20 hours at −180° C. (liquid air); hence, it is not certain whether form II is stable above or below form I (enantiotropic or monotropic system). Form II has been obtained only from thymol or the melt (Figure 2), both on a microscope slide; it is, therefore, of no practical importance and the crystallographic data are limited.

Crystal Morphology (determined by J. W. Cook; checked by W. C. McCrone).

Crystal System. Orthorhombic.

Form and Habit. Prismatic needles or rods elongated parallel to c; showing the forms: prisms {110} and {120}; brachy pinacoid {010}; and bipyramid {111}.

Axial Ratio. $a:b:c$ = 0.519:1:0.410.

Interfacial Angles (Polar). $101\Lambda\bar{1}01 = 77°$; $011\Lambda0\bar{1}1 = 45°$; $110\Lambda1\bar{1}0 = 55°$; $120\Lambda1\bar{2}0 = 88°$.

X-Ray Diffraction Data (determined and checked by S. Siegel, J. F. Whitney, and I. Corvin).

Space Group. P_{bc} or P_{bcm}; ($P222_1$) (*5*).

Cell Dimensions. a = 10.00 Å.; b = 19.25 Å.; c = 7.73° Å. (a = 19.14 Å.; b = 9.96 Å.; c = 7.85 Å.) (*5*). (a = 19.24 Å.; b = 10.04 Å.; c = 7.73 Å.) (*1*).

Formula Weights per Cell. 4; (2) (*1*); (4) (*5*).
Formula Weight. 354.5.
Density. 1.500 ± 0.002 (1.556) (*5*).

Principal Lines[a]

Index	*d*	I/I_1	Index	*d*	I/I_1
200	9.56	0.43	022, 031	3.08	Very weak
111	5.89	1.00	402, 031	3.04	0.66
310	5.37	0.25	231, 222	2.91	0.57
211	5.19	0.10	521	2.83	0.32
020	4.97	0.88	...	2.77	0.27
400	4.79	0.24	430, 700	2.73	0.51
...	4.59	0.20	620	2.68	0.13
220, 311	4.45	0.82	422, 003	2.59	0.06
021	4.22	0.76	132, 040	2.51	0.30
121, 401	4.10	0.50	602, 140	2.46	0.40
320	3.95	Very weak	...	2.42	0.30
500, 221	3.84	0.42	041, 141	2.38	0.40
411, 102	3.78	Very weak	141, 332	2.36	0.20
202, 012	3.61	0.45	241, 023	2.30	0.45
321, 112	3.50	0.42	403, 123	2.25	0.50
420	3.43	Very weak	440, 413	2.18	0.25
030, 212	3.35	0.70	900	2.14	Very weak
511, 130	3.26	0.12	042	2.11	0.25
421	3.17	0.22	142	2.09	0.20
			242, 033	2.05	0.35
			603, 050	2.01	0.35

[a] Additional lines with possible index values are available in the Armour Research Foundation file on request.

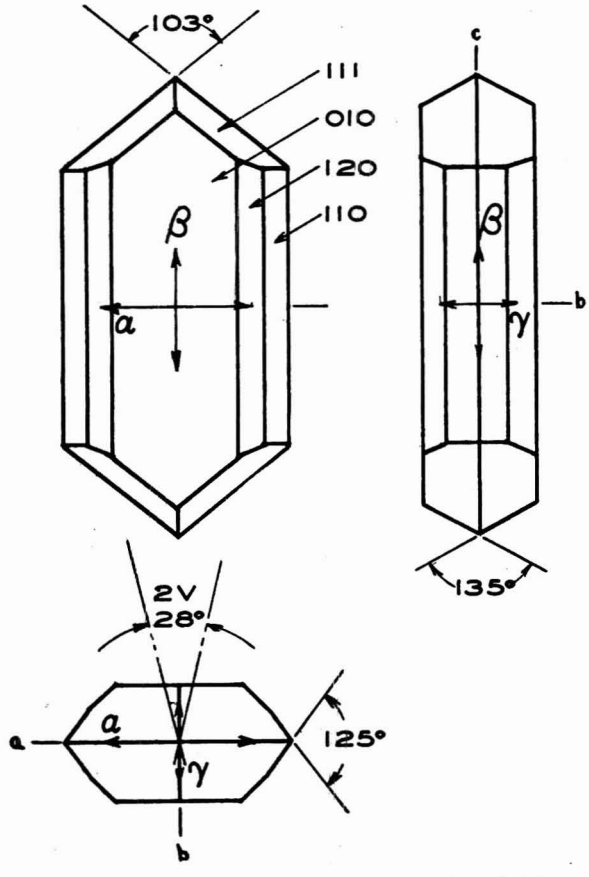


Figure 3. Orthographic Projections of *p,p'*-DDT (Form I)

Optical Properties (determined by W. C. McCrone; checked by J. W. Cook).

Refractive Indices (5893 Å.; 25° C.)
$\alpha = 1.617 \pm 0.002$; (1.618) (*6*)
$\beta = 1.624 \pm 0.002$; (1.626) (*6*)
$\gamma = 1.748 \pm 0.004$; (1.755) (*6*)
Optic Axial Angles (5893 Å.; 25° C.)
$2E = 46°$
$2V = 28°$ (30°) (*6*)
Dispersion. Little or none.
Optic Axial Plane. 001.
Acute Bisectrix. γ.
Sign of Double Refraction. Positive.
Molecular Refraction (*R*) (5893 Å., 25° C.)
$\sqrt[3]{\alpha\beta\gamma} = 1.663$
R (calcd.) = 84.0
R (obs.) = 84.8

Thermal Data (determined by W. C. McCrone; checked by J. W. Cook).

1. *p,p'*-DDT (I) melts at 108.5–109° C. with a slight tendency toward sublimation; *p,p'*-DDT (II) melts below 108° C. The latter is unstable at all temperatures from room temperature to the melting point; it is obtained from fusion by spontaneous crystallization of a supercooled melt (Figure 2). It grows very slowly and may show an off-center Bx_a or optic axis figure [$2E$ = 60–70°, (+), little or no dispersion].

2. *p,p'*-DDT (I) grows rapidly from the melt as rods or needles just below the melting point but grows very slowly as compact spherulites at room temperature (Figure 2).

3. A thymol mixed fusion shows well-formed rods of I or II growing into thymol; I gives a profile angle of 103° (dihedral) with a centered acute bisectrix interference figure (*OAP* crosswise), $2V = 28°$, (+), little or no dispersion.

4. *p,p'*-DDT (I) shows a very interesting and characteristic type of secondary crystal growth under the following conditions. A fusion preparation (about 5 mg. melted between a cover glass and slide) is allowed to crystallize slowly at room temperature in the usual spherulitic habit. After crystallization is complete, the preparation is reheated to 90° to 100° C. for 3 to 5 minutes. Examination of the preparation under crossed Nicols now shows that each spherulite has continued to grow simultaneously into and through its neighbor. This phenomenon has been termed "boundary migration" and is under further investigation (*3*).

I (B). Crystallographic Properties of *p,p'*-DDT, Form II.

Crystals of *p,p'*-DDT (II) can be obtained by strong supercooling from the melt or from thymol on a microscope slide. Most of the properties reported below were obtained on crystals from thymol by either mixed fusion or microrecrystallization from a drop under a cover glass.

Crystal Morphology (determined by W. C. McCrone; checked by J. W. Cook).

Crystal System. Orthorhombic.
Form and Habit. *p,p'*-DDT (II) crystallizes from thymol on a microscope slide as thick tablets showing macropinacoid {100}; prism {110}; brachydome {011}; and macrodome {101}. The crystal was set up on the basis of one view and convenience and the orientation is, therefore, tentative.
Interfacial Angle. $011 \wedge 0\bar{1}1 = 117°$.
Axial Ratio. $b:c = 1:0.61$.

Optical Properties (determined by W. C. McCrone).
Optic Axial Angle. $2E$ = 60–70°.
Dispersion. Little or none.
Optic Axial Plane. 001.
Acute Bisectrix. $b = \gamma$.
Sign of Double Refraction. Positive.

Thermal Data (determined by W. C. McCrone).

1. A strongly supercooled melt will crystallize spontaneously after about 5 minutes as a mixture of forms I and II (Figure 2). The longer the time before nucleation the greater the chance of obtaining form II.

2. The transformation of II to I is very slow at room temperature; rapid above 70° C. The melting point of II is less than 108° C., the melting point of I.

3. Modification II can be crystallized from thymol and gives tablets showing a Bx_0 figure and a profile angle 116°.

4. A mixed fusion with thymol gives random orientations some showing an off-center Bx_a figure, (+); $2E$ = 60–70°; little or no dispersion.

SUMMARY

Details of a project for the collection, checking, and publication of crystal data are presented with an outline for a consistent nomenclature to be used for publication. Data for *p,p'*-DDT

(I), and *p,p'*-DDT (II), are included under the headings: Crystal Morphology, X-Ray Diffraction, Optical Properties, and Thermal Data.

ACKNOWLEDGMENTS

Thanks are due each of the many crystallographers who contributed a great deal of thought and time to the organization of this project. Their offers of assistance and cooperation are sincerely appreciated.

Annette Smedal of the Armour Research Foundation made the density measurements, and helped to assemble and write the data.

Some of this material was presented before the Division of Analytical and Micro Chemistry at the 111th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

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Third Annual Analytical Symposium

L. T. HALLETT, Associate Editor

WITH an attendance of 400 the Third Annual Analytical Symposium, sponsored by the Analytical Division of the Pittsburgh Section of the A.C.S., on February 12 and 13 focused attention on the importance of analysis in the Pittsburgh area. The able symposium committee, headed by G. W. Kelch, may well be proud of its efforts, for the meeting was well organized and the program gave evidence of careful planning and selection of topics and speakers. For this G. R. Anderson deserves great credit. We have mentioned several times before that the Pittsburgh Analytical Group is in the forefront in the organization of analysts and their interests. The impressions we received at the meeting strengthened this opinion.

After a word of welcome by Gilbert Thiessen, Pittsburgh Section chairman, L. T. Hallett dealt briefly with the need for better organization of analytical laboratories, so that research in analysis is organized separately as a group of broad specialists with repetitive analysis closely coordinated with this group.

P. J. Elving outlined the A.C.S. divisional plans for the future and indicated that plans are afoot for heightened tempo in its activities. He mentioned the Symposium on Analytical Methods in Nuclear Chemistry to be held at Northwestern University August 14 and 15, 1948, and the formation of a committee to guide the executive committee in the selection of suitable future topics for national symposia.

Papers not abstracted below are discussed in Dr. Müller's column on instrumentation.

Analytical Research. H. A. FREDIANI, Merck & Co., Rahway, N. J.

Many chemical analytical control methods are the resultant by-products of new product research. As a result many control methods are hand-me-downs acquired from pilot and developmental laboratories and are not necessarily suited to routine control testing. Because of this, it was deemed advisable to set up a formal Analytical Research Department at Merck & Co., Inc. The objectives of this department are fourfold: (1) to establish control analytical methods for new products while these are still in the research and pilot-plant stages; (2) to improve currently used test methods (on regular line products) with respect to sensitivity, specificity, simplicity, precision, and rapidity; (3) to establish analytical techniques properly to evaluate competitor goods; (4) to carry out special routine control testing where complex instrumental methods seem optimum.

In order to maintain high quality standards the Analytical Research Department must not play favorites with any one technique. Each problem is evaluated on its merits and the technique most suited to its solution is applied. This meant the establishment of five general sections in the department, each led by a man well versed in his special field. These sections include: (1) instrumental (use of pH meters, titrimeters, ultraviolet, infrared, filter and flame photometers, conductance measurements, polarimetric, dielectric constant measurements, refractometric, and polarographic); (2) microchemical (use of microscopical techniques for crystallinity, homogeneity, particle size and distribution, isolation and identification of impurities, and crystal identification as well as elementary analysis, determination of functional groups such as ethoxy, methoxy, amino nitrogen, etc., and physical properties such as melting point, freezing point, etc.); (3) spectrographic (emission work for trace element and minor constituents, identification of inorganic contaminants); (4) general (wet chemical methods, gravimetric and volumetric procedures, etc.); (5) statistical (correlation of new and old methods, initiation of proper sampling, establishing of control charts in factory and packaging, and setting up statistically sound chemical studies to be used as basis for new drug applications).

Fundamentally, problems are approached as follows: (1) tentative assignment to one of the section chiefs who gets all known facts together; (2) meeting of section chiefs to decide on proper course of action after reviewing data compiled in (1); (3) assignment to section indicating most promise.

In all this we stress strongly the necessity for collaboration between sections. Ofttimes a problem that looks ideal for spectrographic solution has a far simpler ordinary wet chemical solution.

The Function of a Testing Laboratory. D. R. EVANS, Western Electric Co., Kearny, N. J.

Testing laboratories, like chief chemists, vary considerably in the services rendered and expected. The responsibility for this lies partly with the top levels of management and partly with the chemist. The initiative to improve the situation lies with the chemist. To grasp it he must first have a knowledge of the fundamental purposes, needs, and relationships involved, and then a vision of the vital service he and the laboratory should be able to render. The quickly changing kaleidoscopic situation in industry and in markets, the shortage of basic materials, the availability of new or substitute processes and items, all present real opportunities for the chemist to prove his worth. To do this job, adequate laboratory equipment, tools, methods, and personnel are needed. To acquire these, to use them intelligently and, from the results obtained, to furnish wise guidance and counsel for planning and control, are the responsibilities of those who would operate a modern testing laboratory.

Accurate Analysis of Carbon Monoxide and Carbon Dioxide Gaseous Mixtures. C. H. TOENSING, Carnegie-Illinois Steel Corp., and D. S. MCKINNEY, Carnegie Institute of Technology, Pittsburgh, Pa.

It became apparent after a review of literature that the methods for the accurate analysis of gaseous mixtures containing high percentages of carbon monoxide, and the balance carbon dioxide, were very inadequate. The analytical methods available were found to be involved and applicable mainly to small quantities of carbon monoxide.

Many investigators have stated that gravimetric methods of analyses were to be recommended for carbon dioxide. A very simple gravimetric method was developed for the analysis of gas mixtures containing carbon monoxide and carbon dioxide, using a 500-cc. dry gas sample to increase the analytical accuracy. The

carbon dioxide in the gas sample was absorbed by Ascarite in a weighed absorption bulb, followed by a copper oxide oxidation of the carbon monoxide to carbon dioxide with subsequent absorption and reweighing. Oxygen gas flushed the gas sample through the analytical train and to reoxidize the reduced copper oxide.

The total number of moles present in the original gas sample was determined from the initial pressure and temperature of the gas contained in a calibrated volume, assuming ideal behavior. The number of moles of each gas component was determined from the increase in weight of each absorption bulb from which the mole per cent (or volume per cent) composition was calculated.

A precision of ±0.05% carbon monoxide was obtained from a series of 200 gas analyses using this method over a composition range of 85.0 to 99.5% carbon monoxide. The sources of error are few by this method.

Molar Volume Corrections in Gas Analysis. C. H. TOENSING AND D. S. MCKINNEY.

In most gas analytical procedures it is assumed that the gas mixtures behave ideally; however, this is not necessarily true unless the gas pressure is below 200 mm. of mercury. The molar volumes of various gases are usually not the same. When carbon monoxide is oxidized to carbon dioxide, the difference in molar volumes may introduce a relatively large error in the analytical results, especially if the percentage of carbon monoxide in the gas sample is 30 or more.

Correction data for the molar volume change and the calculations involved for variable-volume, constant-pressure type of gas analysis apparatus (Orsat type) have been published. An investigation of the literature failed to disclose a method of correcting this error for a constant-volume, variable-pressure gas analysis apparatus (Bone and Wheeler type). However, by using the second virial coefficient equation of state for various binary gaseous mixtures, a satisfactory method was developed for making the desired corrections.

These corrections are very easily applied to gas analysis data, and they eliminate a possible source of error often encountered in this type of analytical apparatus.

Analysis of Fluoride-Containing Materials. R. J. ROWLEY, Aluminum Co. of America, New Kensington, Pa.

Many factors must be considered in developing methods for the analysis of fluoride-containing substances. Some properties of fluoride that are responsible for these factors include the unique reaction between hydrofluoric acid and silica, the stable complexes formed between fluoride and aluminum, iron, boron, and silicon, the existence of relatively few insoluble fluoride compounds, and the high volatility of many fluorides.

The determination of fluoride is most successfully accomplished after separation by distillation. In many cases the sample can be dissolved and immediately subjected to distillation; in others there is required preliminary fusion or ashing in alkaline environment. Under certain circumstances a single distillation will not effect a complete separation of fluoride from deleterious impurities; in these cases a double distillation procedure is employed. Following distillation, fluoride may be most accurately determined by either colorimetric or volumetric techniques. These require experience and attention to detail but are capable of yielding excellent results.

Complexation in Chemical Analysis. DAVID F. BOLTZ, Wayne University, Detroit, Mich.

The problem of eliminating the deleterious effect of certain diverse substances is of dominant importance in most analyses. A valuable aid is the utilization of complexation reactions in which complex molecular structures, as exemplified by the heteropoly complexes, are formed. A heteropoly complex is formed by the condensation of two or more oxygen-containing acids. Thus, orthophosphoric and molybdic acids give the yellow heteropoly complex, molybdiphosphoric acid, which can be used in the spectrophotometric determination of phosphorus. This molybdiphosphate complex, upon reduction, produces a heteropoly blue complex which can also be used for the spectrophotometric determination of very small amounts of phosphorus. Ferric ions interfere in the molybdiphosphate method. This interference may be minimized by the complexation of the ferric ions with fluoride ions. A large excess of fluoride ions must be avoided to prevent complexation with the excess molybdate ions. A study of the complex ferric fluoride indicates that it is an interesting stable complex. Certain separations are possible by taking advantage of the relative instability constants of other complex ions. The formation of complexes is especially important in polarographic analysis of samples containing ions having similar half-wave potentials. Although we are still handicapped to some extent by insufficient data on the properties, structures, and reaction mechanisms of complex ions, the potentialities of complexation as an aid in analysis should not be overlooked.

Progress in the Unification of Procedures for the Determination of Iodine in Organic Compounds and Mixtures. DWIGHT L. DEARDORFF, KENNETH L. WATERS, AND GEORGE D. BEAL, Mellon Institute, Pittsburgh, Pa.

It was shown that progress has been made in the unification of the various procedures that have been suggested for the determination of iodine. The discussion included the determination of iodine in pure organic compounds and in mixtures such as iodized oils and mineralized feeds.

Determination of Piperidine and Carbon Disulfide in Presence of Ammonia and Pyridine. J. A. SHAW AND SHERMAN DETRICK, Mellon Institute, Pittsburgh, Pa.

This procedure is the only chemical method in the writers' experience that is satisfactory for this purpose. It depends upon the observation made while working in this field that when caustic soda is added to a water solution containing piperidine dithiocarbamate, one atom of sodium displaces one molecule of piperidine to form one molecule of sodium piperidine dithiocarbamate, which is a very stable salt. It can be boiled down and crystallized from solution without decomposition. It is, therefore, possible to distill off the free organic bases, destroy the dithiocarbamate with sulfuric acid, distill off the liberated carbon disulfide, add an excess of caustic soda and distill the residual piperidine into standard acid, titrate with methyl orange, and calculate the carbon disulfide in the sample. If an excess of carbon disulfide is added to the sample initially, the total piperidine in the sample can be determined in the same way.

A Proposed Method of Expressing Extinction Coefficients of Photometric Test Methods. GRANT WERNIMONT, Eastman Kodak Co., Rochester, N. Y.

If one judges by the relative number of papers being published, photoelectric methods of photometry have all but replaced the visual methods for determining those substances which absorb narrow bands of radiated energy. With more or less standard commercial models of spectrophotometers and filter photometers now available, it would be advantageous for analysts to agree on some uniform method of presenting the results of studies on proposed photometric test methods.

The fundamental relationship upon which many photometric methods are based is the Bouger-Beer law. This law gives the relationship through a proportionality constant, between the transmittancy, the absorption cell thickness, and the concentration of solute in a solution at some given band of radiated energy. Three modifications of the law have been used widely by analysts. In these modifications the proportionality constant has the dimensions of $\frac{1}{\text{solute concentration}}$ and this makes Bouger-Beer law calculations rather complicated.

The Bouger-Beer law is more easily understood and used by analysts if it is stated as follows:

$$\text{Concentration of solute} = E_c \left[\frac{-(\log \text{transmittancy})}{\text{absorption cell thickness}} \right]$$

It is proposed to call E_c the specific extinctance concentration. The numerical value of this constant remains the same when the absorption cell thickness is expressed in centimeters, and the concentration of solute is expressed in units of (1) mg. per liter, (2) micrograms per ml., or (3) parts per million. The constant can be readily converted to other units; it gives an estimate of the relative sensitivity of the test method; it can be readily used to set up working curves for different situations which arise.

Determination of Manganese, Nickel, and Chromium in Type 304, 316, 347, and Similar Steel with the Beckman Spectrophotometer. J. B. CULBERTSON AND R. M. FOWLER, Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N. Y.

A rapid method for the analysis of 18-8 steels with the Beckman spectrophotometer has been developed. This method is based on solution of the sample in perchloric, phosphoric, and hydrofluoric acids, oxidation of the chromium with perchloric in the presence of sulfuric acid quick cooling of the oxidized chromium by adding diluted phosphoric acid, and finally boiling with very dilute hydrochloric acid to reduce any oxidized manganese. Chromium is then determined colorimetrically. An aliquot of the same solution is treated with sodium tartrate, sodium hydroxide, ammonium hydroxide and dimethylglyoxime and the $Ni(C_4H_7O_2N_2)_2O$ color is developed with potassium periodate and measured. A second aliquot is treated with potassium periodate, and the manganese converted to permanganic acid and determined colorimetrically.

Photometric Determination of Arsenic in Copper and Copper-base Alloys. O. P. CASE, American Brass Co., Waterbury, Conn.

In the method described arsenic is separated by reduction to metallic arsenic with hypophosphite ion in 6 *N* hydrochloric acid at 80° to 90° C. The arsenic is collected on a fritted glass filtering funnel of fine porosity and washed with freshly boiled water. The arsenic is then dissolved and oxidized by drawing a dilute iodine solution through the filter into a volumetric flask. An aliquot portion of this solution is treated with an acidified solution of ammonium molybdate and a solution of hydrazine sulfate. Heating at 90° to 100° C. develops the arsenic molybdenum blue complex which is measured photometrically, preferably at 840 millimicrons, although satisfactory measurement may be made at lower wave lengths. The method has been applied to the determination of arsenic in arsenical brass, arsenical copper, and fire-refined copper with results which indicate good precision and accuracy. It is probable that the method may be applied to the determination of arsenic in tin-base, lead-base, and ferrous alloys as well. The method has the advantage of being somewhat more rapid than the conventional distillation-volumetric method and of giving a better recovery of arsenic than distillation separations.

Colorimetric Determination of Columbium and Tungsten in Steel. FRANK MALOOY, Rustless Iron and Steel Division, American Rolling Mill Co., Baltimore, Md.

A direct colorimetric procedure for the determination of columbium in plain and alloy steel has been developed. Use is made of the colored complex that is formed when columbium and hydroquinone react under specified conditions. Measurement of the optical density of the colored complex was made with a Kromatrol photometer, using light peaked at approximately 430 millimicrons. A study of the interfering elements indicates that tungsten and titanium must be absent, as they also form colored complexes with hydroquinone under the conditions specified for the determination of columbium. The effect of known amounts of tungsten on the columbium concentration has been investigated and a correction can be made. Adding known amounts of columbium to various types of stainless steels showed a negligible grade effect when subjected to the recommended procedure. The effect of the water concentration, temperature, and the concentration of stannous chloride, etc., were studied to arrive at the recommended procedure.

Quantitative Spectrographic Analysis of Cemented Carbide Compositions. C. W. HANNA AND JOHN C. REDMOND, Kennametal, Inc., Latrobe, Pa.

The time consumed by wet chemical methods applied to the analysis of cemented carbide compositions made the development of quantitative spectrographic methods very desirable even if low accuracy had to be accepted. Several types of samples and conditions were investigated before the unusual procedure of using finely powdered samples in recessed graphite electrodes and a sparklike discharge was settled upon. The details of the procedure and the results obtained were given. The method gives results of considerable value for control purposes, whereas they could not be obtained in sufficient time by wet methods.

The Use of 8-Hydroxyquinoline for the Colorimetric Determination of Aluminum in Steel. STEPHEN E. WIBERLEY AND L. G. BASSETT, Rensselaer Polytechnic Institute, Troy, N. Y.

The object of this work was to develop a rapid and accurate method for the determination of aluminum in steels of low aluminum content. An appraisal of existing colorimetric methods has been made with a comparison of their good and bad features from an analytical viewpoint. This method has been developed with an emphasis of simplicity, ease of operation, and reproducibility. After being weighed, the sample is dissolved in nitric and perchloric acid, brought to fumes, cooled, diluted, and electrolyzed in a water-jacketed mercury cathode cell until the solution tests free of iron using *o*-phenanthroline in a spot test. The pH is roughly adjusted, the 8-hydroxyquinoline and a buffer are then added to fix the pH within the limits 6.5 ± 1.5, and the aluminum complex of 8-hydroxyquinoline is extracted with chloroform. The resulting solution is measured in a suitable colorimeter or spectrophotometer. The application of the method to various types of samples was described and the effect of the usual variables such as wave length, pH, amount and purity of reagent, and interferences was evaluated.

Current Spectrographic Methods of Nonmetallic Sample Analysis. C. E. HARVEY, Applied Research Laboratories, Glendale, Calif.

The paper presented a discussion of the problems involved in the spectrographic analysis of nonmetallic samples compared to the analysis of metals, the procedures that can be applied to different forms of nonmetallic materials, the critical variables in the analysis, methods of establishing the degree of importance of those variables, methods of eliminating the variables or at least transforming them into experimental constants to achieve a standard condition of analysis, and methods of establishing working curves where no standards are available. The major classifications of sample forms considered are: solid samples, entirely inorganic; solid samples, principally organic; liquid samples, entirely inorganic; liquid samples, principally organic. In addition, the analysis of halogens or other nonmetallic elements is briefly discussed. Briquetting methods with fluxing and heating are necessary to produce standard states with solid samples. Solutions are analyzed by means of a rotating disk. Halogens and other nonmetallic elements are analyzed in partial vacuum.

SYMPOSIUM ON THE ANALYSIS OF INDUSTRIAL WASTES

Determination of Biochemical Oxygen Demand on Industrial Wastes. C. C. RUCHHOFT, Cincinnati Experiment Station, U. S. Public Health Service, Cincinnati, Ohio.

Recent studies have indicated that although the carbonaceous B.O.D. data fit the unimolecular equation, the velocity constant for the rate of oxidation may vary over a wide range. The factors, besides temperature and pH, which affect the B.O.D. rate include the complexity and concentration of the microflora and fauna, the composition and concentration of organic matter in the substrate, the presence of necessary accessory nutrients and of toxic ions, or compounds, and the supply of oxygen. For this reason the B.O.D. determination must be very carefully standardized when applied to industrial wastes. The manometric or oxygen utilometer method may be used on undiluted wastes or the standard excess oxygen dilution method on diluted wastes. The choice of methods depends upon the purpose of study. The results of the two methods are not necessarily comparable and it is not possible to extrapolate results on observations of one day or less to longer periods of incubation. The dilution method will be most useful for the majority of wastes and consequently the detailed technique for its application to industrial wastes is discussed. The techniques that are described include dilution water composition and dilution procedures, pH adjustment and seeding technique, and dissolved oxygen determination modifications to eliminate interferences. Concurrent nitrification during carbonaceous oxidation, calculation of results, derivation of curves of best fit, and interpretation of B.O.D. data on industrial wastes are discussed and wastes are tentatively classified as to suitability for application of B.O.D. determination.

C.O.D. *vs.* B.O.D. of Sewage in Polluted Waters. K. M. MADISON, Mellon Institute, Pittsburgh, Pa.

It is generally recognized that the 5-day B.O.D. method gives low estimates of the degree of sewage pollution in waters containing mine acid (primarily ferric and ferrous sulfates). This has led to the investigation of various chemical methods of measuring the oxygen demand of polluted waters. A modification of the dichromate method of Rhame [*Water Sewage Works*, **94** (5), 192–4 (1947)] has proved satisfactory in the estimation of oxygen demand of sewage and sewage-mine acid mixtures.

Essentially the modified procedure consists of boiling a known volume of sample and 20 ml. of the dichromate sulfuric-phosphoric acid reagent until fuming begins. The temperature of the fuming mixture is reduced until boiling just ceases, and the mixture is left to fume for 4 minutes. Then it is cooled, diluted with 100 ml. of distilled water, and titrated with 0.025 *N* ferrous ammonium sulfate, using sodium diphenylamine as the indicator. A blank is run, using 50 ml. of distilled water instead of the sample.

Sampling and Analyzing Acid Mine Drainage. S. A. BRALEY AND G. A. BRADY, Mellon Institute, Pittsburgh, Pa.

Acid mine drainage and its properties were discussed together with a correlation of these properties and proper methods of sampling and handling of samples preparatory to analysis. The methods of analysis used as compared to the recommended standard methods for water purification and sewage treatment were outlined.

Analytical Procedures for Determination of Metals Affecting Sewage Treatment. MERRILL L. RIEHL, Ohio Department of Health, Columbus, Ohio.

Certain anions and cations, in relatively low concentrations, have a marked effect on sewage treatment processes, especially in

sludge digestion. Analytical procedures were described for the determination of some of the most troublesome of these ions and radicals, including copper, zinc, chromium, iron, and cyanide, by the application of new techniques.

Determination of Metals in Industrial Wastes. H. GLADYS SWOPE, Allegheny County Sanitary Authority, Pittsburgh, Pa.

The analyses considered were those for iron, copper, chromium, vanadium, and cyanide.

Two main difficulties arise in analyzing industrial wastes, the small amounts, many times less than 1.0 part per million, and the many unknown possible interfering ions. No absolutely foolproof method was given for any specific element, since not every known method for the ions was tried, but the difficulties which arose and the method of circumventing them were discussed. In most cases 1 to 2 liters of the sample must be concentrated to 100 to 500 cc. in order even to detect the presence of certain ions.

Small amounts of iron (less than 5 p.p.m.) were determined spectrophotometrically using the *o*-phenanthroline method. Fifty cubic centimeters of the sample were digested and evaporated to dryness with concentrated sulfuric acid, then boiled with 3 *N* hydrochloric acid before adding the hydroxylamine hydrochloride and *o*-phenanthroline and adjusting the pH to between 3 and 8. Copper, chromium, and vanadium had to be removed, if present. For larger amounts of iron the Zimmermann-Reinhardt method was used.

Copper was determined electrolytically, the original waste being concentrated from 2000 to 250 cc. If less than 1.0 p.p.m of copper was present colorimetric methods would have to be used.

Chromium was determined by concentrating 1 to 2 liters of sample to 250 cc. and following the procedure given on p. 152 of Griffin's "Technical Methods of Analysis" (McGraw-Hill), 1927 edition, except that no phosphoric acid was used and the sample was titrated with standard ceric sulfate instead of potassium permanganate.

Vanadium was determined in samples which might also contain chromium; therefore these were run on the same sample. Concentrated sulfuric acid and dilute nitric acid were added to a suitable portion of the sample and the solution was boiled. Strong potassium permanganate was added dropwise and boiling continued for 20 minutes. The manganese dioxide was filtered off and sulfuric acid (1.5 sp. gr.) added. The solution was then cooled to 5° C. and an excess of ferrous sulfate added. Titration with standard ceric sulfate was then carried out. Ammonium hydroxide was added slowly, then sodium acetate and the solution heated to 50° C., and titration again performed with ceric sulfate. This latter titration gives the amount of vanadium present.

Cyanides were determined by the modified Liebig method. Collection and preservation of the original sample are important.

SYMPOSIUM ON MODERN COURSES IN ANALYTICAL CHEMISTRY

Quantitative Analysis, Perspective and Problem. M. G. MELLON, Purdue University, Lafayette, Ind.

Quantitative analysis is the division of chemistry dealing with the determination of the amount of one or more desired constituents in a given sample. The methods used range from the simplicity of applying a hydrion test paper to all that is involved in making a complete analysis of a granite rock. Ultimately, any procedure consists of chemistry, if any is involved, and always of physics.

The chemistry includes whatever transformations are necessary to get the system ready for measurement. Common unit operations are fusion, dissolution, complexation, and separation. The last operation may be volatilization, precipitation, electrodeposition, or extraction. For such processes some modern apparatus, such as Podbielniak stills, are fairly complicated.

Finally comes measurement, the specific method used being preferably that best suited to the situation at hand. Nothing is much simpler, nor more common, than the hydrometer seen at every gasoline filling station. Probably nothing is more complicated than the latest mass or recording emission spectrometer.

Teachers today face a real problem. With only limited time and facilities at their disposal, what should be included in the one short course which is now being given to most chemical graduates? Samples cover the whole range of natural and synthetic materials. Every element in the periodic table, including their isotopes, must be anticipated until proved absent or insignificant. The kinds of possible combinations of these elements are almost endless. To meet this situation, what working knowledge of chemistry should be attempted? Then measurement means physics. Here one finds an ever-increasing variety and complexity of instruments involving especially mechanics, optics, and electronics. For what training in this direction is the teacher of quantitative analysis responsible? What training do industrialists want in our graduates? What is possible in the ordinary colleges these days?

Analytical Techniques. A Course in Quantitative Analysis for Chemical Engineering Students. CARL J. ENGELDER, University of Pittsburgh, Pittsburgh, Pa.

The paper described a new type of course of instruction in quantitative analysis for sophomore chemical and metallurgical engineers, now being given at the University of Pittsburgh. The main purpose is to acquaint the student engineer with the methods, devices, instruments, and principles employed in an analytical laboratory, with more emphasis on treatment of data and computations than on precise manipulation and extreme accuracy of results. The course covers for one-half the semester two simple gravimetric and three volumetric determinations, designed to familiarize the student with the handling of a balance and volumetric apparatus and acquaint him with chemical factors, titers, and normalities as they are applied to factor-weight samples and percentage-volume solutions. The second half of the course covers mainly instrumental analysis in which colorimetric, electrolytic, gas, and coal analysis are introduced together with the use of a pH meter for potentiometric titration.

Metropolitan Microchemical Society of New York

L. T. HALLETT, Associate Editor

THE Metropolitan Microchemical Society of New York held its third annual symposium February 27 to 28. One hundred chemists listened to an interesting and varied program styled for those whose work involves the handling and analysis of small samples.

Recent Developments in Microscopy. KURT J. HEINICKE, Research & Engineering Division, Bausch & Lomb Optical Co., Rochester, N. Y.

The possible use of ultraviolet as a source of light in microscopy was discussed as early as 1904, but the difficulty in developing proper lenses for focusing has delayed its application. Since that time proper lenses and more efficient fluorescent screens and light sources have been developed, and in the near future ultraviolet microscopy will find wide application. In this type of microscopy the monochromatic light is passed through a specimen and a system of lenses, to a photographic plate or a phototube giving resolution to specimens which absorb in the ultraviolet range.

Phase microscopy is essentially converting phase differences created by the specimen into brightness differences clearly discernible by the eye. In this type of microscopy a green or blue light is passed through the specimen, specially developed quartz lenses, and a phase plate to the eye or other receptor. The light, as it passes through the specimen, may be thrown a part of a wave length out of phase, giving resolution which cannot be obtained by ordinary microscopy. By using phase microscopy, quartz placed in a liquid of the same refractive index is clearly discernible. Other examples of better resolution were shown by comparing mouth epithelial cells and the sediment in urine with an ordinary and a phase microscope.

Further development of chemicals fluorescing in the infrared for focusing screens is being carried out. The discovery of these chemicals will open up a new field of infrared photomicrography.

The Application of Infrared Spectroscopy. KONRAD DOBRINER, M.D., Department of Hormone Chemistry, Sloan-Kettering Institute, Memorial Hospital Cancer Center, New York, N. Y.

For some time there has been a need of a method or an instrument for characterizing steroid metabolites found in the urine. Since about 1942, infrared spectrophotometry has been successfully used for this purpose.

In the study of urine from well and diseased persons, it has been necessary to study small amounts (50 micrograms) of the isolated steroids. Infrared study of this small quantity of material has directly contributed to the discovery of new steroid metabolites, quantitative estimates of known steroids, and the determination of position of functional groups, which has led to the exact development of the structures of certain steroids.

Isolation of the steroids from the urine has been made by chromatographic absorption, and an infrared absorption library of about 450 references has been built up. The wave-length absorption of the functional groups has been well established, so that the position of the functional groups of isolated steroid metabolites can be readily established. The bends caused by minimum absorptions, called the fingerprint regions, have also been found important in the characterization of the steroid by pointing out minor differences in structure and purity.

Slides were shown to compare the infrared absorption of steroids isolated from urine with known steroids.

Infrared study of urinary steroid metabolites has led to the isolation of a steroid associated with practically all cancer cases.

Experiences with Microchromatography. RICHARD J. BLOCK, Department of Physiology and Biochemistry, New York Medical College, New York, N. Y.

Paper chromatography for the separation of amino acids, sugars, and fatty acids became widely used after the publication of "Qualitative Analysis of Proteins. A Partition Chromatographic Method Using Paper" in 1944 by Consden, Gordon, and Martin. Its sensitivity and usefulness are indicated by the possibility of identifying approximately 20 amino acids in the hydrolyzate of 0.2 to 0.4 mg. of hydrolyzed protein.

In this method the paper functions only as an inert support for the two solvents and has the advantage over silica gel that it has no retentive action over the moving amino acids. Separation of the amino acids takes place because of the different relative solubilities of each amino acid between the water, which is held by the cellulose fiber, and a solvent not miscible with water, which is allowed to flow slowly up the filter paper past the spot which contains the amino acid mixture.

The separation is carried out in an ordinary, rectangular aquarium, after slight modification, on large sheets of filter paper. A chromatograph may be either one- or two-dimensional. After separation, the acids are identified by treating the paper chemically to produce a color characteristic of each amino acid.

In recent work, rats have been fed radioactive iodine and the protein hydrolyzate of the particular tissue has been separated chromatographically. The radioactive amino acid was then determined chromatographically by cutting the chromatograph into strips and placing the strips in a Geiger counter.

Statistical Methods in Analytical Chemistry. JOHN MANDEL, National Bureau of Standards, Washington, D. C.

A statistician is usually consulted during the preparatory stage of an experiment if statistical treatment of the data is to be successful.

After determining the water-absorptive tendency of synthetic rubber at the Bureau of Standards recently, the question arose as to whether the error involved was due to combined errors of measurement or to differences between the samples removed from several batches of rubber. The 32 data were treated statistically, and it was shown that the error of measurement was small compared to the difference in the samples of rubber from batch to batch.

The validity of Beer's law for the ultraviolet absorption of a solution of GRS rubber in methyl cyclohexane was studied. After plotting optical density *vs.* concentration of the 22 measurements (eleven on two consecutive days), the question arose as to whether the slight deviation of the data from a straight-line plot was due to experimental error or was a true deviation. After statistical treatment of the data by regression analysis, it could be stated that the data did not satisfy Beer's law, although by inspection or line fitting, one might be led to the conclusion that the data did satisfy Beer's law.

Applications of the Automatic Recording Spectrophotometer. E. I. STEARNS, Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

The General Electric automatic recording spectrophotometer can be adapted for use in a number of broad problems for which it was not originally designed if certain modifications are made to the instrument and to the sample holders normally provided.

A certain dye, when applied to wool, dyed the strand of wool but did not have light- or wash-fastness. When the dye was treated with sodium dichromate, the dye on the wool fiber became light- and wash-fast. The spectrophotometer was used to follow this reaction by placing the wool on a specially designed rotating drum and measuring the light reflected from the rotating sample. This gave a more accurate measurement of the color than if the color was measured at any given part of the fiber.

The alcohol concentration of rye whisky has been quantitatively determined by comparing the absorption of the alcohol in rye whisky to that of a sample of known alcohol concentration.

The use of the instrument to determine a reaction rate was illustrated by following the inversion of cane sugar by the spectrophotometer. A special cell was designed and placed in the instrument, and the inversion rate conveniently determined by absorption of the inverted sugar.

The reflectance of printing inks has been determined by smearing samples of ink on the inner side of a right-angle prism and placing the prism in the sample chamber of the instrument.

The identification of an unknown crystal structure can be made by comparing the reflected light of the crystal to the reflected light of known crystal structures. By this means the crystal structure of unknown sample lead chromate was determined by comparing to known standards of the two crystalline forms.

The color of certain materials may be an indication of their purity—for example, β-naphthol when pure is white but when impure is tan. The purity can be determined by measuring the reflected light by passing light through the crystals and a right-angle prism into the instrument. The reflected light can be compared to the reflected light of known purities.

Microbiological Assay Methods. LOUIS SIEGEL, Food Research Laboratories, Long Island City, N. Y.

Microbiological assay compares favorably with chemical assay of many vitamins and drugs, and in many cases makes an assay possible where chemical methods fail. Conditions for a precise and reliable microbiological assay were discussed in detail, including the organisms used and the criteria used to evaluate the assay.

The Analyst's Calendar

Symposium on Spectroscopic Equipment

The Society for Applied Spectroscopy, in cooperation with the Polytechnic Institute of Brooklyn, Brooklyn, N. Y., is completing plans for a symposium on spectroscopic equipment on May 22, under the chairmanship of W. L. Parker. The latest developments in instruments in the fields of absorption and emission spectroscopy will be exhibited.

International Congress on Analytical Chemistry

The International Congress on Analytical Chemistry, meeting June 1 to 3 at Utrecht, Holland, has completed its program, and a limited number of copies may be obtained from the office of ANALYTICAL CHEMISTRY, Washington, D. C. Members will receive preprints of papers in advance of the meeting. All correspondence should be addressed to the general secretary, H. A. J. Pieters, 7 Beatrixlaan, Geleen, Holland.

Symposium on Modern Instrumental Methods of Analysis. Minnesota Section, A.C.S., and Institute of Technology, University of Minnesota, Minneapolis, March 22 to 24.

American Society for X-Ray and Electron Diffraction, joint with Crystallographic Society of America, Yale University, New Haven, Conn., April 1 to 3.

Symposium on Spectroscopic Equipment. Polytechnic Institute of Brooklyn, Brooklyn, N. Y., May 22.

Symposium on Analytical Methods in Nuclear Chemistry. Division of Analytical and Micro Chemistry, Northwestern University, Evanston, Ill., Aug. 13 and 14.

AIDS FOR THE ANALYST.....

Simultaneous Photography of Two Wave-Length Ranges in Spectrochemical Analysis. N. H. Nachtrieb[1], J. G. Conway[2], E. D. Wilson[1], and S. Wexler[3], University of California, Los Alamos Scientific Laboratory, Santa Fe, New Mexico.

THE range of wave lengths photographed at one setting of the camera or slit of commercial spectrographs may not include all the sensitive lines of all the elements to be determined in rare samples. Figure 1 shows a diagram of a commercially available spectrograph (A.R.L.–Dietert) modified so as to direct light from one arc or spark source upon two of the slits at one time.

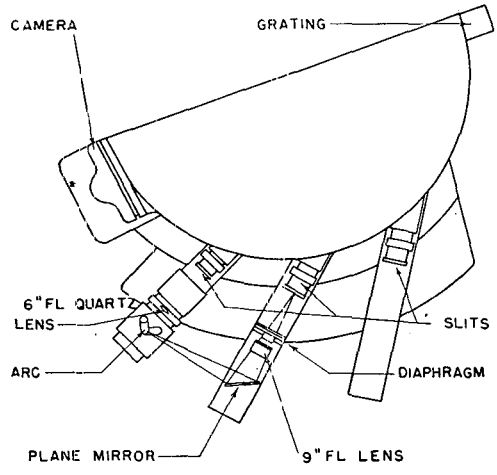

Figure 1. Use of Two Slits to Photograph Two Wave-Length Ranges with One Camera

The camera records the spectrum from 2250 to 4600 Å. of the light which enters the first slit. A second surface mirror and an achromatic lens (9-inch focal length, 2.25-inch diameter) situated as shown on the second optical bench direct a portion of the light through the second slit. The camera receives the spectrum from 4200 to 6700 Å. of light from this slit. Rectangular diaphragms, 1.5 mm. high and 8 mm. wide, are placed at the secondary foci of the grating on the two optical benches. The diaphragm on the second bench is displaced 2 mm. above that on the first bench, so that the spectra of the two regions are juxtaposed rather than superimposed. Eastman type I-N or 103-aF film is sensitive over the combined spectral regions; the latter offers better resolution, contrast, and speed.

There is some compromise of speed, contrast, and resolving power when one photographic emulsion records the spectrum of the whole range 2250 to 6700 Å., and this may be overcome by using two spectrographs mounted on a line facing one another. Figure 2 shows how a 45–90–45° prism may be used, together with a fairly long focus lens (25 inches) in case the optical axes of the two instruments are not in line, either laterally or vertically. The proper position of the prism is determined by visually observing the distribution of intensity along tall spectrum lines and securing it by means of a rigid mounting. Shims may be inserted beneath the prism until photometry of the full slit height

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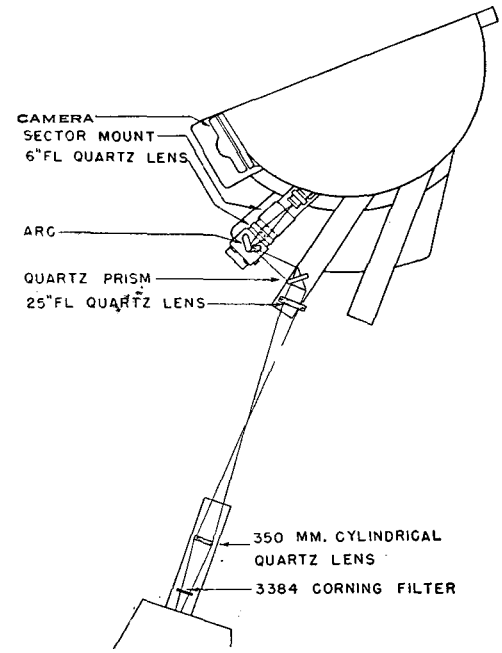

Figure 2. Use of Two Spectrographs to Photograph Two Wave-Length Ranges Simultaneously

lines shows the slit illumination to be uniform. By this arrangement the most suitable photographic emulsion may be selected for the wave-length range of each instrument. In either method the exposure time for the two spectral ranges need not be the same, for each slit possesses its own shutter.

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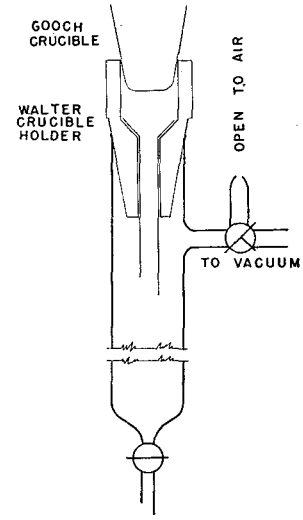

Convenient Filter Flask. S. C. Hindin and J. Grider, Houdry Process Corp., Marcus Hook, Pa.

WHEN filtering with vacuum, removal of filtrate from the usual filter flask is rather awkward. The flask shown in the drawing, which is easily constructed from any of the larger size test tubes, is somewhat more convenient to use. When the volume of filtrate is greater than that of the tube, portions of the filtrate may be taken off without disturbing the filtration more than momentarily. It may be similarly used when a precipitate is washed for removal of soluble salts.