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MICROCHEMISTRY

NOTES ON ANALYTICAL PROCEDURES

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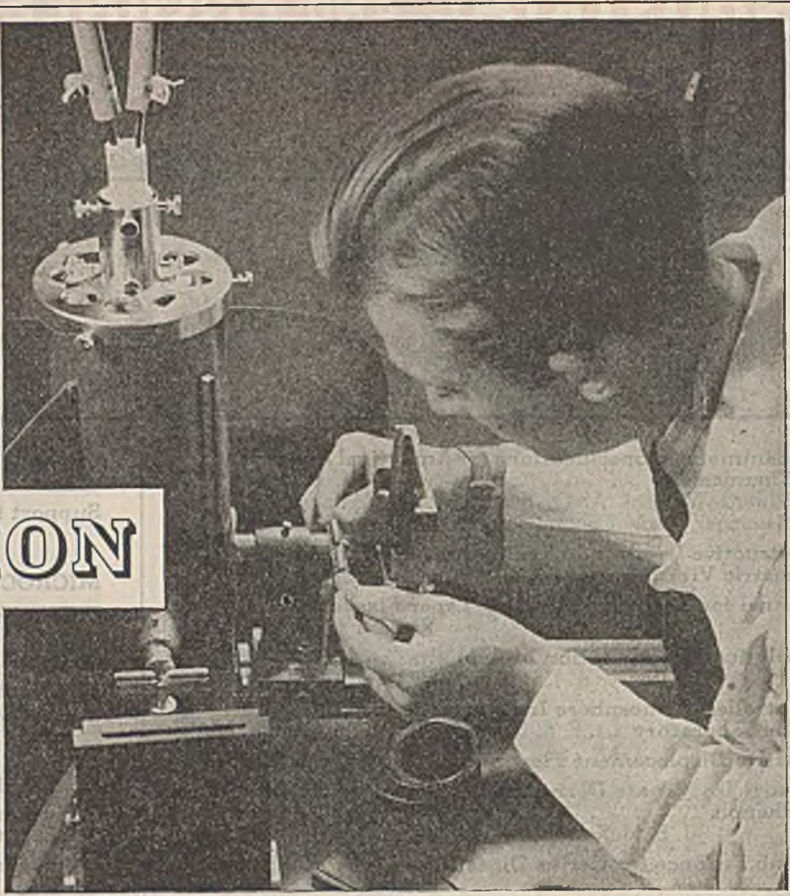

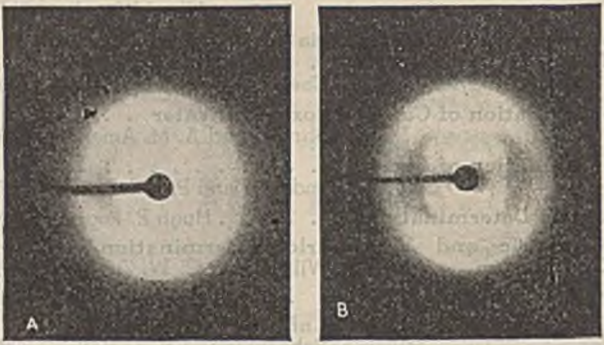
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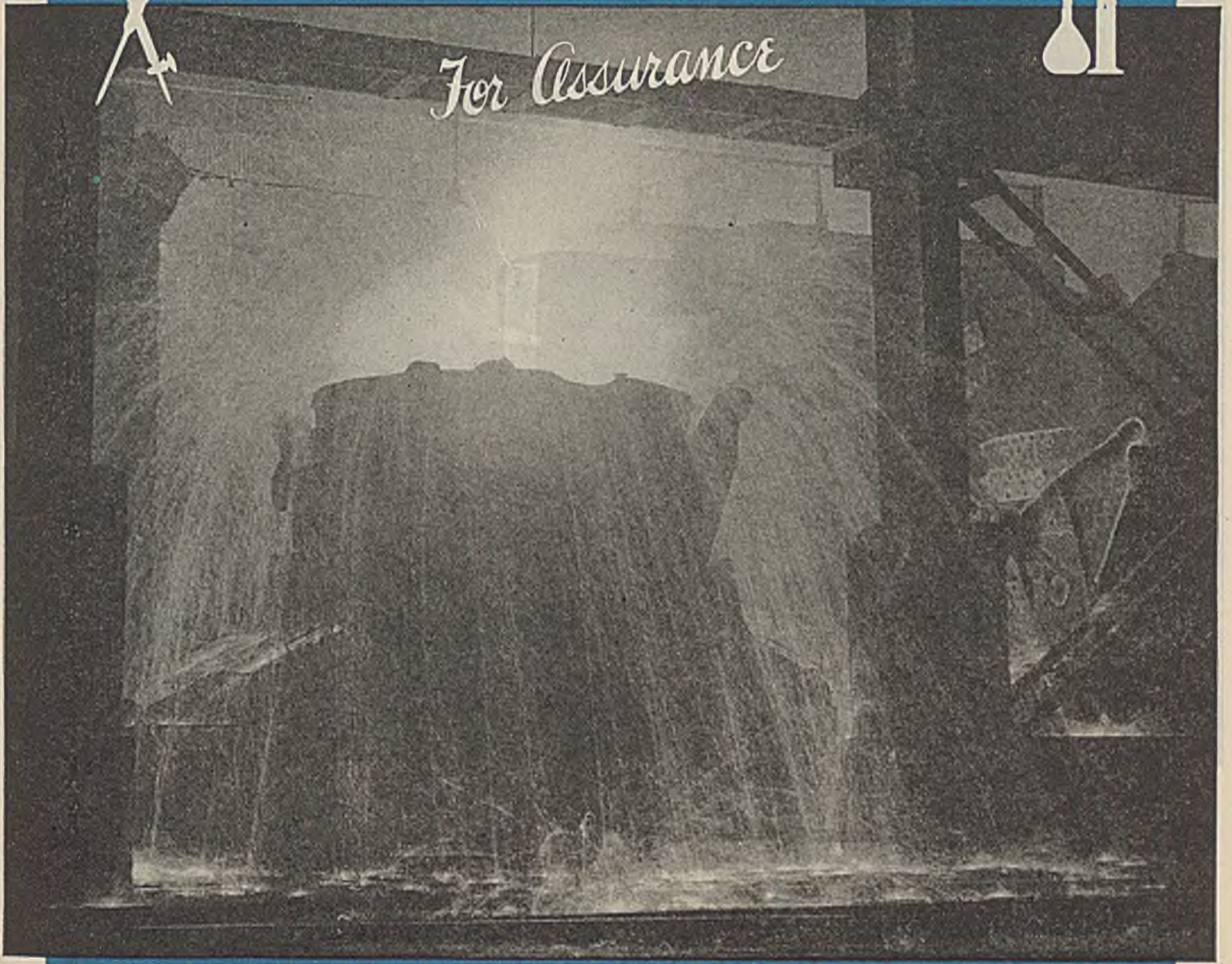
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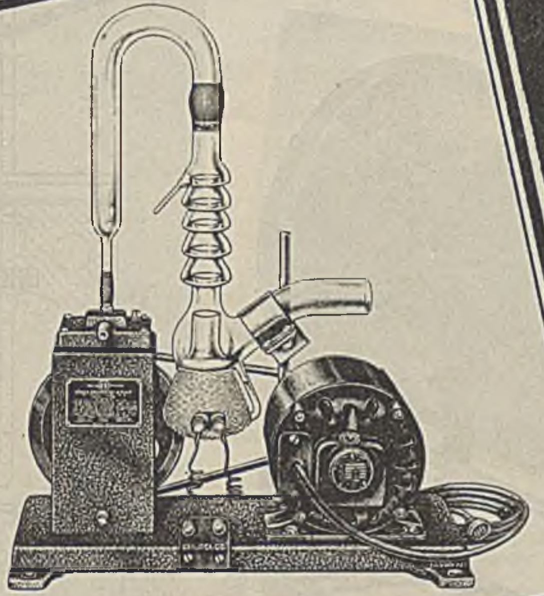

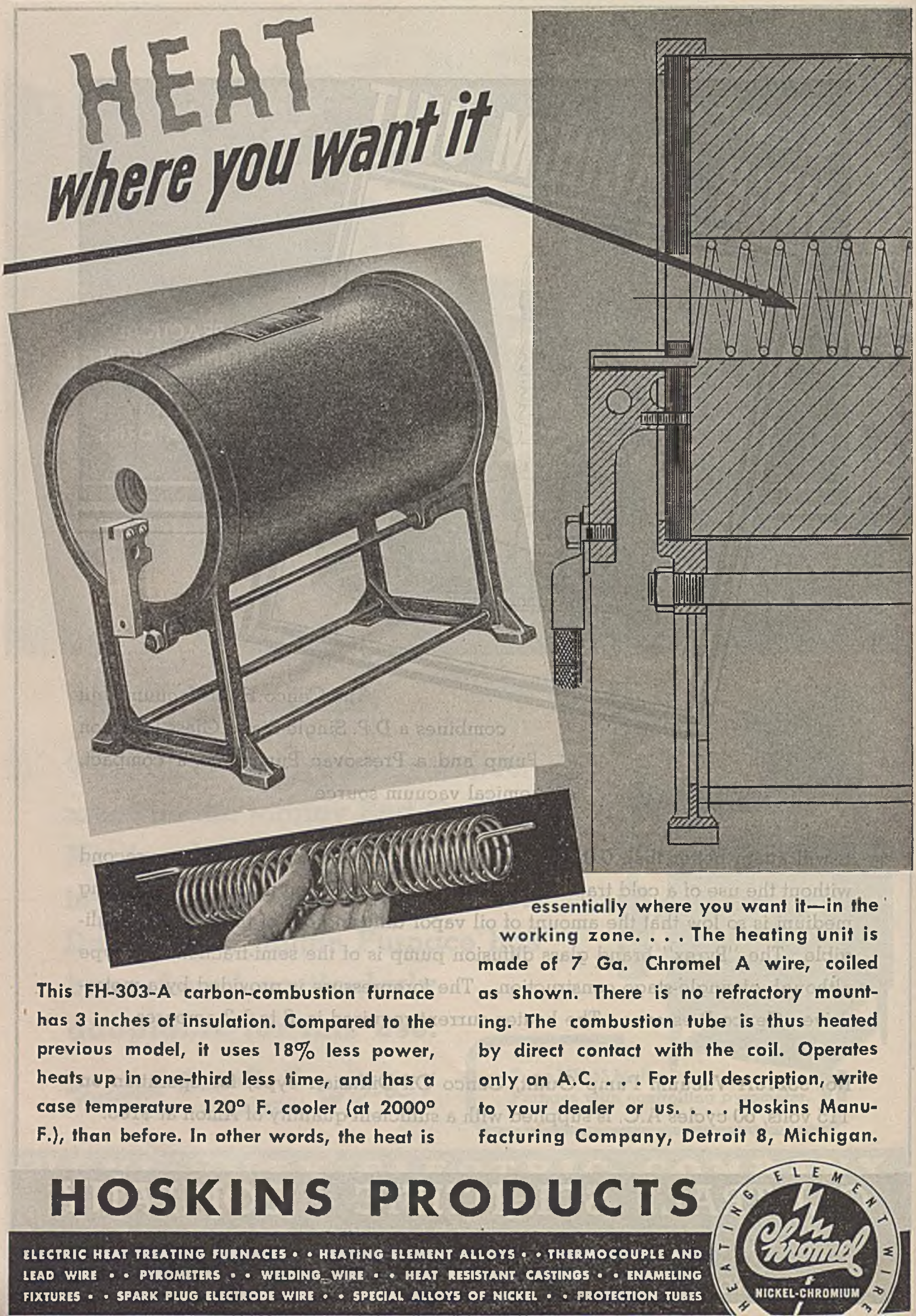
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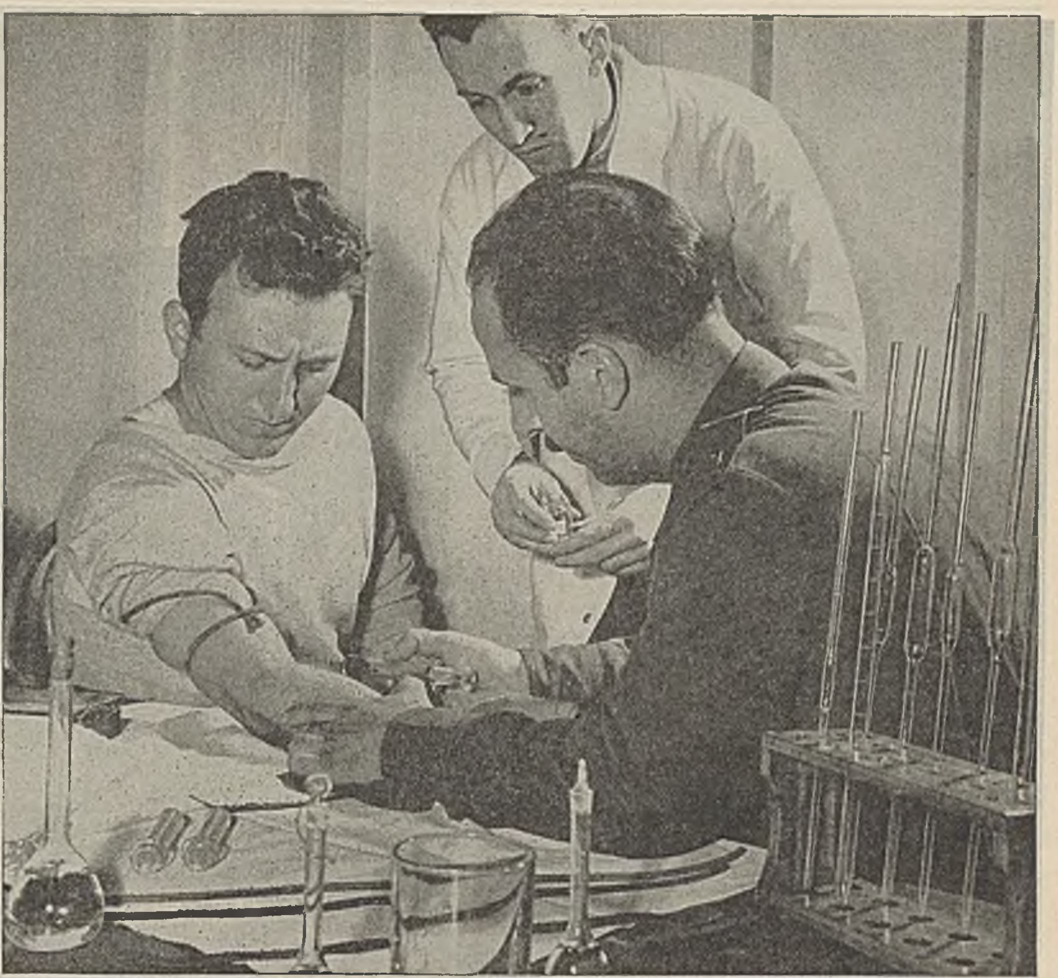

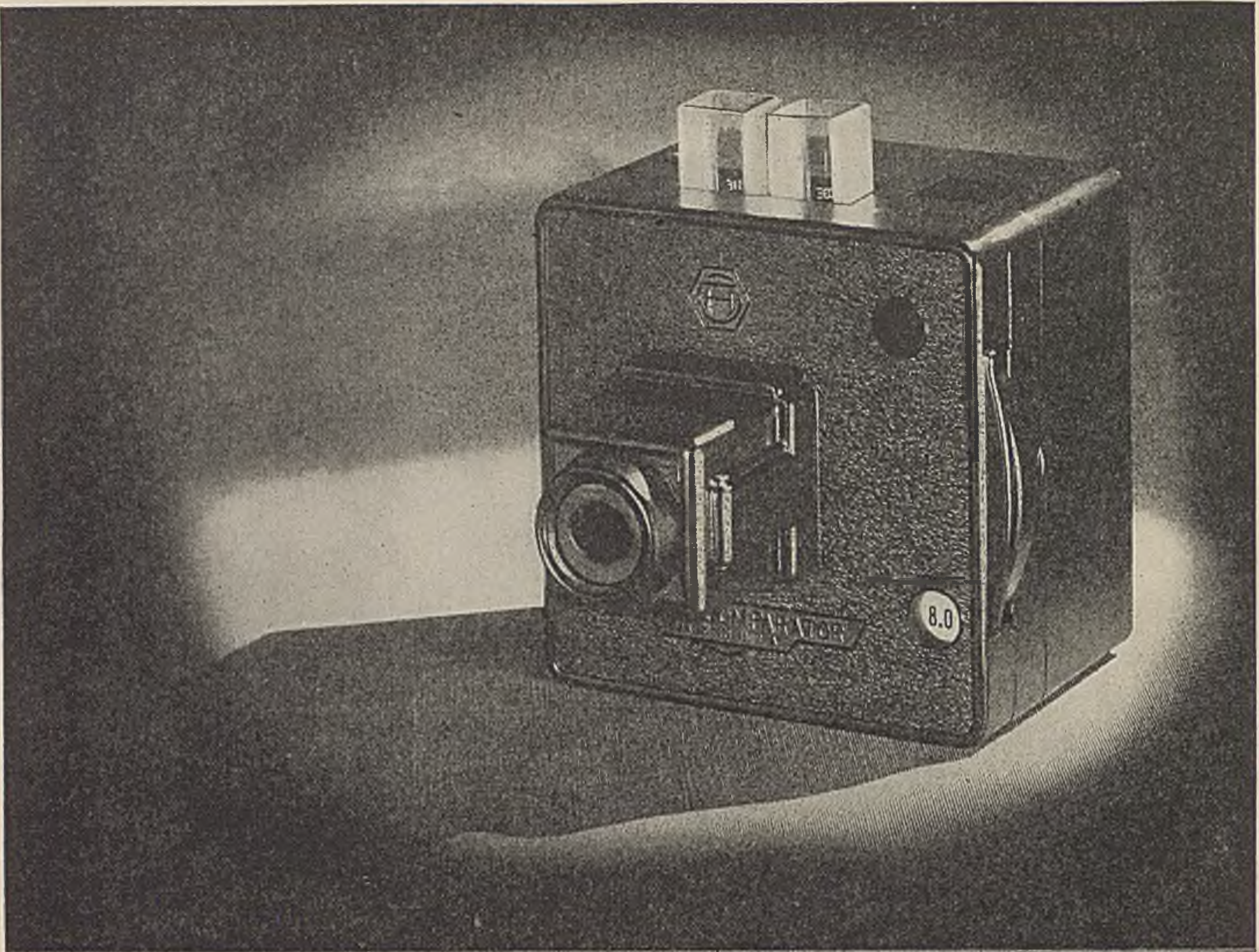
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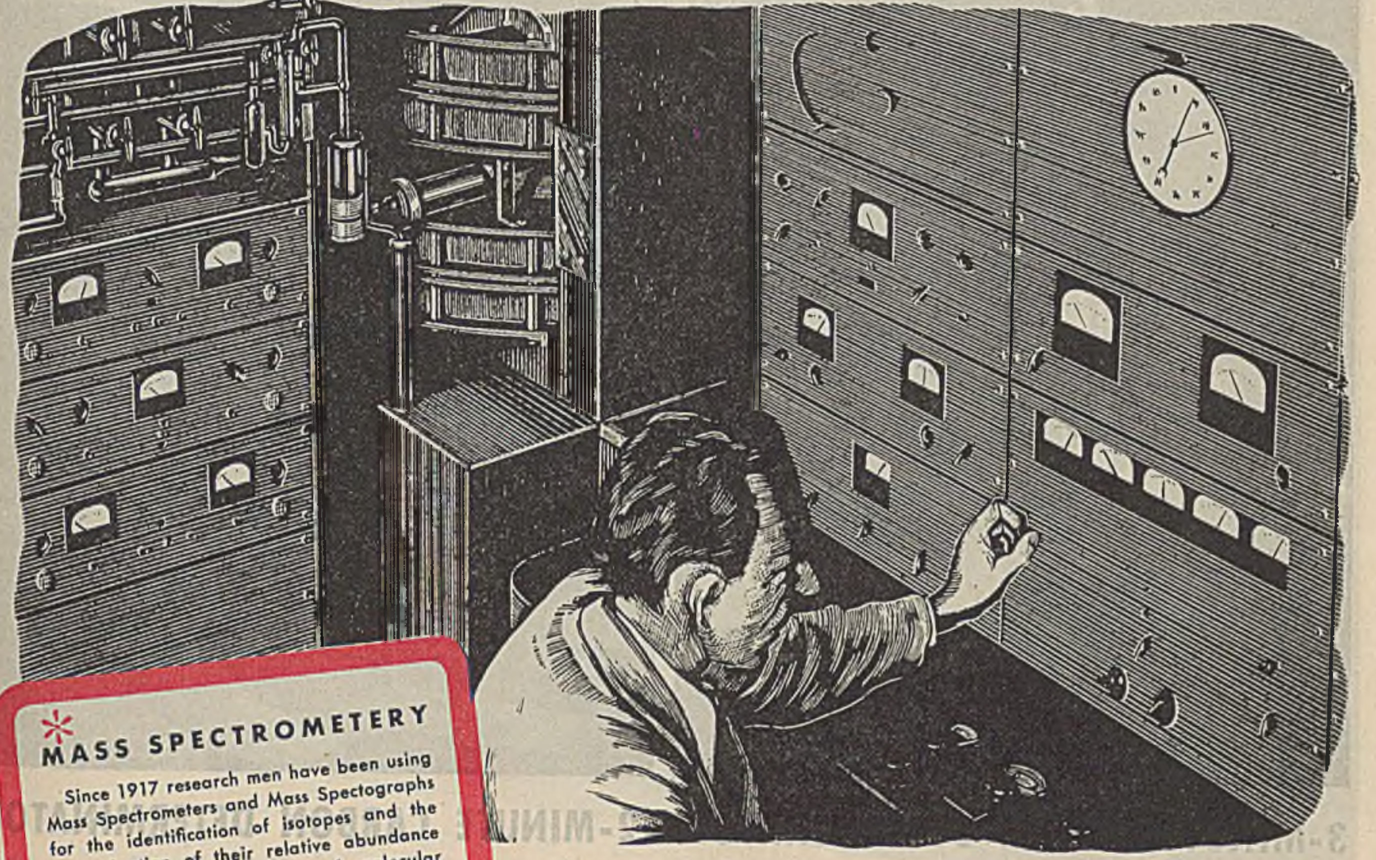

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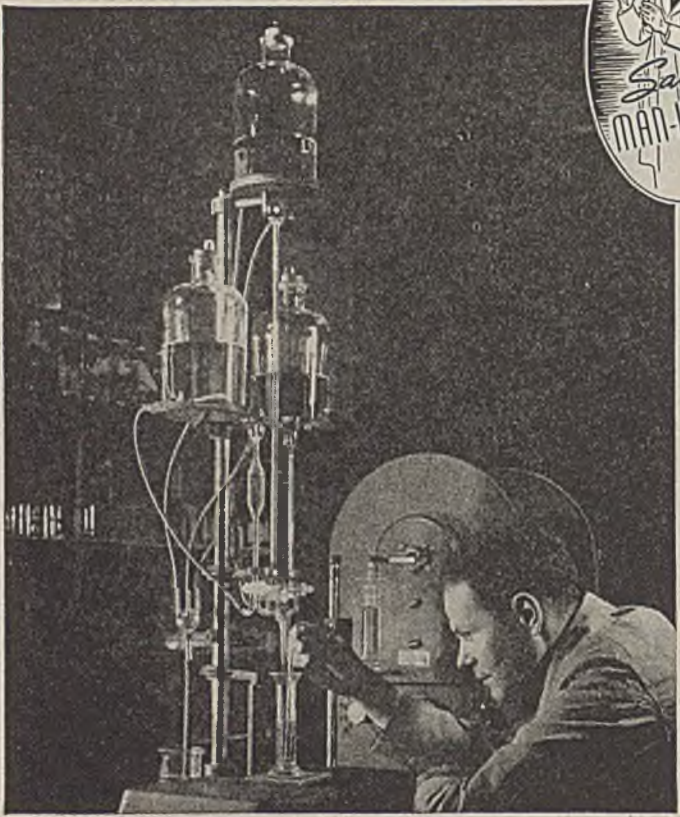

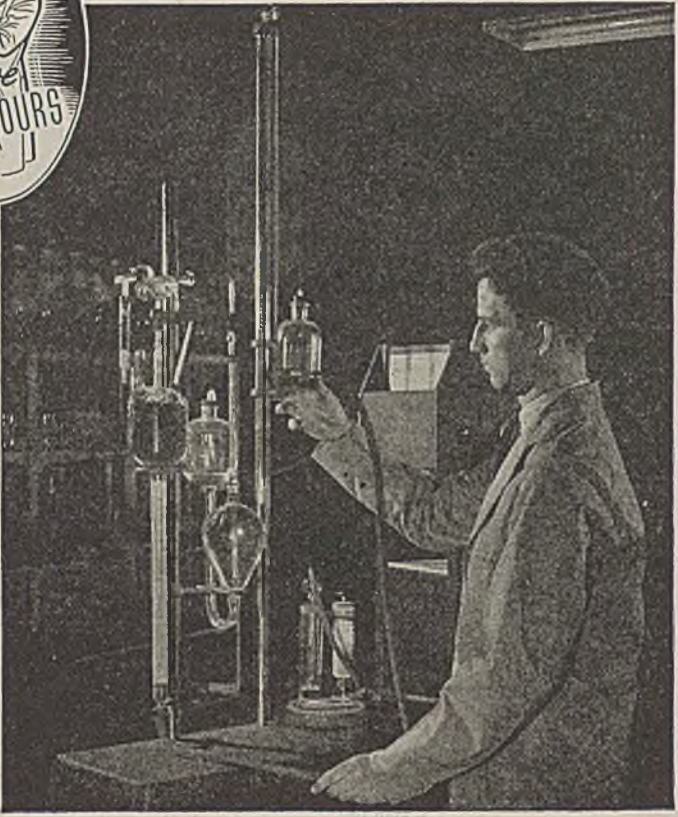

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The determinator has a substantial base and supporting column for holding glassware. Three 2-liter solution bottles insure ample supply of chemicals for the two automatic pipettes and burette.

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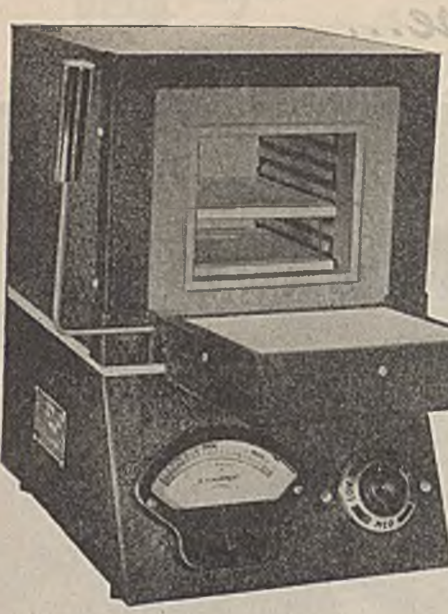

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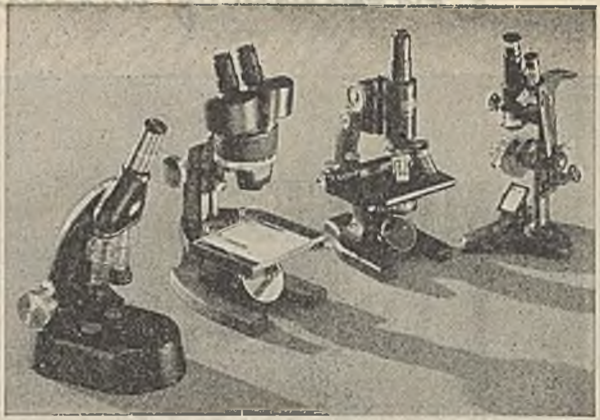

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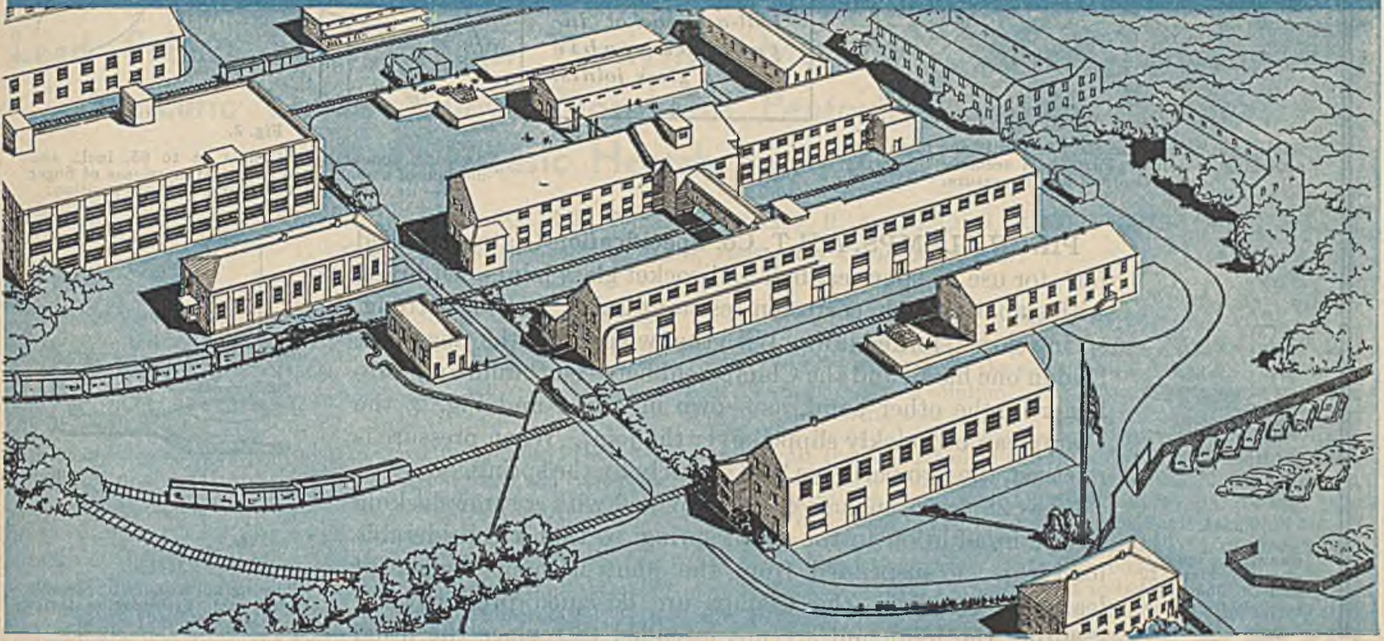

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FOR SPHERICAL BALL-AND-SOCKET GLASS JOINTS

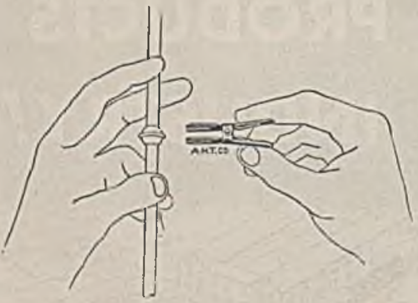


Fig. 1.

Showing appearance of Sizes 12 and 18 and method of attaching to joints. Parts held securely by spring upon release of finger pressure.

For quick, convenient and safe mounting and dismantling of apparatus with spherical ball-and-socket interchangeable ground glass joints.

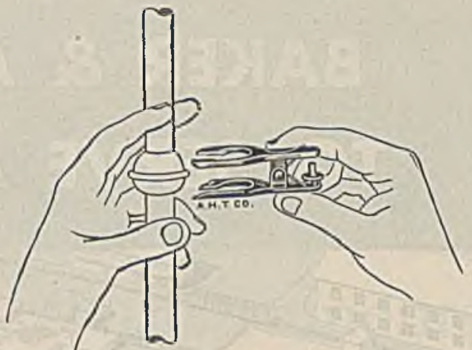


Fig. 2.

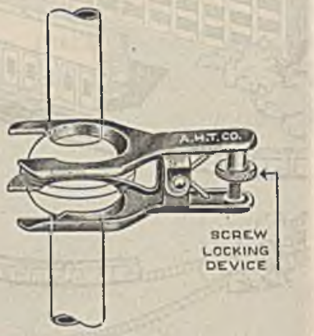
Showing appearance of Sizes 28 to 65, incl., and method of attaching to joint. After release of finger pressure, locking device is screwed into position.

3241.

Showing appearance of Sizes 12 and 18. Joint held securely by spring.

PINCH CLAMPS, A.H.T. Co. Specification (Patent applied for), for use on spherical ball-and-socket glass joints. Of brass, with smooth, black, corrosion-resistant finish, and with strong, spring closed, forked jaws. With the two parts of the glass joint held in one hand, and the Clamp held between thumb and forefinger of the other hand, as shown in Fig. 1 and Fig. 2, the Clamp can be quickly slipped over the joint. When pressure is released, the two parts are held securely by the spring.

Sizes 28 to 65, inclusive, are provided with a screw locking device in addition to the spiral spring, so that a considerable load can be suspended from the joint without danger of leakage. However, the Clamps are designed primarily for securing the joint and are not intended to replace the usual clamps, rings, tripods, etc., as ordinarily used for supporting glassware assemblies. The size number indicates the diameter in millimeters of the ball over which the Clamp fits.



3241.

Showing appearance of Sizes 28 to 65, incl., with locking device screwed into position.

The use of these Clamps adds greatly to the convenience and speed of mounting and dismantling glass apparatus with spherical interchangeable ground joints, and reduces the possibility of breakage in handling.

3241. Pinch Clamps, A.H.T. Co. Specification, as above described.

Size number	12	18	28	35	50	65
Takes spherical joint No.	12/1 to 12/5, incl.	18/7 and 18/9	28/11 to 28/15, incl.	35/20 and 35/25	50/30	65/40
Minimum width of fork opening in jaw, mm.	10	13	21	30	37	48
Each	.55	.65	1.20	1.55	2.25	2.75
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INDUSTRIAL AND ENGINEERING CHEMISTRY
Analytical Edition
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WALTER J. MURPHY, EDITOR

Recommended Specifications for Analytical Reagent Chemicals

Acid Hydriodic with Preservative, Acid Perchloric, Dimethylglyoxime, Lead Subacetate (for Sugar Analysis), Manganese Sulfate Monohydrate, Mercuric Oxide Yellow, Phosphorus Pentoxide, Sodium Phosphate Dibasic Heptahydrate, Zinc

EDWARD WICHERS, A. Q. BUTLER, W. D. COLLINS, P. H. MESSINGER, R. A. OSBORN, JOSEPH ROSIN, AND J. F. ROSS
Committee on Analytical Reagents, American Chemical Society

THE specifications given below comprise the thirteenth group to be published by the committee since 1925, and the first to supplement and amend those appearing in the twelve earlier publications (*1–12*), which were contained in the book, "A.C.S. Analytical Reagents", published in 1941.

The specifications are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for the improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (*1–12*) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (*3*). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

Acid, Hydriodic, with Preservative

Replacing previously published specification for Acid, Hydriodic (*12*).

Note. To avoid danger of explosions this acid should be distilled only in an inert atmosphere.

Requirements

Assay (HI). Not less than 47.0%.
Chloride and Bromide (as Cl). Not more than 0.1%.
Sulfate (SO_4). Not more than 0.005%.
Arsenic (As). Not more than 0.0005%.
Preservative (H_3PO_2). Not more than 1.5%.
Heavy Metals (as Pb). Not more than 0.001%.
Iron (Fe). Not more than 0.001%.

Tests

Assay. Weigh about 50 cc. of water in a 250-cc. glass-stoppered flask; add 0.7 cc. of the acid and weigh again. Add 50 cc. of 0.1 *N* silver nitrate solution, and shake the mixture well. Then add 5 cc. of nitric acid and heat the mixture on the steam bath until the precipitate has acquired a bright yellow color. Cool, and titrate the residual silver nitrate with 0.1 *N* ammonium thiocyanate solution, using ferric ammonium sulfate as the indicator.

Chloride and Bromide. Dilute 1.2 cc. to 100 cc. and take aliquots of 1 cc. and 5 cc. To the 1-cc. aliquot add 0.08 mg. of chloride. Dilute each aliquot to 20 cc., add 1 cc. of ammonium hydroxide, and then slowly, with vigorous stirring, add 2 cc. of a 5% solution of silver nitrate. Heat to boiling for 5 minutes and stir thoroughly. Cool, shake well, and filter. To the filtrate add nitric acid until neutral and then 1 cc. in excess. The turbidity in the aliquot of 5 cc. should not be greater than the turbidity in the 1-cc. portion, to which 0.08 mg. of chloride was added.

Sulfate. Dilute 3 cc. of the acid with 45 cc. of water, neutralize with ammonium hydroxide, and add 1 cc. of hydrochloric acid. Heat to boiling, add 3 cc. of a 10% solution of barium chloride, and allow to stand overnight. If any precipitate is formed, filter, wash thoroughly, ignite, and weigh. The weight of the ignited precipitate should not be more than 0.0006 gram greater than the weight of the ignited precipitate from a blank made with the quantities of reagents used in the test, including filtration and ignition.

Arsenic. Dilute 0.4 gram with 10 cc. of water, add 1 cc. of nitric acid, and evaporate on the steam bath to expel the iodine. Determine the arsenic in the residue by the modified Gutzeit method. Any stain produced should not exceed that produced by 0.002 mg. of arsenic.

Preservative. Weigh about 2 cc., dilute to 20 cc., add 15 cc. of 30% hydrogen peroxide, and allow to stand for 15 minutes. Heat the solution on the steam bath until all the iodine is volatilized and the solution is colorless. Add 50 cc. of water, 1 gram of ammonium chloride, and 15 cc. of magnesia mixture (5.5 grams of magnesium chloride, 7 grams of ammonium chloride, and 13 cc. of ammonium hydroxide per 100 cc. of solution), and allow the precipitate to settle for 10 minutes. Add 40 cc. of diluted ammonium hydroxide (2 + 3), stir for 10 minutes, and allow to stand at room temperature for 4 hours. Filter, and wash the precipitate well with diluted ammonium hydroxide (1 + 19). Dry the residue and ignite it to constant weight. The weight of H_3PO_2 calculated from the weight of magnesium pyrophosphate obtained (factor 0.593) should not be more than 1.5% of the weight of the sample taken for the test.

Heavy Metals. To 1.2 cc. add 3 cc. of sulfuric acid and heat to volatilize the iodine. Add 20 cc. of water, neutralize with ammonium hydroxide, and add 1 cc. of 0.1 *N* hydrochloric acid. Dilute the solution to 50 cc. and pass hydrogen sulfide through the solution. Any brown color should not be darker than is produced by 0.02 mg. of lead in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Make the solution from the preceding test slightly alkaline with ammonium hydroxide. Any green color should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Acid, Perchloric

Replacing previously published specification for Acid, Perchloric 60% (*8*).

Requirements

Assay. Not less than 70% $HClO_4$.
Nonvolatile Matter. Not more than 0.005%.
Chloride (Cl). Not more than 0.001%.
Nitrogen Compounds (as N). Not more than 0.004%.
Sulfate (SO_4). Not more than 0.005%.
Ammonia (NH_3). Not more than 0.001%.
Heavy Metals. To pass test (limit about 0.0005% lead).
Iron (Fe). Not more than 0.0002%.

Tests

Assay. Titrate a weighed portion of the acid, after suitable dilution, with standard alkali hydroxide solution, using phenolphthalein as indicator.

Nonvolatile Matter. Evaporate 10 cc. of the acid and ignite at low red heat. The weight of the residue should not exceed 0.0007 gram.

Chloride. Dilute 2 cc. with 40 cc. of water, add 3 cc. of nitric acid, and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Nitrogen Compounds. Dilute 1 cc. of the sample in a flask with 10 cc. of ammonia-free water, add 10 cc. of 10% sodium hydroxide solution, and about 0.5 gram of aluminum wire in small pieces, and allow to stand for 3 hours protected from loss or absorption of ammonia. Dilute to 50 cc., decant from any insoluble matter, and add 2 cc. of Nessler's reagent. The color should not be greater than is produced by 0.06 mg. of nitrogen as NH_3 in the same volume of a solution containing the quantities of sodium hydroxide and Nessler's reagent used in the test.

Sulfate. Dilute 10 cc. of the acid with 100 cc. of water and neutralize with ammonium hydroxide, using litmus paper as indicator. Add 0.5 cc. of dilute hydrochloric acid (1 + 9) and 5 cc. of 10% barium chloride solution, and allow to stand overnight. Any precipitate of barium sulfate should not weigh more than 0.0020 gram. Correction should be made for the weight obtained on running a blank, including filtration, using the quantities of reagents used in the test. Most of the ammonia should be removed by evaporation, so that only a small quantity of acid will be required for neutralization before acidifying for the precipitation.

Ammonia. Dilute 2 cc. of the sample with 40 cc. of ammonia-free water, add 10 cc. of 10% sodium hydroxide solution and 2 cc. of Nessler's reagent. Any yellow color produced should not be greater than is given by 0.03 mg. of ammonia in the same volume of a solution containing the quantities of sodium hydroxide and Nessler's reagent used in the test.

Heavy Metals, Iron. Dilute 3 cc. with 40 cc. of water, add 5 cc. of hydrogen sulfide water, and make alkaline with ammonium hydroxide. No brown color should be observed. Any greenish color should not be greater than is produced by 0.01 mg. of iron in an equal volume of alkaline sulfide solution.

Dimethylglyoxime

Requirements

Insoluble in Alcohol. Not more than 0.05%.
Residue on Ignition. Not more than 0.05%.
Suitability for Nickel Determination. To pass test.

Tests

Insoluble in Alcohol. Gently boil 2 grams with 100 cc. of ethyl alcohol under a reflux condenser until no more dissolves. Filter on a tared filtering crucible, wash with 50 cc. of alcohol, and dry at 105–110° C. The weight of the insoluble residue should not exceed 0.0010 gram.

Residue on Ignition. Ignite 1 gram at a temperature just high enough to burn off the carbonaceous matter. Cool, add 1 drop of sulfuric acid, and continue the ignition at dull redness for 5 minutes. The weight of the residue should not exceed 0.0005 gram.

Suitability for Nickel Determination. Dissolve 1.00 gram of nickel ammonium sulfate hexahydrate in exactly 50 cc. of water. Dilute 20 cc. of this solution to 100 cc., heat to boiling, and add a solution of 0.25 gram of the dimethylglyoxime in 25 cc. of alcohol. Add diluted ammonium hydroxide (1 + 4), drop by drop, to alkaline reaction, cool, and filter. Add to the filtrate 1 cc. of the nickel ammonium sulfate solution and heat to boiling. A substantial precipitate of nickel dimethylglyoxime should appear.

Lead Subacetate (for Sugar Analysis)

Replacing specification previously published (*10*).

Requirements

Basic Lead (PbO). Not less than 33%.
Insoluble in Acetic Acid. Not more than 0.05%.
Insoluble in Water. Not more than 2.0%.
Moisture (Loss at 100° C.). Not more than 1.5%.
Chloride (Cl). Not more than 0.005%.
Nitrate (NO_3). To pass test (limit about 0.003%).
Substances Not Precipitated by Hydrogen Sulfide. Not more than 0.30%.
Copper (Cu). Not more than 0.005%.
Iron (Fe). Not more than 0.005%.

Tests

Basic Lead. Weigh accurately about 5 grams and dissolve in 100 cc. of carbon dioxide–free water in a 500-cc. volumetric flask. Add 50 cc. of normal acetic acid and 100 cc. of a carbon dioxide–free 3% solution of sodium oxalate. Mix thoroughly, dilute to volume with carbon dioxide–free water, and allow the precipitate to settle. Titrate 100 cc. of the clear supernatant liquid with normal sodium hydroxide, using phenolphthalein indicator. Each cubic centimeter of normal acetic acid consumed is equivalent to 0.1116 gram of PbO.

Insoluble in Acetic Acid. Dissolve 5 grams in 100 cc. of water and 5 cc. of acetic acid, warming if necessary to complete solution. If an insoluble residue remains, filter and wash until the washings are no longer darkened by hydrogen sulfide. Dry at 105–110° C. The weight of the residue should not exceed 0.0025 gram.

Insoluble in Water. Agitate 1 gram in a small stoppered flask with 50 cc. of carbon dioxide–free water and filter at once. Wash with carbon dioxide–free water and dry at 105–110° C. The weight of the residue should not exceed 0.0200 gram.

Moisture. Weigh accurately about 0.5 gram and dry for 2 hours at 105–110° C. Cool and reweigh. The loss in weight should not exceed 1.5%.

Chloride. Dissolve 1 gram in 50 cc. of water and add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.05 mg. of chloride in an equal volume of solution containing the quantities of reagents used in the test.

Nitrate. Dissolve 1 gram in 9 cc. of water containing 5 mg. of sodium chloride. Add 0.7 cc. of acetic acid, 0.2 cc. of indigo carmine solution (1 to 1000), and 10 cc. of sulfuric acid. Stir thoroughly and allow to stand for 10 minutes. The blue color of the clear solution should not be completely discharged.

Solution A. Dissolve 5 grams in 42 cc. of water and 3 cc. of acetic acid, and add 5 cc. of sulfuric acid. After standing for about 10 minutes, filter the solution.

Substances Not Precipitated by Hydrogen Sulfide. Dilute 10 cc. of solution A to 100 cc., pass hydrogen sulfide through the solution to precipitate all the lead, and filter. Evaporate 50 cc. of the filtrate to dryness and ignite gently. The weight of the residue should not exceed 0.0015 gram.

Copper. To 25 cc. of solution A add about 0.05 gram of aluminum chloride and a few crystals of ammonium persulfate. Neutralize with ammonium hydroxide and add a very slight excess. Heat to boiling, cool, and filter. Save the precipitate for the determination of iron. Neutralize the filtrate to phenolphthalein, add 0.25 cc. of acetic acid in excess and 0.25 cc. of a freshly prepared 10% solution of potassium ferrocyanide. Any pink color produced should not exceed that produced by 0.125 mg. of copper in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Wash the precipitate of iron and aluminum hydroxides obtained in the previous test sufficiently to remove most of the acetate. Dissolve the precipitate in 10 cc. of hot dilute hydrochloric acid (1 + 5), wash the paper and dilute to 50 cc. Dilute

20 cc. of this solution to 45 cc. and add a few crystals of ammonium persulfate, 3 cc. of hydrochloric acid, and 3 cc. of a 30% solution of ammonium thiocyanate. The color should not be more than is produced by 0.05 mg. of ferric iron in 45 cc. of water to which are added 3 cc. of hydrochloric acid and 3 cc. of a 30% solution of ammonium thiocyanate.

Manganese Sulfate Monohydrate

Replacing previously published specification for Manganese Sulfate (*12*).

Requirements

INSOLUBLE MATTER. Not more than 0.010%.

CHLORIDE (Cl). Not more than 0.005%.

SUBSTANCES NOT PRECIPITATED BY AMMONIUM SULFIDE. Not more than 0.50%.

IRON (Fe). Not more than 0.002%.

HEAVY METALS (as Pb). To pass test (limit about 0.005%).

NICKEL (Ni). Not more than 0.02%.

ZINC (Zn). Not more than 0.01%.

SUBSTANCES REDUCING PERMANGANATE. To pass test.

Tests

INSOLUBLE MATTER. Dissolve 10 grams in 130 cc. of hot water, and heat on the steam bath for 1 hour. Filter through a tared filtering crucible, wash thoroughly, and dry at 105–110° C. The weight of the insoluble residue should not exceed 0.0010 gram.

CHLORIDE. Dissolve 1 gram in 50 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not exceed that produced by 0.05 mg. of chloride in an equal volume of solution containing the quantities of reagents used in the test.

SUBSTANCES NOT PRECIPITATED BY AMMONIUM SULFIDE. Dissolve 2 grams in about 90 cc. of water and add a sufficient quantity of a freshly prepared solution of ammonium sulfide to precipitate the manganese. Heat on the steam bath for 30 minutes, cool, dilute to 100 cc., mix thoroughly, and filter. Evaporate 50 cc. of the filtrate to dryness in a tared dish, ignite gently, and weigh. The weight of the residue should not exceed 0.0050 gram.

IRON. Dissolve 1 gram in 45 cc. of water, and add 2 cc. of hydrochloric acid, a few crystals of ammonium persulfate, and 3 cc. of a 30% solution of ammonium thiocyanate. Any red color should not be more than is produced by 0.02 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

HEAVY METALS. *Solution A.* Dissolve 1 gram in 20 cc. of water and 1 cc. of 1 *N* hydrochloric acid. *Solution B.* Dissolve 1 gram in 10 cc. of water and 1 cc. of 1 *N* hydrochloric acid and add 10 cc. of hydrogen sulfide water. Solution B should be no darker than solution A.

NICKEL. Dissolve 1 gram in 200 cc. of water. To 20 cc. of this solution add 2 grams of sodium acetate and 10 cc. of hydrogen sulfide water, and allow to stand 1 minute. Add 5 cc. of acetic acid. Any color should not be more than is produced by 0.02 mg. of nickel in 20 cc. of solution containing the quantities of reagents used in the test.

ZINC. Dissolve 2 grams in 50 cc. of water containing 2 cc. of sulfuric acid and add, with thorough agitation, 1 cc. of a 1% solution of potassium ferrocyanide. No turbidity should be produced in 5 minutes.

SUBSTANCES REDUCING PERMANGANATE. Dissolve 7.5 grams in 200 cc. of water containing 3 cc. of sulfuric acid and 3 cc. of phosphoric acid. To this solution add 0.1 cc. of 0.1 *N* potassium permanganate in excess of the amount required to produce a pink color in 200 cc. of water containing 3 cc. of sulfuric acid and 3 cc. of phosphoric acid. The pink color should not be entirely discharged at the end of 1 minute.

Mercuric Oxide, Yellow

Requirements

INSOLUBLE IN HYDROCHLORIC ACID. Not more than 0.030%.

NONVOLATILE MATTER. Not more than 0.050%.

CHLORIDE (Cl). Not more than 0.025%.

SULFATE (SO_4). Not more than 0.020%.

TOTAL NITROGEN (N). Not more than 0.005%.

IRON (Fe). Not more than 0.003%.

Tests

INSOLUBLE IN HYDROCHLORIC ACID. Dissolve 3 grams in 30 cc. of diluted hydrochloric acid (1 + 3) and heat on the steam bath for 1 hour. Filter through a tared filtering crucible, wash well with water, and dry at 105–110° C. The weight of the insoluble residue should not exceed 0.0009 gram.

NONVOLATILE MATTER. Ignite 3 grams in a tared porcelain dish in a well-ventilated hood, cool, and weigh. The weight of the residue should not exceed 0.0015 gram. Save the residue for the determination of iron.

CHLORIDE. Dissolve 1 gram in 50 cc. of water and 1 cc. of formic acid. Add, dropwise, a 10% solution of sodium hydroxide until a small amount of permanent precipitate is formed. Digest under a reflux condenser until all the mercury is reduced to metal and the solution is clear. Cool, filter through a paper that has been washed free of chlorides, and dilute to 100 cc. Dilute 20 cc. of this solution to a total volume of 50 cc. containing 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be more than that in an equal volume of solution containing 0.05 mg. of chloride and the quantities of reagents used in the test.

Solution A. Dissolve 5 grams in 50 cc. of water and 3 cc. of formic acid. Digest under a reflux condenser until all the mercury is reduced to metal and the supernatant liquid is clear. Cool, filter through a well-washed paper, and dilute to 100 cc.

SULFATE. To 10 cc. of solution A add 0.01 gram of sodium carbonate and evaporate to dryness. Dissolve the residue in 10 cc. of water and add 1 cc. of 1 *N* hydrochloric acid. Filter if necessary and add 1 cc. of a 10% solution of barium chloride. Any turbidity should not be more than that produced in a solution containing 0.10 mg. of sulfate, 0.6 cc. of formic acid, and 0.01 gram of sodium carbonate treated in the same way as the solution of the sample.

TOTAL NITROGEN. Dilute 10 cc. of solution A to 55 cc. in a flask suitable for an ammonia distillation, add 15 cc. of a 10% solution of sodium hydroxide and 1 gram of aluminum wire or small chips. Connect the flask, using a spray trap, to a condenser, the tip of which dips below the surface of 10 cc. of 0.1 *N* hydrochloric acid. Distill over 35 cc., and add 5 cc. of a 10% solution of sodium hydroxide and 2 cc. of Nessler's solution. Any color produced should not be greater than that produced in a solution containing 0.025 mg. of ammonia and 0.33 cc. of formic acid treated in the same way as the solution of the sample.

IRON. Dissolve the residue obtained in the test for nonvolatile matter by warming with 9 cc. of hydrochloric acid and a few drops of nitric acid, and dilute to 150 cc. To 50 cc. of this solution add 3 cc. of a 30% solution of ammonium thiocyanate. Any red color should not be greater than that produced by 0.03 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Phosphorus Pentoxide

Requirements

ASSAY (P_2O_5). Not less than 97.0%.

INSOLUBLE MATTER. Not more than 0.02%.

PHOSPHORUS TRIOXIDE (P_2O_3). Not more than 0.02%.

AMMONIA (NH_3). Not more than 0.01%.

ARSENIC (As). Not more than 0.005%.

HEAVY METALS (as lead). To pass test (limit about 0.01%).

Tests

ASSAY. Weigh accurately about 1.5 grams, dissolve in 100 cc. of water, evaporate to 25 cc., and dissolve 5 grams of sodium chloride in the solution. Cool the solution to 15° C. and titrate at this temperature with normal sodium hydroxide, using 3 drops of phenolphthalein indicator solution. Each cubic centimeter of normal alkali consumed corresponds to 0.03549 gram of P_2O_5.

INSOLUBLE MATTER. Dissolve 5 grams in 40 cc. of water (the phosphorus pentoxide must be added to the water in small quantities to prevent excessive heating and sputtering) and warm if necessary to complete solution. Filter through a tared filtering crucible, and set aside the filtrate for solution A. Wash the residue well with water and dry at 105–110° C. The weight of the insoluble residue should not exceed 0.0010 gram.

Solution A. Make up the filtrate from the test for insoluble matter to 50 cc.

PHOSPHORUS TRIOXIDE. To 30 cc. of solution A add 0.20 cc. of 0.1 *N* potassium permanganate solution. Heat to boiling and allow to digest on the steam bath for 10 minutes. The pink color should not be entirely discharged.

AMMONIA. Dilute 5 cc. of solution A to 40 cc., add 10 cc. of a 10% solution of sodium hydroxide and 2 cc. of Nessler's solution. The color should not be more than is produced by 0.05 mg. of ammonia in an equal volume containing the quantities of reagents used in the test.

ARSENIC. Determine the arsenic by the Gutzeit procedure in 1 cc. of solution A. The stain should not be greater than is produced by 0.005 mg. of arsenic.

Heavy Metals. Dilute 5 cc. of solution A to 10 cc. and exactly neutralize with ammonium hydroxide, using 3 drops of phenolphthalein solution as the indicator. Add 50 cc. of 1 *N* sulfuric acid, 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color immediately observed should not be more than is produced by 0.05 mg. of lead in an equal volume of water containing 5 cc. of hydrogen sulfide water.

Sodium Phosphate, Dibasic, Heptahydrate ($Na_2HPO_4.7H_2O$)

Replacing specification for Sodium Phosphate, Dibasic (Disodium Hydrogen Phosphate), previously published (*4*).

Requirements

Insoluble Matter. Not more than 0.005%.
Water of Crystallization. 43 to 50%.
Neutrality. To pass test.
Chloride (Cl). Not more than 0.001%.
Nitrogen Compounds (as N). Not more than 0.001%.
Sulfate (SO_4). Not more than 0.010%.
Arsenic (As). Not more than 0.0005%.
Heavy Metals. To pass test (limit about 0.001% as lead).
Iron (Fe). Not more than 0.001%.

Tests

Insoluble Matter. Dissolve 10 grams in 100 cc. of water, allow to stand on the steam bath for 1 hour, filter through a tared filtering crucible, wash well with water, dry at 105–110° C., cool, and weigh. The weight of the residue should not exceed 0.0005 gram.

Water of Crystallization. Weigh accurately about 1 gram. Dry to constant weight at 105–110° C. The loss in weight should be from 43 to 50%.

Neutrality. Dissolve 3 grams in 30 cc. of water at 15° C. and add 3 drops of phenolphthalein solution. A red color should be produced which should be discharged by the addition of 0.8 cc. of *N* hydrochloric acid. Boil the solution for 2 minutes, cool to 15° C., and dilute to the original volume with cold water. The resulting solution should show no pink color.

Chloride. Dissolve 2 grams in 20 cc. of water, and add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride in an equal volume of solution containing the quantities of reagent used in the test.

Nitrogen Compounds. Dissolve 2 grams in 30 cc. of water, add 20 cc. of a 10% solution of sodium hydroxide and 0.5 gram of aluminum wire in small pieces, and allow to stand for 3 hours protected from loss or access of ammonia. Decant 25 cc. and add 2 cc. of Nessler's solution. The color should not be more than that produced in a similar aliquot of a complete blank to which has been added 0.02 mg. of nitrogen.

Sulfate. Dissolve 10 grams in 100 cc. of water, add 7 cc. of hydrochloric acid, and heat to boiling. Add 5 cc. of a 10% solution of barium chloride, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate forms, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not be more than 0.0025 gram in excess of the weight obtained from a complete blank on the reagents used, including filtration.

Arsenic. Determine the arsenic in a 2-gram sample by the modified Gutzeit method. The stain should not be more than is produced by 0.010 mg. of arsenic.

Heavy Metals. Dissolve 5 grams in 40 cc. of water and exactly neutralize the solution with 1 *N* sulfuric acid, using 3 drops of 1% phenolphthalein solution as indicator. Add 15 cc. of 1 *N* sulfuric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color which is immediately developed should not be greater than that produced by 0.05 mg. of lead in an equal volume of an aqueous solution containing 5 cc. of hydrogen sulfide water.

Iron. Dissolve 5 grams in 100 cc. of water. Dilute 20 cc. of this solution to 40 cc., add 1 cc. of ammonium hydroxide, and 5 cc. of hydrogen sulfide water. Any green color should not be greater than is produced by 0.01 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Zinc

Replacing previously published specifications for Zinc, Low in Arsenic, and Zinc, Low in Lead and Iron (*6*).

Requirements

Arsenic (As). Not more than 0.00002%.
Iron (Fe). Not more than 0.01%.
Lead (Pb). Not more than 0.01%.

Tests

Arsenic. Test 10 grams by the modified Gutzeit method, using 12 cc. of sulfuric acid or 20 cc. of hydrochloric acid, diluted with about 70 cc. of water. Any stain produced should not be more than is produced by 0.002 mg. of arsenic, allowance being made for the blank.

Solution A. Dissolve 2 grams in 15 cc. of diluted hydrochloric acid (1 + 1). When solution is nearly complete add 1 cc. of nitric acid and heat to boiling, or until any residue from the zinc is dissolved. Cool and dilute to 100 cc.

Iron. To 25 cc. of solution A add 2 cc. of hydrochloric acid and 3 cc. of a 30% solution of ammonium thiocyanate, and dilute to 50 cc. Any red color should not be more than is produced by 0.05 mg. of iron in an equal volume containing the quantities of reagents used in the test.

Lead. Dilute 5 cc. of solution A to 20 cc. and add ammonium hydroxide until a small amount of permanent precipitate is formed. Carefully add nitric acid in sufficient amount just to dissolve the precipitate. Pour the resulting solution into 20 cc. of a 10% solution of sodium cyanide, mix thoroughly, and add 0.20 cc. of a 10% solution of sodium sulfide. Any brown color should not be more than is produced by 0.01 mg. of lead in an equal volume containing the quantities of reagents used in the test.

Corrections for Published Specifications

Acetone (2)

Requirements

Specific Gravity at 25°/25° C. Not above 0.788.
Methanol. To pass test (limit about 0.1%).

Test

Methanol. Dilute 5 cc. with water to 100 cc. To 5 cc. of this solution add 0.5 cc. of phosphoric acid and 2 cc. of a 3% solution of potassium permanganate and allow to stand for 10 minutes. Add 1.5 cc. of a 10% solution of oxalic acid and allow to stand until the solution is colorless. Add 5 cc. of diluted sulfuric acid (1 + 3) and 5 cc. of fuchsin–sulfurous acid solution. No blue or violet color should be produced in 10 minutes. To prepare the fuchsin–sulfurous acid solution, dissolve 0.2 gram of fuchsin in 120 cc. of hot water, cool, add 20 cc. of a 10% solution of sodium sulfite and 2 cc. of hydrochloric acid. Dilute the solution to 200 cc. and allow to stand until it is nearly colorless.

Acid, Citric (5)

Test

Heavy Metals. In the second sentence change 7 cc. of ammonium hydroxide to 10 cc. of ammonium hydroxide.

Acid, Oxalic (*1*)

Requirements

Heavy Metals. To pass test (limit about 0.001% as lead).
Iron (Fe). Not more than 0.0005%.

Tests

Nonvolatile. Ignite 5 grams in a porcelain crucible at a low red heat to constant weight. The weight of the residue should not exceed 0.0010 gram. Save the residue.

Heavy Metals. To the residue from the test for nonvolatile matter add about 0.5 cc. of hydrochloric acid and 0.1 cc. of nitric acid, and evaporate to dryness. Dissolve the residue in 1 cc. of 0.1 *N* hydrochloric acid and dilute to 10 cc. Dilute 5 cc. of this solution to 40 cc. and add 10 cc. of hydrogen sulfide water. Any brown color should not be greater than is produced by 0.025 mg. of lead in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Dilute the remaining 5 cc. of the solution of the nonvolatile residue to 45 cc., and add 2 cc. of hydrochloric acid, a few crystals of ammonium persulfate, and 3 cc. of a 30% solution of ammonium thiocyanate. Any red color should not be greater than is produced by 0.0125 mg. of ferric iron in an equal volume of solution containing the quantities of reagents used in the test.

Acid, Phosphoric (4)

Test

Nitrate. Dilute 2 cc. to 10 cc. containing 5 mg. of sodium chloride. Add 0.10 cc. of indigo carmine solution (1 to 1000) and 10 cc. of sulfuric acid. The blue color should not be completely discharged in 5 minutes.

Aluminum and Potassium Sulfate (2)

Requirement

Sodium (Na). To pass test (limit about 0.02%).

Test

Sodium. A 10% solution in hot water tested with a platinum wire in a colorless flame should impart no pronounced yellow color to the flame.

Ammonium Oxalate (1)

Requirements

Heavy Metals. To pass test (limit about 0.001% as lead).
Iron (Fe). Not more than 0.0005%.

Tests

Nonvolatile. Ignite 5 grams in a porcelain crucible at a low red heat to constant weight. The weight of the residue should not exceed 0.0010 gram. Save the residue.

Heavy Metals. To the residue from the test for nonvolatile matter add about 0.5 cc. of hydrochloric acid and 0.1 cc. of nitric acid, and evaporate to dryness. Dissolve the residue in 1 cc. of 0.1 *N* hydrochloric acid and dilute to 10 cc. Dilute 5 cc. of this solution to 40 cc. and add 10 cc. of hydrogen sulfide water. Any brown color should not be greater than is produced by 0.025 mg. of lead in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Dilute the remaining 5 cc. of the solution of the nonvolatile residue to 45 cc., and add 2 cc. of hydrochloric acid, a few crystals of ammonium persulfate, and 3 cc. of a 30% solution of ammonium thiocyanate. Any red color should not be greater than is produced by 0.0125 mg. of ferric iron in an equal volume of solution containing the quantities of reagents used in the test.

Ammonium Persulfate (2)

Requirement

Chloride and Chlorate (as Cl). Not more than 0.001%.

Test

Chloride and Chlorate. Mix 2 grams with 2 grams of sodium carbonate and heat until no more gas is evolved. Dissolve the residue in 20 cc. of water, neutralize with nitric acid, add an excess of 1 cc., and add 1 cc. of a 0.1 *N* silver nitrate solution. Any turbidity should not be greater than that produced by 0.02 mg. of chloride in an equal volume of solution containing the quantities of reagents used in the test.

Barium Carbonate (3)

Tests

Nitrate. To 3 grams in 23 cc. of water containing 15 mg. of sodium chloride add 7 cc. of acetic acid. To 10 cc. of this solution add 0.20 cc. of indigo carmine (1 to 1000) and 10 cc. of sulfuric acid. Heat on the steam bath for 1 hour and stir the precipitate thoroughly several times. The blue color of the clear solution should not be completely discharged.

Strontium and Calcium Salts. Dissolve 3 grams in 30 cc. of water and 4 to 5 cc. of hydrochloric acid, and evaporate to dryness. Powder the residue, add 30 cc. of absolute alcohol, and allow to stand for 30 minutes with occasional shaking. Filter and evaporate 20 cc. of the filtrate to a few cubic centimeters, add about 1 cc. of diluted sulfuric acid (1 + 9), evaporate to dryness, ignite, and weigh. The weight of the residue should not exceed 0.0060 gram.

Barium Chloride (1)

Test

Nitrate and Chlorate. Dissolve 1 gram in 10 cc. of water, and add 0.20 cc. of indigo carmine solution (1 to 1000) and 10 cc. of sulfuric acid. Stir constantly during the addition of the sulfuric acid. Heat on the steam bath for 1 hour and stir the precipitate thoroughly several times. The blue color of the clear solution should not be completely discharged.

Calcium Carbonate (7)

Tests

Sulfate. The weight of the ignited precipitate should not exceed 0.0024 gram.

Magnesium and Alkali Salts. The fourth sentence should read, "To 125 cc. of the filtrate add 0.5 cc. of sulfuric acid, evaporate to dryness, ignite at 700–750° C. for 30 minutes, and weigh."

Calcium Carbonate, Low in Alkalies (7)

Tests

Sulfate. The weight of the ignited precipitate should not exceed 0.0024 gram.

Magnesium and Alkali Salts. The fourth sentence should read, "To 125 cc. of the filtrate add 0.5 cc. of sulfuric acid, evaporate to dryness, ignite at 700–750° C. for 30 minutes, and weigh."

Calcium Chloride ($CaCl_2.2HO_2$) (7)

Tests

Nitrate. Use 0.10 cc. of indigo carmine solution (1 to 1000).

Magnesium and Alkali Salts. The fourth sentence should read, "To 125 cc. of the filtrate add 0.5 cc. of sulfuric acid, evaporate to dryness, ignite at 700–750° C. for 30 minutes, and weigh."

Calcium Chloride, Anhydrous (5)

Test

Magnesium and Alkali Salts. The second sentence should read, "To 100 cc. of the filtrate add 0.5 cc. of sulfuric acid, evaporate to dryness, and ignite at 700–750° C. for 30 minutes."

Carbon Disulfide (4)

Note. Carbon disulfide should be supplied and stored in amber glass containers and protected from direct sunlight.

Chloroform (12)

Note. This reagent normally contains about 0.75% of alcohol as a stabilizer.

Cupric Oxide, Powdered (6)

Test

Carbon Compounds. Ignite 0.6 gram in a stream of carbon dioxide–free air and pass the evolved gases into 20 cc. of diluted ammonium hydroxide (1 + 7), add 2 cc. of a 10% solution of barium chloride, and compare immediately with the standard. The turbidity should not be greater than that produced by 2 cc. of 0.01 *N* sodium carbonate in an equal volume containing the quantities of reagents used in the test.

Cuprous Chloride (7)

Requirement

Arsenic (As). Not more than 0.002%.

Ether (6)

Note. Ether conforming to this specification normally contains about 2% of alcohol and about 0.5% of water.

Requirements

Specific Gravity 25°/25° C. 0.712 to 0.714.
Foreign Odor. To pass test.

Test

Foreign Odor. Allow 10 cc. to evaporate spontaneously to a volume of about 1 cc. in a dry evaporating dish: no foreign odor should be perceptible. Transfer this residue to a piece of clean, odorless absorbent paper: no foreign odor should be perceptible when the last traces of ether evaporate from the paper.

Ether, Absolute (6)

Requirement

Foreign Odor. To pass test.

Test

Foreign Odor. Allow 10 cc. to evaporate spontaneously to a volume of about 1 cc. in a dry evaporating dish: no foreign odor should be perceptible. Transfer this residue to a piece of clean, odorless absorbent paper: no foreign odor should be perceptible when the last traces of ether evaporate from the paper.

Ferric Ammonium Sulfate (2)

Requirement

Nitrate (NO$_3$). To pass test (limit about 0.01%).

Test

Nitrate. Dissolve 2 grams in 15 cc. of water, heat, and pour the hot solution into 6 cc. of diluted ammonium hydroxide (1 + 1). Filter and allow to drain well; to the filtrate add 0.10 cc. of indigo carmine solution (1 to 1000) and 15 cc. of sulfuric acid. The blue color should not be completely discharged in 5 minutes.

Ferric Chloride (9)

Requirement

Sulfate (SO$_4$). Not more than 0.01%.

Tests

Nitrate. To 15 cc. of solution A, add 0.10 cc. of indigo carmine solution (1 to 1000), and 15 cc. of sulfuric acid. The blue color should not be completely discharged in 5 minutes.

Sulfate. Concentrate 120 cc. of solution A to 75 cc., add 1 cc. of hydrochloric acid, heat to boiling, add 10 cc. of a 10% solution of barium chloride, and allow to stand overnight. Filter, wash thoroughly, ignite, and weigh. The weight of the ignited precipitate should not exceed the weight obtained from a complete blank by more than 0.0010 gram.

Glycerol (12)

Requirement

Assay. Not less than 95% by volume.
Use above title in place of "Specific Gravity at 25°/25° C.".

Test

Assay. The specific gravity at 25°/25° C. should not be less than 1.249.

Hydrogen Peroxide (11)

Note. This reagent should be stored in ceresin or ceresin-lined containers.

Lead Acetate (7)

Tests

Solution A. Dissolve 5 grams in 42 cc. of water and 3 cc. of acetic acid, and add 5 cc. of sulfuric acid. After standing for about 10 minutes, filter the solution.

Copper. To 25 cc. of solution A add about 0.05 gram of aluminum chloride and a few crystals of ammonium persulfate. Neutralize with ammonium hydroxide and add a very slight excess. Heat to boiling, cool, and filter. Save the precipitate for the determination of iron. Neutralize the filtrate to phenolphthalein. Add 0.25 cc. of acetic acid and 0.25 cc. of a freshly prepared 10% solution of potassium ferrocyanide. Any pink color should not exceed that produced by 0.125 mg. of copper in an equal volume of solution containing the quantities of reagents used in the test.

Iron. Wash the precipitate of iron and aluminum hydroxides obtained in the previous test sufficiently to remove most of the acetate. Dissolve the precipitate in 10 cc. of hot dilute hydrochloric acid (1 + 5), wash the paper, and dilute to 45 cc. Add a few crystals of ammonium persulfate, 3 cc. of hydrochloric acid, and 3 cc. of a 30% solution of ammonium thiocyanate. The color should not be more than is produced by 0.025 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test.

Substances Not Precipitated by Hydrogen Sulfide. Dilute 20 cc. of solution A to 100 cc., pass hydrogen sulfide through the solution to precipitate all the lead, and filter. Evaporate 50 cc. of the filtrate to dryness and ignite gently. The weight of the residue should not exceed 0.0005 gram.

Lead Dioxide (3)

Test

Other Hydrogen Sulfide Metals. Dissolve 0.5 gram in 5 cc. of nitric acid and 10 cc. of 3% hydrogen peroxide solution. Add 5 cc. of sulfuric acid and evaporate to fumes. Cautiously dilute to 40 cc., allow to stand until the solution is cool and the precipitate has settled. Filter, do not wash, add 10 cc. of sulfurous acid, and boil until the odor of sulfur dioxide disappears. Cool, dilute to 50 cc., and pass hydrogen sulfide through the solution. No red color should be produced, and any darkening should not be more than is produced by 0.10 mg. of lead in an equal volume of solution containing the quantities of reagents used in the test.

Potassium and Sodium Tartrate (6)

Requirement

Ammonia (NH$_3$). Not more than 0.005%.

Test

Ammonia. Dissolve 1 gram in 45 cc. of water, add 2 cc. of a 10% solution of sodium hydroxide and 2 cc. of Nessler's solution. The color should not be more than is produced by 0.05 mg. of ammonia in an equal volume containing the quantities of reagents used in the test.

Potassium Bisulfate, Fused (9)

Requirements

Heavy Metals. To pass test (limit about 0.001% as lead).
Iron (Fe). Not more than 0.002%.

Tests

Solution A. Dissolve 5 grams in 45 cc. of water, add 5 cc. of hydrochloric acid, and boil gently for 10 minutes. Cool and restore volume to 50 cc.

Heavy Metals. Neutralize 20 cc. of solution A to phenolphthalein with ammonium hydroxide, add 0.5 cc. of acetic acid and 10 cc. of hydrogen sulfide water. The color produced should not be more than that produced by 0.02 mg. of lead and 2 cc. of hydrochloric acid in 20 cc. of solution treated in the same way as the solution of the sample.

Iron. Dilute 10 cc. of solution A to 50 cc., add a few crystals of ammonium persulfate and 3 cc. of a 30% solution of ammonium thiocyanate. The color produced should not be more than that produced by 0.02 mg. of iron and 1 cc. of hydrochloric acid in an equal volume of solution containing the quantities of reagents used in the test.

Potassium Chlorate (3)

Test

Nitrogen. Change the last sentence to, "The color should not be more than that produced in a similar aliquot of a complete blank to which has been added 0.02 mg. of nitrogen."

Potassium Hydroxide (1)

Tests

Potassium Hydroxide and Carbonate. Accurately weigh 35 to 40 grams, dissolve, and dilute to 1 liter, using carbon dioxide-free water. Use a 50-cc. aliquot of this solution for the titration instead of 10 cc. of solution A.

Phosphate. Neutralize 10 cc. of solution A with nitric acid and dilute to 50 cc. Add 10 cc. of nitric acid, neutralize with ammonium hydroxide using phenolphthalein indicator, and add 0.5 cc. of nitric acid in excess. Add 50 cc. of ammonium molybdate solution, shake the solution (at about 40° C.) for 5 minutes, and allow to stand for 0.5 hour. Any precipitate formed should not be more than is formed when 0.10 mg. of phosphate is treated by the above procedure, except that the control should include the residue from evaporation of the quantity of nitric acid used to neutralize 10 cc. of solution A.

Iron. Neutralize 25 cc. of solution A to phenolphthalein with hydrochloric acid, add 1 cc. in excess, and dilute to 50 cc. Add a few crystals of ammonium persulfate and 3 cc. of a 30% solution of ammonium thiocyanate. The red color should not exceed that produced by 0.10 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test. The control should contain residue from evaporation of the quantity of hydrochloric acid used to neutralize 25 cc. of solution A.

Heavy Metals. Neutralize 25 cc. of solution A to phenolphthalein with hydrochloric acid and add a slight excess. Exactly neutralize with ammonium hydroxide, add 0.5 cc. of acetic acid, and saturate with hydrogen sulfide. The darkening should not exceed that produced by 0.15 mg. of silver in an equal volume of solution containing the quantities of reagents used in the test. The standard should contain residue from evaporation of the quantity of hydrochloric acid used to neutralize 25 cc. of solution A.

Potassium Oxalate (*11*)

Requirement

Iron (Fe). Not more than 0.001%.

Tests

Solution A. To 5 grams in a 150-cc. beaker add 5 cc. of sulfuric acid. Heat under a well-ventilated hood until decomposition is complete and heavy fumes of sulfuric acid are given off. Cool and dilute to 100 cc.

Heavy Metals. Neutralize 10 cc. of solution A with ammonium hydroxide to the end point of phenolphthalein, add 0.5 cc. of acetic acid, and dilute to 25 cc. Cool and add 10 cc. of hydrogen sulfide water. The color should not be more than that produced in a solution of the same volume containing 0.5 cc. of sulfuric acid and 0.01 mg. of lead neutralized with ammonium hydroxide and otherwise treated in the same way.

Iron. To 20 cc. of solution A add a few crystals of ammonium persulfate and 3 cc. of a 30% solution of ammonium thiocyanate, and dilute to 50 cc. The color should not be more than that produced by 0.01 mg. of iron and 1 cc. of sulfuric acid in an equal volume of solution containing the quantities of reagents used in the test.

Sodium Bisulfate, Fused ($NaHSO_4$) (5)

Requirements

Heavy Metals. To pass test (limit about 0.001% as lead).

Iron (Fe). Not more than 0.002%.

Tests

Solution A. Dissolve 5 grams in 45 cc. of water, add 5 cc. of hydrochloric acid, and boil gently for 10 minutes. Cool and restore volume to 50 cc.

Heavy Metals. Neutralize 20 cc. of solution A to phenolphthalein with ammonium hydroxide, add 0.5 cc. of acetic acid and 10 cc. of hydrogen sulfide water. The color produced should not be more than that produced by 0.02 mg. of lead and 2 cc. of hydrochloric acid in 20 cc. of solution treated in the same way as the solution of the sample.

Iron. Dilute 10 cc. of solution A to 50 cc., add a few crystals of ammonium persulfate and 3 cc. of a 30% solution of ammonium thiocyanate. The color produced should not be more than that produced by 0.02 mg. of iron and 1 cc. of hydrochloric acid in an equal volume of solution containing the quantities of reagents used in the test.

Sodium Carbonate, Anhydrous (2)

Test

Chloride. The first sentence should read, "Dissolve 1 gram in 20 cc. of warm water, add 2 cc. of nitric acid, cool, and add 1 cc. of 0.1 *N* silver nitrate solution."

Sodium Hydroxide (*1*)

Tests

Sodium Hydroxide and Carbonate. Accurately weigh 35 to 40 grams, dissolve, and dilute to 1 liter, using carbon dioxide-free water. Use a 50-cc. aliquot of this solution for the titration instead of 10 cc. of solution A.

Phosphate. Neutralize 10 cc. of solution A with nitric acid and dilute to 50 cc. Add 10 cc. of nitric acid, neutralize with ammonium hydroxide, using phenolphthalein indicator, and add 0.5 cc. of nitric acid in excess. Add 50 cc. of ammonium molybdate solution, shake the solution (at about 40° C.) for 5 minutes, and allow to stand for 0.5 hour. Any precipitate formed should not be more than is formed when 0.10 mg. of phosphate is treated by the above procedure, except that the control should include the residue from evaporation of the quantity of nitric acid used to neutralize 10 cc. of solution A.

Iron. Neutralize 25 cc. of solution A to phenolphthalein with hydrochloric acid, add 1 cc. in excess, and dilute to 50 cc. Add a few crystals of ammonium persulfate and 3 cc. of a 30% solution of ammonium thiocyanate. The red color should not exceed that produced by 0.10 mg. of iron in an equal volume of solution containing the quantities of reagents used in the test. The standard should contain residue from evaporation of the quantity of hydrochloric acid used to neutralize 25 cc. of solution A.

Heavy Metals. Neutralize 25 cc. of solution A to phenolphthalein with hydrochloric acid and add a slight excess. Exactly neutralize with ammonium hydroxide, add 0.5 cc. of acetic acid, and saturate with hydrogen sulfide. The darkening should not exceed that produced by 0.15 mg. of silver in an equal volume of solution containing the quantities of reagents used in the test. The standard should contain the residue from evaporation of the quantity of hydrochloric acid used to neutralize 25 cc. of solution A.

Sodium Nitrate (4)

Requirement

Calcium, Magnesium, and Ammonium Hydroxide Precipitate. Use this title instead of present title of "Calcium and Magnesium Precipitate". The limit remains the same.

Test

Calcium, Magnesium, and Ammonium Hydroxide Precipitate. The second sentence should read, "If any precipitate is formed, filter, wash with diluted ammonium hydroxide (1 + 9), ignite, and weigh."

Sodium Oxalate (*1*)

Requirements

Neutrality. To pass test (limit of alkalinity equivalent to 0.042% Na_2CO_3, limit of acidity equivalent to 0.022% of $NaHC_2O_4$).

Heavy Metals. To pass test (limit about 0.002% as lead).

Iron (Fe). Not more than 0.001%.

Tests

Solution A. To 5 grams in a 150-cc. beaker add 5 cc. of sulfuric acid. Heat under a well-ventilated hood until decomposition is complete and heavy fumes of sulfuric acid are given off. Cool and dilute to 100 cc.

Heavy Metals. Neutralize 10 cc. of solution A with ammonium hydroxide to the end point of phenolphthalein, add 0.5 cc. of acetic acid, and dilute to 25 cc. Cool and add 10 cc. of hydrogen sulfide water. The color should not be more than that produced in a solution of the same volume containing 0.5 cc. of sulfuric acid and 0.01 mg. of lead neutralized with ammonium hydroxide and otherwise treated in the same way.

Iron. To 20 cc. of solution A add a few crystals of ammonium persulfate and 3 cc. of a 30% solution of ammonium thiocyanate, and dilute to 50 cc. The color should not be more than that produced by 0.01 mg. of iron and 1 cc. of sulfuric acid in an equal volume of solution containing the quantities of reagents used in the test.

Sodium Peroxide (4)

Test

Iron. Dissolve 1 gram in 10 cc. of water, add 5 cc. of hydrochloric acid, and evaporate to dryness. Treat the residue with 3 cc. of hydrochloric acid, dissolve in 45 cc. of water, add a few crystals of ammonium persulfate, and 3 cc. of a 30% solution of ammonium thiocyanate. The color should not be greater than that produced by 0.03 mg. of ferric iron in an equal volume of solution containing the quantities of reagents used in the test.

Sodium Sulfate, Anhydrous (2)

Test

Calcium, Magnesium, and Ammonium Hydroxide Precipitate. Second sentence should read, "Allow to stand overnight."

Sodium Sulfite, Anhydrous (*11*)

Requirements

Assay. Not less than 97% Na_2SO_3.

Free Alkali. To pass test (limit of alkalinity equivalent to 0.15% Na_2CO_3).

Test

Free Alkali. The last sentence should read, "Not more than 0.3 cc. of 0.1 N acid should be required to neutralize the solution."

Sodium Tungstate (*12*)

Test

Alkalinity. Dissolve 2 grams in 50 cc. of cold water and add 2 drops of thymol blue indicator. A blue color should be produced which is changed to a yellow color by the addition of not more than 0.4 cc. of 0.1 N acid.

Specifications Previously Published

(1) Committee on Analytical Reagents, Ind. Eng. Chem., 17, 756 (1925).
(2) *Ibid.*, 18, 636, 759 (1926).
(3) *Ibid.*, 19, 645 (1927).
(4) *Ibid.*, 19, 1369 (1927).
(5) *Ibid.*, 20, 979 (1928).
(6) Ind. Eng. Chem., Anal. Ed., 1, 171 (1929).
(7) *Ibid.*, 2, 351 (1930).
(8) *Ibid.*, 3, 221 (1931).
(9) *Ibid.*, 4, 154 (1932).
(10) *Ibid.*, 4, 347 (1932).
(11) *Ibid.*, 5, 289 (1933).
(12) *Ibid.*, 12, 631 (1940).

Presented in connection with the report of the Committee on Analytical Reagents at the 105th Meeting of the American Chemical Society, Detroit, Mich.

Destructive Irradiation Technique of Spectrophotometric Vitamin A Assay

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DURING the past 15 years many studies have been made of the two in vitro methods of vitamin A assay in an attempt to replace the laborious and time-consuming animal-feeding method by a more rapid and precise means of determining vitamin A potency.

The spectrophotometric assay, while rapid, finds simple application limited to fish liver oils and food oils of fairly high potency. As the potency of the oil decreases, the extraneous absorption at the wave length of the maximum absorption of vitamin A becomes greater, and there is therefore a lower limit of potency, below which the spectrophotometric technique gives rise to apparent potencies greater than the actual vitamin A content. The practice of saponifying oils of low potency lowers the limit of applicability somewhat.

The colorimetric method of Carr and Price (*2*) has been used to some extent in miscellaneous products containing vitamin A, particularly to trace the occurrence and storage in the various tissues of the animal body (*1*, *3*, *4*, *13*).

In 1934 the International Committee approved the spectrographic method as an alternate to the biological assay (*9*) but it has, as yet, been used almost exclusively in the assay of fish liver oils. The method has been shown to be applicable to butterfat (*8*, *14*), and attempts have been made to apply it to other food extracts (*5*, *7*).

The difficulty in obtaining an extract of a food product or animal tissue, which would be sufficiently free from interfering extraneous absorption to measure the vitamin absorption directly, suggests the use of the destructive irradiation technique as first suggested by Peacock (*15*). As was pointed out by Demarest (*6*), the validity of this method depends upon three assumptions: (1) the irradiation process destroys vitamin A, the end product of the destruction having no appreciable absorption at 3280 Å. (2) Substances present other than vitamin A undergo no appreciable change in their absorption at 3280 Å. during the irradiation. (3) The irradiation causes quantitative destruction of the vitamin present. Whether or not these three conditions can be satisfied seems still to be a subject of controversy (*6*, *12*).

Since absorption of ultraviolet radiation is characteristic of all unsaturated organic linkages and of conjugated systems in particular, it was felt that filtered radiations from a mercury vapor arc, limited as closely as possible to the absorption range of the vitamin, offered the most logical opportunity of attaining specificity in the photolysis process.

APPARATUS

The absorption was carried out by means of a Hilger medium quartz spectrograph combined with a double disk rotating sector photometer, the source of radiation being a water-cooled, low-pressure, hydrogen discharge tube. The spectrograph slit was kept at a constant setting of approximately 0.09 mm.

The spectrograms were made using fused quartz absorption cells, similar to Hilger type C, and were recorded on 10 × 25 cm. (4 × 10 inch) photographic plates (Eastman 33), isodensity points being picked out by visual comparison with the aid of an opal-glass spectrum viewer and a small hand lens (4×).

Destructive irradiations were carried out with a Hanovia quartz mercury vapor arc, laboratory model, 110 volt, direct current, the lamp always being turned on 10 minutes before irradiations were begun. The spectrograph cell containing the solution to be irradiated was placed in a small, water-jacketed tin can (5 cm. deep, 5 cm. in diameter) which was fitted to be covered with the filter or filters desired. [Two filters were used: (1) red-purple Corex A (C. G. No. 986), 3 mm. thick and 5 cm. square; (2) an optical quartz cell, 5 cm. in diameter, containing 5 cc. of 0.2 M potassium hydrogen phthalate resulting in a depth of solution of about 1 mm.] The can was raised into the hood of the lamp during the irradiation, so that the cell being irradiated was about 18 cm. from the mid-section of the arc.

MATERIALS

Cyclohexane. A special grade was obtained (Eastman No. 702) and redistilled before use. In cases where the cyclohexane contained benzene or other impurities, it was purified by treating with fuming sulfuric acid. Each new or purified lot of solvent was compared spectrographically with distilled water and with the last solvent used.

Ethyl Alcohol. Ethanol 95% was treated with silver nitrate and potassium hydroxide and the filtered solvent then refluxed with M-phenylenediamine dihydrochloride and distilled.

Wet Ether for Extractions. Anhydrous ether was shaken periodically with about $^1/_3$ its volume of 5% aqueous po-

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tassium hydroxide for 2 to 3 hours and distilled slowly from the alkaline solution. This solvent was always purified less than 24 hours before use.

Dry Ether. Anhydrous ether was distilled onto sodium wire and used as required from the storage bottle.

PROCEDURES

Unsaponifiable Fraction of Reference Oil. The procedure of Wilkie (*17*) was used with the following modifications. A portion of 300 to 400 mg. of oil was taken for a sample and refluxed for 10 minutes with 5% alcoholic potassium hydroxide. Following the ether extractions 100 cc. of water were poured through the combined ether extracts without agitation. The water layer was drawn off and the ether solution washed with 3 to 5 cc. of water, with vigorous shaking. The resulting emulsion was broken by a final wash with 100 cc. of water, the water again being poured in without agitation. The washed ether extract was filtered by suction through a layer of anhydrous sodium sulfate on a sintered-glass funnel into a ground-glass vacuum distillation apparatus. The filter and anhydrous sodium sulfate were washed with two small portions of anhydrous ether and the solvent was removed at room temperature, under reduced pressure, and in an atmosphere of nitrogen. The cyclohexane was introduced by means of a small, side-arm separatory funnel before the vacuum was broken. The cyclohexane solution was then transferred to a volumetric flask and made up to volume. The remaining air was displaced with nitrogen and the spectrographic assay run within 24 hours.

As was pointed out by McFarlane and Sutherland (*12*), vaseline should not be employed as a stopcock lubricant in the separatory funnels. Glycerol was used in this work and found to be satisfactory.

Unsaponifiable Extract of Animal Tissues. The animal tissues were dissected out, placed in a weighed cork-stoppered 50-cc. Erlenmeyer flask, reweighed, and covered with 5% aqueous potassium hydroxide. (Care was taken to remove all fatty tissue and the tissues were blotted carefully with paper toweling to remove excess blood.) The air in the flask was displaced with nitrogen and the tissues were stored in the dark, under refrigeration until assayed.

On removal from storage, the flasks were placed in a water bath at 80° C. for 5 minutes or until complete dissolution occurred, cooled, and the tissue solution was transferred to a 50-cc. separatory funnel. The solution was shaken with 5 cc. of ethanol followed by 25 cc. of wet ether. [As was found by Davies (*3*), a preliminary shaking with alcohol makes it possible to extract 90% or more of the vitamin A with a single ether extraction.] The water layer was drained into a second separatory funnel and again extracted with 25 cc. of wet ether. The ether extracts were then combined in a reflux flask with a boiling chip and the ether was boiled off in a 60° C. water bath.

The residue was cooled, 25 cc. of ethanol and 3 cc. of 50% aqueous potassium hydroxide were added, and the mixture was refluxed in a water bath for 10 minutes, using a ground-glass reflux. This solution was cooled, 30 cc. of water were added, and the whole was transferred to a 250-cc. separatory funnel. From here on the sample was treated as given above for the unsaponifiable fraction of a cod-liver oil.

Solutions of muscle tissue prepared in this manner were always clear and colorless but became somewhat turbid when irradiated. Occasionally this turbidity formed when the prepared solution had to be stored in the refrigerator overnight, in which case filtering into the absorption cells solved the difficulty. The following step, however, invariably led to a clear, colorless final solution with no tendency to become turbid either on refrigeration or irradiation.

After saponification the sample was cooled, 30 cc. of water and 10 drops of saturated sodium sulfate were added, and the flask was allowed to stand 5 to 10 minutes in an ice bath. The solution was then filtered into a separatory funnel (Whatman No. 44) and the flask and filter were washed with a few cubic centimeters of a mixture of half 95% ethanol and half water, saturated with sodium sulfate. The extraction was then carried out as usual.

From applications of this treatment to preparations of muscle tissue, liver tissue, and cod liver oil, it appears that such a "salting out" does not cause any appreciable loss of vitamin A.

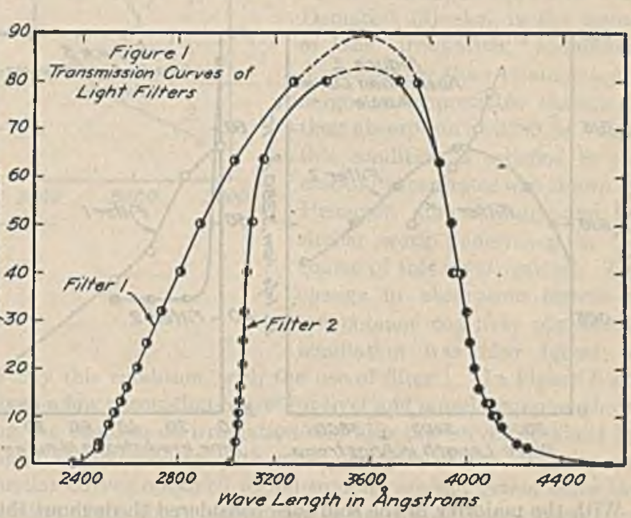
In the course of this work specific extinction coefficients were determined by three different methods—(1) direct measurement, (2) irradiated measurement, and (3) modified photometry.

The direct measurement is generally used in spectrographic work, in which case the spectrogram is taken with one absorption cell containing the solution under test and the other cell filled with pure solvent. The specific extinction coefficient is represented by the symbol $E^{1\%}_{1\text{ cm.}}$.

In the second case two spectrograms are taken: one a direct measurement as above, and the other a measurement of the same preparations left in the cells, the solution having been irradiated. In this case the symbol $E^{1\%}_{1\text{ cm. irrad.}}$ is used, where

$$E^{1\%}_{1\text{ cm. irrad.}} = E^{1\%}_{1\text{ cm. (original)}} - E^{1\%}_{1\text{ cm. (residual)}}$$

The method of modified photometry as suggested by De (*5*) requires but one spectrogram, in which case both cells are filled with the solution under test, the solvent cell being irradiated before the spectrogram is taken. The symbol $E^{1\%}_{1\text{ cm. mod.}}$ will be used in this case.



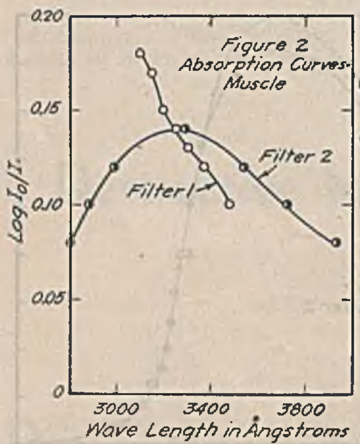
It is obvious that methods 2 and 3 should give the same specific extinction coefficient for any given solution and also a measure of those constituents of the solution which are destroyed by irradiation—i.e., vitamin A if the effect of irradiation can be made specific for the vitamin.

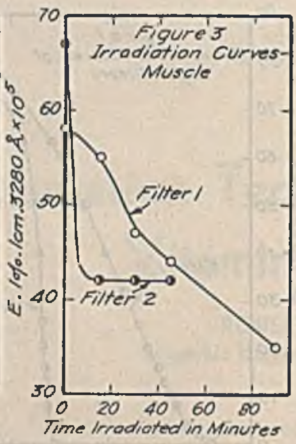
EXPERIMENTAL

Instrument Factor. Specific extinction coefficients ($E^{1\%}_{1\text{ cm.}}$) of the unsaponifiable fraction of U.S.P. reference oil 2, as measured ten times over a period of 9 months, ranged from 0.69 to 0.80, the mean being 0.73 with an average deviation of ±0.03, the instrument factor calculated therefrom being 2330.

Thus, the precision of the method when applied to oils, including changes in the oil on aging and differences introduced by the saponification and extraction processes, amounts to approximately ±4%. The working factor used in potency calculations was the mean value given rounded off to 2300. Both the *E* value and the factor above gave satisfactory checks with other laboratories running spectrophotometric assays on the same unsaponifiable fraction and whole oil preparations.

Light Filters and Effect of Filtered Radiation. In the selection of light filters to cut down the radiation of the full mercury vapor arc, two conditions should be satisfied: (1) The filter should cut out, as thoroughly as possible, the radiations in the range from 2000 to 3000 Å. (2) The remaining radiations from 3000 to 4000 Å. should be as intense as possible. It was felt that since almost all the extraneous absorption due to constituents of the fish oils other than vitamin A lies in the range from 2000 to 3000 Å., radiations of the mercury arc from 3500 Å. to longer wave lengths should have no appreciable effect on the solutions studied, and need not be considered. The two chief maxima of the oils lie generally at about 2300 and 2700 Å. These maxima completely overshadow the vitamin absorption, except in the case of concentrates of vitamin A, and therefore are the most probable sources of change in extraneous absorption when exposed to light radiations of the proper wave length. For the irradiation studies two filters were used—filter 1: red-purple Corex A, C. G. No. 986; filter 2: C. G. No. 986 plus phthalate filter. The use of potassium acid phthalate solution as a filter for ultraviolet light was first suggested by Saunders (*16*). It is particularly applicable for this work since it cuts out completely all light radiations of wave lengths shorter than 3000 Å. The transmission curves of these two filters are shown in Figure 1. The transmission curves as shown do not give a true picture of the influence of each on the effective radiations of the mercury vapor arc. The effect of these curves on the absolute intensities of the ultraviolet spectrum of the low intensity quartz mercury arc, as given by McAlister (*11*), should be considered.





With the majority of the solutions considered throughout this work the effect of filter 1 was found to be sufficient to make insignificant those changes in extraneous absorption which occur during irradiation. With all solutions of muscle tissue and with a few low-potency preparations of liver tissue the use of filter 2 was required to obtain anything like a specific effect for vitamin A. (Filter 2 might well be used for all samples regardless of potency.) In Figure 2 are given the absorption curves for muscle preparations employing modified photometry, using filter 1 in one case and filter 2 in the other. Figure 3 shows the effects of the two filters on the rate at which the vitamin is destroyed in a preparation of muscle tissue.

From Figure 2 it will be seen that, in spite of the very low potency of this sample (less than 3 I.U. per gram), and the presence of large amounts of other absorbing constituents, the use of filter 2 produced a curve very much more similar to that of pure vitamin A than the corresponding curve obtained with filter 1. The destruction curve in Figure 3 using filter 2 shows a clean-cut decrease in absorption at 3280 Å. reaching a steady minimum value. This closely resembles the destruction curves found for other tissues, oils, and vitamin A itself. With filter 1, on the other hand, the destruction curve shows no tendency to level out as it does with filter 2.

Table I. E Values and Factors for U.S.P. Oil 2

(Determined by direct and irradiation techniques)

Sample	$E^{1\%}_{1\text{ cm.}}$ Direct	Irradiation	Factor Direct	Irradiation
1	0.78	0.70	2180	2430
2	0.72	0.63	2360	2700
3	0.80	0.67	2120	2540
4	0.78	0.72	2180	2360
5	0.73	0.63	2330	2700
Mean	0.76	0.67	2240	2540
Av. deviation	±0.03	±0.03	(2200)	(2500)
% av. deviation	±3.9	±4.5		

Decomposition on Irradiation. The questions which first arose in the use of destructive irradiation were those which Demarest (*6*) expressed in his conditions 1 and 3—i.e., does the irradiation destroy vitamin A leaving no absorbing end products, and how long should the irradiation be continued to ensure quantitative destruction? The work of Neal *et al.* (*14*) indicates that the disappearance of absorption at 3280 Å. is accompanied by a quantitative loss of biological activity; thus the disappearance of the absorption at 3280 Å. may be interpreted as indicating the destruction of the vitamin A molecule by irradiation. The practice in this investigation was to determine for each new sample which differed in nature or potency from the last considered, the time necessary to attain 100% decomposition—i.e., the irradiation time required to give an E value which was unchanged on further irradiation. This irradiation time was then used on assaying the remaining samples of the particular tissue or oil. For the great majority of samples the irradiation was carried out for 30 minutes, this time being used for any material which indicated complete destruction in 30 minutes or less.

In Figure 4 are given a few decomposition curves characteristic of all those obtained. A study of these curves, keeping in mind the large range of potency of the materials represented, indicates satisfaction of the two conditions stated above. The fact that the residual absorption found in samples of low potency is not due to an end product of the vitamin A decomposition, but rather to the end absorption of a constituent of the oil or tissue unaffected by the irradiation, is shown by the liver curves, which go to zero absorption even in the case of liver of lowest potency. Final proof of this fact lies with the curve of crystalline vitamin itself.

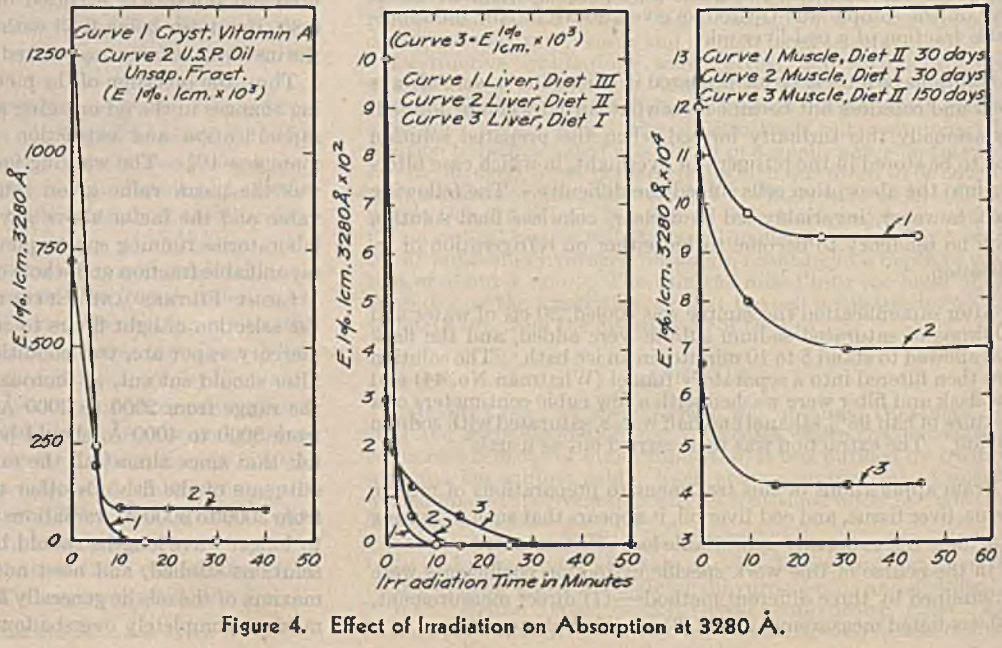


Figure 4. Effect of Irradiation on Absorption at 3280 Å.

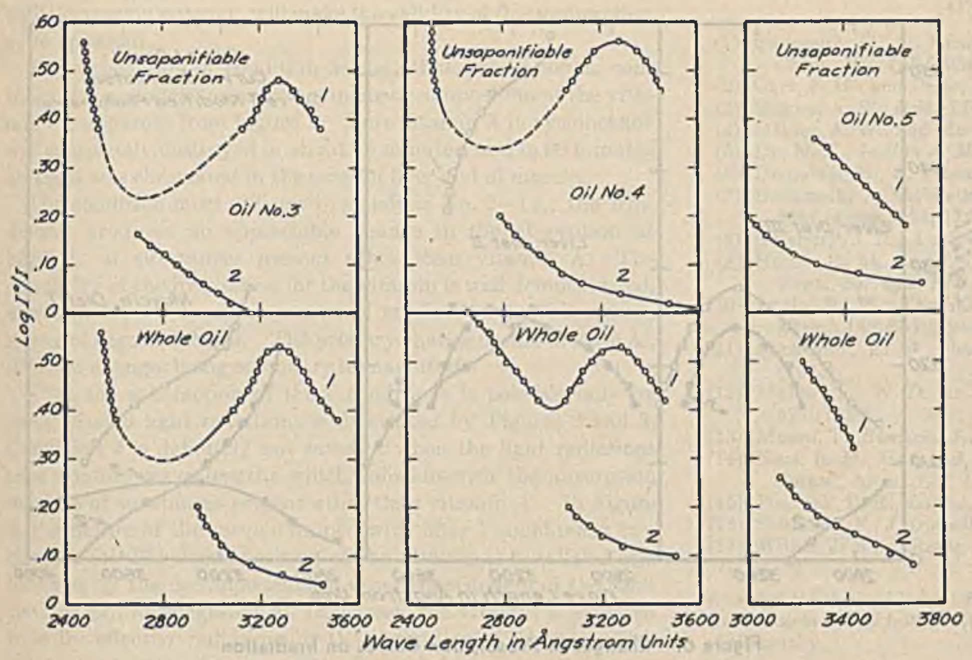


Figure 5. Absorption Curves

1. Direct 2. Irradiated

Irradiation of Fish Liver Oils and Concentrates. In the course of this study it was noticed that the destructive irradiation of preparations of U.S.P. oil 2 never caused the E value to decrease to a value of zero. In substantiation of this, a group of U.S.P. oil preparations were measured by both the direct and irradiation methods (Table I).

The results show a distinct difference between the values of $E^{1\%}_{1\,\mathrm{cm.}}$ and $E^{1\%}_{1\,\mathrm{cm.\ irrad.}}$ which is greater than the average deviation. In view of the results of the preceding section, the determination of the instrument factor by means of $E^{1\%}_{1\,\mathrm{cm.}}$ would result in a value from 8 to 12% too low and would thus introduce an error of the same magnitude into all calculations of vitamin A potency, using the factor thus obtained. In all calculations of biological potency from E values in this work, the "modified" factor of 2500 was used in place of the "direct" factor of 2300. The value of 2500 for the instrument conversion factor compares very favorably with the results obtained earlier with U.S.P. oil 1. These average values were $E^{1\%}_{1\,\mathrm{cm.}} = 1.21$, giving a factor of 2480 (2500).

In an attempt to clarify this situation, a series of determinations was made on six oils ranging in potency from 50 to 260,000 I.U. per gram, using both the direct and irradiation methods. These results are presented in Table II, and show clearly the differences in the applicability of the two methods. In so far as the relative potencies of the oils allow, the results also indicate approximate limits of potency, below which the methods are in error due to extraneous absorption. As was found in Table I, the unsaponifiable preparation of U.S.P. oil 2 does fall below the lower limit of potency of the direct method. Further proof of this is easily seen from the absorption curves of 3 of these oils, before and after irradiation, as plotted in Figure 5. The gradually increasing extraneous absorption of the oil itself with decreasing potency has become so great in the case of oil 4 that it can no longer be neglected, even in the unsaponifiable fraction. The destructive irradiation technique, on the other hand, can be employed with oils of potencies as low as this, even on the whole oil itself, and when saponification is carried out, can be applied to oil samples at least as low as 240 I.U. per gram.

Change in Absorption Curves Produced by Irradiation. The last condition, which must be satisfied in order to make the destructive irradiation technique valid as a measure of vitamin A, is that stated as condition 2 by Demarest (*6*)—i.e., in the course of the irradiation, substances present other than vitamin A undergo no appreciable change in their absorption at 3280 Å. That this condition is satisfied in the case of concentrates was shown by Demarest and is supported by similar work undertaken in the course of this investigation. The change in absorption curves of low-potency cod liver oils during irradiation was also found to satisfy this condition, with the use of filter 1. In Figure 6 are given a few absorption curves for liver and muscle samples, showing the changes on irradiation and also the curves obtained by modified photometry with other samples of the same tissue. Similar curves obtained for oil samples are not given, since the validity of the above assumption in the case of these low-potency tissues is more open to question than in the case of oil preparations with potencies 300 to 1500 times as great. The potencies of the tissues in these three cases were 221, 13, and 1 I.U. per gram respectively.

In the case of Figure 6 (left) the shape of the absorption curve is very similar to that of vitamin A and falls completely to zero on irradiation. The curve obtained by modified photometry is also similar in characteristics and indicates that irradiation causes a maximum change in absorption at 3280 Å., changes at all other wave lengths being secondary. The curve obtained by calculating $E^{1\%}_{1\,\mathrm{cm.\ irrad.}}$ for curves 1 and 2 resembles 3 very closely. It seems highly probable that, in this case, changes in the absorption at 3280 Å. of constituents other than vitamin A are negligible. The potency of the liver represented by Figure 6 (center) is a great deal lower than that just considered, and the absorption of vitamin A becomes merely an inflection point on the primary curve of the tissue oil. The change of absorption is still a maximum at 3280 Å., however, as shown best by curve 3, and condition 2 is fairly well satisfied in this case also. The extraneous absorption in the case of muscle tissue is very great and the absorption of vitamin A is almost completely masked. Curve 3

Table II. Direct and Irradiated Measurements of Vitamin A Potency of Concentrates, Fish Liver Oils, and Oil Dilutions

Oil No.	Whole Oil: Known Potency	Whole Oil: Potency direct	Whole Oil: Potency irradiated	Whole Oil: Difference, direct and irradiated	Unsaponifiable Fraction: Potency direct	Unsaponifiable Fraction: Potency irradiated	Unsaponifiable Fraction: Difference, direct and irradiated	Difference, Whole Oil and Unsaponifiable Irradiated
	I.U. per gram			%	*I.U. per gram*[a]		%	%
1	260,000	237,000	237,000	0	225,000	225,000	0	6
2	60,000	72,500	72,500	0	60,000	60,000	0	21
3	2,400	2,750	2,400	14	2,500	2,500	0	4
4[b]	1,700	2,020	1,700	19	1,875	1,670	12	2
5[c]	240	450	275	64	325	240	35	14
6[d]	46	250	87	187	140	70	100	38

[a] I.U. per gram of original oil.
[b] U.S.P. oil 2.
[c] Oil 3 diluted 1–10 by weight with corn oil.
[d] Oil 3 diluted 1–50 by weight with corn oil.

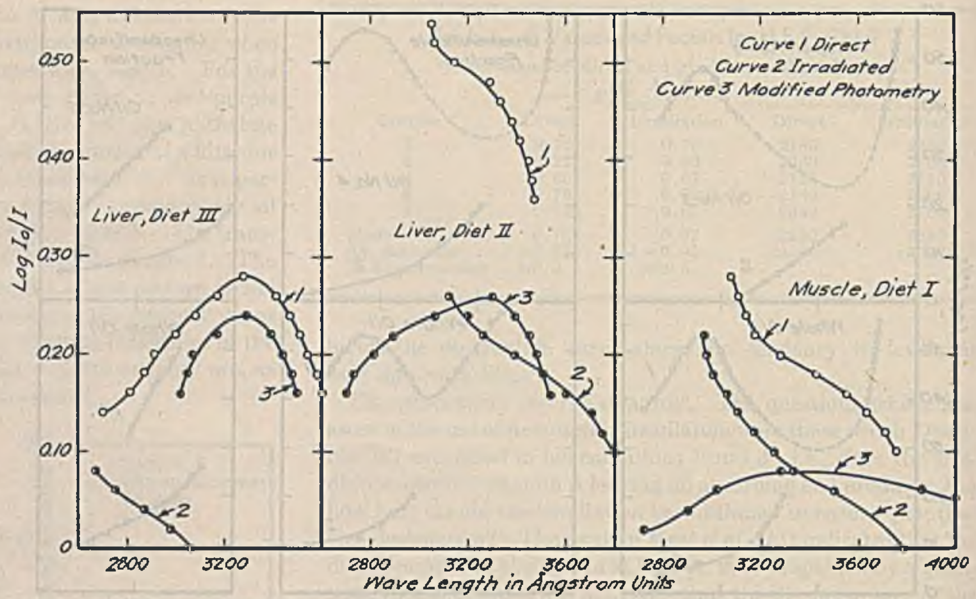


Figure 6. Changes in Absorption Curves on Irradiation

still has its maximum at 3280 A., however, and condition 2 is again satisfied as well as might be expected for a material of such low potency. The extraneous absorption in the case of muscle preparations bears about the same relation to the vitamin absorption as it did for the low-potency oil shown in Figure 5 (right) although the potency of the oil was about 250 times that of the muscle.

Carotenoid Interference. In determining vitamin A by a spectrophotometric measurement, the question arises as to how much of the absorption at 3280 Å. may be due to the carotenoids. In the case of butterfat the absorption at 3280 Å., which may be due to an end absorption of the carotene maxima at 4500 Å. and 4800 Å., becomes large enough to require consideration. However, in comparing the transmission curves of several prepared solutions of animal tissues with that of pure β-carotene, it was shown that the greatest interference by carotene at 3280 Å. amounted to less than 0.01 unit on the log I_0/I scale.

Recovery Experiments. In a procedure, such as is used in the preparation of the solutions of animal tissues, involving saponification, extraction, washing, and a change of solvents, two conditions must be satisfied—(1) the process must be specific in separating the constituent desired from the materials which would interfere in the quantitative measurement of that constituent, and (2) the recovery in the final solution of the substance to be determined must be as quantitative as possible.

In the case of a material like an animal tissue, condition 1 could not be completely satisfied, but, as the results show, the separation is sufficient to allow measurements to be made within a certain limit of error.

In order to test the extent to which condition 2 is satisfied, recovery experiments were carried out using supplemented and unsupplemented samples of liver and muscle tissue. The recovery in the final solutions, of the supplements added to the tissues, ranged, for the most part, from 88 to 99%. In the cases of the extremely low-potency muscle tissues, the effect of the supplement is so much closer to the precision of the measurements that calculations in terms of per cent recovery have a limited meaning. The results obtained indicated clearly, however, that the vitamin A of the sample is recovered efficiently in the final solution.

Precision of Measurements on Animal Tissues. The precision of measurement, in the case of a cod liver oil, was approximately ±4%. In another part of this work (*10*), it was found that the values obtained, with the same tissue from different but comparable test animals, varied from each other by as much as ±40%. It was felt that the precision of any one measurement was much better than these results indicated, the much larger variations found being due to differences in the rates of growth and storage of the experimental animals.

In Table III are shown the results obtained when several samples of one large portion of a tissue were run on consecutive days.

It is evident that the precision of the measurements on a homogeneous sample of liver tissue is as good as that found for cod liver oils. With the muscle samples, the precision shown is also of the same order and the probable error might be expected to lie between the value given above and that caused by ±0.02 precision in the spectrographic measurement in terms of log I_0/I—i e., in this case between ±5 and ±16%.

Table III. Precision of Measurement with Animal Tissues

Sample No.		Liver Potency *I.U./g.*	Muscle Potency *I.U./g.*
1		217	0.95
2		217	0.95
3		220	0.95
4		225	1.10
5		227	0.95
6		219	...
	Mean	221	0.98
	Av. deviation	±3.5	±0.05
	% av. deviation	±2	±5

DISCUSSION

In order to adopt the destructive irradiation technique as a method for the quantitative estimation of vitamin A, the validity of the three assumptions previously stated must be demonstrated. On the basis of the work just described, it is considered that these three conditions have been shown to be satisfied, under the conditions used, for fish liver oils and preparations of animal tissues over a very wide range of potency.

The bioassay results of Neal *et al.* (*14*), on unsaponifiable preparations before and after irradiation, demonstrate the complete loss of biological potency, which parallels a total loss of absorption at 3280 Å. The curves of Figure 4 show that the irradiations carried out, using the filters indicated, cause very similar decomposition curves for all types of materials studied. In the case of the liver samples the absorption at 3280 Å. is completely removed, indicating 100% decomposition of vitamin A. This is strongly supported by the destruction shown in the case of the crystalline vitamin A alcohol. On the basis of these destruction curves it may be said that condition 1 is satisfied—i.e., irradiation causes the destruction of vitamin A and the end products of the destruction have no absorption at 3280 Å. The similarity of the destruction curves and the consistent leveling out of these curves in from 10 to 30 minutes, with no additional change on continued irradiation, make credible the assumption that this same quantitative destruction occurs when residual absorption is present, provided irradiation is continued until the level portion of the curve is reached. A study of the absorption curves of Figures 5 and 6, observing the steady increase in extraneous absorption with decreasing potency, will make the validity of this assumption more apparent.

The satisfaction of condition 3—i.e., that irradiation is continued long enough to ensure complete decomposition of the vitamin—is apparent from Figure 4. Pure vitamin A in cyclohexane was completely destroyed in about 15 minutes, and in 30 minutes or less it was eliminated in the cases of liver and of muscle.

The condition most difficult to satisfy is No. 2—i.e., the irradiation produces no appreciable change in the absorption at 3280 Å. of substances present other than vitamin A. The specificity of the irradiation for the vitamin is well demonstrated, however, for all types of materials studied, in the absorption curves of Figures 5 and 6. The primary change occurs at 3280 Å., all other changes being secondary in magnitude.

That the satisfaction of these conditions is possible only by using filtered light radiations is illustrated by Figures 2 and 3. Condition 2 is definitely not satisfied when the light radiations used contain wave lengths which coincide with the absorption maxima of substances present other than vitamin A. In Figure 3, the nature of the curve obtained with filter 1 could mean two things: (1) The decomposition of the vitamin is paralleled and followed by the decomposition of other constituents of the solution, or (2), as suggested by Demarest, the vitamin is screened from the effective radiations by the absorption of other constituents. The result of this second effect would be a much greater irradiation time required to obtain complete destruction of the vitamin.

The value of a method of vitamin A assay employing destructive irradiation is apparent in the application of the method to oils of a wide range of potency, as shown in Table II. Direct measurement of the whole oil dilution has often been employed in the case of high-potency oils, common practice having been to dispense with saponification for oils with a potency of 10,000 I.U. per gram or more. Direct measurement of unsaponifiable preparations is applicable to potencies of approximately 2500 I.U. per gram or more. The applicability of the irradiation technique used on whole oil preparations is even lower than this, and would probably go to values of 1000 I.U. per gram or less. Employing both saponification and irradiation, the assaying of oils as low as 200 I.U. per gram or lower is possible. These limits will, of course, vary with the nature of the material assayed, and with the saponification and extraction technique used.

In the light of what has been said thus far, it would seem that $E^{1\%}_{1\,\text{cm. mod.}}$ or $E^{1\%}_{1\,\text{cm. irrad.}}$ might be more dependable measures of vitamin A potency than $E^{1\%}_{1\,\text{cm.}}$. The results obtained with the second U.S.P. oil (Table I) indicate the introduction of an error of 8 to 12% by the assumption that $E^{1\%}_{1\,\text{cm.}}$ is a measure of vitamin A only. This error would carry over into calculated instrument factors and any spectrophotometric assays made on other preparations, using this factor. The similarity of the factors calculated from $E^{1\%}_{1\,\text{cm. irrad.}}$ for U.S.P. oil 2 and $E^{1\%}_{1\,\text{cm.}}$ for U.S.P. oil 1 (2500 in each case) suggests that the extraneous absorption in the case of the latter was small enough at 3280 Å. to give rise to no significant error in direct measurement. This is indicated, but not proved, by the results obtained with oil 3 in Table II.

It would seem possible, on the basis of the work presented, that the destructive irradiation technique may be the means of increasing the scope of the determination of vitamin A by in vitro methods. Certainly the value of $E^{1\%}_{1\,\text{cm.}}$ for preparations of materials containing vitamin A should be interpreted carefully, unless considerable research has been done on substances of comparable chemical nature, with respect to the nature of the absorption curve and the effects of irradiation.

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The author wishes to take this opportunity to express his sincere gratitude to Arthur W. Thomas for his interest and helpful criticisms throughout this investigation.

LITERATURE CITED

(1) Baumann, C. A., Riising, B. M., and Steenbock, H., *J. Biol. Chem.*, 107, 705 (1934).
(2) Carr, F. H., and Price, E. A., *Biochem. J.*, 20, 497 (1926).
(3) Davies, A. W., *Ibid.*, 27, 1770 (1933).
(4) Davies, A. W., and Moore, T., *Ibid.*, 28, 288 (1934).
(5) De, N. K., *Indian J. Med. Research*, 24, 737 (1937).
(6) Demarest, B., *Z. Vitaminforsch.*, 9, 20 (1939).
(7) Dornbush, A. C., Peterson, W. H., and Olson, F. R., *J. Am. Med. Assoc.*, 114, 1748 (1940).
(8) Edisbury, J. R., *Analyst*, 65, 484 (1940).
(9) Hume, R. M., and Chick, H., Med. Research Council, Special Rept., *Ser.* 202, IV (1935).
(10) Little, R. W., Thomas, A. W., and Sherman, H. C., *J. Biol. Chem.*, 148, 441 (1943).
(11) McAlister, E. D., *Smithsonian Misc. Collections*, 87, No. 17 (1933).
(12) McFarlane, W. D., and Sutherland, A. J., *Can. J. Research*, 16, 421 (1938).
(13) Moore, T., *Biochem. J.*, 24, 692 (1930).
(14) Neal, R. H., Haurand, C. H., and Luckmann, A. H., IND. ENG. CHEM., ANAL. ED., 13, 150 (1941).
(15) Peacock, P. R., *Lancet*, 11, 328 (1926).
(16) Saunders, F., *J. Optical Soc. Am.*, 16, (1928).
(17) Wilkie, J. B., *J. Assoc. Official Agr. Chem.*, 23, 336 (1940).

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A Funnel for Use with Standard Taper Flasks

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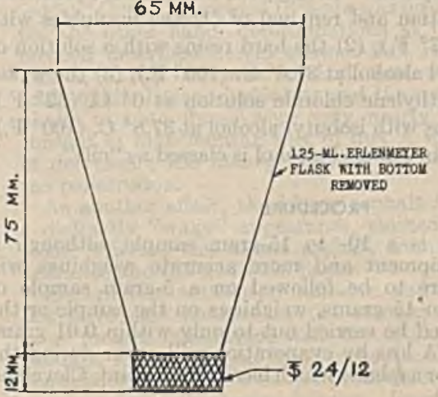
A TIME-HONORED method of adding solids to narrow-mouthed containers involves the use of a sheet of paper rolled into a funnel. Every chemist is familiar with the drawbacks of this device, and most of them have managed to spill an embarrassing amount of material in its use.

An important routine analysis in this laboratory requires the quantitative transfer of a fairly large amount of solid to a small weighing bottle having a standard taper stopper. The awkwardness of balancing a paper funnel in this operation, and the danger of loss of material in the fold of the paper, definitely suggested an improvement in this line.

The funnel shown in the illustration was accordingly constructed, and has been found highly satisfactory in practice. Because it fits firmly into the neck of the flask, the question of balancing is obviated. Since it is made of glass, the danger of particles sticking or getting lost in cracks is greatly reduced. The slope of the walls being fairly steep, solids do not tend to pile up in the funnel.

The funnel has also been found useful in pouring large amounts of liquids and solids into other flasks, with and without ground joints, as the pouring is speeded by the steep walls and wide stem opening.



Analytical Fractionation of Asphalts

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A procedure is described for the solvent separation of asphalts into five fractions: hexane-insolubles, hard resins, soft resins, oils, and waxes. Since all solvents employed boil above room temperatures, the method requires only ordinary laboratory glassware. All fractions are recoverable, an advantage in that they may be studied to characterize the asphalt further. The accuracy and precision of the method are discussed. Data are given to show the averages and ranges of fractions and the properties of fractions recovered from 37 oxidized and 7 straight-run asphalts, and to illustrate some applications of the method in study of asphalts.

INSIGHT into behaviors of asphalts is usually best obtainable from knowledge of the component fractions. Separation into fractions serves to characterize the asphalt. Recombinations of the fractions may be made to determine the effects of their proportions on the properties of the resulting blends. Such studies are both fundamental and practical, for they describe basic means of adjusting the fractional composition of asphalts to obtain desired action in service.

Although division into fractions with highly distinctive properties may readily be accomplished through selective solvents or adsorbents, all the laboratory methods which have been described have shown serious disadvantages.

Marcusson (*14*, cf. *2*) in 1916 described a technique whereby the insolubles are precipitated with naphtha, and the resins adsorbed by fuller's earth. The oils are extracted from the fuller's earth with naphtha, and the resins thereafter removed by washing the earth with carbon disulfide. Various modifications of this method have been described, in all of which the resins are removed by adsorption. Important as these procedures are, it remains questionable if the resin fraction can be recovered from the clay in an unchanged condition. Uniformity of results between laboratories is difficult to achieve, even though adsorbents prepared by standard procedures are used. More recent possible methods depend upon propane as the precipitant (*8, 10, 13*). The primary objection to the usage of propane or of hydrocarbon gases in laboratory procedures is the notable difficulties of handling.

A method, utilizing only solvents boiling above atmospheric temperatures, which permits direct recovery and weighing of all fractions and can be practiced in ordinary laboratory equipment, was proposed by Grant and Hoiberg (*6*) in 1940. That procedure, while successful with asphaltic crudes of relatively low wax content, did not completely separate waxes from the resin fractions of paraffinic-base asphalts.

A revision is described here whereby this difficulty is in large part overcome. Further refinement is introduced by separating resins into two fractions, "hard resins" and "soft resins", separate knowledge of which possesses essential value in interpretation of the behavior of asphalts. Briefly, the method here presented consists in precipitation and removal of (1) the insolubles with hexane at 25° C. (77° F.), (2) the hard resins with a solution of cyclohexane–isobutyl alcohol at 37.8° C. (100° F.), (3) the waxes with an acetone–methylene chloride solution at 0° C. (32° F.), and (4) the soft resins with isobutyl alcohol at 37.8° C. (100° F.). The portion soluble in isobutyl alcohol is classed as "oils".

PROCEDURE

Basis of analysis is a 10- to 15-gram sample, although if desired smaller equipment and more accurate weighings will permit the procedure to be followed on a 5-gram sample of asphalt. With 10 to 15 grams, weighings on the sample or the fractions derived need be carried out to only within 0.01 gram.

VOLATILE OILS. A loss by evaporation will occur during the analysis of road oils or asphalts which have a flash point, Cleveland open cup, below about 232° C. (450° F.). This loss can be reported as such or the volatile oils may be removed prior to the analysis by a vacuum and/or a steam distillation.

HEXANE-INSOLUBLES. The sample of asphalt, flux, or oil is weighed into a 3-liter flask, and 50 ml. of commercial mixed hexanes are added per gram of sample. With high-melting asphalts, and in the absence of efficient mechanical agitation, heating and refluxing of the solution or addition of the asphalt as a powder is necessary to disperse the material in a reasonable time. (The agitation provided by a Ro-Tap sieve shaker has been found to disperse the asphalts rapidly.)

The solution is cooled in a water bath for 1 hour at 25° ± 1° C. (77° ± 2° F.) and filtered twice, with suction. The first filtration, which removes the bulk of the insolubles, is through two sheets of filter paper, such as a Whatman No. 50 on top of a Sargent No. 500, in a Büchner funnel. The second filtration is through a No. F sintered-glass Büchner funnel. After each filtration, the insolubles are washed with the minimum quantity of hexane which will produce clear washings. The washings are added to the filtrate.

The final filtrate is distilled over a water bath until about 150 ml. of solution remain. This is transferred to a centrifuge bottle (a 250-ml. Pyrex sterilizer bottle is suggested) which has been previously weighed to the nearest 0.01 gram. The remaining hexane is evaporated, with removal of the last traces accomplished under reduced pressure. The residue is weighed and the insoluble content calculated.

HARD RESINS. To the residue in the centrifuge bottle is weighed a solution of 80% isobutyl alcohol–20% cyclohexane (by volume) equal to eight times the weight of hexane-solubles. The mixture is refluxed for 15 minutes with occasional shaking to hasten solution. Periodic agitation during this time has been found necessary to obtain reliable results on resin content, especially in the analysis of asphalts of high resin content. After cooling to 65.6° ± 3° C. (150° ± 5° F.), 1.80 ml. of an isobutyl alcohol solution containing 2.0% by weight of sodium hydroxide are measured from a buret into the centrifuge bottle for each 100 grams of 80% isobutyl alcohol–20% cyclohexane solution used in dissolving the petrolenes. The mixture is thoroughly agitated, cooled in a water bath held at 37.8° ± 0.5° C. (100° ± 1° F.), and maintained at this temperature for at least 5 minutes. The mixture is then centrifuged for 5 minutes at 37.8° ± 1.5° C. (100° ± 3° F.).

The solution of oil, wax, and soft resins is quickly decanted from the centrifuge bottle through a Gooch crucible containing an asbestos mat into a tared 250-ml. Soxhlet extraction flask. The bottle and filter are rinsed with 21 ml. of a solution of 80% isobutyl alcohol and 20% cyclohexane by volume which has been heated to 37.8° C. (100° F.). The solvent is used in three 7-ml. portions. Since the purpose is to rinse the surfaces free of solution containing oil, wax, and soft resins, and not further to extract the hard resins, this operation should also be carried out quickly. The last portion of the wash solution which cannot be decanted is pipetted from the centrifuge bottle.

The resinous material collected in the Gooch crucible is washed into the centrifuge bottle with hexane or light solvent naphtha. The solvents are distilled from the bottle, with the last traces removed under reduced pressure. The residue is reported as hard resins.

The oils, waxes, and soft resins are recovered under reduced pressure and weighed before continuing the extraction.

WAXES. To the oil, wax, and soft resin residue are added 10 parts by weight of a solvent containing 1 volume of acetone to 2 volumes of methylene chloride. After as complete solution as is possible of the residue, the mixture is cooled to 0° ± 0.3° C. (32° ± 0.5° F.). The precipitated wax is removed by filtering under slightly reduced pressure through a Whatman No. 42 or other hard-surfaced filter paper held in a cold funnel maintained at 0° ± 0.3° C. (32° ± 0.5° F.). The addition of dry ice to hexane or other light solvent provides a convenient method of maintaining the desired temperature in the cold funnel. Three 7-ml. portions of the dewaxing solvent at 0° C. (32° F.) are used to wash the wax.

The wax is dissolved from the filter paper with hexane into the flask in which the precipitation was made and the solvent distilled over a lamp bank. Final trace of the solvent is removed under reduced pressure. The weighed residue is reported as wax.

The remainder of oil and soft resin solution is transferred to a

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tared centrifuge bottle, recovered under reduced pressure, and weighed before continuing the extraction.

Oils and Soft Resins. To the residue in the centrifuge bottle is added isobutyl alcohol equal to six times the weight of the oils and soft resins. The mixture is refluxed for 15 minutes. After cooling to 65.6° ± 3° C. (150° ± 5° F.), 0.50 ml. of an isobutyl alcohol solution containing 2.0% by weight sodium hydroxide is measured from a buret into the centrifuge bottle for each 100 grams of isobutyl alcohol used. The cooling and centrifuging procedure at 37.8° C. (100° F.) is then followed as for the separation of the hard resins.

The oil solution is decanted from the centrifuge bottle through an asbestos mat held in a Gooch crucible into a weighed extraction flask. The centrifuge bottle and filter are washed with three 7-ml. portions of isobutyl alcohol heated to 37.8° C. (100° F.).

The residue is washed from the crucible with hexane into the centrifuge bottle. The solvent is distilled from the centrifuge bottle under reduced pressure and the residue reported as the percentage of soft resins.

The oils are separated from the solvent under reduced pressure and weighed, or if their recovery is not desired they may be reported by difference.

Solvents. Mixed hexanes (from Phillips Petroleum Company, Special Products Division, Bartlesville, Okla.), of nil unsaturate content, and with an initial boiling point of not less than 54° C. (130° F.) and a dry point not greater than 71° C. (160° F.) were employed to precipitate the insolubles.

The isobutyl alcohol (from Eastman Kodak Company, Chemical Sales Division, Rochester, N. Y.), Eastman grade, boiled in the range of 105–108° C. (221–226° F.).

The cyclohexane (Eastman), with a density at 25° (77° F.) of 0.77 ± 0 .01 gram per ml., boiled in the range of 78–81° C. (172–176° F.). While the Eastman grade was preferred, selected batches of the practical grade were found to give essentially the same yields of hard resins. Use of other batches of the practical grade of higher density lowered the yield of resins.

The methylene chloride (Eastman), practical grade, boiled in the range of 39–43° C. (102–109° F.).

The acetone (Eastman), practical grade, boiled in the range of 55–57° C. (131–135° F.).

Characterization of Recovered Fractions. Knowledge of the character of the precipitated fractions is of importance in relating the composition to properties and behavior of asphalts. Methods which may be followed to determine the refractive index and specific gravity, and to calculate the specific dispersion and refractive intercept have been described (*6*, *7*).

With the high-melting hard resin fraction difficulty was had in reading an Abbe refractometer. An approximate procedure followed was to estimate the refractive index and drum reading for blends of low-viscosity lubricating oils and the resins, and then to extrapolate the data to zero oil content.

The melting point of the wax fractions was determined by the procedure recorded by Knowles and Levin (*13*).

The viscosity of the oil fractions was determined with microviscometers of the type described by Cannon and Fenske (*5*).

Pour points of the oils were determined in an 8 × 50 mm. test tube one-third full of the oil fraction, since an insufficient amount of this fraction was available for filling the standard A.S.T.M. tube. The test tube was closed by a cork carrying an A.S.T.M. cloud and pour test thermometer. The test tube was fitted through a stopper into a standard cloud and pour point test jar and the annular space filled with a light lubricating oil. The assembly was heated in a water bath to about 49° C. (120° F.), removed to a standard cooling bath, and observation made as required by the procedure described under A.S.T.M. Designation D97-39.

Equipment. The arrangements used in the centrifuging and filtering of wax, and in the evaporation of small volumes of solvents, are discussed only for the sake of illustration. Many modifications are possible.

A G.E. centrifuge, Size 1, Type C, was heated by blowing air through an opening in the cover. The air was heated by passage over a 500-watt electric element held in an insulated brass cylinder 9 cm. in inside diameter × 38 cm. Cold air was by-passed into the heated stream to maintain the temperature of the air leaving the centrifuge through the bottom drain opening at 38.3° C. (101° F.), at which temperature the whirling bottles were found to remain at 37.8° ± 0.5° C. (100° ± 0.5° F.). When temperature of the outlet air rose above 38.3° C. (101° F.), slight lifting of the cover of the centrifuge was found to admit sufficient air to reduce the temperature the desired extent. The centrifuge was operated at about 1800 r.p.m.

The cold funnel was constructed from the upper half of a carbon disulfide can, 12 cm. in inside diameter × 8.5 cm. A lip was soldered on to reduce the opening of the can to a diameter of 8 cm., leaving, however, a notched-out portion for the introduction of dry ice and a thermometer. A 9-cm. outside diameter glass funnel, held in place by a rubber stopper set in the outlet for the can, could then fit tightly to the lip to prevent the cooling liquid from splashing into the funnel. The outside of the can was insulated.

A lamp bank was constructed as a convenience in evaporating small amounts of light solvents, as hexane and the wax precipitating solvents. Seventy-five-watt light bulbs were enclosed in a 9.5-cm. diameter × 21-cm. metal cylinder, provided with a screened top and arranged in banks of 4.

DEVELOPMENT OF REVISED PROCEDURE

The original procedure (*6*) was based on the removal of the insolubles with pentane, precipitation of the total resin fraction at 54.4° C. (130° F.) with isobutyl alcohol, and separation of the waxes from the oils at 0° C. (32° F.) with a solvent consisting of 60% acetone and 40% methylene chloride by volume. These conditions were suitable in selectively precipitating fractions from naphthenic-base asphalts. Trials with paraffin-base asphalts of high wax content showed, however, that an appreciable portion of the wax was precipitated along with the resin fraction. Two obvious changes were possible to improve the separation of the resin and wax fractions. Actually, a combination of these modifications was devised.

The solvent used to precipitate the resin fraction could be modified to become a better solvent for wax, providing that the resin fraction would still be precipitated. As a less practical equivalent, the temperature at which the resins were precipitated 54.4° C. (130° F.) could be raised.

The wax could be precipitated from the resin-wax-oil mixture if a dewaxing solvent with a high solubility for resins could be found.

Revision of Dewaxing Procedure. Many of the unsettled discussions of the influence of wax on service behavior of asphalts are the result of the wide range of properties exhibited by hydrocarbons which can properly be included under the descriptive term "wax". The determined wax content of a given asphalt can vary greatly, dependent on the method employed in the determination. Both types of paraffins, those which are solid or liquid at ordinary temperatures, or only the higher melting compounds may be recovered. A selection of conditions which will precipitate the fraction most informative of the composition and behavior of asphalts is desirable. Some of the phenomena are listed below which led to the belief that knowledge of only the higher melting waxes would usually be of greater importance.

Blown asphalts from a light Arkansas asphalt, flux A, were about 30 points higher in penetration at 25° C. (77° F.) than an asphalt of the same melting point blown from another light Arkansas asphalt, flux B. Determinations on both fluxes at −17.8° C. (0° F.) yielded 16% of a wax liquid at room temperature. On the other hand, determinations at 0° C. (32° F.) by the method described herein showed flux B to contain 3.0% and flux A, 10.5% of a wax solid at room temperature. The contents of the hexane-insolubles and the resins from the blown asphalts of both fluxes were very nearly identical. The higher content of high melting wax of flux A was apparently effective in decreasing the homogeneity of the asphalt, thereby raising the penetration.

As another effect, the blown asphalt from flux A, which has a distinctly "waxy" appearance, stained paper to a dark olive color, whereas the blown asphalt from B was normal in appearance and did not stain paper.

Experiences with poor adhesion and the noncuring of road oils have also pointed to the content of high-melting waxes as of greater importance than the total paraffin content. It is thought that as the oil fraction becomes heavier during service the higher melting waxes are precipitated to form a nonhomogeneous and noncohesive binder. Road oils of this type that

Table I. Dewaxing Trials with Various Solvents

Dewaxing Solvent[b]	Blank on Cylinder Stock[a]				Determination on 40% Wax–60% Cylinder Stock Blends						
	Solvent ratio	Temp. of ppt.		Cylinder stock insoluble	Solvent ratio	Temp. of ppt.		Wax found	Wax found less blank	Error	Refractive index of wax, n_D^{50}
	G./g. cylinder stock	° C.	° F.	%	G./g. blend	° C.	° F.	%	%	%	
Methyl isobutyl ketone	22.8	−17.8	0	4.3	23.5	−17.8	0	39.1	34.8	5.2	1.481
Methyl isobutyl ketone	23.0	0.0	32	1.2	23.4	0.0	32	26.9	25.7	14.3	1.482
35% acetone, 65% benzene	10.1	0.0	32	2.5	10.0	0.0	32	25.9	23.4	27.0	1.490
60% acetone, 40% methylene chloride	9.9	0.0	32	64.5	10.0	10.0	50	76.0	..	..	1.488
50% acetone, 50% methylene chloride	9.9	0.0	32	47.5	9.6	10.0	50	68.2	..	..	1.487
33.3% acetone, 66.7% methylene chloride	10.0	0.0	32	1.0	10.0	0.0	32	39.1	38.1	1.9	1.477

[a] Refractive index at 50° C. (n_D^{50}) = 1.512. [b] Proportions given by volume.

fail to set often reduce by the A.S.T.M. method to a 100 penetration residue that is grainy, noncohesive, and waxy in appearance.

With these effects of waxes in mind it was decided to include with the oil fraction that portion of the paraffin fraction which is liquid at ordinary temperatures. The properties of this fraction would probably be sufficiently unique to be reported separately. However, this would introduce an additional complexity in the method which should not generally be necessary, since the average properties of the oils can be indicated by physical measurements, such as specific dispersion. However, if the composition is to be determined in connection with a study of the properties of the asphalt at low temperatures, it seems likely that more exact knowledge of the content of the lower melting paraffins would be important, since at low temperatures these would presumably also be solid in the asphalt. In such a case, separation could be accomplished by further dewaxing of the oils, or the wax could be precipitated by the procedure recommended herein but at a temperature lower than 0° C. (32° F.)

Selection of Dewaxing Solvent. Relatively few solvents have been discussed in the literature with regard to their selective solubility for highly resinous oils and for high-melting petrolatum waxes. Usually the solvents have been investigated and classified according to their solubility for a dewaxed refined oil and refined paraffin. An exception is the acetone–methylene chloride solutions used in separating waxes from petroleum and its lubricating fractions (*11*). Acetone-benzene solutions are also used commercially to dewax untreated lube oil stocks (*12*). Hexone (methyl isobutyl ketone) has been reported to be satisfactory for the quantitative dewaxing of propane-soluble heavy lube oils (*13*).

The results of dewaxing trials with these three solvents, all of which have properties suitable for laboratory dewaxing procedures, are shown in Table I. The heavy cylinder stock of 245 seconds Saybolt Universal viscosity at 98.9° C. (210° F.) used in the trials was obtained by propane-deasphaltizing an asphaltic flux. Wax was recovered from a portion of the stock by dewaxing at −17.8° C. (0° F.) with 4 volumes of a solvent containing 35% acetone and 65% benzene by volume. The recovered wax was reprecipitated at −17.8° C. (0° F.), using 10 volumes of solvent to 1 volume of wax, and then cleaned by mild acid and clay treatment. The final wax with a refractive index at 50° C. (122° F.) of 1.478 melted at 63.3° C. (146° F.).

Results indicate that of the three best solvents for the cylinder stocks, the 33.3% acetone–66.7% methylene chloride solution recovered the wax at 0° C. (32° F.) with the smallest error. The refractive index of the wax precipitated by this solvent was the same as that of the wax added to the cylinder stock, showing that no resinous material was precipitated from the heavy cylinder stock.

Content of High Melting Waxes in Petrolatum. Two petrolatums were dewaxed at 0° C. (32° F.) with various ratios of the 33.3/66.7% acetone–methylene chloride solvent. The properties of the petrolatums, the variation in wax content with solvent ratio, and the properties of the separated wax and oils are given in Table II. The results are believed to be indicative of the variation which would be expected in wax recovery from an asphalt with a change in solvent ratio. This is especially so since petrolatums I and II were derived from residual oils and, therefore, contained the high-melting waxes normally present in asphalts.

The variation in wax content with the solvent ratio, calculated from the weights of solvents used and wax found, is shown graphically by Figure 1. The content of wax precipitated at ratios above 80 decreases only slightly with increase in the ratio. Since in the usual asphalt analysis the ratio of the acetone–methylene chloride solvent to the determined wax content is near or above 100, the type and amount of wax recovered should be essentially independent of the exact ratio established by the procedure.

The oils recovered, which at the higher ratios represented a substantial portion of the petrolatum, were highly paraffinic, as shown by refractive indices. However, for reasons previously discussed, it is believed that these oils properly belong in the oil fraction because of their liquid character at ordinary temperatures. Dewaxing at 0° C. (32° F.) with the acetone–methylene chloride solvent thus appeared to be satisfactory for the purpose in mind.

Modification of Solvent to Precipitate Resin Fraction. Since the results with the acetone–methylene chloride solvent (Table I) had indicated that the wax determination could be run on a highly resinous stock without coprecipitation of the resins, a solvent to increase the solubility of waxes could be added to the precipitant for resins. Two solvents, toluene and cyclohexane, which boil in the desired range and are fairly good solvents for wax, were blended with the isobutyl

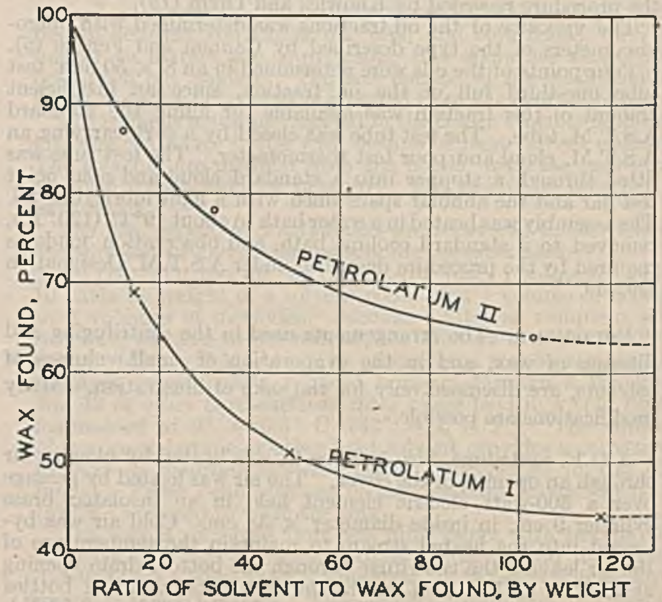

Figure 1. Dewaxing of Petrolatums at 0° C. (32° F.)

alcohol. Precipitations were completed with the alcohol solvents on asphalts from which the pentane-insolubles had previously been precipitated.

The contents of resins obtained are shown in Table III. Since the resin content determined according to the original procedure had been 51 and 78% on the blended asphalt and flux, respectively, the reduction in yield upon adding the toluene or the cyclohexane was very marked. Nevertheless, the wax precipitated at 0° C. (32° F.) with the acetone–methylene chloride dewaxing-solvent had a refractive index low enough to indicate but little resin contamination. The wax recovery was slightly higher from the soft resin-oil-wax mixtures soluble in the toluene–isobutyl alcohol solvents, but the wax was lower in melting point.

Table II. Wax Content of Petrolatum at 0° C. (32° F.)

(At various ratios of 33.3% acetone–66.7% methylene chloride solvent)

Properties of petrolatum	I			II		
Melting point, ° C.	62.0			72.5		
Melting point, ° F.	143.5			162.5		
Density at 65° C., g./ml.	0.842			0.834		
Refractive index at 65° C. (n_D^{65})	1.466			1.464		
Specific dispersion	99			99		
Refractive intercept	1.044			1.047		
Oil and wax content of petrolatum						
Ratio of solvent to petrolatum, by wt.	10	25	52	10	25	66
Ratio of solvent to wax found, by wt.	14.5	49	118	11.5	32	103
Wax found, %	69	51	44	87	78	64
Oil found, %	31	49	56	13	22	36
Total	100	100	100	100	100	100
Properties of wax						
Refractive index at 65° C. (n_D^{65})	1.470	1.462	1.461	1.468	1.464	1.462
Melting point, ° C.	...	67.2	68.9	...	75.0	75.0
Melting point, ° F.	...	153	156	...	167	167
Properties of oil						
Refractive index at 25° C. (n_D^{25})	1.487	1.485	1.483	1.494	1.491	1.486
Pour point, ° C.	...	12.8	15.7	...	21.1	26.7
Pour point, ° F.	...	55	60	...	70	80
Appearance of oil	...	Reddish brown	Reddish brown	...	Very dark brown	Very dark brown

Solubilities of Petrolatum. The solubilities of petrolatum in the cyclohexane– and toluene–isobutyl alcohol solvents and in pentane and hexane are shown by Table IV. The two petrolatums used in the trials were the same as previously described, and their properties are given in Table II. The ratios of solvents to waxes were selected to correspond to ratios which normally occur during separation of the fractions from asphalts according to the procedure developed herein. Column 5 lists calculated concentrations of wax in an asphalt which would correspond to these ratios. For the trials with the isobutyl alcohol solutions the calculations were based upon an asphalt containing 15% of insolubles and the use of 8 parts by weight of solvent per part of insoluble free asphalt.

The solubility of the petrolatums was found to be appreciably lower in pentane than in hexane. Consequently, hexane instead of pentane was adopted to determine the insoluble content.

The solubility of petrolatum I in the isobutyl alcohol solutions was high, above 98%. Petrolatum II, of higher melting point, was less soluble, with 92% dissolved at a solvent ratio equivalent to that in an asphalt containing 7.3% of wax. No appreciable increase in solubility of II was found upon increasing the cyclohexane content of the isobutyl alcohol from 20 to 22.5% or substituting 20% of toluene for the cyclohexane.

With 92% solution of petrolatum II the wax content found would be 6.4% instead of the correct value of 7.3%. The other portion, 0.9%, of wax would be partially precipitated by the hexane, the remainder with the hard resins. Since the solubility of wax would be increased during actual analyses by the presence of resins and oils in the solvent, it was decided that further studies could best be made on asphalts containing known contents of wax. Also, as described below, the use of an aqueous ammonia solution as a flocculent for the resins was discontinued with a probable increase in solubility for wax in the isobutyl alcohol solutions.

Precipitation of Resins. *Addition of Cyclohexane to Isobutyl Alcohol.* Cyclohexane was selected in preference to toluene for addition to the isobutyl alcohol. The addition of 20% by volume improved the solvency of the alcohol for wax to about the same extent as did toluene. A definite advantage was the precipitation of a larger fraction of resins by the cyclohexane solution, as shown by data of Table II. Unless the resin fraction represents about 10% or more of the asphalt, characterization tests are difficult and changes in the fraction which occur in service or processing cannot readily be followed. The lower boiling point of cyclohexane would also make easier the removal of the last traces of solvent.

Separation of Soft Resins. Since addition of cyclohexane to the isobutyl alcohol markedly increased the solvency of the alcohol for resins, the fraction of the asphalt remaining after dewaxing would be highly resinous. A further separation of resins from the oils was indicated. Preliminary trials showed that precipitation at 37.8° C. (100° F.) with isobutyl alcohol removed a large part of the remaining resin fractions. To distinguish between the two resin fractions, the precipitate formed with the 20% cyclohexane–80% isobutyl alcohol solution was designated as hard resins, and the precipitate with the isobutyl alcohol, soft resins.

Precipitating Agents for Resin Fractions. With the change from pentane to hexane to remove the insolubles, difficulty was found in precipitating the hard resins when ammonium hydroxide was used as the flocculent. Incomplete settling of the resins was obtained even after prolonged centrifuging. With the use of hexane a fraction was apparently shifted from the insolubles to the hard resins which was very difficult to flocculate. An increase in the concentration of ammonium hydroxide was not desirable, since additional water to lower the solubility of wax would then be present. Consequently, other agents were tried. A chemical used to break crude oil-water emulsions, Visco 242A, and a wetting agent, Aerosol OT 100%, were unsuccessful. Sodium hydroxide in a concentration of 0.03% by weight in the cyclohexane–isobutyl alcohol solution was found to settle the hard resin fraction rapidly. The addition of 0.01% of sodium hydroxide to the isobutyl alcohol solution was sufficient to flocculate the soft resin fraction. The added caustic is probably precipitated with the wax fraction and in the average analysis would increase the percentage of wax by about 0.2%.

ANALYSIS OF ASPHALTS

Asphalts of High Petrolatum Content. The recovery obtained of fractions from asphalts to which known amounts of high-melting petrolatum had been added is shown by Table V. The calculated compositions of the asphalts as given are based upon determined compositions of the asphalt blanks and of the oil and wax contents of the added petrolatum. The wax contents of the petrolatums were selected from the graph of Figure 1 at the actual dewaxing ratio employed in the analysis, rather than by assigning an average wax content to the petrolatum at an average solvent ratio. The difference between the calculated and experimental contents of wax in the asphalts then is a direct measure of the recovery of wax from the asphalt and does not include the effect of change in dewaxing solvent ratio. Actually, unless the wax content is high, above about 8%, the ratio is in the range wherein a change will have only a slight effect on wax recovery. Four asphalts listed in Table V, which contained

Table III. Resin Precipitating Trials with Various Solvents

Asphalt	Resin Precipitating[a] Solvent	Ratio of Solvent Added[b]	Temp. of Ppt.		Hard Resins Found	Wax Added Plus Blank	Wax Found	Melting Point		Refractive Index of Wax, n_D^{65}
			° C.	° F.	%	%	%	° C.	° F.	
Blended	15% toluene 85% isobutyl alcohol	8	37.8	100	12.1	7.8	7.6	54.4	130	1.482
Blended	20% toluene 80% isobutyl alcohol	8	37.8	100	6.0	7.8	8.4	55.0	131	1.482
Blended	20% cyclohexane 80% isobutyl alcohol	8	37.8	100	15.8	7.8	7.4	62.2	144	1.489
Flux	20% cyclohexane 80% isobutyl alcohol	6.8	37.8	100	11.4	...	8.0	65.6	150	1.487
Flux	20% cyclohexane 80% isobutyl alcohol	6.8	40.6	105	8.3	...	7.6	66.1	151	1.484

[a] Proportions given by volume.
[b] Wt. of solvent divided by wt. of pentane-insoluble free asphalt.

from 10.9 to 14.3% of wax, were dewaxed at solvent ratios of from about 70 to 40, respectively. If calculated values for wax had been based on an assumed ratio of 100, the values would have been lower by 0.7 to 1.5%, respectively. Then comparisons with the experimental values would have shown the recovery of wax higher than was actually the case.

An average difference of +0.4% was found between the calculated and experimental values for hexane-insolubles, with a maximum difference of 1.8%. The larger differences were shown in analysis of asphalts to which petrolatum II had been added. Precipitation of waxes probably occurred. The average wax content of the asphalts was high, 9.7%, and solubility trials (Table IV) had shown that petrolatum I or II would not be completely soluble in hexane at such concentrations. Also, possibly, the weight of insolubles precipitated was increased because of the increased paraffinicity of the hexane-asphalt solution, owing to the large weight of petrolatum contained in the asphalt. This effect should be small, however, because of the large volumes of hexane used.

The recovery of resins from the petrolatum-asphalt blends was higher by an average of 1.8 and 2.4% than that calculated for the hard and soft resins, respectively. The increase in these fractions could be due to coprecipitation of waxes from the petrolatums and/or to precipitation of fractions wider in molecular weight range because of the greater paraffinicity of the precipitating mixture caused by the high petrolatum content. Thus, a portion of the soft resins would be precipitated with the hard resins and a portion of the higher molecular weight oils with the soft resins.

Since the recovered wax accounted for about 93% of the calculated wax values, and an additional 4% was presumably precipitated with the hexane-insolubles, it was evident that the paraffinicity of the deresinating solvents was largely responsible for the increased yield of hard resins. With the soft resins there was a possibility that some of the large content of paraffinic oils contained in the added petrolatum were precipitated by the isobutyl alcohol at 37.8° C. (100° F.). As an indirect check, recovery of the soft resins was made with solvents having greater solubility for paraffins by using isobutyl alcohol containing 5 and 10% of cyclohexane, analyses 8 and 9 of Table V, respectively. The yield of resins was again greater than calculated by about the same amount, which should not have been the case if paraffins were precipitated.

Some resin contamination in the wax was indicated by the values for specific dispersion which were greater than 100. The melting points of the recovered wax, with one exception, did not agree with those of the added wax. Melting points on five of the recovered waxes were lower by 3° to 12° C. (5° to 22° F.), while on three the values were greater by more than 13° C. (24° F.). The lowering of melting points of the waxes is probably caused by the previous precipitation of a small portion of higher melting waxes with the insolubles and hard resins and by the presence of minor amounts of resins and oils in the waxes. The increase in melting point of three of the waxes could possibly be attributed to coprecipitation of very high-melting resins. However, an analysis of blended asphalt A containing 16 2 grams of petrolatum I per 100 grams of asphalt with precipitation of the wax at −6.7° C. (20° F.) did not show an increased precipitation of resins: A yield of 9.0% of a wax with a specific dispersion value of 111 and melting at 64° C. (147° F.) was obtained. Maintaining of a dewaxing temperature of 0° C. (32° F.) or above is thus apparently not critical in so far as precipitation of resins with wax is concerned.

Accuracy. The differences between the calculated and experimental values, shown in Table V, are low for a method dependent upon batch solvent separations. Since there is no definite dividing line between the resins and oils, the differences shown are not of great significance except to indicate that with asphalts of high wax content there is a shift in the line of separation. The accuracy of recovery of the insolubles and waxes is sufficiently high for most studies which might be made of

Table IV. Solubility of Petrolatum in Various Solvents

Solvent[a]	Petrolatum	Ratio Solvent to Petrolatum	Ratio Solvent to Wax Content of Petrolatum	Calculated Wax Content of Asphalt Based on Solvent-Wax Ratios	Temp. of Test		Petrolatum Found Soluble
		Ml./g.	Ml./g.	%	° C.	° F.	%
Pentane	I	686	1560	3.2	25	77	100.0
Pentane	I	344	784	6.4	25	77	98.0
Pentane	II	1280	2000	2.5	25	77	95.8
Pentane	II	439	685	7.3	25	77	93.2
Hexane	I	686	1560	3.2	25	77	100.0
Hexane	I	344	784	6.4	25	77	99.6
Hexane	II	1280	2000	2.5	25	77	99.0
Hexane	II	439	685	7.3	25	77	94.9
		G./g.	G./g.				
20% cyclohexane 80% isobutyl alcohol	I	93.4	212	3.2	37.8	100	99.2
20% cyclohexane 80% isobutyl alcohol	I	46.7	106	6.4	37.8	100	98.2
20% cyclohexane 80% isobutyl alcohol	II	174	272	2.5	37.8	100	96.7
20% cyclohexane 80% isobutyl alcohol	II	59.6	93.1	7.3	37.8	100	92.5
22.5% cyclohexane 77.5% isobutyl alcohol	I	93.4	212	3.2	37.8	100	99.0
22.5% cyclohexane 77.5% isobutyl alcohol	I	46.7	106	6.4	37.8	100	99.0
22.5% cyclohexane 77.5% isobutyl alcohol	II	174	272	2.5	37.8	100	96.6
22.5% cyclohexane 77.5% isobutyl alcohol	II	59.6	93.1	7.3	37.8	100	92.1
20% toluene 80% isobutyl alcohol	I	80.8	184	3.7	37.8	100	99.6
20% toluene 80% isobutyl alcohol	II	114	179	3.8	37.8	100	94.7

[a] To all isobutyl alcohol–solvent blends 0.25% by volume of 27% NH_4OH solution was added. This solution was used as flocculator for resins in original procedure.

Table V. Recovery of Fractions from Asphalts Containing Added Petrolatum

(Results based on average values from two duplicate determinations)

Analysis No.	Asphalt	Petrolatum Type	Petrolatum Added	Calculated Values H.I.	Calculated Values H.R.	Calculated Values S.R.	Calculated Values O.	Calculated Values W.	Difference between Calculated and Determined Values H.I.	H.R.	S.R.	O.	W.	M. P. of Added Wax		M. P. of Wax Found		Specific Dispersion of Wax Found × 10⁴
			G./100 g. asphalt	G./100 g.					G./100 g.					° C.	° F.	° C.	° F.	
1	Blended A	I	16.2	9.5	16.6	33.2	33.5	7.2	+0.1	+3.0	+2.9	−5.4	−0.3	69	156	82+	180+	120
2	Blended B	II	12.9	9.3	13.1	35.9	33.7	8.0	+1.1	−0.1	+1.7	−2.3	−0.4	75	167	75	167	109
3	Paving, 98 penetration	I	29.1	11.3	30.0	22.2	22.1	14.3	+0.9	+3.5	+4.1	−6.6	−2.1	67	152	60	141	130
4	Paving, 98 penetration	II	17.7	12.4	33.0	24.4	16.0	14.3	+1.8	+3.0	−0.1	−3.2	−1.9	75	167	64	148	128
5	Oxidized light[a] flux	I	12.8	30.6	8.1	16.0	37.6	7.7	−0.3	+1.8	+3.1	−4.0	−0.7	68	155	65	149	105
6	Gulf Coast SC-6 road oil	I	29.1	11.8	7.1	10.4	57.3[b]	10.9	−0.2	−0.7	+4.3	−4.0	−0.2	68	155	61	141	117
7	Mexican SC-6 road oil	II	17.7	16.0	10.3	9.9	50.3[c]	11.8	+0.6	+1.4	−0.2	−2.7	+0.5	75	167	63	145	128
8[d]	Blended A	I	16.2	9.9	16.2	27.8	39.7	6.4	−0.5	+2.1	+2.1	−3.4	−0.4	69	156	82+	180+	118
9[e]	Blended A	I	16.2	9.5	16.5	20.8	46.3	6.8	0.0	+2.0	+3.6	−4.1	−0.5	69	156	82+	180+	119
								Av. difference	+0.4	+1.8	+2.4	−4.0	−0.7					

[a] S.P. (R. and B.) 95° C. (203° F.), penetration at 25° C. (77° F.) 23.
[b] Loss of volatile oils by evaporation during analysis, 2.5%.
[c] Loss of volatile oils by evaporation during analysis, 1.7%.
[d] Blend of 5% cyclohexane, 95% isobutyl alcohol by vol. used to ppt. soft resins.
[e] Blend of 10% cyclohexane, 90% isobutyl alcohol by vol. used to ppt. soft resins.

Table VI. Precision of Method

(Deviation from average of two determinations run on 60 different samples of asphalts, grams per 100 grams of original sample)

	Average Deviation	Maximum Deviation	Percentage of Samples on Which Deviation Was Greater than ±0.50
Hexane-insolubles	±0.28	±0.9	20
Hard resins	±0.31	±1.1	15
Soft resins	±0.32	±1.2	23
Oils	±0.31	±1.2	23
Waxes	±0.28	±0.9	17

asphalt. An exception would be if knowledge of the melting points of the wax fraction were important. Then other methods designed only for the determination of waxes should be followed, such as those dependent upon the resin adsorption by clay (*16*), or the removal of the resins by acid or aluminum chloride (*4*), or by propane (*13*).

PRECISION. Deviations shown by results of duplicate determinations on 59 asphalts derived from Venezuelan, Mexican, California, Gulf Coast, and various Mid-Continent crudes and refined Trinidad asphalt are given in Table VI. The asphalts ranged from road oils through penetration grades to blown products melting (ring and ball) at 104° C. (220° F.). One cracked road oil was included; other asphalts showed a negative spot when tested by the Oliensis unmodified procedure (*3*).

The average deviations were near ±0.3 for each of the five fractions, and for about 80% of the samples the results did not deviate from the average by more than ±0.50 gram per 100 grams of samples. The maximum deviation for all fractions was, on an average, ±1.1 grams per 100 grams of sample. Thus, with two determinations on a sample the average is likely to be precise to within ±0.50 gram and with three determinations the average will probably be within ±0.3 gram per 100 grams of sample.

COMPARISON OF WAX CONTENTS. The methylene chloride-acetone dewaxing solvent was found to precipitate contents of waxes intermediate between those obtained by the Holde (*9*, cf. *1*) and the U.O.P. (*16*) methods, as shown by data of Table VII.

The waxes by the Holde method were essentially free of nonparaffinic material. The drastic heat treatment received during the process apparently converted all resinous materials into lighter oils soluble in the dewaxing solvent. That some of the paraffins are also cracked in the process is shown by the low yield obtained of a low melting point wax.

The U.O.P. method, which depends on clay adsorption to remove resinous material that otherwise might be coprecipitated with the wax, yielded very high contents of waxes from all the asphalts. This method is thus suitable for determining what might be termed the "total content" of waxes, knowledge of which should be of value in interpreting the low-temperature behavior of asphalts. The inclusion of the paraffinic oil with the higher melting waxes did not greatly lower the melting point. This was also noticed in dewaxing trials at various ratios with petrolatums I and II, Table II. The contamination of the waxes with resins apparently has a much greater effect on reduction of melting point. This is probably the reason why the melting point of the wax precipitated by the methylene chloride-acetone solvent from the oxidized flux is lower than that of the wax recovered from the same asphalt by the U.O.P. method, as shown by the difference in specific dispersions of the waxes.

AVERAGE RESULTS OF ANALYSES. Tables VIII and IX list the ranges and average weights of fractions and the properties of fractions separated from blown and straight-run asphalts. The 37 oxidized asphalts were blown chiefly from fluxes reduced from Mid-Continent crudes and blends of these fluxes, but included one California and one Venezuelan oxidized asphalt. The seven 85/100 penetration straight-run asphalts, all of which showed a negative Oliensis spot test (*3*) in standard naphtha, were

Table VII. Comparison of Wax Contents of Four Asphalts Recovered by Three Methods

Asphalt	Methylene Chloride and Acetone at 0° C. (32° F.) Wax found	Melting point		Specific dispersion × 10⁴	Holde Wax found	Melting point		Specific dispersion × 10⁴	U.O.P. Method No. A-46-40 Wax found	Melting point		Specific dispersion × 10⁴
	%	° C.	° F.		%	° C.	° F.		%	° C.	° F.	
Mid-Continent flux 1	5.1	59.4	139	125	1.8	51.7	125	95	17.8	53.9	129	115
Mid-Continent flux 2	5.9	50.0	122	113	2.5	47.8	118	100	26.0	46.7	116	115
Oxidized paraffinic-base flux	11.3	62.2	144	126	2.9	52.2	126	98	22.9	65.6	150	108
Paving asphalt	2.3	82+	180+	106	1.5	51.1	124	98	8.7	61.1	142	115

Table VIII. Averages and Ranges of Fractions in Asphalts

	37 Asphalts Oxidized from Bases Reduced from Various Crudes			7 Straight-Run Asphalts Reduced from Different Crudes		
	Minimum	Maximum	Av.	Minimum	Maximum	Av.
S.P. (R. and B.), ° C. (° F.)	69 (157)	104 (220)	93 (200)	43 (110)	48 (119)	46 (115)
Penetration at 25° C. (77° F.)	9	47	25	85	98	92
Hexane-insolubles, %	23	36	32	4	20	15
Hard resins, %	2	33	16	11	39	26
Soft resins, %	13	28	22	22	30	26
Oils, %	10	45	26	14	54	29
Waxes, %	1.0	11.3	4.6	1.4	7.3	3.4

Table IX. Averages and Ranges of Properties of Fractions in Asphalts

Fraction	Hard Resins			Soft Resins			Oils			Waxes		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
37 Asphalts Oxidized from Bases Reduced from Various Crudes												
Density at 65° C., g./ml.	0.946	1.013	0.993	0.910	0.982	0.937	0.898	0.929	0.911	0.853	0.890	0.875
Refractive index[a] at 65° C. (n_D^{65})	1.56	1.59	1.57	1.51	1.55	1.53	1.503	1.535	1.512	1.472	1.498	1.483
Specific dispersion × 10⁴[a]	220	290	240	160	240	190	141	199	156	114	142	130
Refractivity intercept[a]	1.07	1.10	1.08	1.05	1.07	1.06	1.035	1.070	1.056	1.026	1.055	1.047
S.U. viscosity at 98.9° C. (210° F.)	..	..	..	..	..	..	131	1110	215	..	..	..
M.P. of wax, ° C.	..	..	..	..	..	..	..	..	..	47	82+	..
7 Straight-Run Asphalts Reduced from Different Crudes[b]												
Density at 65° C., g./ml.	0.987	1.030	1.012	0.946	0.995	0.962	0.920	0.948	0.937	..	..	..
Refractive index[a] at 65° C. (n_D^{65})	1.58	1.63	1.60	1.54	1.58	1.55	1.525	1.544	1.530	..	..	..
Specific dispersion × 10⁴[a]	230	330	260	200	260	220	159	210	177	..	..	..
Refractivity intercept[a]	1.080	1.115	1.091	1.063	1.082	1.069	1.056	1.070	1.061	..	..	..
S.U. viscosity at 98.9° C. (210° F.)	..	..	..	..	..	..	540	1462	831	..	..	..

[a] Precision of determination on hard and soft resins was low because of difficulty of reading Abbe refractometer.

[b] Wax contents were low and characterizations were run on only two samples. Therefore, averages and ranges cannot be given.

reduced from two Arkansas, one Venezuelan, two Mid-Continent, one Texas, and one California crude.

The wide range in content of fractions indicates that the method of analysis is highly sensitive to difference in composition of asphalts. With methods based upon adsorption of resins by clay the variation in content and the total content would be less, since the selection is dependent more upon polarity, while isobutyl alcohol, like propane, precipitates fractions more on the basis of molecular weight. An advantage in precipitating relatively large fractions is the greater accuracy of observing changes in composition of asphalts with processing or with service.

The average and range in properties of the fractions obtained upon analysis are shown in Table IX. A wide range in the character of the components was found, as would be expected of fractions precipitated on the basis of molecular weight. While the ranges overlap for the different fractions, the averages are widespread.

APPLICATIONS. The need to interpret more fully the changes occurring in asphalts under service conditions and during refinery processing led to development of the method of fractionation described herein. Then compositions could be adjusted, in accordance with empirical relations to behavior, by blending various available residues or extracts or by change in refinery processing to make available stocks relatively rich in needed fractions. Results of some analyses are given below to illustrate a few of the possible applications.

Steam and vacuum reduction of an asphalt from a penetration of 190 to 36 produced changes in fractions as shown by Table X. The softening point (ring and ball) increased from 38.9° to 54.4° C. (102° to 130° F.) to maintain the penetration temperature susceptibility (*15*) very nearly constant. As expected, the first overhead products were largely oils, but to reach lower penetrations loss of soft resins also occurred. The aromaticity of the fractions remaining in the asphalt did not change greatly, as is shown by the nearly constant values for specific dispersion. The oil fraction became much more viscous.

Air blowing of the straight-reduced asphalt of 36 penetration markedly increased the content of hexane-insolubles at the expense of the resins, especially the hard resins. These changes in the fractional composition, which are graphed on Figure 2 *vs.* softening point for both the distillation and blowing operations, served to decrease the penetration and to raise the softening

Table X. Analyses of Asphalts

	Straight-Reduced			Air-Blown from Asphalt of 36 Penetration		
Properties of asphalts						
Penetration at 25° C. (77° F.)	190	89	36	13	9	1
Softening point (R. and B.), ° C. (° F.)	38.9 (102)	45.0 (113)	54.4 (130)	85.0 (185)	96.1 (205)	173.3 (344)
PTS × 100[a]	4.5	4.7	4.6	3.0	2.7	0.2
Fractions, % by wt.						
Hexane-insolubles	11.4	12.3	14.8	26.9	31.4	51.3
Hard resins	39.5	41.2	45.5	36.6	36.1	19.6
Soft resins	26.8	27.8	25.0	22.3	20.9	16.9
Oils	20.4	15.8	12.3	11.9	10.0	11.1
Waxes	2.1	2.9	2.5	2.0	1.8	1.6
Total	100.2	100.0	100.1	99.7	100.2	100.5
Ratio of total resins to hexane-insolubles	5.8	5.6	4.7	2.2	1.8	0.7
Specific dispersion of fractions[b] × 10⁴						
Hard resins	235	230	235	216	231	232
Soft resins	193	194	188	189	189	172
Oils	166	173	166	158	168	154
Viscosity of oils, S.U.S. at 98.9° C. (210° F.)	446	862	932	949	993	644

[a] $$\text{PTS} = \frac{\log 800 - \log \text{pen. at } 25^\circ \text{ C.}}{\text{S.P. (R. and B.)}^\circ \text{ C.} - 25}$$

[b] Calculated from values of density and of refractive index as determined with an Abbe refractometer. Determinations of refractive index were made on resins at 65° C. (n_D^{65}) and on oils at 25° C. (n_D^{25}). Determinations of density were made on resins at 65° C. and on oils at 25° C.

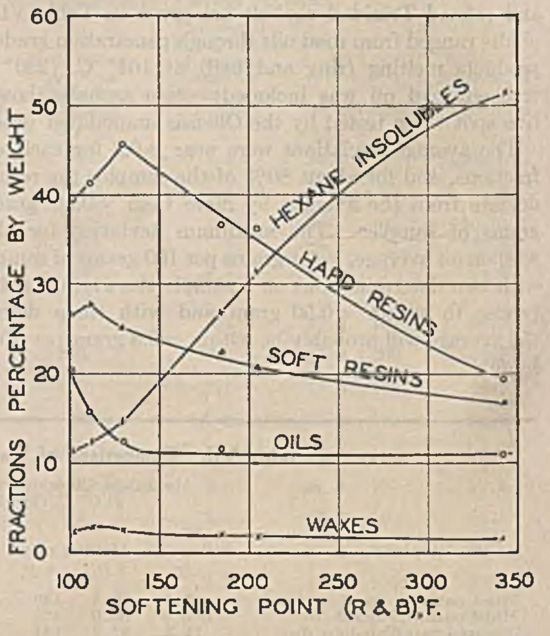

Figure 2. Change in Fractions during Distillation and Air-Blowing of Asphalts

Table XI. Analyses of Asphalts

(Air-blown from bases of varying consistency straight-reduced from smackover crude oil and analysis of smackover asphalt)

	Blown Asphalts					Straight-Reduced
Properties of base						
Float at 50° C. (122° F.), seconds	78	83	140	530	740	750
Penetration at 25° C. (77° F.)	...	...	...	110	91	89
Softening point (R. and B.), ° C., (° F.)	...	...	...	44.4 (112)	46.1 (115)	45.0 (113)
Properties of blown asphalt						
Penetration at 25° C. (77° F.)	28	34	23	15	18	89
Softening point (R. and B.), ° C. (° F.)	96.1 (205)	83.3 (182)	95.0 (203)	94.4 (202)	83.3 (182)	45.0 (113)
PTS × 100	2.0	2.3	2.2	2.5	2.8	4.7
Fractions in blown asphalt, % by wt.						
Hexane insolubles	33.6	31.2	32.3	33.1	29.4	14.2
Hard resins	10.1	12.8	22.3	32.8	30.9	42.5
Soft resins	22.6	23.8	21.6	20.3	25.9	25.9
Oils	31.9	29.2	21.8	11.5	11.5	14.3
Waxes	3.2	3.3	2.8	2.9	3.2	3.2
Total	101.4	100.3	100.8	100.6	100.9	100.1
Ratio of total resins to hexane insolubles	1.0	1.2	1.4	1.6	1.9	4.8
Specific dispersion of fractions × 10^4 [a]						
Hard resins	245	241	242	231	237	234
Soft resins	188	195	188	191	183	188
Oils	158	151	159	169	161	166
Viscosity of oils, S.U.S. at 98.9° C. (210° F.)	171	205	262	366	621	701

[a] Calculated from values of density and of refractive index as determined with an Abbe refractometer. Determinations of refractive index were made on resins at 65° C. (n_D^{65}) and on oils at 25° C. (n_D^{25}). Determinations of density were made on resins at 65° C. and on oils at 25° C.

Table XII. Analyses of Solvent Extracts and Propane Precipitates

Stock	Agent	Viscosity of Extracts and Precipitates S.U.S. at 98.9° C. (210° F.)	Fractions Found, % by Wt.						Specific Dispersion × 10^4 of Fractions[a]			Viscosity of Oil Fractions S.U.S. at 98.9° C. (210° F.)
			H.I.	H.R.	S.R.	O.	W.	Total	H.R.	S.R.	O.	
Heavy lube	Phenol	780	0.0	0.0	10.9	89.6	0.2	100.7	...	214	196	558
Residuum	Furfurol	1770	0.2	1.1	24.1	73.4	1.3	100.1	...	243	242	899
Residuum	Chlorex	1093	0.8	0.0	9.3	85.6	3.5	99.2	...	160	162	116
Residuum	Propane	567 (Saybolt Furol at 210° F.)	0.0	71.5	16.2	9.9	3.3	100.9	242	216	156	501
Residuum	Propane	916	0.0	56.9	25.7	14.8	3.3	100.7	...	149	153	412
Asphaltic residuum	Propane	[b]	35.0	50.0	9.1	5.0	1.2	100.3	290	275	213	...

[a] Calculated from values of density and of refractive index as determined with an Abbe refractometer. Determinations of refractive index were made on resins at 65° C. (n_D^{65}) and on oils at 25° C. (n_D^{25}). Determinations of density were made on resins at 65° C. and on oils at 25° C.

[b] Softening point (R. and B.), 103° C. (218° F.). Penetration at 25° C. (77° F.), 1.

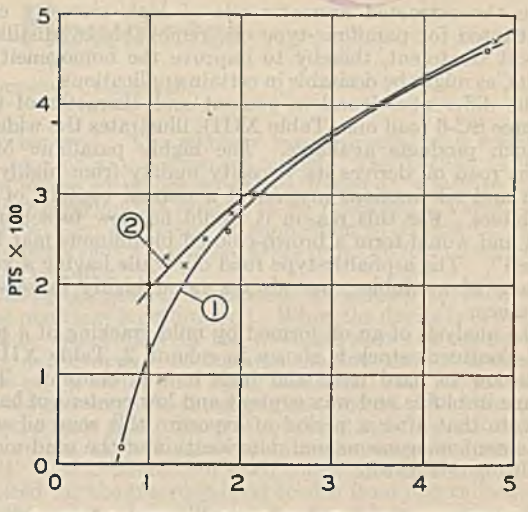

Figure 3. Penetration-Temperature Susceptibility vs. Ratio of Total Resins to Hexane-Insolubles

point of the asphalt, and therefore to lower greatly the penetration-temperature susceptibility. This decrease was found to be related to the ratio of the total resin to the hexane-insoluble content, as is shown by curve 1 of Figure 3. The character of the fractions obtained from the air-blown asphalts was remarkably constant, as shown by measurements of specific dispersion and viscosity of the oils, until a softening point above 96.1° C. (205° F.) had been reached. Thereafter, the soft resin and oil fractions from the asphalt became less aromatic and the oil fraction was lowered in viscosity, as shown by the data on the fractions from the asphalt melting at 173.3° C. (344° F.).

In manufacture of blown asphalts it is necessary in many instances to obtain products of approximately the same softening point but of varying penetration. The common practice, with residues available from a given crude oil, is to air-blow bases of varying viscosity. In general, the higher the viscosity of the base the lower will be the penetration of the blown asphalt at a given melting point. The fractional compositions of a series of such asphalts, all melting within the range of 82.2° to 96.1° C. (180° to 205° F.), but prepared from bases of varying consistency are shown by Table XI. A nearly constant content of hexane-insolubles was found in this series. The result of blowing an asphalt base of lower oil content but with an essentially constant ratio of resins to insolubles is thus to obtain an end product of given melting point but with a higher ratio of resins to insolubles, since less conversion of resins to insolubles has occurred. The ratio of total resins to hexane-insolubles for the blown asphalts and for a straight-run asphalt of 87 penetration from the same crude, analysis of which is also shown in Table XI, was again found related to penetration-temperature susceptibility (curve 2, Figure 3). Values for penetration-temperature susceptibility are at a slightly higher level than shown by data on the blown asphalts of Table X, since the asphaltic crude bases involved, although similar, were different.

The fractional compositions of three solvent extracts and of three propane precipitates are shown in Table XII. Although no direct comparison may be made of the action of the different refining agents because of the difference in starting stocks, the precipitating action of propane as compared with extracting effect of the selective solvents is readily apparent. Such analyses indicate the value of extracts and precipitates in blending procedures for adjusting compositions of petroleum residua. Thus, for example, the propane precipitates contain large contents of resins and could therefore be added to residua to raise their penetration-temperature susceptibility and increase ductility;

Table XIII. Analyses of Road Oil

Crude Base	Paraffinic	Paraffinic	Asphaltic
Properties of road oil			
Viscosity, S. Furol at 60° C. (140° F.), seconds	440	640	700
Flash point, Cleveland open cup, ° C. (° F.)	316 (600)	210 (410)	154 (310)
Spot test	Neg.	Pos.	Neg.
Specific gravity at 25° C./25° C. (77° F./77° F.)	0.963	1.034	0.990
Fractions, % by wt.			
Hexane insolubles	2.5	12.2	18.9
Hard resins	19.4	2.6	12.1
Soft resins	38.7	16.6	11.6
Oils	31.2	58.8	54.5
Waxes	8.2	5.9	1.1
Loss of oils by evaporation	0.0	3.9	1.8
Total	100.0	100.0	100.0
Specific dispersion of fractions × 10^4 [a]			
Hard resins	303	...	...
Soft resins	204	238	...
Oils	162	247	150
Refractive index of hard resin, n_D^{65}, ° C.	1.577	1.623	1.589
Viscosity of oils, S.U.S. at 98.9° C. (210° F.)	261	139	106

[a] Calculated from values of density and of refractive index as determined with an Abbe refractometer. Determinations of refractive index were made on resins at 65° C. (n_D^{65}) and on oils at 25° C. (n_D^{25}). Determinations of density were made on resins at 65° C. and on oils at 25° C.

while the extracted aromatic oils of high viscosity could be substituted for paraffinic-type oils removable by distillation or solvent treatment, thereby to improve the homogeneity of asphalts, as might be desirable in certain applications.

The differences found in content and character of fractions in three SC-6 road oils (Table XIII), illustrates the wide variety of such products available. The highly paraffinic Mid-Continent road oil derives its viscosity mainly from highly viscous resin and oil fractions instead of a normal content of hexane-insolubles. For this reason it would be slow to set upon the road and would form a brown-colored bituminous mat likely to "bleed". The asphaltic-type road oil, while having a very high content of insolubles, has always rated highly in service performance.

The analysis of an oil formed by mild cracking of a paraffinic Mid-Continent stock is shown in column 2, Table XIII. This oil is low in hard resin and high in wax content. The high hexane-insoluble and wax content and low content of hard resins indicate that after a period of exposure this road oil would become nonhomogeneous and deterioration of the road mat would result for this reason.

SUMMARY

The procedure of analysis has been found adequate for accurate classification of asphalts from widely differing sources according to the content and character of their five main fractions. The method is suitable for products varying in consistency from road oils to highly blown products. While only a few trials have been made on cracked asphalts, the treatment is thought also to be applicable in the separation of their fractions, except for some products produced by high level cracking which, although resinous, are largely insoluble in hexane. Other petroleum products which contain some or all of the fractions found in residua may also be subjected to analysis, such as extracts and precipitates from lubricating stocks and lubricating oils which have been in heavy-duty service.

ACKNOWLEDGMENT

The authors wish to express their appreciation to John W. Poole for many helpful suggestions and to Janet M. Lemley for assistance in the laboratory determinations.

LITERATURE CITED

(1) Abrahams, Herbert, "Asphalts and Allied Substances", 4th ed., p. 993, New York, D. Van Nostrand Co., 1938.

(2) *Ibid.*, p. 1007.

(3) American Association of State Highway Officials, Washington, D. C., "Standard Specifications for Highway Materials and Methods of Sampling and Testing", Part II, 4th ed., p. 113, 1942.

(4) Betts, R. L., and Wirsig, H. D., Ind. Eng. Chem., Anal. Ed., 15, 478 (1943).

(5) Cannon, M. R., and Fenske, M. R., *Ibid.*, 10, 297 (1938).

(6) Grant, F. R., and Hoiberg, A. J., *Proc. Assoc. Asphalt Paving Technologists*, 12, 87 (1940).

(7) Hoiberg, A. J., Ind. Eng. Chem., Anal. Ed., 14, 323 (1942).

(8) Hoiberg, A. J., Hougen, O. A., and Zapata, Jos., Univ. of Wis. Eng. Expt. Sta., *Bull.* 86 (1939).

(9) Holde, D., "Untersuchung der Kohlenwasserstoffole und Fette", p. 45, Berlin, Julius Springer, 1913.

(10) Holmes, A., and Raphael, A. L., *Proc. Assoc. Asphalt Paving Technologists*, 8, 105 (Jan. 1937).

(11) Horne, J. W., and Holliman, W. C., *Bur. Mines Tech. Paper* 583 (1938).

(12) Kalichevsky, V. A., "Modern Methods of Refining Lubricating Oils", 1st ed. p. 60, New York, Reinhold Publishing Corp., 1938.

(13) Knowles, E. C., and Levin, Harry, Ind. Eng. Chem., Anal. Ed., 13, 314 (1941).

(14) Marcusson, Julius, *Z. angew. Chem.*, 29, I, 21 (1916).

(15) Pfeiffer, J. Ph., and Van Doormaal, P. M., *J. Inst. Petroleum Tech.*, 22, 414 (1936).

(16) "U.O.P. Laboratory Test Methods for Petroleum and Its Products", 2nd ed., p. A-21, Chicago, Universal Oil Products Co., 1943.

A Controlled-Atmosphere Induction Melting Furnace for the Laboratory

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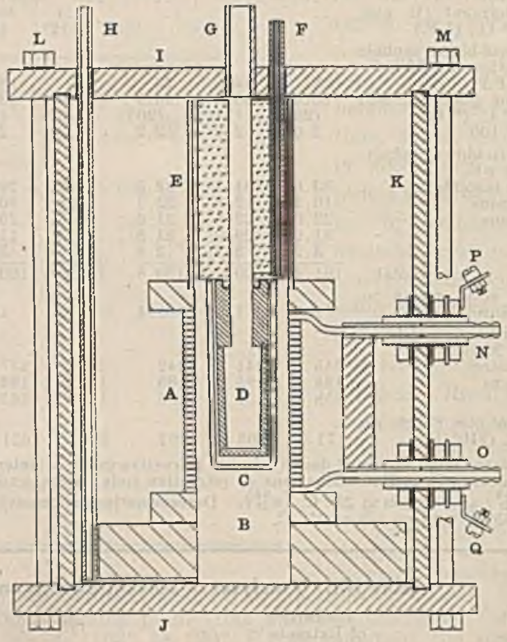

THE most common controlled-atmosphere (or vacuum) furnace for melting small metal samples by induction has been described frequently and is supplied as standard equipment by the Ajax Electrothermic Corporation. Its construction entails the use of silica tubing which is fragile, expensive, and difficult to work without special glass-blowing equipment. The disadvantages in the use of silica have led to the development in this laboratory of a less delicate piece of equipment which serves the same purpose and can be constructed in a few hours in a well-equipped shop.

Important construction features are shown in the diagrammatic drawing. In essence, the heating unit is merely enclosed by a gas-tight shell so that the entire assembly, including the furnace coil, can be evacuated or flushed with inert gas.

The water-cooled heating coil, *A*, is connected with the converter cables at *P* and *Q* and with water lines at *N* and *O*. It is the standard coil supplied with the 3 kv.-amp. furnace assembly. The Alundum thimble, *C*, contains the melting crucible, *D*, and is surrounded with Norconite, *B*, or other suitable insulating powder. A layer of sheet mica, rolled into a cylinder, separates this powder from the cooling coil, and prevents its lateral escape. The assembly, *E*, above the melting crucible, serves to diminish the upward radiation from the molten charge, while permitting a clear view of the charge through sight tube *G*.

This whole unit is surrounded by the chamber formed by fiber plates, *I* and *J*, and leucite (or metal) cylinder, *K*. Rubber gaskets in the grooves of the top and bottom plate and at the water-cooled electrical connections render the entire assembly gas-tight when compressed by the six vertical bolts, *L*, *M*, etc., and the brass nuts and washers of the cooling tubes. The gas input and exit tubes, *H* and *F*, are sealed with DeKhotinsky cement to the top plate, as is also *G*. The temperature of the molten charge may be determined either by an optical pyrometer, sighted through a cemented window at *G*, or by a thermocouple, within a gas-tight protection tube, inserted into the charge through *G* and cemented at the top. Insulation is unnecessary outside the water-cooled coil and the bolts are far enough from the induction currents to remain cool, despite crucible temperatures of 1500° C. or above. The crucible and contents cool rapidly when the current is interrupted and may be replaced in a few minutes by removal of the top plate and the radiation shields.

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Positive Displacement Flowmeter

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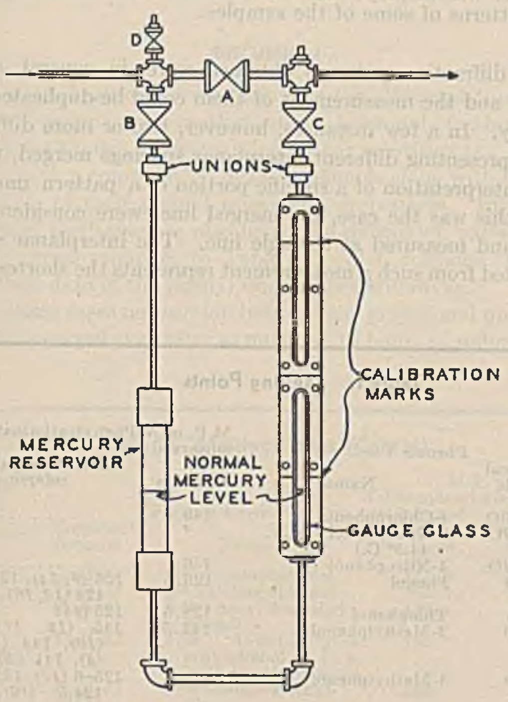
IN LABORATORY and pilot-plant work, particularly when continuous processes are studied, it is often necessary to measure the rate of flow of small, sometimes pulsating or irregularly flowing streams which may vary in density or viscosity. In many such instances it is inconvenient or impossible to use conventional orifice- or Venturi-type meters, rotameters, or calibrated tanks. Obviously, some form of positive displacement meter is desirable for such service; but unfortunately most commercially available meters of this type are either too large or have pressure, temperature, or other limitations which make them unsuitable.



A problem often encountered in these laboratories which is thus complicated is the measurement of recycle or "combined feed" streams in continuous cracking pilot plants. Often these streams are hot and are subject to changes in temperature and composition in the course of a run. Usually they are transferred by a reciprocating pump, and always the continuity of their flow must be maintained. While alternately used surge tanks, pump stroke calculation, and calibrated orifices or rotameters can be employed with some success, all these methods have certain drawbacks in such use. The device described below (*1*) was developed especially for this service and has been in use about 2.5 years. It is also applicable to many other flow-measurement problems, and has been found particularly useful in obtaining rapid, approximate measurements of flow rates even when the quantity flowing over a long period is determined by more accurate means, such as calibrated charge tanks. Its chief advantages are simplicity of construction and operation; applicability over wide ranges of temperature, pressure, and stream composition; and a positive calibration which does not change with operating conditions or fluid properties.

The diagram shows the particular design of this flowmeter which has been most generally used in the author's laboratories. It consists essentially of a U-tube, one leg of which is a gage glass, the other a reservoir for mercury, water, or other liquid heavier than and immiscible with the flowing stream. A Jerguson "Reflex" type glass has been used most commonly because it allows operation at high temperatures and pressures, but any glass satisfactory for the prevailing conditions may be used. The mercury reservoir can be a suitable length of pipe or any convenient vessel. The U-tube is connected by means of unions to valves *B* and *C*, which in turn join the line carrying the stream to be measured. Valve *A* is interposed between the point of connection of *B* and *C*. The crosses and plugs shown and valve *D* are provided for convenience in filling and cleaning.

Before the gage glass is connected, its volume between two convenient markings is determined. When the device is in operation the flow is normally in the direction shown in the sketch, with *A*, *B*, and *C* open. To measure the flow rate, *A* is closed, forcing the oil (or other fluid being measured) into the mercury reservoir, the mercury into the gage glass, and oil out of the gage glass into the main line. Since as much oil is forced out of the system as enters, the net rate of flow in the main line remains unchanged. The measurement itself consists in determining the time required for the mercury level to rise from one calibration mark to the other, thus filling a known volume. When this measurement is completed, *A* is reopened, and the mercury seeks its own level. Here again, since oil is discharged from one leg as rapidly as it enters the other, no interruption in the net flow occurs.

Calculation of the flow rate from the observed time is simple. Thus, if the calibrated volume is V gallons, and the time required to fill it is t minutes, the rate of flow, R, in gallons per minute, is obtained by the equation $R = \frac{V}{t}$. In one typical example, the calibrated volume was 0.046 gallon and the observed filling time was 30 seconds. The rate of flow was then $\frac{0.046}{30} \times 60 = 0.092$ gallon per minute.

While the design described is cheap, simple, and highly satisfactory, it can be modified to meet particular demands and utilize existing apparatus. The calibrated volume should be of such a size that the time required for a single determination is neither so long as to be inconvenient nor so short as to be inaccurate. The author has found 30 to 60 seconds satisfactory.

More elaborate modifications of the basic design have been suggested (*1*) for applications where an automatically determined rate or a record of total flow is desired. While the device was developed for, and to date has been limited to, the measurement of liquid streams varying from liquid propane to heavy recycle oil, it can also be used for measuring gas streams by taking proper account of the compression of the gas on the upstream side of the meter, using a low-density sealing liquid, and limiting the variation in liquid level to a low value.

LITERATURE CITED

(1) McAfee, Jerry, U. S. Patent 2,325,695 (Aug. 3, 1943).

THIS device was described by L. S. Kassel of the U.O.P. Research and Development Laboratories at the round table discussion on pilot-plant design, construction, and operation, Division of Petroleum Chemistry, 106th Meeting of the AMERICAN CHEMICAL SOCIETY, Pittsburgh, Pa.

Course in Instrumental Methods of Analysis and Control

An ESMWT course in instrumental methods of analysis and control will be given at the University of Southern California, Los Angeles, starting June 12. The course now being taught by Sidney W. Benson is to be expanded for the summer session to 7 hours of laboratory work and one hour of lecture each week for 15 weeks, devoted to study of the applications of physical properties of chemical substances to the analysis and control of chemical processes, and including laboratory work with basic instruments such as pressure gages, flowmeters, rotameters, thermocouples, potentiometric circuits, colorimeters, spectrophotometers, and electronic relays.

Phenyl Isocyanate Derivatives of Certain Alkylated Phenols

Melting Points and X-Ray Powder Diffraction Data

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As positive means for identifying alkylated phenols, the authors have prepared phenyl isocyanate derivatives of a large number of phenols, and in this paper present tables of melting points and x-ray powder diffraction data.

AS A result of recent developments, considerable quantities of alkylated phenols are finding use in the preparation of synthetic plastics, rubber, germicides, fungicides, and related substances. Because of this increasing interest in alkylated phenols, the authors have undertaken to develop an easy and positive means for their identification. One widely used method for such purposes is the determination of the characteristic melting point of the aryl *N*-phenylcarbamate formed by the reaction of a phenol with phenyl isocyanate. As this procedure has been shown to be satisfactory, it was decided to prepare these derivatives of a large number of phenols which were available, and then to ascertain their melting points and also to obtain their x-ray powder diffraction data. Either the melting point or the x-ray powder diffraction pattern of the phenyl isocyanate derivative is usually sufficient for identification of the parent phenol, but a consideration of both determinations gives results which are unequivocal.

The melting points of a number of such phenolic derivatives have been listed by Morgan and Pettet (*14*) and by Steinkopf and Höpner (*16*); a few relevant supplemental data are given by other investigators. No previous publications have been found in which x-ray powder diffraction data are presented for these derivatives, although the value of such information for the identification of compounds possessing crystalline structure has been pointed out by Hanawalt and co-workers (*7*, *8*), Davey (*3*), and others.

PROCEDURES

The method of preparation of the aryl *N*-phenylcarbamates was based upon the procedures given by Steinkopf and Höpner (*16*) and Weehuizen (*21*). A small quantity of the phenolic substance (ca. 1 gram) was mixed with a slight molar excess of phenyl isocyanate in a 20-cm. (8-inch) test tube fitted with a reflux condenser and to this reaction mixture were added 8 to 10 ml. of a petroleum distillate (b.p. 170–200° C.) previously fractionated from kerosene. The reaction was completed by gently refluxing for 1 to 4 hours (usually 4). After product was cooled, the crystals which formed were recovered by filtration and purified by recrystallization from petroleum ether, benzene, or a mixture of these solvents. The purified derivative was dried under room conditions and its melting point was determined using a calibrated Anschütz thermometer.

The x-ray diffraction patterns of the aryl *N*-phenylcarbamates were secured by the usual Debye-Scherrer-Hull method. A small portion of the material was finely powdered, packed into a short length of 19-gage stainless steel hypodermic needle tubing of 0.7-mm. internal diameter, compressed with a plunger, and finally extruded as a cylinder of the same diameter. The steel tubing was mounted in a camera of 57.3-mm. effective diameter in such a manner that only the extruded part of the specimen appeared in the x-ray beam. The photograms were made with filtered CuK$_\alpha$ radiation having an effective wave length of 1.539 A. A camera of 171.9-mm. effective diameter was employed to obtain better resolution of the diffraction patterns of some of the samples.

The diffraction patterns obtained were, in general, sharply defined and the measurement of them could be duplicated satisfactorily. In a few instances, however, two or more diffraction lines representing different interplanar spacings merged, making exact interpretation of a specific portion of a pattern uncertain. When this was the case, the merged lines were considered as a group and measured as a single line. The interplanar spacing calculated from such a measurement represents the shortest inter-

Table I. Melting Points

X-Ray Diffraction Pattern No.	Phenols Used: Empirical formula	Phenols Used: Name	M.P. of *N*-Phenylcarbamates, ° C.: Observed by authors	M.P. of *N*-Phenylcarbamates, ° C.: Literature values and references
1	C_6H_5ClO	4-Chlorophenol	148.5	....
2	$C_6H_5NO_3$	2-Nitrophenol (m.p. 44.5° C.)	[a]	....
3	$C_6H_5NO_3$	4-Nitrophenol	156	....
4	C_6H_6O	Phenol	126.5	126 (*6*, *14*), 125.5 (*13*), 124 (*12*, *16*), 122 (*10*)
5	C_6H_6S	Thiophenol	128.5	125 (*15*)
6	C_7H_8O	2-Methylphenol	142.5	145 (*12*, *17*), 144.5 (*16*), 144 (*14*), 143 (*5*), 141 (*20*)
7	C_7H_8O	3-Methylphenol	124.5	125–6 (*17*), 125 (*5*, *14*), 124.5 (*16*), 121–2 (*20*)
8	C_7H_8O	4-Methylphenol	113	115 (*5*, *14*), 114 (*12*, *16*, *17*), 112–13 (*20*)
9	C_7H_8S	4-Methylthiophenol	132	....
10	$C_8H_{10}O$	2-Ethylphenol	143.5	141 (*16*, *19*), 140–1 (*2*), 140 (*18*)
11	$C_8H_{10}O$	3-Ethylphenol	137[b]	138.8 (*16*), 138 (*11*)
12	$C_8H_{10}O$	4-Ethylphenol	120.5	120 (*11*, *16*, *19*)
13	$C_8H_{10}O$	2,3-Dimethylphenol	173.5	176 (*16*)
14	$C_8H_{10}O$	2,4-Dimethylphenol	103[c]	112 (*14*, *16*), 111.8–122.2 (*4*), 102 (*5*, *17*)
15	$C_8H_{10}O$	2,5-Dimethylphenol	166	162 (*5*, *14*, *16*), 160–1 (*1*)
16	$C_8H_{10}O$	3,4-Dimethylphenol	119.3	120 (*14*, *16*)
17	$C_8H_{10}O$	3,5-Dimethylphenol	149.5	151 (*5*, *16*), 148 (*14*)
18	$C_9H_{12}O$	2,4,6-Trimethylphenol	143	142 (*16*), 141–2 (*9*), 140–2 (*1*)
19	$C_{10}H_{13}ClO$	2-*tert*-Butyl-4-chlorophenol	133	....
20	$C_{10}H_{14}O$	4-*tert*-Butylphenol	148.5	....
21	$C_{11}H_{14}O$	4-Methyl-2-(β-methylallyl)phenol	98.5	....
22	$C_{11}H_{16}O$	4-*tert*-Amylphenol	108	....
23	$C_{11}H_{16}O$	4(or 6)-*tert*-Butyl-2-methylphenol (b.p. 135° C. at 20 mm.)	139.5	....
24	$C_{11}H_{16}O$	6(or 4)-*tert*-Butyl-2-methylphenol (b.p. 123° C. at 20 mm.)	189	....
25	$C_{11}H_{16}O$	4(or 6)-*tert*-Butyl-3-methylphenol (b.p. 129° C. at 20 mm.)	133	....
26	$C_{11}H_{16}O$	2-*tert*-Butyl-4-methylphenol	155	....
27	$C_{12}H_{10}O$	4-Phenylphenol	167.5	....
28	$C_{12}H_{14}O_3$	2,6-Diacetyl-3,5-dimethylphenol (m.p. 109° C.)	[a]	....

[a] These phenols did not form phenyl isocyanate derivatives.

[b] This value was had only after thorough drying of the sample. Without drying, a value of 124° C. was obtained consistently.

[c] This value was found consistently even after several recrystallizations and drying.

planar spacing of the group considered and is followed by the letter D in Table II.

Certain flaky organic crystals tend to pack anisotropically, which results in preferred orientation of the crystallites in the extruded specimen when prepared in the manner employed in this work. Since it is necessary that the powdered specimen employed for a Debye-Scherrer-Hull diffraction photogram contain crystallites randomly oriented, diffraction data were secured for a number of the compounds studied, using a rotating powdered sample loosely packed in a thin-walled nylon tube in order to determine whether anisotropic packing of the extruded specimens occurred. Patterns obtained with loosely packed specimens checked those secured with extruded specimens, and inasmuch as all the compounds studied were similiar, these data were taken to indicate that there was no preferred orientation of crystallites in the extruded specimens examined.

DISCUSSION

The phenols studied were mainly of the alkylated type, where the alkyl groups were methyl, ethyl, isopropyl, *tert*-butyl, and *tert*-amyl, although a few contained other substituents. In Table I is set forth a complete list of these phenols along with the melting points of their phenyl isocyanate derivatives. In the first column of this table are also listed the diffraction pattern numbers for cross reference to Table II, which contains the x-ray diffraction data of the phenyl isocyanate derivatives.

In certain cases no reaction between the phenol and phenyl isocyanate occurred even after as much as 15 hours of refluxing. In

Table I. Melting Points (Cont'd)

X-Ray Diffraction Pattern No.	Phenols Used: Empirical formula	Phenols Used: Name	M.P. of N-Phenylcarbamates, ° C.: Observed by authors	M.P. of N-Phenylcarbamates, ° C.: Literature values and references
29	$C_{12}H_{16}O$	2-Cyclohexylphenol	111.5	....
30	$C_{12}H_{16}O$	4-Cyclohexylphenol	145.5	....
31	$C_{12}H_{18}O$	2-*tert*-Amyl-4-methylphenol	124	....
32	$C_{12}H_{18}O$	4(or 6)-*tert*-Butyl-3-ethylphenol (b.p. 142° C. at 20 mm.)	156	....
33	$C_{12}H_{18}O$	2-*tert*-Butyl-4-ethylphenol	134	....
34	$C_{12}H_{18}O$	4(or 6)-*tert*-Butyl-2,3-dimethylphenol (b.p. 130° C. at 20 mm.)	216	....
35	$C_{12}H_{18}O$	6-*tert*-Butyl-2,4-dimethylphenol	173	....
36	$C_{12}H_{18}O$	4-*tert*-Butyl-2,5-dimethylphenol	144	....
37	$C_{12}H_{18}O$	4-*tert*-Butyl-2,6-dimethylphenol	160	....
38	$C_{12}H_{18}O$	6-*tert*-Butyl-3,4-dimethylphenol	142	....
39	$C_{12}H_{18}O$	2,6-Diethyl-3,5-dimethylphenol	226	....
40	$C_{13}H_{20}O$	3,5-Diisopropyl-2-methylphenol	198.5	....
41	$C_{13}H_{20}O$	3,5-Diisopropyl-4-methylphenol	256	....
42	$C_{14}H_{22}ClO$	2,6-Di-*tert*-butyl-4-chlorophenol (m.p. 78° C.)	[a]	....
43	$C_{15}H_{24}O$	4,6-Di-*tert*-butyl-2-methylphenol	163.5	....
44	$C_{15}H_{24}O$	4,6-Di-*tert*-butyl-3-methylphenol	171.5	....
45	$C_{15}H_{24}O$	2,6-Di-*tert*-butyl-4-methylphenol (m.p. 69.5° C.)	[a]	......
46	$C_{16}H_{24}O$	2-*tert*-Butyl-4-cyclohexylphenol	170	....
47	$C_{16}H_{26}O$	4,6-Di-*tert*-butyl-3-ethylphenol	182.5	....
48	$C_{16}H_{26}O$	2,6-Di-*tert*-butyl-4-ethylphenol (m.p. 43.5° C.)	[a]	....
49	$C_{16}H_{26}O$	4,6-Di-*tert*-butyl-2,3-dimethylphenol	216	....
50	$C_{18}H_{30}O$	2,4,6-Tri-*tert*-butylphenol (m.p. 131° C.)	[a]	....
51	$C_{20}H_{32}O$	2,6-Di-*tert*-butyl-4-cyclohexylphenol (m.p. 115.5° C.)	[a]	....

[a] These phenols did not form phenyl isocyanate derivatives.

Table II. Powder Diffraction Data[a]

1[b]. 4-Chlorophenyl N-phenylcarbamate

d		I/I_1
5.9		W
5.4		W
4.61	(1)	VS
4.41		W
4.28		W
4.16		W
4.05		W
3.89		M
3.71	(2)	S
3.62		VW
3.48		VW
3.18	(3)	S
3.09		M
2.99		W
2.88		VW
2.69		W
2.30		W
2.24		VW
2.19		VW
1.90		VW
1.86		VW
1.81		VW

2.[b] 2-Nitrophenol

d		I/I_1
7.5	(3)	S
6.2		VW
5.9	(2)	S
5.0		M
4.86		W
3.87		M
3.65		W
3.25D	(1)	VS
3.10		W
3.01		W
2.92		W
2.76		VW
2.64		W
2.55		W
2.47		W
2.43		VW
2.31		VW
2.26		W
2.19		VW
2.13		M
2.09		VW
2.02		VW
1.96		W
1.92		VW
1.85		W
1.82		VW
1.75		VW
1.73		W
1.64		VW

3[b]. 4-Nitrophenyl N-phenylcarbamate

d		I/I_1
21.0D		W
10.4D		W
6.3		VW
5.9		W
5.3		VW
4.94		W
4.63D	(1)	VS
4.14		M
4.03		M
3.82	(2)	VS
3.58	(3)	VS
3.47		W
3.39		W
3.32		W
3.17		W
3.05		W
3.00		VW
2.83		VW
2.70		VW
2.66		VW
2.58		W
2.47		VW
2.34		W
2.29		VW
2.24		W
2.16		VW
2.08		W
2.02		W
1.89		W
1.84		W

4. Phenyl N-phenylcarbamate

d		I/I_1
6.8		M
4.36D	(1)	VS
3.98	(2)	S
3.48D		S
3.21		S
3.09		W
2.96		W
2.71D	(3)	S
2.63		M
2.53		M
2.46		M
2.30		M
2.21		M
2.12		M
1.99		M
1.90		W
1.83		M
1.74		M
1.66		W
1.60		W
1.53		W
1.47		VW
1.41		VW
1.35		VW
1.30		VW
1.18		VW
1.10		VW
1.08		VW

5[b]. S-Phenyl N-phenylthiocarbamate

d		I/I_1
7.9	(3)	S
7.0		W
6.7		W
6.2		W
5.5		M
4.78	(1)	VS
4.56		VW
4.30	(2)	S
4.22		W
4.10		W
4.03		W
3.89		W
3.58		VW
3.33D		M
3.19		W
3.01		W
2.85		W
2.72		W
2.61		M
2.49		VW
2.41		VW
2.28		W
2.14		VW
2.09		VW
2.03		VW
1.89		VW
1.84		VW

6. 2-Methylphenyl N-phenylcarbamate

d		I/I_1
7.6		S
6.1		W
5.2	(1)	VS
4.61	(2)	VS
4.20	(3)	VS
3.62D		S
3.17		S
2.85		W
2.62		W
2.43		W
2.30		W
2.09		M
1.99		M
1.87		VW
1.67		VW
1.60		VW

7[b]. 3-Methylphenyl N-phenylcarbamate

d		I/I_1
8.2		S
7.5		VW
6.4		VW
5.3	(3)	S
5.0		VW
4.61	(2)	S
4.47		VW
4.22	(1)	VS
4.03		M
3.78		W
3.64		W
3.50		W
3.38		VW
3.29		VW
3.17		M
3.05		VW
2.89		W
2.81		W
2.68		VW
2.54		W
2.42		W
2.37		W
2.30		VW
2.25		VW
2.19		VW
2.09		VW
2.02		VW
1.96		VW

8. 4-Methylphenyl N-phenylcarbamate

d		I/I_1
4.66	(1)	VS
4.03	(2)	S
3.67	(3)	S
3.14		M
2.96		VW
2.64		W
2.33		M
1.99		VW
1.89		VW

9[b]. S-4-Methylphenyl N-phenylthiocarbamate

d		I/I_1
10.9		S
10.0		S
8.3		VW
6.7		VW
5.8		M
5.3		VW
4.86		M
4.48	(1)	VS
3.80		M
3.59	(2)	S
3.49		S
3.24		VW
3.08	(3)	S
2.99		VW
2.84		W
2.57		M
2.52		W
2.42		W
2.31		W
2.19		W
2.12		W
1.95		VW
1.92		VW
1.80		VW
1.76		VW

[a] d = interplanar spacing in Ångstroms; I/I_1 = estimated relative intensity; S = strong; M — medium; W = weak; V = very. Three strongest lines indicated in decreasing order of intensity by (1), (2), and (3). For explanation of D see text.

[b] Data obtained using a camera of 171.9-mm. effective diameter.

Table II. Powder Diffraction Data[a] (Cont'd)

10. 2-Ethylphenyl *N*-phenylcarbamate

d		I/I_1
7.9		S
6.3		M
5.4	(2)	VS
4.71		S
4.22	(1)	VS
4.07		S
3.67	(3)	S
3.20D		S
2.98		W
2.77		M
2.59		M
2.41		M
2.28		W
2.13		M
1.98		W
1.80		W
1.72		M
1.51		VW
1.44		VW
1.37		VW
1.25		VW
1.17		VW

11. 3-Ethylphenyl *N*-phenylcarbamate

d		I/I_1
7.9		S
6.2		M
5.3	(2)	S
4.63	(3)	S
4.18	(1)	VS
4.03		S
3.62		S
3.22		S
2.94		M
2.70		M
2.61		M
2.40		S
2.25		W
2.14		M
1.98		W
1.85		W
1.72		W
1.66		W
1.59		W
1.49		VW
1.42		W
1.17		VW

12. 4-Ethylphenyl *N*-phenylcarbamate

d		I/I_1
7.3		M
6.5		W
5.5		W
4.73	(2)	S
4.32	(1)	VS
3.94	(3)	S
3.58		M
3.25D		S
2.83		M
2.58		W
2.45		W
2.27		W
2.15		W
2.06		W
1.88		W
1.79		W
1.65		W
1.55		VW
1.47		VW

13. 2,3-Dimethylphenyl *N*-phenylcarbamate

d		I/I_1
7.8		M
6.2		W
5.4	(3)	S
4.66	(2)	VS
4.24	(1)	VS
3.99		M
3.68		S
3.21D		S
3.01		W
2.75		W
2.68		W
2.58		W
2.40		M
2.22		VW
2.12		M
2.06		W
1.95		VW
1.86		VW
1.78		VW
1.70		VW

14. 2,4-Dimethylphenyl *N*-phenylcarbamate

d		I/I_1
5.6		M
5.1		M
4.52	(1)	VS
4.30		M
4.05		W
3.65	(3)	M
3.31	(2)	S
3.02		W
2.76		W
2.57		W
2.43		W
2.28		VW
2.16		VW
2.04		VW
1.96		VW
1.88		VW
1.74		VW
1.66		VW

15[b]. 2,5-Dimethylphenyl *N*-phenylcarbamate

d		I/I_1
7.7	(2)	S
7.2		W
6.6		M
5.6		W
5.0		W
4.56	(3)	S
4.33	(1)	VS
4.05		S
3.91		S
3.80		W
3.60		W
3.50		M
3.44		M
3.34		M
3.25		M
3.16		W
2.99		M
2.93		W

16. 3,4-Dimethylphenyl *N*-phenylcarbamate

d		I/I_1
8.2		M
6.7		M
5.5		S
4.83	(3)	VS
4.30	(2)	VS
3.70	(1)	VS
3.38		S
3.21		M
2.89D		M
2.71		W
2.53		M
2.23		M
2.08		VW
2.00		W
1.90		M
1.82		W
1.66		VW
1.58		VW
1.22		VW

17. 3,5-Dimethylphenyl *N*-phenylcarbamate

d		I/I_1
7.7	(3)	S
5.7	(2)	S
4.76		S
4.16	(1)	VS
3.70		M
3.38		M
3.20		M
2.88		M
2.55		W
2.40		M
2.15		M
1.89D		W
1.82		W
1.72		W
1.63		W
1.43		W
1.18		VW
1.08		VW

18. 2,4,6-Trimethylphenyl *N*-phenylcarbamate

d		I/I_1
8.1		S
7.1		M
6.3		M
5.8	(2)	S
4.83	(1)	VS
4.61		W
4.03	(3)	S
3.81		S
3.59		S
3.26		M
2.91D		M
2.74		W
2.68		W
2.59		W
2.37		M
2.23		W
2.19		W
2.11		VW
1.96		W
1.83		W
1.76		VW

19. 2-*tert*-Butyl-4-chlorophenyl *N*-phenylcarbamate

d		I/I_1
8.5	(3)	S
5.5		S
4.83	(2)	VS
4.32		S
3.05	(1)	VS
3.26		M
3.02		M
2.89		M
2.68		M
2.40		VW
2.26		VW
2.08		W
1.92		W
1.81		W
1.64		VW
1.52		VW

20. 4-*tert*-Butylphenyl *N*-phenylcarbamate

d		I/I_1
7.8		M
7.4		W
6.2		M
4.56	(1)	VS
3.98	(2)	S
3.68		W
3.25	(3)	S
3.04		M
2.88		W
2.71		W
2.34		M
2.11		W
1.98		W
1.87		W
1.63		W
1.55		VW

21. 4-Methyl-2(β-methylallyl)phenyl *N*-phenylcarbamate

d		I/I_1
6.4		S
5.8		M
4.97		S
4.28	(1)	VS
3.82	(2)	S
3.34	(3)	S
3.18		W
2.96		W
2.67		W
2.51		W
2.31		M
2.23		VW
2.00D		M
1.92		M
1.81		M
1.66		W
1.59		W

22. 4-*tert*-Amylphenyl *N*-phenylcarbamate

d		I/I_1
8.1		W
6.5	(2)	S
4.59D	(1)	VS
4.36		M
3.79D	(3)	S
3.35		M
3.09		M
2.83		M
2.47		M
2.31		W
2.19		W
1.99		W
1.86		VW
1.74		VW
1.65		VW

23. 4(or 6)-*tert*-Butyl-2-methylphenyl *N*-phenylcarbamate

d		I/I_1
6.6		M
4.78D	(1)	VS
4.28		M
3.94		M
3.51	(2)	S
3.12	(3)	S
2.86		M
2.67		W
2.39		M
2.28		W
2.09		W
1.82		W
1.62		W

24. 6(or 4)-*tert*-Butyl-2-methylphenyl *N*-phenylcarbamate

d		I/I_1
7.7		VW
6.4	(1)	VS
6.2		VW
5.6		VW
4.86	(2)	VS
3.94D	(3)	VS
3.40		S
3.14		M
2.82		M
2.47		M
2.28		M
2.07		W
1.96		W
1.77		VW
1.61		VW

25[b]. 4(or 6)-*tert*-Butyl-3-methylphenyl *N*-phenylcarbamate

d		I/I_1
12.0		S
8.1		M
7.3	(3)	S
6.3		M
5.9		W
5.2		VW
4.82	(1)	VS
4.19	(2)	S
3.71		M
3.54		W
3.21		W
2.89		W

26. 2-*tert*-Butyl-4-methylphenyl *N*-phenylcarbamate

d		I/I_1
8.6		M
7.5		W
6.4		M
5.4	(3)	S
4.81	(1)	VS
4.28D		S
3.63	(2)	S
3.27		W
3.02		M
2.89		M
2.68		W
2.23		VW
2.11		W
1.90		W
1.80		W
1.66		VW
1.53		VW
1.43		VW
1.36		VW

27. 4-Phenylphenyl *N*-phenylcarbamate

d		I/I_1
8.4		M
6.9		M
5.8		M
5.0		M
4.38	(1)	VS
4.18	(2)	S
3.98	(3)	S
3.57		S
3.14		S
2.93		M
2.64		M
2.33D		M
2.11		W
1.99		W
1.84		W
1.63		VW

28. 2,6-Diacetyl-3,5-dimethylphenol

d		I/I_1
6.7D	(3)	S
5.7D		M
4.78		M
4.28		M
3.82	(2)	VS
3.39	(1)	VS
3.28		W
3.12		M
2.87		M
2.58D		M
2.41		M
2.26		M
2.15		VW
2.07		W
1.98		W
1.89		W
1.84		W
1.71		M

29. 2-Cyclohexylphenyl *N*-phenylcarbamate

d		I/I_1
6.6		M
6.1		M
4.94	(2)	S
4.26D	(1)	VS
3.55		M
3.26	(3)	M
3.10		W
2.92		W
2.61		VW
2.47		M
2.31		VW
2.13		VW
2.03		VW
1.84		VW
1.67		VW
1.62		VW

30. 4-Cyclohexylphenyl *N*-phenylcarbamate

d		I/I_1
7.8		S
6.7		S
4.47D	(1)	VS
3.98	(2)	VS
3.67		M
3.20D	(3)	S
2.97		S
2.70		M
2.53		W
2.41		M
2.32		W
2.22		M
2.11		W
1.66		M
1.61		VW
1.53		VW
1.47		VW

31. 2-*tert*-Amyl-4-methylphenyl *N*-phenylcarbamate

d		I/I_1
8.6		M
6.5		S
5.5	(3)	S
5.1	(1)	VS
4.30		S
3.65	(2)	VS
3.34		M
3.14		M
2.93		M
2.72		M
2.49		M
2.27		M
2.12		M
1.90D		M
1.84		M
1.80		M
1.66		M
1.39		VW
1.26		VW
1.22		VW
1.12		VW
1.05		VW

32. 4(or 6)-*tert*-Butyl-3-ethylphenyl *N*-phenylcarbamate

d		I/I_1
7.2	(3)	S
5.4		W
4.78	(1)	VS
4.59		M
3.99	(2)	S
3.57		M
3.37		M
3.04		M
2.68		W
2.47		VW
2.35		VW
2.25		VW
2.08		M
1.91		W
1.77		VW
1.55		VW

33. 2-*tert*-Butyl-4-ethylphenyl *N*-phenylcarbamate

d		I/I_1
7.3		M
5.7	(3)	S
4.63D	(1)	VS
4.36		S
3.81	(2)	VS
3.62		VW
3.26		M
3.04		M
2.86		VW
2.69		VW
2.55		W
2.30		M
2.22		W
2.03		M
1.95		W
1.86		M
1.78		W
1.63		VW

[a] d = interplanar spacing in Ångstroms; I/I_1 = estimated relative intensity; S = strong; M = medium; W = weak; V = very. Three strongest lines indicated in decreasing order of intensity by (1), (2), and (3). For explanation of D see text.

[b] Data obtained using a camera of 171.9-mm. effective diameter.

Table II. Powder Diffraction Data[a] (Cont'd)

34. 4(or 6)-*tert*-Butyl-2,3-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
6.7	(2)	VS
6.2		W
4.81	(1)	VS
3.90D	(3)	S
3.48		S
3.16		M
2.86		W
2.74		VW
2.61		VW
2.47		W
2.33		M
2.12		VW
2.05		VW
1.96		M
1.85		VW
1.77		VW
1.67		VW
1.61		VW
1.49		VW
1.40		VW
1.35		VW

35. 6-*tert*-Butyl-2,4-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
8.0		W
6.6	(1)	VS
5.8		M
4.83	(2)	VS
4.16	(3)	VS
3.73		S
3.26		S
3.09		S
2.92		W
2.62		W
2.47		M
2.19		S
2.07		W
1.90		M
1.78		VW
1.64		VW
1.59		VW
1.26		VW
1.17		VW
1.08		W

36. 4-*tert*-Butyl 2,5-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
8.4		M
6.5	(2)	S
5.5		W
4.71	(3)	S
4.32		W
3.86	(1)	VS
3.52		S
3.37		M
3.04		M
2.68		W
2.57		W
2.30		M
2.17		VW
2.05		W
1.87		W

37. 4-*tert*-Butyl-2,6-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
9.4		S
6.6D	(3)	VS
5.8		VW
4.83	(2)	VS
4.26	(1)	VS
3.84		VS
3.67		W
3.50		W
3.17		S
2.76		M
2.39		M
2.17		M
2.05		W
1.96		M
1.88		VW

38. 6-*tert*-Butyl-3,4-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
8.9		M
7.2	(2)	S
5.5		M
4.89		M
4.34	(1)	VS
4.00		M
3.62	(3)	S
3.40		M
3.14		M
2.82		M
2.66		W
2.52		W
2.39		W
2.21		M
2.10		M
1.96		M
1.81		M
1.71		VW
1.63		VW

39. 2,6-Diethyl-3,5-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
6.2	(2)	S
5.7		W
4.94	(1)	VS
4.41		M
3.79		S
3.62		W
3.48		W
3.19	(3)	S
2.68		W
2.46		W
2.33		W
2.17		W
1.98		W
1.91		VW
1.81		W
1.65		W
1.60		W
1.48		VW
1.28		VW
1.24		VW

40. 3,5-Diisopropyl-2-methylphenyl *N*- phenylcarbamate

d		I/I_1
6.6	(2)	S
5.7		M
4.97	(1)	VS
4.38		M
3.98		M
3.35		M
3.13	(3)	M
2.70		W
2.34		W
2.23		W
1.95		W
1.84		VW
1.63		VW
1.58		VW

41. 3,5-Diisopropyl-4-methylphenyl *N*-phenylcarbamate

d		I/I_1
8.6		M
7.6		M
6.4		S
4.89	(1)	VS
4.66		M
4.16		S
3.81	(3)	S
3.54		W
3.16	(2)	S
2.97		VW
2.72		M
2.46		W
2.24		M
2.14		W
1.97		W
1.84		W
1.77		W
1.56		VW
1.47		VW

42. 2.6-Di-*tert*-butyl-4-chlorophenol

d		I/I_1
7.5	(2)	S
6.4		M
4.78	(1)	VS
4.36	(3)	S
4.22		S
3.82		M
3.23		M
3.01		W
2.80		W
2.66		VW
2.51		W
2.39		W
2.20		M
1.92		VW
1.66		VW

43. 4,6-Di-*tert*-butyl-2-methylphenyl *N*-phenylcarbamate

d		I/I_1
7.9		M
6.4	(2)	S
5.7		M
4.86	(1)	VS
3.98	(3)	S
3.78		M
3.27		M
3.17		M
2.67D		W
2.30		W
2.19		W
2.09		W
1.94		VW
1.81		VW
1.66		VW
1.60		VW
1.48		VW

44. 4,6-Di-*tert*-butyl-3-methylphenyl *N*-phenylcarbamate

d		I/I_1
7.8		M
7.1		M
6.5		M
5.3	(2)	VS
4.47	(1)	VS
4.16		M
3.79		M
3.35	(3)	S
2.88		S
2.76		W
2.59		W
2.23		M
2.08		M
1.91		W
1.79		W
1.67		VW
1.55		VW

45[b]. 2,6-Di-*tert*-butyl-4-methylphenol

d		I/I_1
8.5	(3)	S
7.6		S
6.7		W
6.1	(1)	VS
5.8		W
5.1		S
4.66		W
4.52		VW
4.28	(2)	S
4.08		W
3.86		M
3.65		M
3.37		M
3.27		VW
3.10		W
2.92		W
2.81		M
2.75		VW
2.68		VW
2.47		W
2.30		W
2.16		W
2.10		W
2.05		M
1.95		W
1.88		W
1.82		W
1.73		VW
1.70		VW
1.59		W
1.56		VW
1.52		VW

46. 2-*tert*-Butyl-4-cyclohexylphenyl *N*-phenylcarbamate

d		I/I_1
7.5		M
7.1		W
5.7		M
4.71	(1)	VS
4.30	(2)	M
4.10		W
3.96		W
3.70		M
3.26		M
2.86	(3)	M
2.47		VW
2.32		W
2.14		W
2.05		VW
1.88		W
1.79		VW
1.60		VW
1.26		VW
1.08		VW

47. 4,6-Di-*tert*-butyl-3-ethylphenyl *N*-phenylcarbamate

d		I/I_1
8.6		S
7.4	(3)	S
6.7		M
6.1		W
5.1	(1)	VS
4.54D	(2)	S
4.24		S
3.86		S
3.48		S
3.25		S
2.79		VW
2.54		W
2.41		W
2.24		M
2.06		M
1.98		VW
1.85		VW
1.75		VW

48. 2,6-Di-*tert*-butyl 4-ethylphenol

d		I/I_1
8.3		S
6.3	(1)	VS
5.2	(3)	S
4.63		S
4.34	(2)	VS
3.73		M
3.44		M
3.22		M
2.93		M
2.52		W
2.28		M
2.10		M
2.00		W
1.87		W

49. 4,6-Di-*tert*-butyl-2,3-dimethylphenyl *N*-phenylcarbamate

d		I/I_1
8.0	(3)	VS
7.2		M
5.8		S
5.4		W
4.59	(1)	VS
4.32	(2)	VS
3.71		S
3.39		M
3.16		M
2.88		W
2.68		VW
2.48		VW
2.24		M
2.08		M
1.92		M

50. 2,4,6-Tri-*tert*-butylphenol

d		I/I_1
8.0	(3)	S
6.6		W
5.1	(1)	VS
4.49	(2)	S
3.68		M
3.29		W
2.96		W
2.76		M
2.47		M
2.29		W
2.18		W
2.02		M
1.95		W
1.81		W
1.68		W
1.60		VW
1.26		VW
1.16		VW

51. 2,6-Di-*tert*-butyl-4-cyclohexylphenol

d		I/I_1
8.7		W
6.5D		M
5.8		W
5.1	(2)	S
4.59	(1)	VS
4.18	(3)	S
4.00		VW
3.82		VW
3.47		M
3.14		W
2.82		W
2.49		M
2.33		VW
2.23		W
2.09		W
1.92		W

[a] d = interplanar spacing in Ångstroms; I/I_1 = estimated relative intensity; S = strong; M = medium; W = weak; V = very. Three strongest lines indicated in decreasing order of intensity by (1), (2), and (3). For explanation of D see text.

[b] Data obtained using a camera of 171.9-mm. effective diameter.

such instances the pertinent data in Tables I and II refer to the phenol itself and a footnote to Table I points out these exceptions. In a very few cases, the specific structure of the phenol was not known, and for these compounds an alternative structure is given in parentheses and the boiling point of the compound is indicated. For example, two mono-*tert*-butyl derivatives of *o*-cresol are probable in which the *tert*-butyl radical is in either the 4 or 6 position. To the isomer boiling at 135° C. at 20 mm., the formula 2-methyl-4(or 6)-*tert*-butylphenol was assigned, while to the one boiling at 123° C. at 20 mm. was given the formula 2-methyl-6(or 4)-*tert*-butylphenol.

Phenols which would not form aryl *N*-phenylcarbamates by reaction with phenyl isocyanate were, in general, of the type in which both positions ortho to the hydroxyl were occupied by large groups which hindered the activity of the hydroxyl hydrogen. Specifically, these were 2,6-diacetyl-3,5-dimethylphenol, 2,6-di-*tert*-butyl-4-chlorophenol, 2,6-di-*tert*-butyl-4-cyclohexylphenol, 2,4,6-tri-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, and 2,6-di-*tert*-butyl-4-ethylphenol. 2-Nitrophenol reacts only to a very limited extent with phenyl isocyanate (*6*) and for this reason the properties of its derivative are not included in this paper.

The nonreactivity of 2,6-di-*tert*-butyl substituted phenols is interesting in that it makes possible the removal of admixed 2-*tert*-butyl substituted phenols upon treatment of such mixtures with phenyl isocyanate. Advantage of this fact was taken in the preparation of 2-*tert*-butyl-4-cyclohexylphenyl-*N*-phenylcarbamate from a mixture of 2-*tert*-butyl-4-cyclohexylphenol and 2,6-di-*tert*-butyl-4-cyclohexylphenol. The aryl *N*-phenylcarbamate obtained had a sharp melting point indicating its purity, and its elementary analysis (calculated: C, 78.59; H, 8.32; found: C, 78.54; H, 8.19) indicated that only the mono-*tert*-butyl derivative reacted with the phenyl isocyanate.

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LITERATURE CITED

(1) Auwers, K., *Ber.*, 32, 17 (1899).
(2) Baeyer, A., and Seuffert, O., *Ibid.*, 34, 40 (1901).
(3) Davey, W. P., *Gen. Elec. Rev.*, 25, 565 (1922).
(4) Fichter, F., and Schetty, G., *Helv. Chim. Acta*, 20, 150 (1937).
(5) Fromm, E., and Eckard, H., *Ber.*, 56, 948 (1923).
(6) Gumpert, F., *J. prakt. Chem.*, 32, 278 (1885).
(7) Hanawalt, J. D., and Rinn, H. W., Ind. Eng. Chem., Anal. Ed., 8, 244 (1936).
(8) Hanawalt, J. D., Rinn, H. W., and Frevel, L. K., *Ibid.*, 10, 457 (1938).
(9) Hey, D. H., *J. Chem. Soc.*, 1931, 1581.
(10) Hofmann, A. W., *Ber.*, 4, 246 (1871).
(11) Kruber, O., and Schmitt, A., *Ibid.*, 64, 2270 (1931).
(12) Leuckart, R., *J. prakt. Chem.*, (2) 41, 301 (1890).
(13) Morel, A., *Bull. soc. chim.*, (3) 21, 823 (1899).
(14) Morgan, G. T., and Pettet, A. E. J., *J. Chem. Soc.*, 1931, 1124.
(15) Snape, H. L., *Ber.*, 18, 2428 (1885).
(16) Steinkopf, W., and Höpner, T., *J. prakt. Chem.*, 113, 137 (1926).
(17) Stoermer, R., and Boes, J., *Ber.*, 33, 3013 (1900).
(18) Stoermer, R., and Kahlert, B., *Ibid.*, 35, 1630 (1902).
(19) Vavon, G., and Mitchovitch, V. M., *Bull. soc. chim.*, (4) 45, 961 (1929).
(20) Weehuizen, M. F., *Rec. trav. chim.*, 37, 266 (1918).
(21) *Ibid.*, 37, 355 (1918).

Bomb Furnace for Carius Digestion

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THE oxidation of organic material in a sealed glass tube at high temperatures and pressures, as first used by Carius for the determination of halides (*1*), is still used for the determination of halides, sulfur, and nitrogen. The pressure tubes are made of heavy Jena glass or Pyrex; they are carefully flame-sealed, avoiding any strain in the glass, and are heated to temperatures as high as 300° C. in a bomb furnace. The pressure developed within the tubes is so great that they frequently explode, causing considerable damage (*2*). In carrying out halide determinations in this laboratory, there have been several such explosions. The author has therefore devised a bomb furnace in which the danger of explosion is eliminated.

In principle, the glass pressure tube is heated in an atmosphere whose pressures approximate the pressure developed within the tube. A diagram of the furnace (built by the Bigelow Boiler Works, New Haven, Conn.) is shown in Figure 1. It consists of a steel tube 70 cm. in length, 4 cm. in diameter, and closed at one end. The wall of the steel tube is 3 mm. thick. The open end has a flange measuring 13 cm. in diameter and 3 cm. in thickness, to which a cap of similar dimensions can be bolted. The cap has attached to it a steam pressure gage reading up to 910 kg. (2000 pounds), a safety valve, and a manual valve. The furnace is built to operate safely up to 910 kg. (2000 pounds) and the safety valve is adjusted to open at 700 kg. (1500 pounds). The steel tube is supported in a vertical position by a metal frame and is heated at its lower end by vertical gas burners.

To use the furnace, water is placed in the vertical steel tube to a depth of about 20 cm. The sealed glass bomb, about 25 cm. in length, is suspended by a short piece of cord tied at one end to a hook drawn out at the sealed end of the tube, and at the other end to a short metal bar laid across the mouth of the steel tube. The glass bomb must not dip into the water and must not come into contact with the wall of the steel tube. This is easily accomplished if the furnace is perfectly vertical. A gasket is placed on the flanged open end of the furnace and the cap is bolted into position. With the manual valve open, the gas burners are lighted and when the vapor starts to escape from this valve, it is closed. Heating is continued until the desired temperature is reached as estimated by the pressure on the gage. The flame is then adjusted to maintain this pressure. At the end, the flame is turned off and the furnace is allowed to cool until the pressure reading is not more than a few pounds. The manual valve is then opened and the cap is removed.

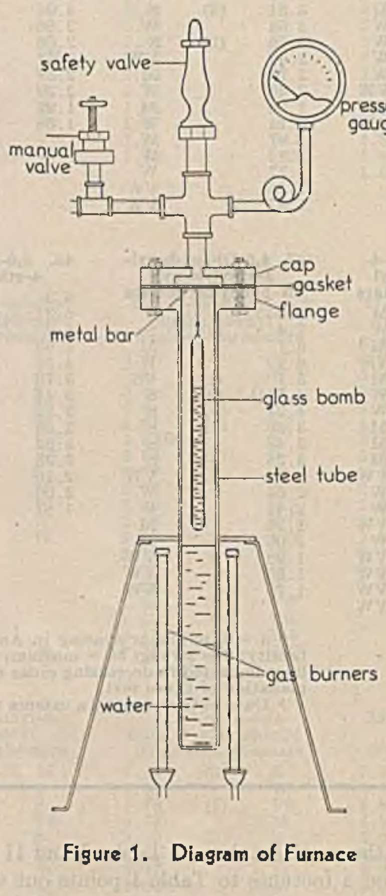

Figure 1. Diagram of Furnace

The author has carried out many Carius digestions with this furnace, using Pyrex tubes of ordinary thickness, without losing one. Although the unit illustrated holds only 1 pressure tube, a multiple unit can be easily constructed. Besides the determinations of halides, sulfur, and nitrogen, many other procedures used in laboratories, such as aminization, must be carried out in glass bombs at high temperatures. For such purposes, the type of furnace described here is useful in eliminating the danger of explosion.

LITERATURE CITED

(1) Carius, L., and Houben, J., "Die Methoden der organische Chemie", Vol. 1, pp. 59–63, Leipzig, G. Thieme, 1925.
(2) Gordon, C. L., *J. Research Natl. Bur. Standards*, 30, 107 (1943).

Direct Photometric Determination of Silicon in Copper-Base Alloys

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A new method for the direct photometric determination of silicon in copper-base alloys offers considerable advantage over the regular gravimetric method in speed and simplicity of operation. Determinations of silicon in a group of manganese bronze samples containing up to 0.15% of silicon show good agreement with results obtained by the regular gravimetric method. The optimum conditions for the development and evaluation of the silicomolybdate color complex in the presence of copper are discussed. A method for overcoming the interference of phosphorus is described.

THE usual gravimetric determination of silicon in copper-base alloys (*2*) is a rather lengthy and exacting procedure. Two dehydrations must be made to ensure complete separation of the silicon and where, as is often the case, insoluble silicides remain undecomposed after the first dehydration, these must be fused with sodium carbonate and carried through two more dehydrations. These multiple dehydrations of the large amount of salts resulting from a 5-gram sample must be made slowly and carefully to avoid spattering. Besides the time consumed by dehydration, considerably more time must be spent in filtering, igniting, weighing, and volatilizing the separated silica and reweighing the platinum crucible.

In the present emergency, when large volumes of samples must be handled daily and results reported quickly, a simpler and more rapid method for this determination is highly desirable. A photometric method seemed to offer the best possibility along these lines.

A survey of the literature revealed that practically all the proposed colorimetric methods for the determination of silicon (*17*, *20*) depend upon the formation of a silicomolybdate complex by the reaction of silicic acid and ammonium molybdate in a moderately acid solution. This method is often credited to Dienert and Wandenbulcke (*3*) in the recent literature, but the reaction was used for the colorimetric determination of silica as long ago as 1898 by Jolles and Neurath (*6*). The method in various modifications has been used for the determination of silicon in fresh water (*3*, *6*, *9*), in sea water (*13*, *18*, *19*), in boiler-feed water (*15*), in tissue (*8*), in iron and steel (*11*), and in aluminum- and magnesium-base alloys (*1*, *4*, *5*, *12*). No reference could be found to the use of this reaction for the determination of silicon in copper-base alloys.

That the reaction has not been so employed is probably due to difficulty in obtaining complete solution of the silicon when ordinary acids are used for dissolving these alloys. The thought occurred that if the samples were dissolved by adding a little hydrofluoric acid to the regular dissolving acid, and the excess hydrofluoric acid was inactivated by the addition of boric acid (*14*), it should be possible to obtain a solution of the sample which could be treated directly with ammonium molybdate to develop the silicomolybdate color complex. Experiment showed this to be true. Solution of the sample must, of course, take place in a platinum container and all contact with glass must be avoided until after the addition of the boric acid, as hydrofluoric acid attacks glassware.

Presumably the following reactions take place: Silicides are dissolved by action of the hydrofluoric acid, forming silicon tetrafluoride which reacts with water to form silicic acid and fluosilicic acid. Since the amount of silicic acid is small, it does not precipitate. The boric acid reacts with the excess hydrofluoric acid, forming fluoboric acid (*7*). Experiment has shown that the silicon in fluosilicic acid reacts with ammonium molybdate to produce the same color as an equivalent amount of silicon in silicic acid. The hydrofluoric acid also appears to form stable complexes with tin and iron when these are present in the sample, preventing the precipitation of metastannic acid and the formation of the colored iron molybdate complex noted by Thayer (*18*). Free hydrofluoric acid prevents, or greatly retards, the formation of the silicomolybdate complex.

PROPOSED METHOD

SOLUTIONS AND REAGENTS REQUIRED. Dilute Nitric Acid (1 to 2). Dilute 1 volume of reagent nitric acid with 2 volumes of water.

Hydrofluoric Acid (48%), reagent grade. Even the best grades of hydrofluoric acid appear to contain a small amount of fluosilicic acid.

Boric Acid (saturated solution). Dissolve 65 grams of reagent boric acid crystals, H_3BO_3, in 1 liter of hot water. Cool to room temperature.

Ammonium Molybdate (10%). Dissolve 100 grams of reagent ammonium molybdate crystals, $(NH_4)_6Mo_7O_{24}.4H_2O$, in hot water. Cool and dilute to 1 liter. Filter if the solution is not clear.

Citric Acid (10%). Dissolve 100 grams of reagent citric acid crystals, $C_6H_8O_7.H_2O$, in water and dilute to 1 liter.

Standard Silicate Solution (1 ml. = 0.0001 gram of silicon). Fuse 0.2141 gram of pure anhydrous silica, SiO_2, with 2 grams of sodium carbonate in a platinum crucible. Heat at slightly above fusion temperature for about 15 minutes, cool, and dissolve the melt in warm water, using a platinum dish for a container. Cool the solution and transfer to a 1000-ml. volumetric flask. Dilute to the mark and mix thoroughly. Store the solution in a wax or hard-rubber bottle.

PREPARATION OF CALIBRATION CURVE (for alloys containing up to 0.20% silicon). Weigh portions of high-purity copper equivalent to the amount of copper (±25 mg.) present in a 1-gram sample of the alloy under test. Very fine pieces of metal (35-mesh) and light, feathery drillings should be avoided, as they react too vigorously with the dissolving acid. Transfer to platinum crucibles of at least 20-ml. capacity fitted with covers. Somewhat larger crucibles are preferable if available. To each portion of metal add 10 drops of hydrofluoric acid (0.3 to 0.4 ml.) followed by an amount of dilute nitric acid (1 to 2) equivalent to 0.6 ml. for each 100 mg. of metal plus 6 ml. in excess. Cover the crucibles and let stand until the vigorous reaction has subsided, when they may be placed on the steam plate to complete solution. With the aid of a long-stemmed hard-rubber or plastic funnel, transfer the contents of the crucibles to 200-ml. volumetric flasks containing 25 ml. of boric acid solution. Rinse the crucibles and sides of the flasks and immediately swirl the flasks to mix the solutions thoroughly. From a microburet add amounts of standard silicate solution to cover the desired range of silicon in steps of 0.2 mg. Cool the solutions to room temperature and add 10 ml. of ammonium molybdate solution to each. Dilute to the mark and mix thoroughly. Let the solutions stand for 15 minutes and read the transmission or relative density of the color with a photometer at approximately 410 millimicrons. Plot the photometer readings against milligrams of silicon, or per cent of silicon. The curve approximates a straight line. Alternately, a calibration curve may be plotted by using several carefully analyzed samples of the alloy under test as standards, covering as wide a range of silicon content as possible.

While this method of calibration automatically compensates for the reagent blank, this blank may vary for different lots of reagents, and it is desirable to run either a synthetic standard or an analyzed sample of the alloy under test to determine whether or not a correction should be applied each time a new lot of reagents is used.

PROCEDURE FOR SAMPLES. Treat a 1- to 1.0050-gram sample of the alloy under test exactly as described above, omitting addition of the standard silicate solution. Read per cent silicon directly from calibration curve.

Table I. Silicon in Ounce Metal

(National Bureau of Standards Standard Sample 124, per cent composition: copper, 83.77; zinc, 5.46; tin, 4.69; lead, 4.78; iron, 0.38; nickel, 0.45; antimony, 0.23; sulfur, 0.071; phosphorus, 0.037; silicon, 0.075. Evelyn photoelectric colorimeter, filter 400)

Citric Acid Added	Colorimeter Reading	Silicon, Per Cent		Difference
		Colorimetric	B. of S. certificate	
Ml.				
0	30.75	0.086	0.075	+0.011
0	31.00	0.085	0.075	+0.010
5	35.50	0.073	0.075	−0.002
5	35.00	0.074	0.075	−0.001
5	35.00	0.074	0.075	−0.001
5	35.00	0.074	0.075	−0.001
5	34.75	0.075	0.075	0.000
5	34.50	0.076	0.075	+0.001

DISCUSSION

The method of solution causes no significant loss of silicon volatilized as silicon tetrafluoride, provided the crucibles are covered and the pieces of sample metal are not so fine as to cause an exceedingly vigorous reaction which would bring the metal to the surface of the solution. Samples of silicon bronze containing as high as 15 mg. of silicon have been dissolved in this way with no significant loss of silicon.

The amount of hydrofluoric acid added in dissolving the sample should be kept to the minimum necessary for complete solution of the silicon (and tin if present); 0.3 to 0.4 ml. is ample for amounts of silicon up to 15 mg. This amount of hydrofluoric acid (48% reagent grade) may contain as much as 0.1 mg. of silicon as fluosilicic acid.

The amount of boric acid solution used is not critical, provided enough is present to react with the excess hydrofluoric acid. Using the technique described in the proposed method, 25 ml. of a saturated solution of boric acid are ample for inactivating the excess hydrofluoric acid. If desired, 1 gram of dry boric acid crystals may be added directly to the sample contained in the platinum crucible after solution is complete, the crucible being heated gently until the boric acid dissolves. Alternately, the solution of the sample may be mixed with a saturated boric acid solution in a platinum dish. The last two techniques obviate the necessity for using a funnel of nonsilicate material in transferring to the volumetric flask.

The amount of diluted nitric acid (1 to 2) used in dissolving the sample affects the color developed considerably; 12 to 14 ml. of acid for a 1-gram sample diluted to 200 ml. give the most intense color. The optimum pH for maximum color intensity was found to be 0.75 to 1.25, using the quinhydrone electrode. This pH is somewhat lower than has been recommended by Knudson *et al.* (*9*) but is in substantial agreement with the findings of Schwartz (*15*).

At the pH recommended, the full color of the silicomolybdate complex develops almost immediately and does not fade appreciably for at least 30 minutes.

Eight to 10 ml. of 10% ammonium molybdate solution in a total volume of 200 ml. give the maximum color development. Less molybdate retards the color development, but amounts in excess of 10 ml. do not appreciably increase the intensity of the color.

Investigation of the spectral transmittance of each of the two colored components of the copper nitrate–silicomolybdate solution showed that the maximum transmittance of the copper nitrate occurred below 430 millimicrons and that the maximum absorption of the silicomolybdate complex occurred at 410 to 420 millimicrons. These findings indicate the use of a filter which has a maximum transmission between 400 and 430 millimicrons. Schwartz and Morris (*16*) have recommended a filter transmitting in the neighborhood of 410 millimicrons for maximum sensitivity in reading the color values of silicomolybdate solutions.

The maximum sensitivity of the silicomolybdate color read at approximately 410 millimicrons is obtained when the concentration of silicon is not greater than 1.0 mg. per 100 ml. While a detailed procedure is given only for those copper-base alloys which contain not more than 0.20% silicon, and the recommended amounts of reagents are based upon a 1-gram sample diluted to 200 ml., preliminary experiments with silicon bronze alloys indicate that by suitable dilution or the use of a smaller sample to bring the concentration of the silicon into the most sensitive range, copper-base alloys containing up to 3.50% of silicon may be analyzed by this method.

A few elements other than silicon also form colored complexes with molybdic acid, notably phosphorus, germanium, and arsenic (*10*). Of these, the arsenic complex is not formed at room temperature, and germanium is a very rare constituent of copper-base alloys. Infrequently a small amount of phosphorus may occur as an impurity in copper-base alloys containing silicon. Under the analytical conditions described in the proposed method, a given amount of phosphorus develops somewhat less than half the color intensity of an equal amount of silicon. For practical purposes, amounts of phosphorus less than 0.01% appear to have no significant influence on the silicon determination. Where phosphorus is present in amounts large enough to cause interference, the colored phosphorus complex may be selectively destroyed by the addition of citric acid (*15*). Oxalic acid which has been recommended for this purpose by Schwartz (*15*) cannot be used in the presence of copper, owing to the insolubility of copper oxalate.

Table II. Silicon in Manganese Bronze

(Approximate per cent composition: copper, 60; tin, up to 2.50; iron, 1; manganese, 0.03; silicon, up to 0.15; zinc, balance. Evelyn photoelectric colorimeter, filter 400)

Sample No.	Colorimeter Reading	Silicon, Per Cent		Difference
		Colorimetric	Gravimetric	
8,194	46.50	0.050	0.050	0.000
	46.00	0.051		+0.001
13,520	36.25	0.072	0.067	+0.005
	36.75	0.070		+0.003
13,519	35.50	0.073	0.070	+0.003
	34.75	0.075		+0.005
7,725	35.25	0.074	0.071	+0.003
	35.25	0.074		+0.003
8,159	36.25	0.071	0.073	−0.002
	35.75	0.072		−0.001
4,627	34.25	0.076	0.078	−0.002
	35.25	0.074		−0.004
13,518	28.00	0.095	0.092	+0.003
	27.25	0.098		+0.006
7,721	28.75	0.093	0.093	0.000
	28.25	0.094		+0.001
8,907	26.00	0.102	0.101	+0.001
	25.00	0.106		+0.005
7,969	23.25	0.114	0.112	+0.002
	22.50	0.117		+0.005
6,952	23.25	0.114	0.113	+0.001
	23.00	0.115		+0.002
7,967	24.00	0.110	0.116	+0.006
	22.75	0.116		0.000
8,201	20.00	0.130	0.131	−0.001
	21.00	0.125		−0.006
8,167	18.50	0.140	0.133	+0.007
	18.25	0.141		+0.008
8,165	16.25	0.155	0.154	+0.001
	17.00	0.150		−0.004

To determine silicon in the presence of phosphorus, the sample is treated as described under Proposed Method until the ammonium molybdate has been added, then the sample solution is diluted to 175 ml. and let stand for 10 minutes. Five milliliters of 10% citric acid are added, diluted to the mark, and mixed thoroughly, and the color value is read at once.

Under the above conditions the phosphorus complex is bleached almost at once, while the silicon complex is not significantly affected for several minutes; 5 ml. of 10% citric acid are sufficient to destroy the color developed by 2.5 mg. of phosphorus.

Samples of National Bureau of Standards ounce metal (Standard Sample 124) containing 0.037% phosphorus and 0.075% silicon were analyzed colorimetrically for silicon, both with and without additions of citric acid. Results are shown in Table I.

RESULTS ON COMMERCIAL COPPER-BASE ALLOYS

Samples of manganese bronze, having a composition of approximately 60% copper, up to 2.50% tin, 1% iron, 0.03%

manganese, up to 0.15% silicon, and the balance zinc, were analyzed for silicon both by the regular gravimetric method using 5-gram samples and by the colorimetric method here presented. Results are shown in Table II. Good agreement between the silicon values obtained by the two methods is indicated. Individual determinations were usually reproducible within 5%. All the photometric readings were taken with an Evelyn photoelectric colorimeter, using the Evelyn No. 400 filter which has a transmission range of 380 to 430 millimicrons.

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LITERATURE CITED

(1) Aluminum Co. of America, "Chemical Analysis of Aluminum", 2nd ed., p. 64, 1941.
(2) Am. Soc. Testing Materials, "A.S.T.M. Methods of Chemical Analysis", p. 189, 1943.
(3) Dienert, F., and Wandenbulcke, F., *Compt. rend.*, 176, 1478 (1923).
(4) Dow Chemical Co., "Dowmetal Laboratory Methods", *Bull.* DM41, p. 21 (1941).
(5) Hadley, W. H., *Analyst*, 66, 468 (1941); 67, 5 (1942).
(6) Jolles, A., and Neurath, F., *Z. angew. Chem.*, 11, 315 (1898).
(7) Kendall, J., "Smith's Inorganic Chemistry", 2nd revised ed., pp. 659, 667, New York, D. Appleton-Century Co., 1937.
(8) King, E. J., *J. Biol. Chem.*, 80, 25 (1928).
(9) Knudson, H. W., Juday, C., and Meloche, V. W., Ind. Eng. Chem., Anal. Ed., 12, 270 (1940).
(10) Krumholz, P., *Z. anorg. allgem. Chem.*, 212, 91 (1933).
(11) Pinsl, H., *Arch. Eisenhüttenw.*, 9, 223 (1935).
(12) Pinsl, H., *Z. Metallkunde*, 27, 107 (1935).
(13) Robinson, R. J., and Spoor, H. J., Ind. Eng. Chem., Anal. Ed., 8, 455 (1936).
(14) Schrenk, W. T., and Ode, W. H., *Ibid.*, 1, 201 (1929).
(15) Schwartz, M. C., *Ibid.*, 6, 364 (1934); 14, 893 (1942).
(16) Schwartz, M. C., and Morris, L. W., *Ibid.*, 15, 20 (1943).
(17) Snell and Snell, "Colorimetric Methods of Analysis", Vol. 1, 2nd ed., p. 517, New York, D. Van Nostrand Co., 1936.
(18) Thayer, L., Ind. Eng. Chem., Anal. Ed., 2, 276 (1930).
(19) Thompson, T., and Houlton, H., *Ibid.*, 5, 417 (1933).
(20) Yoe, J. H., "Photometric Chemical Analysis", Vol. 1, p. 366, New York, John Wiley & Sons, 1928.

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Determination of Germanium in Steel

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A gravimetric method for the analysis of germanium in steel which is free from any known interference, consists of separation of germanium by distillation of the tetrachloride, precipitation of germanium in the distillate with tannin, and ignition to the oxide. This method yielded entirely satisfactory results, the average error being of the order of 0.001% in steels containing up to 0.5% of germanium. Using synthetic standards, it was shown to be applicable to steels containing up to 0.5% of germanium, or up to 5% of germanium if a 1-gram sample is used instead of 10 grams. With a single distillation apparatus, an average of four determinations a day can be completed.

DURING an investigation at the Naval Research Laboratory, it was necessary to analyze several samples of steel for germanium. No method for the determination of germanium in steel was found in the literature; however, by suitable modifications of the methods given for the analysis of residues and ashes, it was possible to work out a satisfactory method for determining moderate amounts of germanium in steel.

The most convenient method for the separation of germanium from practically all other elements normally present in steel is distillation of germanium tetrachloride from a hydrochloric acid solution; this method was devised by Buchanan (5) for separating germanium from germaniferous zinc oxide residues. Tin and arsenic may be expected to accompany germanium into the distillate, but contamination by tin can be avoided by adding sulfuric acid to the solution before distillation (9). Contamination by arsenic can be completely eliminated through the method of Dennis and Johnson (7) by distilling in a current of chlorine and using an efficient still head. Under these conditions arsenic trichloride is oxidized to the less volatile pentachloride and a separation from germanium may be obtained.

However, the separation of germanium from moderate amounts of arsenic is unnecessary, since Davies and Morgan (6) have shown that germanium may be satisfactorily determined in the presence of arsenic by precipitation of the former with tannic acid. The oldest gravimetric method for germanium is Winkler's, in which germanium sulfide is precipitated from strong acid solution, treated with nitric acid, and ignited to the oxide (*13*). Because of the danger of loss in this procedure, Johnson and Dennis (*11*) prefer to dissolve the sulfide in ammonium hydroxide and then to oxidize with hydrogen peroxide; in either case, complete precipitation of germanium as the sulfide requires 24 hours or longer, and arsenic is also precipitated. Other methods are precipitation of the 8-hydroxyquinolate of germanomolybdic acid (*3*, *4*) and colorimetric determination of the blue reduction product obtained by treating germanomolybdic acid with ferrous sulfate (*10*). The colorimetric method is subject to interferences from traces of arsenic, silica, and phosphorus.

Preliminary work indicated the superiority of the tannin method over other published procedures for the determination of germanium. Slow evaporation to dryness of a pure germanium solution containing hydrofluoric, hydrochloric, perchloric, and sulfuric acids, followed by ignition to the oxide (*2*) gave accurate results in this laboratory, but was too time-consuming. Determination of germanium by precipitation and weighing as magnesium orthogermanate (*12*) gave high results in preliminary experiments, as has been noted by others (*6*).

It seemed best to separate germanium, with a small amount of arsenic, from the other elements present in steel by distillation from a solution containing hydrochloric and sulfuric acids, and then to precipitate the germanium in the distillate with tannic acid.

EXPERIMENTAL

Mixtures of 10 grams of various germanium-free steels with weighed amounts of Adam Hilger's "spectroscopically standardized" grade of germanium metal, ground to pass a 100-mesh sieve, were analyzed by the procedure described below. The results obtained are shown in Table I.

The germanium-bearing steels under investigation were analyzed by the same method (Table II).

RECOMMENDED PROCEDURE

Transfer 10.00 grams of the germanium steel sample to a 500-ml. round-bottomed flask with standard taper neck and add a mixture of 10 ml. of nitric acid and 100 ml. of 1 to 4 sulfuric acid. When most of the action has ceased, boil the mixture

Table I. Analysis of Steel-Germanium Mixtures

(100-mesh metallic germanium + 10 grams of steel)

Germanium Taken Gram	Germanium Found Gram	Error Gram
0.0024	0.0022	−0.0002
0.0051	0.0051	0.0000
0.0051	0.0053	+0.0002
0.0127	0.0128	+0.0001
0.0178	0.0177	−0.0001
0.0259	0.0259	0.0000
0.0401	0.0402	+0.0001
0.0466	0.0464	−0.0002
0.0510	0.0511	+0.0001
	Av.	0.0001

Table II. Analysis of Germanium Steels

Sample	Germanium Added to Steel during Melting, Approximate %	Germanium Found %
GHB	0.053	0.051 0.052 0.053
GHC	0.11	0.102 0.102
GHD	0.17	0.161 0.162 0.160 0.161 0.161

gently for 30 minutes to ensure complete solution of the germanium. Cool somewhat and add 5 grams of copper turnings to destroy the excess of nitric acid. Boil 3 minutes to expel oxides of nitrogen.

Wash down the inside of the flask with enough water to make the total volume about 150 ml., and cool the solution in an ice bath. Add 200 ml. of hydrochloric acid and immediately connect to the distilling apparatus (Figure 1). An efficient fractionating device, the Widmer column, is included in the distilling apparatus in order to minimize contamination by higher-boiling metal chlorides. Details of the construction of the column are given by Adkins and McElvain (*1*). Two precautions are taken against suck-back during distillation: a pressure-equalization pinchcock, *C*, is provided at the top of the fractionating column and a safety bulb, *B*, 5 cm. (2 inches) in diameter is included in the adapter.

Start the distillation, adjusting the rate of heating so that the constant-boiling hydrochloric acid distills over at the rate of one drop in about 5 seconds, and collect 20 to 30 ml. of distillate in 100 ml. of ice-cold water in the receiver. Nearly all the germanium tetrachloride (b.p. 86° C.) comes over before any of the constant-boiling acid.

Disconnect the apparatus, wash the adapter with a jet of water, and add 2 grams of hydroxylamine hydrochloride to the distillate to reduce any oxidizing substances. With stirring, add 30 ml. of a fresh 5% tannin solution, and then a few drops of methyl red indicator. Add ammonia until the solution is alkaline, then make it barely acid by dropwise additions of sulfuric acid and add 10 drops in excess. Davies and Morgan (*6*) state that acidity as high as 1.0 *N* sulfuric acid is permissible. The 10-drop excess in a volume of 200 ml. gives an acidity of about 0.08 *N*, which seems to be well within the safe limits. Heat the mixture to incipient boiling and allow to stand until the flocculent precipitate has settled and the solution is cool.

Filter the precipitate through a 15-cm. No. 40 Whatman paper, washing until completely free of chlorides with a wash water containing 50 grams of ammonium nitrate, 5 grams of tannin, and 5 ml. of nitric acid per liter. Ignite cautiously at first in a weighed platinum crucible, then at 600° C. for about an hour. Allow to cool, treat with 5 drops of sulfuric acid and 3 ml. of nitric acid, and evaporate to dryness to destroy most of the remaining carbon. Ignite again below 600° C. until all carbon is burned off and finally ignite the white residue at 900° to 1000° C. for 10 minutes and weigh as germanium dioxide.

Correct for the weight of a blank obtained by carrying 10 grams of germanium-free steel through the procedure, and multiply the weight of germanium dioxide in grams by 6.941 to obtain the percentage of germanium in the steel.

DISCUSSION

Preliminary work showed that hydrochloric acid could be substituted for sulfuric acid in the tannin precipitation procedure, and that considerable variations in the amounts of hydrochloric and nitric acids present in the distillate caused no difficulty.

Entirely satisfactory results were obtained through the use of the recommended procedure, which gave a reproducibility of 0.002% in comparison with another recent method for germanium (*4*), the reproducibility of which is stated as 0.02%; but extreme care must be taken to wash the precipitate completely free of chlorides, or loss of germanium will occur upon ignition.

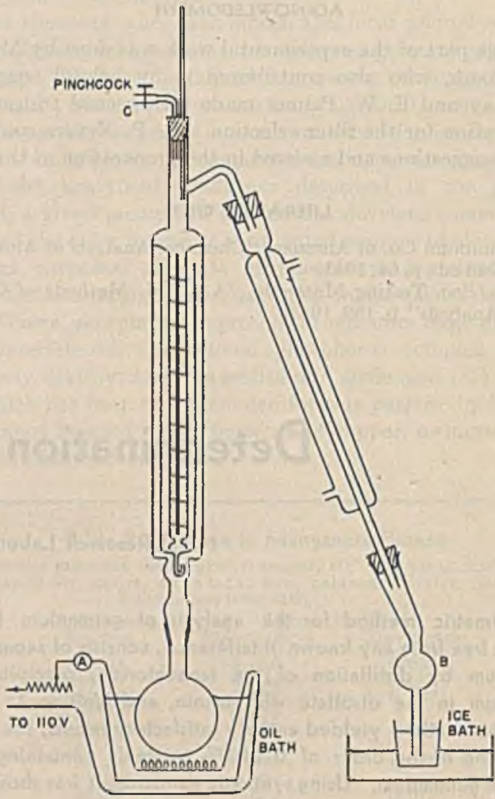

Figure 1. Distilling Apparatus

The ignition must be performed at 900° to 1000° C. Above this range, germanium dioxide begins to volatilize; below it, results are too high, perhaps because of incomplete decomposition of germanium sulfate.

Germanium tetrachloride vapors are reported to be difficult to condense (*2, 8*). Several trials were made for the purpose of determining whether germanium was lost because of incomplete condensation, but no germanium was ever found in the wash water of a Milligan gas-washing bottle through which the gases were led after bubbling through the ice water.

An effort was made to determine whether any germanium was present in the insoluble residue remaining after solution and distillation of a germanium steel.

This insoluble residue was filtered off, washed thoroughly first with hot 1 to 9 hydrochloric acid and finally with hot water, ignited, and fused with sodium carbonate and sodium nitrate. The melt was dissolved in water and then acidified with sulfuric acid, 200 ml. of hydrochloric acid were added, and the solution was distilled and analyzed for germanium as usual. With a 10-gram sample of steel GHD, no germanium was found in the acid-insoluble residue. When 50-gram samples were treated in the same manner, GHB was found to contain 0.002% and GHC 0.003% of acid-insoluble germanium.

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LITERATURE CITED

(1) Adkins, H., and McElvain, S. M., "Practice of Organic Chemistry", p. 102, New York, McGraw-Hill Book Co., 1933.

(2) Aitkenhead, W. C., and Middleton, A. R., Ind. Eng. Chem., Anal. Ed., 10, 633–5 (1938).

(3) Alimarin, I. P., and Alekseeva, O. A., *J. Applied Chem.* (U.S.S.R.), 12, 1900 (1939).

(4) Alimarin, I. P., Ivanov-Emin, B. N., Medvedeva, O. A., and Yanovskaya, C. Y., *Zavodskaya Lab.*, 9, 271 (1940).

(5) Buchanan, G. H., J. Ind. Eng. Chem., 8, 585 (1916); 9, 661 (1917).

(6) Davies, G. R., and Morgan, G. T., *Analyst*, 63, 388–93 (1938).

(7) Dennis, L. M., and Johnson, E. B., *J. Am. Chem. Soc.*, 45, 1380 (1923).

(8) Foster, L. S., Drenan, J. W., and Williston, A. F., *Ibid.*, 64, 3042 (1942).

(9) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis", pp. 233–4, New York, John Wiley & Sons, 1929.

(10) Hybbinette, A.-G., and Sandell, E. B., Ind. Eng. Chem., Anal. Ed., 14, 715 (1942).

(11) Johnson, E. B., and Dennis, L. M., *J. Am. Chem. Soc.*, 47, 790 (1925).

(12) Müller, J. H., *Ibid.*, 44, 2493 (1922).

(13) Winkler, C., *J. prakt. Chem.*, 142, 228 (1886).

Determination of Magnesia in Magnesite and Dolomite

A Potentiometric Method

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The magnesia content of magnesites and dolomites may be determined by potentiometric titration, using a glass electrode. Excess acid present on solution of the sample is neutralized with analytical reagent calcium carbonate. The titration is made in a hot 50% solution of alcohol, with standard carbonate-free caustic. Weak bases such as iron, aluminum, and titanium normally present in magnesite and dolomite do not interfere. The method attains an accuracy which compares favorably with that of the ammonium phosphate procedure for magnesium and is much less time-consuming.

THE determination of magnesia in magnesite and dolomite by precipitation as magnesium ammonium phosphate is tedious and time-consuming. Hildebrand and Harned (*1*) attempted to determine magnesia in limestone potentiometrically by means of a hydrogen electrode. Zhukov and Gortikov (*3*) and Treadwell and Bernasconi (*2*) investigated a potentiometric system for estimating magnesia, employing antimony as the indicator electrode.

The potentiometric method described in this paper makes use of a glass electrode–saturated calomel system. The magnesium salt is titrated in a hot 50% solution of alcohol with standard sodium hydroxide. The excess acid normally present after solution of the sample is neutralized with carbonate-free caustic or with analytical reagent calcium carbonate. The latter markedly minimizes the error due to weak bases. All titrations are made using a Leitz Titrimeter Model G & D. No absolute potential values are listed in this investigation.

REAGENTS

Standard sodium hydroxide (carbonate-free), 1.054 *N*. Standard magnesium chloride solution (10.554 grams of pure magnesium per liter). Calcium carbonate, analytical reagent. Thymolphthalein indicator, 0.1% alcoholic solution. Ethyl alcohol, 95%.

PROCEDURE

Weigh a 2.000-gram sample into a 400-ml. beaker, add 20 ml. of 1 to 1 perchloric acid, cover the beaker with a Speedyvap watch glass, and take to dryness on a hot plate. Add 100 ml. of distilled water and 10 drops of concentrated hydrochloric acid, boil briefly to aid in dissolving the salts, and add analytical reagent calcium carbonate to neutralize the free hydrochloric acid, finally boiling to remove the excess carbon dioxide. (If sodium hydroxide is used, neutralize electrometrically at room temperature.) Add 100 ml. of ethyl alcohol and 2 ml. of thymolphthalein indicator, and transfer to the electrometric titrator, keeping the solution near boiling with the aid of an electric hot plate. Turn on the mechanical stirrer and add a few milliliters of standard hydroxide. Permit the solution to come to equilibrium and adjust the titrator, using the maximum sensitivity. Continue the titration.

The addition of the remainder of the sodium hydroxide affects the galvanometer reading only slightly until the end point is reached. The thymolphthalein indicator warns of the nearness of the end point by turning a deep blue. Add the titrant in 0.1-ml. portions near the end of the titration for most satisfactory results. The greatest deflection of the galvanometer for an addition of 0.1 ml. of titrant may be taken as the end point. If more accuracy is desired, a graph of the end point may be made. The latter method was employed in this paper.

DISCUSSION

Table I shows the standardization of a carbonate-free caustic solution using a standard magnesium chloride solution, which was prepared from pure magnesium metal dissolved in dilute hydrochloric acid. By this method, the caustic was found to be 1.054 *N*. Standardized against c.p. potassium acid phthalate, its normality was 1.053. The results in this paper are based on the former value.

The excess hydrochloric acid is neutralized potentiometrically, prior to the titration of the magnesium ion, by the use of a carbonate-free sodium hydroxide solution or by the addition of a slight excess of analytical reagent calcium carbonate. The latter reagent proved superior and is considered standard for this procedure.

Table II shows that stick antimony may be used as the indicator electrode without interference from the calcium ion in the titration of magnesium chloride solutions. While results re-

Table I. Potentiometric Standardization of a Caustic Solution (Carbonate-Free)

(Showing effect of calcium on glass indicator electrodes. Magnesium present, 0.5277 gram)

Caustic Used, Ml.	Indicator Electrode	Neutralizing Reagent
41.17	Antimony	Sodium hydroxide
41.22	Antimony	Sodium hydroxide
41.08	Antimony	Sodium hydroxide
41.18	Antimony	Sodium hydroxide
41.22	Glass	Sodium hydroxide
41.26	Glass	Sodium hydroxide
41.18	Glass	Sodium hydroxide
41.13	Glass	Calcium carbonate
41.20	Glass	Calcium carbonate
41.20	Glass	Calcium carbonate
41.15	Glass	Calcium carbonate
41.20	Glass	Calcium carbonate
41.20	Glass	Calcium carbonate
41.20	Glass	Calcium carbonate

Table II. Electrometric Titration of Magnesium Chloride[a]

(In the presence of calcium chloride, using antimony as the indicator electrode, magnesium present, 0.5277 gram)

Calcium Present Gram	Magnesium Recovered Gram	Magnesium Error Gram
0.200	0.5289	+0.0012
0.200	0.5277	0.0000
0.200	0.5279	+0.0002
0.400	0.5277	0.0000
0.400	0.5279	+0.0002
0.400	0.5277	0.0000
0.600	0.5279	+0.0002
0.600	0.5277	0.0000
0.600	0.5277	0.0000

[a] Excess hydrochloric acid present neutralized electrometrically with carbonate-free sodium hydroxide.

corded in this table are excellent, the antimony indicator electrode frequently shows a tendency to drift at the end point. It gives unreliable results (not cited) in the presence of certain other ions studied in this investigation.

The analytical reagent calcium carbonate effectively precipitates the weak bases of titanium, aluminum, and ferric iron, making possible the direct titration of magnesium. In most instances, it is not necessary to filter the solution after neutralization with calcium carbonate. If this becomes necessary, however, the weak bases precipitated in this manner usually filter well, even permitting the use of suction. Appreciable amounts of aluminum, sulfate, or phosphate ions make filtration necessary. The phosphates normally occurring in magnesite and dolomite have no deleterious effect on the final results. Perchlorate, nitrate, and chromate ions are without influence if the determination is made using a glass indicator electrode. If manganese is present in quantities greater than 5 mg., it must be oxidized to manganese dioxide by the addition of bromine water. After neutralization with calcium carbonate, the solution is boiled until the excess bromine is removed.

Table III. Effect of Metallic Ions on Potentiometric Estimation of Magnesium (as Chloride) Using a Glass Electrode

(Magnesium present, 0.5277 gram)

Iron Present Gram	Aluminum Present Gram	Manganese Present Gram	Titanium Present Gram	Chromium Present Gram	Magnesium Found Gram
0.001	....	....	....	...	0.5277
0.001[a]	....	....	....	...	0.5277
0.005	....	....	....	...	0.5281
0.005[a]	....	....	....	...	0.5277
0.010	....	....	....	...	0.5270
0.010[a]	....	....	....	...	0.5274
0.025	....	....	....	...	0.5268
0.050[a]	....	....	....	...	0.5284
0.050	....	....	....	...	0.5289
...	0.005	....	....	...	0.5270
...	0.010	....	....	...	0.5277
...	0.015	....	....	...	0.5270
...	0.020	....	....	...	0.5277
...	0.020	....	....	...	0.5264
...	0.025	....	....	...	0.5264
...	0.025	....	....	...	0.5251
...	....	0.0011	....	...	0.5264
...	....	0.0022	....	...	0.5272
...	....	0.0055	....	...	0.5283
...	....	0.0110	....	...	0.5328
...	....	0.0110[b]	....	...	0.5264
...	....	0.0100[b]	....	...	0.5277
...	....	0.0100[b]	....	...	0.5277
...	....	0.0100[b]	....	...	0.5289
...	....	....	0.005	...	0.5277
...	....	....	0.010	...	0.5277
...	....	....	0.025	...	0.5277
...	....	....	....	0.002	0.5289
...	....	....	....	0.005[a]	0.5277
...	....	....	....	0.010	0.5280
0.005	0.0003	....	0.0001	...	0.5277
0.005	0.0005	....	0.0010	...	0.5267
0.010	0.0025	....	0.0010	...	0.5277
0.010	0.0050	....	0.0050	...	0.5277
0.025	0.0125	....	0.0100	...	0.5277
0.025	0.0050	0.002	0.0050	0.002	0.5277
0.025	0.0050	0.002	0.0050	0.002	0.5277

[a] Excess hydrochloric acid neutralized with standard caustic (carbonate-free) using electrometric titrator. Analytical reagent calcium carbonate used to neutralize all other samples.

[b] Manganese oxidized with bromine water. Calcium carbonate then added and excess bromine removed by boiling.

Table III shows the effect of individual elements on the determination of magnesium. The results are based on a differential electrometric end point, which appears to give greater precision and accuracy than titrating to a given value on the galvanometer scale, as is often recommended.

Table IV shows a comparison of potentiometric and gravimetric (magnesium ammonium phosphate) results for magnesia in a series of magnesite samples. The fourth column records the total percentage for all elements found in a sample of magnesite with which the gravimetric value for magnesia was used and the fifth column represents the total percentage using the potentiometric value.

It is believed that the accuracy of this method compares favorably with that of the ammonium phosphate procedure for magnesia. The time required to make a single determination or a series of analyses is greatly reduced. In general, it is not essential to make a separation from elements commonly associated with magnesite and dolomite.

Table IV. Potentiometric and Gravimetric (Magnesium Ammonium Phosphate) Results on Magnesite Samples

Sample No.	Magnesia Found		Total for Magnesite Analysis	
	Gravimetric %	Electrometric %	Gravimetric %	Electrometric %
1	46.10	46.19	99.60	99.69
2	45.90	46.37	99.30	99.77
3	46.20	46.13	100.04	99.97
4	46.40	46.34	99.70	99.64
5	46.10	46.13	99.90	99.93
6	46.10	46.25	99.90	100.05

Bureau of Standards dolomite sample 88 was dissolved in hydrochloric acid and the magnesium content determined potentiometrically. Values of 21.55 and 21.50% magnesia were obtained. This checks well against the Bureau of Standards value of 21.48% magnesia.

Most precipitated calcium carbonates contain quantities of magnesia which would lead to high results. Therefore, it is extremely important that analytical reagent calcium carbonate be used in this procedure. Some magnesite samples dissolve slowly in hydrochloric acid; consequently it has been found best in this laboratory to dehydrate the sample with perchloric acid. Best results are obtained by titrating the sample near its boiling point in a 50% solution of alcohol. These conditions lend sharpness to the end point. Thymolphthalein indicator assists in warning of the nearness of the end point, although it is in no way essential. A few milliliters of standard caustic are added to the sample before adjusting the instrument for the titration, since a considerable change in potential occurs with the first addition of caustic. A Beckman high-temperature glass electrode, No. 8990T, is recommended.

SUMMARY

Magnesia in dolomite and magnesite may be determined directly by potentiometric titration in a hot 50% solution of alcohol. A procedure to eliminate the interference of weak bases such as ferric iron, aluminum, and titanium is described. The determination is rapid and simple, requiring but a few minutes for a single sample. The accuracy attained is comparable to that of the gravimetric ammonium phosphate method for magnesia.

LITERATURE CITED

(1) Hildebrand and Harned, *8th Intern. Congr. Applied Chem.*, 1, 217–25 (1912).
(2) Treadwell and Bernasconi, *Helv. Chim. Acta*, 13, 500–9 (1930).
(3) Zhukov and Gortikov, *J. Russ. Phys. Chem. Soc.*, 61, 2055–72 (1929).

Determination of Carbon Dioxide in Water

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An improved method for determining total carbon dioxide in water is capable of a precision of ±1 p.p.m. even in the presence of rather large amounts of interfering substances such as phosphates. It is believed that this is the best precision that can be obtained using open flasks for the titration. The method uses apparatus readily available in any laboratory, and requires no knowledge of the nature or concentration of interfering substances, except sulfides.

During the years 1931 to 1933, a number of papers (*2*, *3*, *5*, *7*, *8*, *9*) were published on the determination and interpretation of alkalinity in boiler waters. This work led to the acceptance of the evolution method of Partridge and Schroeder (*7*) for carbon dioxide as a tentative standard by the American Society for Testing Materials (*1*). The authors' experience indicates that this is the most precise method for determining carbon dioxide, but it suffers as a plant method from the fact that it is rather slow and requires special apparatus that is not easily portable nor always available. This, and the realization by steam plant operators that carbon dioxide may cause serious corrosion in condensate return lines, indicate the need for a rapid, accurate titration method requiring only apparatus readily available in any laboratory.

With the exception of the evolution method (*1*), titration methods, especially when used to determine small amounts of carbon dioxide (*8*), are defective in one or more of the following respects: (1) Indicators used do not change color at optimum pH values. (2) Titration is carried out by observing color change, and not to precise pH values. (3) Corrections due to the presence of interfering substances are uncertain.

The method described overcomes these defects by titrating the sample between two properly selected end points, acidifying and boiling off the carbon dioxide, cooling the sample, and retitrating between the same two end points. The difference between the two titrations gives the carbon dioxide in the sample. Titration between two end points is necessary to ensure the same effect of the interfering substances for the titration before and after boiling.

SELECTION OF END POINTS

Titration curves were calculated as described by Schroeder (*8*) for carbon dioxide ranging from 4.4 to 440 p.p.m. and for a mixture of 44 p.p.m. of carbon dioxide with 95 p.p.m. of phosphate, using the values of the dissociation constants for carbon dioxide and phosphoric acid selected by Latimer (*4*). Inflection points (most rapid change of pH per unit of titrant) for the bicarbonate stage in the titration were very close to pH 8.5 in the absence of phosphate. The corresponding inflection point for the carbon dioxide–phosphate mixture occurred at pH 8.8. Inflection points for the free carbon dioxide stage shifted from pH 5 at the lowest carbon dioxide concentration to pH 4 at the highest, and were practically unaffected by phosphate. Since high precision is desired for small amounts of carbon dioxide, pH values 8.5 and 5 were selected. pH values 9 and 5 are slightly better in water containing phosphates.

In order to check the selection of pH 8.5 and 5.0 as end points, a number of samples were titrated using thymol blue and bromocresol green as indicators, with the results shown in Table I. Carbon dioxide was added as sodium carbonate and phosphate as potassium monohydrogen phosphate, with other substances as shown. End points were determined by comparison with LaMotte colorimetric standards. Titrations were conducted in open flasks, but as rapidly as possible to avoid contamination from the air. The sample volume was 100 ml. In all samples except No. 11, the agreement between the known carbon dioxide in the water and that found by analysis is within ±1 p.p.m. A few samples were titrated using a glass electrode for the end-point determination. Repeated titrations differed by as much as 1 p.p.m. It is therefore believed that greater precision than ±1 p.p.m. cannot be obtained in open flasks, because of chance loss of carbon dioxide to or gain from the atmosphere.

Table I. Results of Titration from pH 8.5 to pH 5

(Using thymol blue and bromocresol green indicators)

Test No.	Known CO_2 in Water	Known PO_4 in Water	Other Substances in Water	Apparent CO_2 Unboiled sample, A	Apparent CO_2 Boiled sample, B	Net CO_2	Error
	P.p.m.	*P.p.m.*	*P.p.m.*	*P.p.m.*	*P.p.m.*	*P.p.m.*	*P.p.m.*
1	51	47.5	....	80.1	30.4	50.7	−0.3
2	25.5	23.75	....	40.2	14.9	25.3	−0.2
3	11.0	47	....	40.3	29.7	10.6	−0.4
4	5.5	33	....	20.5	16.4	4.1	−1.1
5	2.75	16.5	....	11.5	9.3	2.2	−0.55
6	5.0	47.5	71 Na_2SO_4 10 Oxalic acid 10 Citric acid	37.5	31.6	5.9	+0.9
7	6.0	47.5	71 Na_2SO_4 10 Oxalic acid 10 Citric acid	37.8	31.2	6.6	+0.6
8	6.6	47.5	71 Na_2SO_4 10 Oxalic acid 10 Citric acid	37.2	31.7	5.5	−1.1
9	6.6	47.5	71 Na_2SO_4 10 Oxalic acid 10 Citric acid	37.2	30.4	6.8	+0.2
10	11.0	...	50 Na_2SO_4	10.3	0.0	10.3	−0.7
11	516.5	...	Contamination not known	540.0	21.2	518.8	+2.3
12	7.25	...	10 ml. of 0.02 *N* NaOH 209 p.p.m. $NaNH_4HPO_4 \cdot 4H_2O$	70.0	63.3	6.7	−0.55
13	44.3	6.0	2 $NaAlO_2$ 30 Na_2SO_3 12 NaCl	57.7	12.4	45.3	+1.0

Figures in column A and B corrected for the amount of acid necessary to change pure water from pH 8.5 to pH 5.0, equivalent to 0.6 p.p.m. of CO_2.

Errors caused by improper sampling and handling of the sample for analysis may greatly exceed the errors indicated above. Water samples for carbon dioxide should be analyzed promptly, and should be transferred from one vessel to another by siphoning rather than by pouring. The siphon should be immersed well below the water surface in the vessel being sampled and should deliver the sample to the bottom of the receiving vessel.

SELECTION OF INDICATORS

Because of the blue alkaline color of both thymol blue and bromocresol green, they cannot be used together in the same sample. Each determination of Table I required the titration of four samples. A search was therefore made for indicators that could be used together in the same sample, and that were sufficiently stable to resist the necessary boiling, in order that a determination could be made on a single sample. Considering only indicators showing intense color contrast, methyl red, bromocresol green, and methyl orange were selected for the pH range 4 to 5, and thymol blue, phenolphthalein, and *o*-cresolphthalein for the pH range 8 to 9. Trials of pairs of these indicators led to the selection of methyl red mixed with *o*-cresolphthalein as the best pair, with methyl red mixed with phenolphthalein as a close second choice.

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REAGENTS REQUIRED

Mixed Indicator Solution. Dissolve 0.1 gram of methyl red and 0.1 gram of *o*-cresolphthalein in 200 ml. of 50% alcohol (phenolphthalein may replace *o*-cresolphthalein).

Buffer Solution. Prepare buffer solutions for pH 8.5 and 5.0. If preferred, a pH 9.0 buffer may replace pH 8.5 buffer.

Acid. Hydrochloric or sulfuric acid, 0.02 *N*.

Base. Approximately 0.02 *N* sodium hydroxide, carbonate-free, prepared by diluting a clear, saturated solution of sodium hydroxide with well-boiled distilled water, is satisfactory. Keep in a heavily waxed bottle, protected from atmospheric contamination by a guard tube of Ascarite or soda lime.

PROCEDURE

1. Select two flasks of the size and type to be used in the titration (250-ml. Erlenmeyer flasks are satisfactory). Place 100 ml. of pH 8.5 buffer in one and 100 ml. of pH 5.0 buffer in the other, to each add 0.4 ml. of mixed methyl red–*o*-cresolphthalein indicator, and cork the flasks. After some practice, more or less indicator may be preferred, but the volume used in the buffered solutions should always be the same as that used in the sample.
2. In a third flask, add 0.4 ml. of mixed indicator to 100 ml. of the water to be tested.
3. Titrate to pH 8.5 (matching the buffered solution), using 0.02 *N* hydrochloric acid if the sample is more alkaline than pH 8.5 or 0.02 *N* sodium hydroxide if it is more acid. If sodium hydroxide is used, record the volume required as V_{1X} (see below, interfering substances in sodium hydroxide solution).
4. Titrate from pH 8.5 to pH 5 (again matching the buffered solution) with 0.02 *N* hydrochloric acid. Record the volume used as V_1.
5. Acidify by adding 20% more of the 0.02 *N* hydrochloric acid than was required for V_1, but in no case less than 5 drops of this solution. Boil the solution vigorously for 2 minutes over a strong flame.
6. Cool the flask rapidly in running water to room temperature, add 0.02 *N* sodium hydroxide until the pH is 8.5, and record the volume of base required as V_{2X}. Now titrate the sample from pH 8.5 to pH 5 with 0.02 *N* hydrochloric acid and record the volume of acid used as V_2.

INTERFERING SUBSTANCES IN SODIUM HYDROXIDE SOLUTION

The sodium hydroxide solution is used only to adjust the pH of the sample to 8.5; hence, its exact normality need not be known. However, it may contain appreciable quantities of carbon dioxide, which would be titrated by the acid, and for which corrections must be made. The magnitude of the correction is determined as follows:

To 80 ml. of carbon dioxide–free distilled water add 0.4 ml. of mixed indicator and sufficient 0.02 *N* sodium hydroxide to bring the pH to 8.5. Then titrate to pH 5 using 0.02 *N* hydrochloric acid. Let the volume of acid used be *A*. Add immediately 20 ml. of 0.02 *N* sodium hydroxide and again titrate with 0.02 *N* hydrochloric acid, noting the volume required to change the pH from 8.5 to 5. Let this volume be *B*. Disregard the volume of acid required to titrate the 20 ml. of base to pH 8.5. The volume of acid required to titrate the carbon dioxide in 1 ml. of base is then:

$$\frac{B-A}{20} = X$$

CALCULATION OF CARBON DIOXIDE

The carbon dioxide in the sample is calculated by the following formula:

$$\underset{\text{(p.p.m.)}}{CO_2} = K \times \frac{1000}{V_s} \times N\,[(V_1 - V_{1X} \times X) - (V_2 - V_{2X} \times X)]$$

where K = 45.56 if the titration from pH 8.5 to 5 is used
or K = 43.95 if the titration from pH 9 to 5 is used
V_s = sample volume in ml. (usually 100 ml.)
N = normality of HCl solution
V_1, V_2 = ml. of acid required to titrate, respectively, unboiled and boiled sample from pH 8.5 to 5 (or pH 9 to 5 if these end points are used)
V_{1X}, V_{2X} = ml. of base used to adjust unboiled and boiled sample, respectively, to pH 8.5 (or 9)
X = ml. of acid required to titrate CO_2 in 1 ml. of base from pH 8.5 to 5 (pH 9 to 5)

The numerical value of *K* differs slightly from 44.01 (the molecular weight of carbon dioxide) since not exactly one equivalent of carbon dioxide is titrated between the pH values chosen (*3*, *5*). To calculate *K* for a pH range other than those given above, the later tables of McKinney (*6*) should be used.

In many water supplies, the concentration of interfering substances remains practically constant, as evidenced by the constancy of the titration on the sample after expulsion of the carbon dioxide by boiling. In such cases, titration of the boiled sample need only be run often enough to determine $(V_2 - V_{2X} \times X)$ in the formula above. The time required to run a single complete test is approximately 10 minutes. When a series of tests is run, the average time per determination is approximately 5 minutes, since a second sample may be titrated while the first is boiling and cooling.

ACID GASES OTHER THAN CARBON DIOXIDE

Water supplies may be encountered containing sulfur dioxide or hydrogen sulfide or their salts. In the pH range 8.5 to 5, sulfites are titrated from SO_3^{--} to HSO_3^- and sulfides are titrated from HS^- to H_2S. Sulfites, at the low concentrations used in industrial water treatment, do not interfere with the carbon dioxide determination, as is indicated by sample 13, Table I. This is as expected, since the solubility of sulfur dioxide, corrected for ionization, is about 40 times that of carbon dioxide and in addition only approximately 5% of the sulfur dioxide is in the un-ionized form at pH 3 (the approximate pH at which the carbon dioxide is boiled off). The sulfur dioxide is therefore not boiled off and is properly accounted for by the titration after boiling.

The properties of hydrogen sulfide are similar to those of carbon dioxide. Its solubility is approximately 3 times that of carbon dioxide and at pH 3 it is practically all in molecular form. Hence, it will be boiled off with the carbon dioxide, thus causing high results by the present method. The results may be corrected for hydrogen sulfide by the following procedure.

Collect the distillate from step 5 of the procedure in cadmium chloride solution and determine hydrogen sulfide therein in the same manner as for sulfur in steel by the "evolution method". Correct the carbon dioxide (p.p.m.) calculated from the formula given above by subtracting

$$H_2S\text{ (p.p.m.)} \times \frac{44.01}{34.08} \times 0.9800 = H_2S\text{ (p.p.m.)} \times 1.266$$

if the titration from pH 9 to 5 is used, or

$$H_2S\text{ (p.p.m.)} \times \frac{44.01}{34.08} \times 0.9618 = H_2S\text{ (p.p.m.)} \times 1.242$$

if the titration from pH 8.5 to 5 is used.

Samples containing large quantities of either hydrogen sulfide or sulfur dioxide cannot be successfully titrated by the procedure described in this paper, because of rapid reduction of the methyl red on boiling.

LITERATURE CITED

(1) Am. Soc. Testing Materials, Standards, Part III, p. 1549 (1942) (D513-38T).
(2) Collins, L. F., and Schroeder, W. C., Ind. Eng. Chem., Anal. Ed., 4, 278 (1932).
(3) Hecht, Max, and McKinney, D. S., *Power Plant Eng.*, 35, 602, 649 (June, 1931).
(4) Latimer, W. M., "Oxidation Potentials", New York, Prentice Hall, 1938.
(5) McKinney, D. S., Ind. Eng. Chem., Anal. Ed., 3, 192 (1931).
(6) McKinney, D. S., *Proc. Am. Soc. Testing Materials*, 41, 1290 (1941).
(7) Partridge, E. P., and Schroeder, W. C., Ind. Eng. Chem., Anal. Ed., 4, 271, 274 (1932).
(8) Schroeder, W. C., *Ibid.*, 5, 389 (1933).
(9) Straub, F. G., *Ibid.*, 4, 290 (1932).

Determination of Iron

A Study of the o-Phenanthroline Method

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A critical study was made of the o-phenanthroline method. The rate of color development was influenced by the order of, and time interval between, additions of reagents, temperature of solutions, type and amount of phosphate, and the length of time the solutions stood before being read in the photometer. If the reaction was adjusted with sodium citrate instead of acetate and the citrate was added after the hydroquinone and o-phenanthroline at temperatures above 20° C., iron was completely recovered.

DURING some nutrition experiments, the iron content of the rations and of individual yolks and whites of eggs was determined by the *o*-phenanthroline method (*2, 3, 4*). In this method, the ashed materials are dissolved in dilute hydrochloric acid. Sodium acetate is added to aliquots to adjust the pH to 3.5, hydroquinone to reduce the iron, and *o*-phenanthroline to develop an orange-pink color. Iron in the form of *o*-phenanthroline complex is evaluated by means of a photometer using a Corning No. 430 blue-green filter. Certain difficulties developed and a study of the method was therefore made.

EXPERIMENTAL

The addition of acetate to solutions of the ash of the materials used frequently produced turbid solutions which could not be read directly in the photometer (a Cenco Sheard-Sanford Photelometer was used). Other acetates besides sodium were tried with the same result. Cowling and Benne (*1*), working with plant ash, overcame this by adding ammonium citrate before the pH was adjusted to 3.5 by acetate. It occurred to the authors that citrate might replace the acetate in adjusting the pH and thus eliminate the turbidity. To check this hypothesis, aliquots of an acid solution of the ash of a poultry ration were adjusted to pH 3.5 with sodium acetate, sodium citrate, or potassium citrate solution. The acetate gave a cloudy solution which required centrifugation, whereas the citrates were clear. All three, however, gave correct iron values. The rate of color development with sodium citrate was the same as with the acetate but it was somewhat slower with potassium citrate.

Since sodium citrate was more satisfactory than the acetate for adjusting the pH, the range in pH over which it could be used and still retain maximum color development was ascertained. To aliquots of ashed egg white, yolk, or poultry ration, 0.5 to 22 ml. of a 25% sodium citrate solution were added and the pH and iron determined. Maximum color development occurred above pH 2.5 and it remained maximum to pH 5, which was as high as was obtained with the amounts of citrate used.

If the final solutions stood either 30 or 60 minutes before reading in the photometer, the order of addition of reagents was found to be of significance. Whenever the solution used to adjust the reaction to pH 3.5 was added first, as in the Hummel and Willard procedure (*3*), or was added second, results were inconsistent (Table I). Both the acetate and citrate behaved in the same way. If, however, both the hydroquinone and *o*-phenanthroline were added before the pH-adjusting solution, determinations checked well. The relative order in which hydroquinone and *o*-phenanthroline were added was unimportant. If solutions stood for 120 minutes, the order of addition of reagents was not critical.

The time that elapsed between the addition of the acetate and other reagents was of no consequence when iron salts by themselves were used. With solutions of ashed egg yolk and white, however, this time interval was important; the longer the interval, the less iron was determined. To investigate the possibility that the phosphorus, which was present in the materials to an appreciable extent in proportion to the iron, might have caused these low results, ferrous sulfate and sodium pyrophosphate solutions were mixed, dried on the steam bath, and ashed overnight in the muffle. Only 34% of the iron was recovered. Other salts of phosphoric acid were then investigated in a similar manner. In Table II are given the data on the recovery of iron from solutions when these salts were present in an iron-phosphorus ratio similar to that of egg white. In general, if the adjusting solution, whether acetate or citrate, was added first, poor recoveries were obtained; these were even worse with ashed samples. When the acetate or citrate was added last, recoveries were complete in the case of unashed but not ashed materials.

A possible explanation for the failure to determine the iron in the unashed solutions when the pH-adjusting solution was added first is that an iron-phosphate complex is formed which does not react with the *o*-phenanthroline. In the ashed samples, it is probable that an insoluble iron meta- or pyrophosphate is formed which does not dissolve in the dilute hydrochloric acid.

Cowling and Benne (*1*) reported that if solutions of ferrous sulfate and sodium pyrophosphate were heated in a water bath

Table I. Effect of Order of Addition of Reagents upon Iron Determination in Solutions of Ashed Egg Yolk, Egg White, and Poultry Ration

Order of Addition of Reagents			Egg Yolk				Egg White, Citrate		Poultry Rations, Citrate	
			Acetate		Citrate					
1st	2nd	3rd	30 min.	60 min.	30 min.	120 min.	30 min.	120 min.	30 min.	120 min.
			Per cent recovery of iron							
A	HQ	*o*-P	77	84	75	100	81	95	92	100
A	*o*-P	HQ	83	89	74	100	91	96	89	100
HQ	A	*o*-P	99	99	78	100	91	100	94	100
o-P	A	HQ	100	99	82	100	83	100	95	100
HQ	*o*-P	A	100	100	100	100	100	100	100	100
o-P	HQ	A	100	100	100	100	100	100	100	100

A = solution used to adjust to pH 3.5.
HQ = hydroquinone.
o-P = *o*-phenanthroline.

Table II. Effect of Phosphates upon Recovery of Iron from Ferrous Sulfate Solution

(Fe:P = 1:100, read after 30 minutes)

Phosphate	Sodium Acetate Added				Sodium Citrate Added			
	First, Unashed	Last, Unashed	First, Ashed	Last, Ashed	First, Unashed	Last, Unashed	First, Ashed	Last, Ashed
	%	%	%	%	%	%	%	%
None	100	100	100	100	100	100	98	100
$CaH_4(PO_4)_2.H_2O$	88	100	80	100	90	100	91	92
$CaHPO_4.2H_2O$	96	100	48	92	88	100	96	98
$(NH_4)H_2PO_4$	80	100	48	76	86	100	83	85
$(NH_4)_2HPO_4$	72	100	40	52	88	100	76	82
KH_2PO_4	100	100	60	88	88	100	96	97
K_2HPO_4	72	100	12	84	86	100	67	88
$NaH_2PO_4.H_2O$	80	100	24	80	83	100	79	80
$Na_2HPO_4.12H_2O$	72	100	20	100	86	100	52	74
$Na_3PO_4.12H_2O$	48	100	72	100	90	100	71	95
$Na_4P_2O_7$	...	...	...	...	88	100	52	80
$NaNH_4HPO_4.4H_2O$	...	...	...	...	90	100	55	69
H_3PO_4	...	...	...	...	88	100	52	67

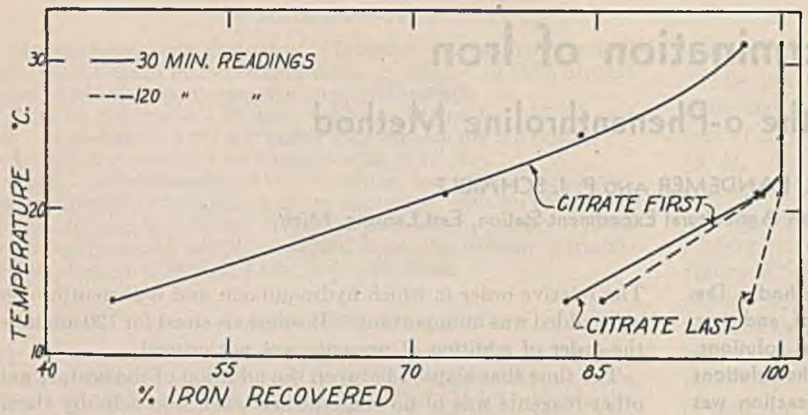

Figure 1. Effect of Temperature and Time of Standing upon Recovery of Iron from Egg White Ash

Citrate added either first or last

for one hour after the addition of the reagents, color developed completely in the presence of considerable phosphorus as pyrophosphate. But they added the acetate before the other reagents to unashed substances. The authors show in Table II that, if either acetate or citrate is added last to unashed materials, heating is unnecessary. In an additional experiment, it was determined that, with solutions of ashed materials, heating as long as 60 minutes on a steam bath did not produce maximum color when the pH-adjusting solution was added first; furthermore, the longer the interval between the addition of this solution and the other reagents, the less the color developed.

The effect of temperature of the solutions before mixing was also investigated (Figure 1). At 14° C., less than half of the iron was determined in egg white ash when the citrate was added first and over 80% when the citrate was added last. At 21° and 25° C., about 75 and 85%, respectively, were found if the citrate was added first, whereas complete recoveries were obtained if the citrate was added last. At 31° C., practically complete recoveries were obtained no matter whether the citrate was added first or last. These data were obtained from readings after the solutions stood 30 minutes. If the solutions stood 120 minutes, the order of addition of reagents was immaterial except at 14° C. Similar results were obtained with egg yolk and a poultry ration. From this it is apparent that the temperature of the room or of the solutions is an important factor in the conduct of the procedure, particularly if the adjusting solution is added first.

To find the relative effect of temperature and the amount of citrate necessary for proper pH upon the rate of color development, varying quantities of 1 to 4 hydrochloric acid were added to aliquots of a solution of an ash from a poultry ration. These aliquots were adjusted to pH 3.5 with sodium citrate and the color was developed with hydroquinone and *o*-phenanthroline. Four different temperatures were used. If readings were made after 30 minutes, at any one temperature, the greater the amounts of citrate, the less the percentage of iron determined (Figure 2). For any given concentration of citrate, the lower the temperature, the less the percentage of iron determined. In other words, those solutions that required large amounts of citrate to produce a pH of 3.5 also required a higher temperature to produce maximum color. When the solutions stood 120 minutes, except at 14° C., neither the temperature nor volume of citrate affected the recovery of iron. If the citrate is added last, these complications do not arise.

Inasmuch as individual titrations to determine the amount of citrate required to adjust the reaction to pH 3.5 slow up the procedure considerably, it was decided to find out if an average volume of citrate could be used when samples of similar materials of about the same size are analyzed. A number of samples of egg yolk of approximately the same weight were ashed, dissolved in acid, and made up to the same volume. Two aliquots of each solution were analyzed for iron. To the first was added the amount of citrate required to give pH 3.5 as determined by titration; to the second, the approximate average of the volumes of citrate required for the first aliquots. Good agreement between the two procedures was attained (Table III). The volume of citrate required for similar materials can be found by titrating about a dozen samples and using the whole number of milliliters just greater than the average of these values. This can be done because the maximum color develops over a fairly wide pH range. Much labor, therefore, can be saved if an average volume of citrate is used instead of the varying volumes found by titrations when approximately equal samples of like materials are being analyzed.

The procedure as outlined below is simple and has been found satisfactory by the authors.

REAGENTS

Iron Standard Solution (1 mg. of iron per ml.). Dissolve 1 gram of electrolytic iron in 50 ml. of 10% sulfuric acid and dilute to 1 liter with distilled water.

Table III. Comparison of Amounts of Citrate Obtained by Individual Titrations with Average of These Titrations

(Based upon determination of iron in a series of egg yolk samples

Yolk	Citrate Required	Iron Found	
		Individual titrations	Average of titration
Grams	*Ml.*	γ	γ
3.39	5.7	40.5	41.0
3.41	6.0	39.5	39.2
3.45	5.4	33.5	33.7
3.50	5.2	33.0	32.5
3.51	5.5	35.5	34.7
3.51	4.7	43.7	44.0
3.53	6.0	36.7	37.2
3.56	4.6	34.0	33.5
3.58	5.4	48.0	47.5
3.59	5.6	51.2	51.0
3.67	4.9	40.7	41.0
3.81	5.1	45.0	45.2
	Av. 5.34	40.1	40.1

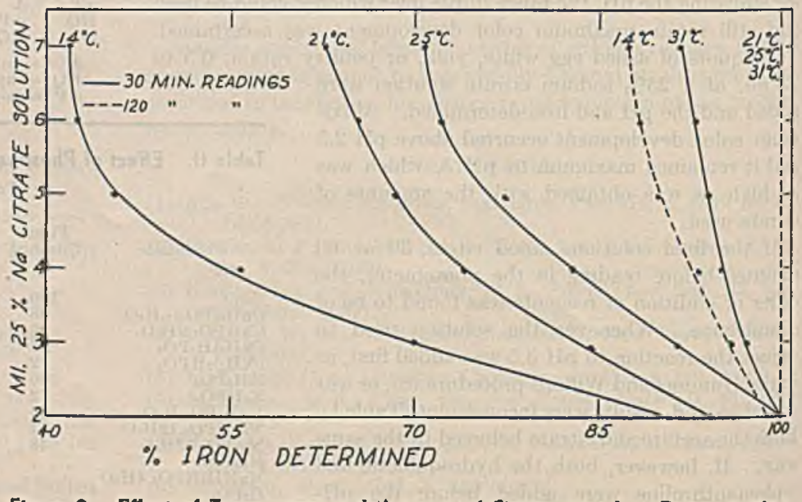

Figure 2. Effect of Temperature and Amount of Citrate upon Iron Determination

Sodium Citrate Solution. Dissolve 250 grams of sodium citrate in distilled water and make up to 1 liter.

Hydroquinone Solution. Dissolve 1 gram of hydroquinone in 100 ml. of distilled water. Store in refrigerator and discard if any color develops.

o-Phenanthroline Solution. Add 150 ml. of almost boiling distilled water to 0.5 gram of *o*-phenanthroline in a 200-ml. volumetric flask. When cool, make up to volume. Store in refrigerator and discard if any color develops.

PROCEDURE

Pipet an aliquot of the unknown solution containing an iron concentration suitable for the range of the photometer into a 25-ml. volumetric flask, add 1 ml. of the hydroquinone, 2 ml. of the *o*-phenanthroline, and the proper amount of the citrate solution, and make up to volume. Let stand 30 minutes at a temperature above 20° C. and read in the photometer, using a blank made fom the reagents in the same way for the 100 setting (this eliminates correcting for iron in the reagents). Use 1-cm. absorption cells and a 12.5-mm. No. 430 dark-shade blue-green Corning molded glass filter. Convert readings into concentrations of iron by referring to a curve made from the iron standard solution in exactly the same manner.

SUMMARY

Sodium citrate was found more satisfactory than the acetate in adjusting the reaction for the development of the color of the iron-*o*-phenanthroline complex.

If the pH was adjusted before the introduction of *o*-phenanthroline, the rate of color development was influenced by such factors as the time interval between the addition of reagents, temperature of the solutions, type and amount of phosphate present, amount of citrate, and length of time the solutions stood before being read in the photometer. If the sodium citrate was added after the hydroquinone and *o*-phenanthroline at temperatures above 20° C., these factors did not adversely affect the recovery of iron. Under these conditions, maximum color developed when the solutions stood only 30 minutes.

For samples of similar materials of approximately the same size, it was found expedient to use an average volume of citrate rather than to titrate each sample individually.

The procedure for the *o*-phenanthroline determination of iron, modified as a result of the study is presented.

LITERATURE CITED

(1) Cowling, Hale, and Benne, E. J., *J. Assoc. Official Agr. Chem.*, 25, 555 (1942).
(2) Fortune, W. B., with Mellon, M. G., IND. ENG. CHEM., ANAL. ED., 10, 60 (1938).
(3) Hummel, F. C., and Willard, H. H., *Ibid.*, 10, 13 (1938).
(4) Saywell, L. G., and Cunningham, B. B., *Ibid.*, 9, 67 (1937).

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Furfural Determination

Iodine Method for Hydrolyzed Wood Liquors

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A rapid method has been developed for the determination of furfural. It is based on the oxidation of furfural to furoic acid by iodine in alkaline solution, and with aqueous solutions of pure furfural shows excellent precision and is highly accurate. With samples that contain other iodine-consuming constituents in addition to furfural slightly high results are obtained, but the precision is satisfactory. The method is well suited for control work in which accuracy is second in importance to the rapidity with which determinations may be made.

BECAUSE of the large number of furfural analyses required for control work in the author's laboratory, a simple and rapid method with a reasonable degree of accuracy was desired. The rapid bisulfite method of Jolles (*3*) and the bromine method of Hughes-Acree (*2*), both volumetric, were not practical, owing to the nature of the samples and the specific control conditions required by the methods. The gravimetric phloroglucinol (*1*) and 2,4-dinitrophenylhydrazine (*7*) methods gave sufficiently accurate results, but were much too slow. The phloroglucinol precipitation method was found to be the most practical and was used until the development of the present procedure.

A slight excess of iodine in strongly alkaline solution reacts quantitatively with furfural. In an approximately 1 *N* sodium hydroxide solution the hypoiodite, which is formed from the iodine, oxidizes the furfural quantitatively to furoic acid. By a method based on this reaction most of the difficulties found with the other methods have been eliminated.

Pure furfural in aqueous solution can be determined accurately by this reaction. However, furfural used by the author is obtained from hydrolyzed wood liquors and is present in aqueous solution with lower boiling constituents which are termed "heads". Owing to the presence of these heads in the furfural samples, it has been necessary to devise a method that would compensate for their iodine consumption. Furfural in solution with the heads is determined by carrying out a blank reaction on each sample in slightly alkaline solution in which the iodine preferentially reacts with essentially all the heads or lower alcohols, aldehydes, etc., but with only 12.5% of the furfural present, the furfural being oxidized to furoic acid. Then by the regular sample reaction in a 1 *N* sodium hydroxide solution the iodine required by all the furfural and heads is found and thus the total furfural in the sample is calculated.

DEVELOPMENT OF METHOD

REGULAR SAMPLE REACTION. Pervier and Gortner (*6*) first tried the use of iodine in alkaline solution as a method for determining furfural. Although they gave very few details of their work, they reported that the results could not be duplicated. Later Kline and Acree (*4*) also tried iodine in alkaline solution for determining furfural according to their method for determining aldose sugars (*5*). They gave no details of their work and reported only that negative results were obtained. Although very little information on the work of the previous investigators is given in the literature, it seems that their lack of success was due mainly to use of too large furfural samples and too low an alkalinity.

In the present work it has been found that the oxidation of furfural to furoic acid by iodine in alkaline solution is a function of the alkalinity. Approximately 100 mg. of pure furfural is as large a sample as can be oxidized quantitatively, regardless of the alkali concentration. With samples of furfural much larger than this, the oxidation is not quantitative, apparently because of the rapid formation of iodate and iodide before the hypoiodite originally formed has a chance to react witb all the furfural present.

Figure 1 shows the effect of alkalinity on the oxidation of furfural to furoic acid by iodine when the reaction is carried out for 20 minutes at room temperature in a reacting volume of

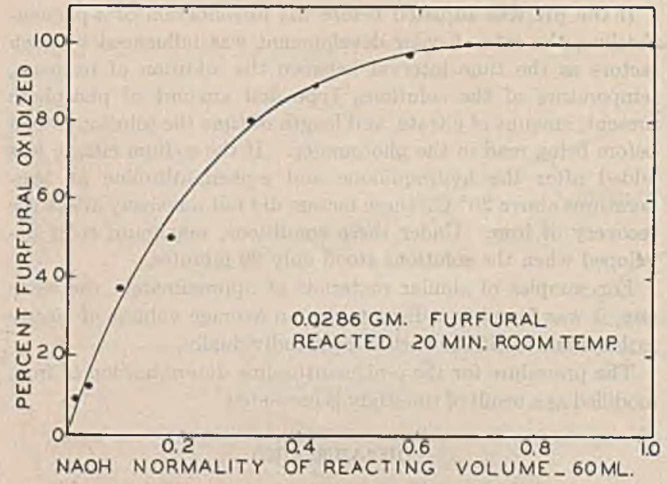

Figure 1. Effect of Alkalinity on Per Cent Furfural Oxidized

approximately 60 ml. Although the curve shows the oxidation to become quantitative when the alkalinity of the reaction mixture approaches 0.7 *N*, the conditions established for carrying out the reaction require an approximately 1 *N* sodium hydroxide solution to ensure complete oxidation. When the reaction was carried out in a 1 *N* sodium hydroxide solution a quantitative yield of furoic acid was isolated by extracting with ethyl ether and identified by melting point and mixed melting point with an authentic sample. The furfural used was redistilled and gave a purity of 100% by precipitating with phloroglucinol in 12% hydrochloric acid and by using Krober's tables.

Figure 2 gives the rate of oxidation of various concentrations of furfural when carried out at room temperature in a reacting volume of approximately 60 ml. of 1 *N* sodium hydroxide solution. The curves show that the oxidations are complete in 4 to 10 minutes, depending upon the size of the samples, and that additional time up to 30 minutes does not alter the reaction. If furfural samples as large as 100 mg. are used the time of the reaction should be increased to approximately 20 minutes to ensure complete oxidation. A slight increase in temperature does not affect the reaction other than to speed up the oxidation slightly.

BLANK REACTION. While the iodine required by the furfural is dependent upon the alkalinity, as shown in Figure 1, the iodine consumed by the heads is essentially independent of this factor. Conditions were established for the blank reaction whereby the heads consumed iodine to the same extent as they did in the regular sample reaction, and in which a consistent percentage of the furfural present was oxidized. By using 10 to 40 mg. of furfural in a reacting volume of approximately 60 ml. containing 10 ml. of 0.1 *N* iodine and the iodine equivalent of alkali or 2 ml. of *N* sodium hydroxide, 12 to 13% of the furfural is oxidized consistently. Furoic acid equivalent to an oxidation of 12.5% of the furfural has been isolated quantitatively from the reaction mixture and identified by melting points. The remaining 87.5% of furfural was shown to be left unchanged by accounting for it through precipitation with phloroglucinol in 12% hydrochloric acid.

Figure 3 gives the rate of the oxidation of furfural for various sized samples when this blank reaction is carried out at room temperature. From the curves it is seen that no further oxidation takes place after 18 to 20 minutes. A slight increase in temperature causes no change in the percentage of furfural oxidized, the only effect being to speed up the reaction slightly.

To determine the difference in the amount of iodine consumed by the heads in the blank and the sample reactions, a portion of the heads with a boiling range of 35° to 60° C. was fractionated from the crude furfural solution and 9 mg. reacted with the iodine under each set of conditions. These low-boiling heads were used as they could be obtained free of furfural and constituted the major and most reactive portion of the impurities. Table I gives these results and shows a difference of only 0.1 ml. of 0.1 *N* iodine in the amount of iodine consumed by the heads in the blank and the sample reactions under the specific conditions outlined in the method.

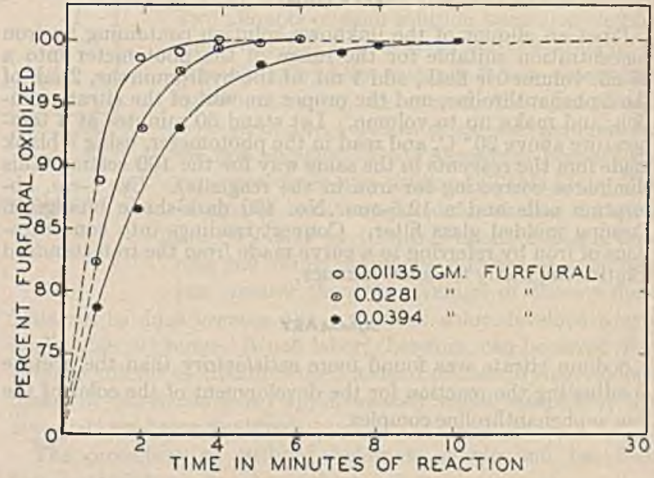

Figure 2. Rate of Sample Reaction at Room Temperature

After establishing the conditions for carrying out the blank reaction in which 12.5% of the furfural was oxidized and after showing from Table I that the iodine consumed by the impurities was essentially the same in both the blank and sample reactions, a comparison was made between the determination of furfural by this method and the phloroglucinol precipitation method. All samples were steam-distilled from their crude furfural solutions and the comparative results are given in Table II.

METHOD

Two aliquots of distillate containing 10 to 40 mg. of furfural are placed in 250-ml. wide-mouthed Erlenmeyer flasks. To these samples 4 or 5 drops of phenol red or any suitable aqueous indicator are added. One of the samples is made exactly neutral with sodium hydroxide and the other approximately so. The former is then employed as the blank and the latter as the regular sample.

Table I. Iodine Consumed by Heads (9-Mg. Sample)

Time	0.1 *N* I_2 Consumed Blank reaction	 Sample reaction
Min.	*Ml.*	*Ml.*
5	1.10	1.20
10	1.15	1.45
15	1.25	1.45
20	1.35	1.45
30	1.35	1.45

Table II. Comparison of Iodine and Phloroglucinol Precipitation Methods

Sample No.	Per Cent Furfural Phloroglucinol	 Iodine
1	3.26	3.17
2	3.45	3.40
3	3.44	3.41
4	3.23	3.13
5	3.37	3.42
6	3.50	3.53
7	2.93	2.96
8	2.46	2.46
9	3.10	3.10
10	3.10	3.06
Av.	3.18	3.16

To the blank, which is exactly neutral, are added 2 ml. of 1 *N* sodium hydroxide and then 10 ml. of 0.1 *N* iodine, the sample being swirled on addition of the iodine to ensure thorough mixing. After this addition the volume is adjusted to approximately 60 ml. with water and the solution allowed to stand at room temperature for 18 to 20 minutes.

To the regular sample, which was made approximately neutral, are added 10 ml. of approximately 6 *N* sodium hydroxide. Immediately following this, 10 ml. of 0.1 *N* iodine are added and the solution is swirled during the addition. The volume is then adjusted to 60 ml. or approximately 1 *N* with respect to the sodium hydroxide and the solution allowed to stand at room temperature for 10 to 12 minutes. It is important that the sodium hydroxide be added before the iodine, since to obtain a quantitative oxidation the alkali concentration has to be rather high at the beginning of the reaction. Otherwise, the iodine is converted to the iodate and iodide by the strong alkali before the hypoiodite initially formed has a chance to oxidize all the furfural quantitatively.

To the blank reaction, after standing 18 to 20 minutes, is added approximately 0.5 ml. of 6.5 *N* sulfuric acid. The excess iodine which is released from the iodate and iodide that has formed is titrated with 0.1 *N* sodium thiosulfate using starch indicator. The milliliters of thiosulfate are recorded as *B*.

Approximately 10 ml. or an excess of the 6.5 *N* sulfuric acid is added to the regular sample after it has stood 10 to 12 minutes and the excess iodine released is titrated with standard thiosulfate as in the blank reaction. The milliliters of thiosulfate required are recorded as *S*. The value of $B - S$ gives the milliliters of 0.1 *N* iodine required to oxidize 87.5% of the furfural present in the sample to furoic acid.

Calculation: Grams of furfural in sample =

$$\frac{(B - S) \times N \text{ of thiosulfate} \times 0.048}{0.875}$$

METHOD AS APPLIED TO DETERMINATION OF XYLOSE

To determine xylose by this method, by first converting the xylose to furfural with 12% hydrochloric acid, the regular Tollens distillation had to be modified.

Because the distillate has to be made neutral before the determination of furfural, only a 25-ml. aliquot of the acid distillate can be used, since the total reacting volume cannot exceed 60 ml. Thus it is necessary to use a larger sample of xylose than is called for in the Tollens distillation, so that the 25-ml. aliquot of the distillate will contain the appropriate amount of furfural. Xylose from the Eastman Kodak Company was used in this work and gave a purity of 100% when Krober's tables were used after the xylose had been converted to furfural by the regular Tollens distillation (*1*). In using the larger samples of xylose the following conditions were established for the conversion of the xylose to furfural in 12% hydrochloric acid.

From 0.6 to 1 gram of xylose is placed in a 1-liter balloon flask fitted with a dropping funnel and connected to a condenser by means of a Clark distilling head. Then 250 ml. of 12% hydrochloric acid are added to the xylose in the flask and distilled with an open flame at the rate of 50 ml. per 20 minutes, 50 ml. of 12% hydrochloric acid being added through the dropping funnel as 50 ml. distills over. In this manner 450 ml. of distillate are collected requiring a total time of 3 hours, the distillate is made to 500 ml., and 25-ml. aliquots are taken for furfural analysis according to method given.

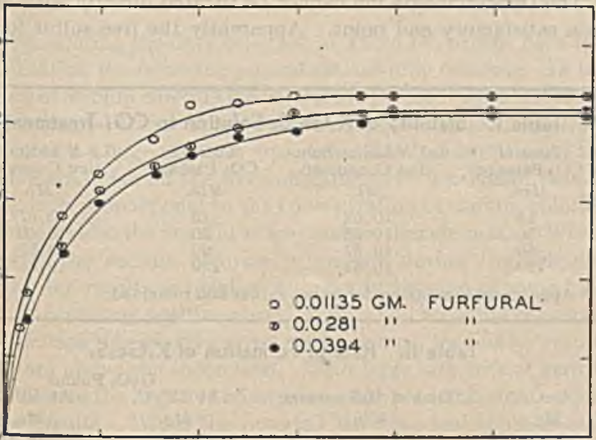

Figure 3. Rate of Blank Reaction at Room Temperature

Table III. Conversion of Xylose to Furfural by Modified Tollens Method

Xylose	Furfural Formed Phloroglucinol method	 Iodine method	Conversion Based on I_2 Method
Grams	*Gram*	*Gram*	%
0.5990	0.330	0.324	84.4
0.8702	0.485	0.472	84.6
0.8350	0.450	0.445	83.2
0.9990	0.545	0.543	84.8
0.9948	0.542	0.540	84.7
0.9950	0.544	0.534	84.3
1.0004	0.552	0.544	85.0
			Av. 84.5

By the use of the larger samples under the same conditions as employed above, the conversion of xylose to furfural is found to be 84.5% of the theoretical rather than the 88 to 89% found in the regular Tollens distillation. Thus the factor 0.54 is used to convert the furfural formed back to xylose instead of the Tollens factor of 0.57. Table III gives results for the conversion of pure xylose to furfural by this modified method.

SUMMARY AND DISCUSSION

A simple and rapid method for the determination of furfural has been developed. Furfural in pure aqueous solution can be determined accurately, by a quantitative oxidation, according to the regular sample reaction. In the presence of other iodine-consuming constituents, the method gives slightly high results but the precision is excellent. The results, even in the presence of these impurities, are slightly more accurate than with the phloroglucinol precipitation method which is considered a standard in most laboratories.

The interfering substances are in general those that will give the iodoform reaction at room temperature, although the blank reaction compensates almost quantitatively for these materials. No investigation has been made of the reaction between iodine in alkaline solution and methyl furfural or hydroxymethyl furfural. It is known, however, from the literature (*8*) that a method using iodine in alkaline solution is given as the basis for determining hydroxymethyl furfural in honey and there is little doubt but that iodine reacts with methyl furfural as well. The rapiditp and excellent precision of the method have proved very satisfactory in this laboratory since its development 4 years ago.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Assoc. Official Agr. Chem., "Official and Tentative Methods of Analysis", 4th ed., p. 344 (1935).
(2) Hughes, E. E., and Acree, S. F., Ind. Eng. Chem., Anal. Ed., 6, 123 (1934).
(3) Jolles, Adolph, *Z. anal. Chem.*, 45, 196 (1906); 46, 764 (1907).
(4) Kline, G. M., and Acree, S. F., *Bur. Standards J. Research*, 8, 25–35 (1932).
(5) Kline, G. M., and Acree, S. F., Ind. Eng. Chem., Anal. Ed., 2, 413 (1930).
(6) Pervier, N. C., and Gortner, R. A., Ind. Eng. Chem., 15, 1255 (1923).
(7) Reynolds, H., Osburn, O. L., and Werkman, C. H., *Iowa State Coll. J. Sci.*, 8, 433 (1933).
(8) Troje, E., *Z. Ver. deut. Zucker-Ind.*, 75, 635–72 (1925).

Gravimetric and Volumetric Determination of Germanium

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A volumetric method for germanium was developed, based on the quantitative formation of potassium thiogermanate in acetate-buffered solution by treatment with potassium sulfide, removal of the excess hydrogen sulfide by carbon dioxide, and titration of the sulfur with iodine. The presence of large concentrations of sodium chloride leads to both a positive and a negative error in the application of this method, depending on conditions. The negative error is due to the adsorption of the sulfide ion on the free sulfur formed by titration with iodine, while the positive error is probably connected with the formation of a higher sulfide. Germanium is quantitatively precipitated by 5,6-benzoquinoline as a complex oxalate. Although the compound cannot be weighed directly, it can be ignited to germanium dioxide, thus affording a good gravimetric method. High concentrations of sodium chloride prevent this precipitation.

WILLARD and Zuehlke (*4*) recently reported the preparation of potassium thiogermanate. This compound serves as the basis of a volumetric method for germanium. Germanium dioxide, in acetate-buffered media, may be quantitatively converted to potassium thiogermanate by treatment with hydrogen sulfide or potassium sulfide:

$$2Ge(OH)_4 + 5H_2S + 2KAc = K_2Ge_2S_5 + 2HAc + 8H_2O$$

The excess hydrogen sulfide is removed by passing a rapid stream of carbon dioxide through the solution, after which the sulfide ion is determined by treatment with an excess of standard iodine solution and back-titration with sodium thiosulfate solution:

$$K_2Ge_2S_5 + 5I_2 + 8H_2O = 5S + 2Ge(OH)_4 + 8HI + 2KI$$

REAGENTS

Germanium dioxide solution, approximately 2 grams of germanium dioxide dissolved in 1 liter of water. This solution is stable and remains perfectly clear.

Acetic acid, 2.5 molar.

Potassium sulfide solution, approximately 8 grams of potassium hydroxide dissolved in 100 ml. of water and saturated with hydrogen sulfide. The solution was cooled to 0° C. during the saturation with hydrogen sulfide to avoid formation of thiosulfate and polysulfide by atmospheric oxidation.

Standard iodine solution, approximately 0.1 *N*.

Standard sodium thiosulfate solution, approximately 0.1 *N*.

PROCEDURE

A measured aliquot of the germanium dioxide solution was transferred to a 25-cm. (10-inch) test tube and diluted to 25 ml., and 20 ml. of potassium sulfide solution were added, followed by 15 ml. of acetic acid solution. The acid was allowed to run down the side of the test tube to promote better mixing of the solution and to avoid a violent effervescence of hydrogen sulfide at the surface. The solution was allowed to stand for 5 minutes.

Carbon dioxide was bubbled through the solution rapidly by means of a delivery tube extending to the bottom of the test tube. A mechanical stirrer was used to break up the bubbles of carbon dioxide to promote more efficient removal of the excess hydrogen sulfide. Twenty minutes' passage of the gas was found to be sufficient to give a negative test for hydrogen sulfide in the issuing gases by lead acetate test paper.

The solution was transferred to a large beaker and diluted to 1 liter. A measured excess of standard iodine solution was added, allowed to stand for 15 minutes, and back-titrated with standard sodium thiosulfate solution using starch solution as an indicator. The end point may be determined to ±0.05 ml.

DISCUSSION

The success of the thiogermanate method depends upon the stability of potassium thiogermanate in acid solution. It was previously reported that a solution of potassium thiogermanate contains insufficient free sulfide ion to precipitate cobalt or nickel sulfide. The carbon dioxide treatment readily removes the excess hydrogen sulfide from solution without decomposing the thiogermanate. Further experiments were made by subjecting a solution of potassium thiogermanate to a rapid stream of carbon dioxide. Samples were withdrawn periodically and titrated with iodine to observe the decrease in sulfide-ion concentration with time. The results (Table I) show that the loss after 2 hours' treatment is negligible.

In order to attain complete reaction between hydrogen sulfide and germanium dioxide it is essential that a high concentration of sulfide ion be applied. The reaction is rapid but, nevertheless, incomplete when only the equilibrium concentration of a saturated solution of hydrogen sulfide is used. The data given in Table II were obtained by treating buffered solutions of germanium dioxide with a constant flow of hydrogen sulfide for varying periods of time. The excess hydrogen sulfide was removed and the solutions were titrated in the usual manner. Although the reaction is nearly complete after 5 minutes, quantitative combination is not attained even after 20 minutes.

The data in Table II indicate that the hydrogen sulfide-germanium dioxide system behaves as though an equilibrium is rapidly established a little short of complete reaction. Prolonged treatment with hydrogen sulfide is without beneficial effect but quantitative results are obtained when a condition of supersaturation is maintained for a short period of time by the addition of potassium sulfide.

Experiments concerned with the effect of temperature on the completeness of reaction are in agreement with this concept. Increasing the temperature decreases the solubility of hydrogen sulfide and, in general, decreases the amount of sulfur combined. Solutions of germanium dioxide buffered with acetic acid and potassium acetate were treated with hydrogen sulfide for 15 minutes at various temperatures. The amount of sulfur combined was determined in the usual manner. At 25° C. the reaction was 96% complete while at 80° C. only 65% of the germanium reacted in 15 minutes. In unbuffered solution only 70 and 11% reaction was obtained at these two temperatures, respectively.

The thiogermanate ion cannot be titrated directly with iodine to a satisfactory end point. Apparently the free sulfur formed

Table I. Stability of $K_2Ge_2S_5$ Solution to CO_2 Treatment

Time of CO_2 Passage	0.1 *N* Iodine Solution Consumed	Time of CO_2 Passage	0.1 *N* Iodine Solution Consumed
Min.	*Ml.*	*Min.*	*Ml.*
15	10.58	15	10.67[a]
30	10.58	30	10.40
60	10.57	60	10.39
120	10.51	120	10.34

[a] Apparently some excess hydrogen sulfide still remained.

Table II. Rate of Formation of $K_2Ge_2S_5$

GeO_2	Time of H_2S passage	GeO_2 Found	
		At 25° C.	At 40° C.
Mg.	*Min.*	*Mg.*	*Mg.*
48.6	5	47.9	47.7
48.6	10	48.1	48.1
48.6	15	48.3	48.5
48.6	20	48.2	

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Table III. Determination of Germanium by Thiogermanate Method

GeO_2 Taken	GeO_2 Found	GeO_2 Taken	GeO_2 Found
Mg.	*Mg.*	*Mg.*	*Mg.*
52.2	52.2	39.9	39.9
52.2	52.1	29.8	29.8
52.2	52.2	20.0	20.0
52.2	52.1	10.0	9.9
49.8	49.8		

in the reaction adsorbs some of the thiogermanate ion and thereby prevents complete reaction and leads to a fading end point. The extent of this adsorption was shown to be dependent upon the concentration of electrolyte present. By dilution to a volume of 1 liter before titration a true end point was obtained. This dilution serves not only to reduce the concentration of electrolyte but also the concentration of the thiogermanate ion in equilibrium with the free sulfur as it is formed. The amount of iodine consumed when the equivalent of 50 mg. of germanium oxide was titrated in a volume of 250 ml. rather than 1 liter was found to be about 2% less than the true value.

This method is fairly simple, requires about 1.5 hours for a single determination, and is capable under favorable conditions of yielding precise results, as is shown in Table III.

INFLUENCE OF SODIUM CHLORIDE ON THIOGERMANATE METHOD

Germanium is usually separated for analysis by distillation as the tetrachloride, or more probably, as a complex acid of the type H_2GeCl_6. Since this distillation is most efficiently carried out from constant-boiling hydrochloric acid, the final determination of germanium must frequently be made in a solution containing large amounts of chloride ion. It has already been shown that high concentrations of electrolyte lead to a false end point in the thiogermanate method. Accordingly an investigation was undertaken to determine the effect of sodium chloride on the application of this method. These experiments may be divided into three series:

1. Varying amounts of sodium chloride were added to the solution just prior to titration.
2. Varying amounts of sodium chloride were added to the solution prior to the sulfiding reaction.
3. Varying amounts of sodium chloride were added to the solution prior to the sulfiding reaction and the sulfur retained was determined by an inverse titration technique. In this procedure a solution containing an excess of iodine was diluted to about 800 ml. and the thiogermanate solution was added slowly with stirring. The sulfur was thereby formed in a solution containing very little unreacted thiogermanate ion and the sodium chloride was allowed to reach its highest concentration only at the end of the reaction. The results of these experiments are given in Table IV.

In considering the data collected in Table IV, except for a few irregularities, the following generalizations may be made. In the absence of sodium chloride the results are precise within the limits of experimental error. When sodium chloride is added just before the titration a large negative error arises due to adsorption of the thiogermanate ion on the free sulfur formed. The magnitude of this error is proportional to the concentration of sodium chloride present and also the amount of germanium dioxide taken. When, however, the sodium chloride is present during the sulfiding process, the results are higher, apparently because of some kind of a compensating positive error. With small amounts of germanium dioxide this positive error predominates, leading to results which are above the theoretical. With large amounts of germanium dioxide the negative adsorption error predominates, leading to low results. When the inverted titration technique is used the results are generally higher than those obtained by the usual method, owing to the partial elimination of the negative adsorption error.

The low results in the sodium chloride solutions are unquestionably due to an adsorption error. The high results which arise when the sodium chloride is present during the sulfiding reaction are, on the contrary, not easily explained. This positive error may be connected in some manner with the formation of a higher sulfide of the type $K_2Ge_2S_7$ (*1*), but not enough information concerning these thiogermanates is available at this time to arrive at any satisfactory conclusion.

The thiogermanate method, under favorable conditions, is capable of yielding results precise to 0.1 mg. of germanium, owing to its low equivalent weight in the thiogermanates (1 ml. of 0.1 *N* iodine solution is equivalent to 2.092 mg. of germanium dioxide, or to 1.452 mg. of elemental germanium). The scope of the method is seriously limited, however, by the sodium chloride error, since germanium is usually separated by distillation from constant-boiling hydrochloric acid. Undoubtedly many specific analytical situations do exist in which the method could be advantageously employed, particularly where the amount of germanium is low. Since germanium is frequently encountered as a minute constituent, the possibility of applying this method on the micro scale should not be overlooked.

Table IV. Effect of Sodium Chloride on Thiogermanate Method

	GeO_2 Found				
				NaCl Added before Sulfiding	
GeO_2 Taken	No NaCl added	Grams of NaCl added	NaCl added after sulfiding	Normal titration	Inverted titration
Mg.	*Mg.*		*Mg.*	*Mg.*	*Mg.*
10.0	9.9	20	...	...	10.8
		30	9.5	9.8	10.8
20.0	20.0	20	20.0	20.4	20.9
		30	18.8	20.4	20.6
29.8	29.8	20	29.3	29.7	29.6
		30	29.9	29.3	29.6
39.9	39.9	20	38.9	39.4	39.3
		30	37.9	38.8	38.8
49.9	49.8	20	48.5	48.6	49.3
		30	47.6	48.0	49.2

INTERFERING SUBSTANCES

Metals which form insoluble sulfides at a pH of 4.6 must be absent.

GRAVIMETRIC METHOD

Willard and Toribara (*3*) showed that tin forms a complex oxalate and assigned the formula $K_6Sn_2(C_2O_4)_7$ to its potassium salt. Tchakirian (*2*) attempted to prepare the analogous compound of germanium but found that the potassium salt was too unstable to isolate. He did, however, establish the existence of trioxalatogermanic acid, $H_2Ge(C_2O_4)_3$, by isolating it as the quinine and strychnine salts. It was found that 5,6-benzoquinoline also forms an insoluble derivative with trioxalagogermanic acid which shows promise as an analytical precipitant for germanium.

Reagents. Germanium dioxide solution, approximately 2 grams of germanium dioxide dissolved in 1 liter of water.

5,6-Benzoquinoline oxalate solution. Ten grams of 5,6-benzoquinoline (may be obtained from the Eastman Kodak Company) were treated with 5 grams of oxalic acid dissolved in 50 ml. of water. The suspension was heated to promote solution of the base, filtered while hot, and diluted to 500 ml.

Experimental. Measured aliquots of the germanium dioxide solution were diluted to 400 ml., treated with 5 grams of oxalic acid, and heated to promote the formation of trioxalatogermanic acid. Twenty-five milliliters of the reagent solution were added. Upon cooling to room temperature the derivative was precipitated in long crystalline needles. The solutions were allowed to stand overnight to ensure complete precipitation, and filtered. After washing with a dilute solution of oxalic acid and the reagent, the precipitate was ignited in a platinum crucible in a muffle at 700° to 800° C. to a pure white residue of germanium dioxide. Precipitation was found to be quantitative, as shown by Table V.

Table V. Precipitation of Germanium with 5,6-Benzoquinoline

GeO_2 Taken *Mg.*	GeO_2 Found *Mg.*	GeO_2 Taken *Mg.*	GeO_2 Found *Mg.*
84.3	84.2	49.9	49.9
54.2	54.0	49.9	50.1

5,6-Benzoquinoline would appear to be a superior precipitant for germanium for the following reasons: The precipitation procedure is simple and yields a product of very high molecular weight. The crystalline precipitate is easy to filter and wash and there is accordingly little danger of contamination by foreign ions. The precipitate is readily converted to germanium dioxide.

A specimen of 5,6-benzoquinoline trioxalatogermanate was purified by recrystallization from water. Weighed samples were ignited to the oxide and from the loss in weight a ratio of 1.98 moles of base for each mole of germanium was calculated. Because a definite composition was indicated, an attempt was made to precipitate the derivative in pure form and to weigh it directly. In all these attempts some of the reagent was coprecipitated, even when its concentration was reduced to the point where quantitative precipitation of the germanium was no longer obtained. The precipitate was also found to lose weight slowly in a desiccator and to come to a constant value only after 30 hours.

A concentration of 20 to 30 grams of sodium chloride in a volume of 400 ml. completely prevented precipitation of this derivative. It would appear that the germanium is firmly bound in a complex ion of the type $GeCl_6^{--}$ under these conditions and therefore fails to form the oxalate complex which is necessary for precipitation.

Of the other members of the fourth periodic group, titanium, zirconium, and tin are known to form complex oxalates. 5,6-Benzoquinoline was found to give a precipitate when solutions of these elements were treated by the same procedure as was used for germanium. The precipitate formed with tin resembles that of germanium very closely, while the products obtained with titanium and zirconium appeared to be much more insoluble and flocculent in nature. These compounds are being investigated.

Interfering Substances. All elements which form insoluble oxalates when treated with oxalic acid must be absent. Titanium, zirconium, tin, and to a lesser extent, iron, form complex oxalates which are precipitated by the reagent.

LITERATURE CITED

(1) Schwartz, R., and Geise, H., *Ber.*, 63, 779 (1930).
(2) Tchakirian, A., *Ann. chim.*, 12, 415 (1939).
(3) Willard, H. H., and Toribara, Y. K., *J. Am. Chem. Soc.*, 64, 1759 (1942).
(4) Willard, H. H., and Zuehlke, C. W., *Ibid.*, 65, 1887 (1943).

From a dissertation submitted by C. W. Zuehlke to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy in chemistry.

Support for Kjeldahl Flasks

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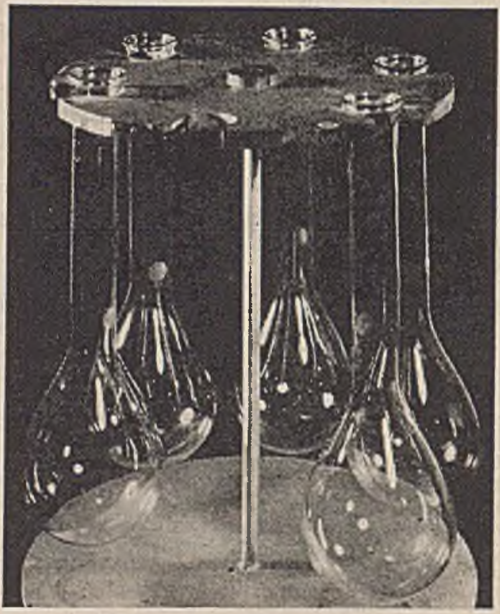
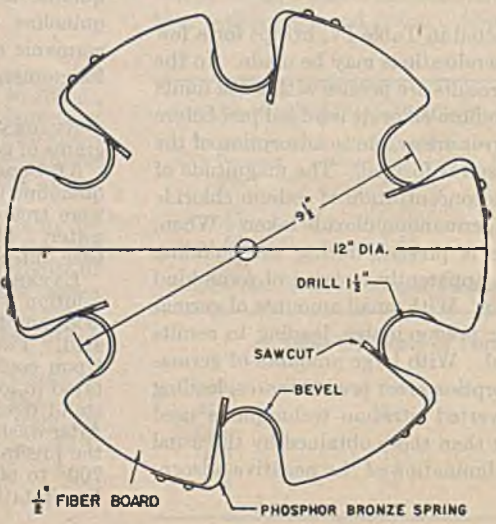
Because of their peculiar shape, with round bottom and elongated wide neck, Kjeldahl flasks do not fit into any rack ordinarily found in a chemical laboratory. Tall rectangular supports have been used with clamps holding the flasks, but such arrangements are unstable and working the clamps is inconvenient and time-consuming. It is considered desirable to have a support which will grasp the flask, hold it firmly, yet release it with one movement. Furthermore, it should hold the flasks vertically, and provide easy access to each flask, as samples are measured into them.



The necks and lips of the flasks are not uniform in size; therefore, the holding device cannot be rigid if it is to accommodate these differences. To solve this problem in this laboratory, a holder of simple design has been made. The beveled openings are provided with a spring (see drawing). The fiberboard (or plastic) disk has six places for flasks, although any number can be used. This disk is constructed so that it rotates on a central shaft and each flask is equally accessible. To stabilize the support, a heavy circular base of metal is employed, with a diameter of 35 cm. (14 inches) extending out as far as the widest part of the hanging flask.

The upper portion of the neck of the flask is pushed into the disk opening, so that, when the flask drops down, it catches on the bevel and is held firmly by the spring about 1.25 cm. (0.5 inch) below the lip. To remove a flask from the rack it is merely necessary to raise it straight up and slide it out.



This stand is very useful in holding the flasks while either solid or liquid samples are measured into them. It is substantial enough to support several 800-ml. flasks and their contents with no tendency to tip. Ammonia distillations and nitrogen digestions have been facilitated considerably by this inexpensive and easily constructed support.

Colorimetric Determination of 2,4-Dinitroanisole

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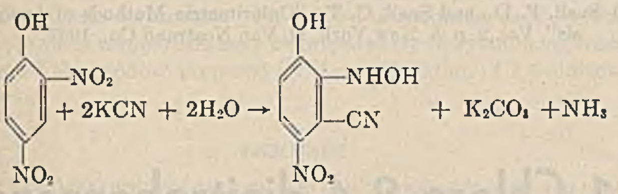
THE development of insecticidal dusts (*2*, *5*) containing 2,4-dinitroanisole has raised the problem of a suitable method for the determination of this compound in insecticidal compositions. The presence of a yellow color in some preparations due to other materials, such as pyrethrum oleoresin, made it impractical to use the yellow color of 2,4-dinitrophenol produced by the action of alkalies on 2,4-dinitroanisole as the basis of a photometric method. Use was made of the purpuric acid reaction (*1*, *3*, *4*), in which potassium cyanide reacts with *m*-dinitro compounds to give red-brown to violet colors. By analogy, the reaction with 2,4-dinitroanisole is presumed to be similar to that for 2,4-dinitrophenol, which is as follows:



[The equation given by Anger (*1*) and reproduced by Feigl (*4*) is not balanced and could be made to balance only if potassium carbonate is a product rather than potassium bicarbonate, as given by Feigl.]

Feigl (*4*) described this test for a number of *m*-dinitro compounds but did not list 2,4-dinitroanisole, which the authors found to give a red color with the potassium cyanide reagent. He did list 1-chloro-2,4-dinitrobenzene, which sometimes occurs as an impurity in 2,4-dinitroanisole and would therefore interfere. However, a specific method for determining 1-chloro-2,4-dinitrobenzene in 2,4-dinitroanisole has been developed (*6*). In the case of 2,4-dinitroanisole (and 1-chloro-2,4-dinitrobenzene) heating was not found to be necessary for rapid development of the color, but does seem to be necessary for many of the other *m*-dinitro compounds, such as 2,4-dinitrophenol and dinitrocyclohexylphenol.

The following procedure was developed for an insecticidal dust (*2*) containing 2% of 2,4-dinitroanisole, 2% of *N*-isobutyl undecylenamide, enough pyrethrum oleoresin to give 0.2% of total pyrethrins, and 1% of an antioxidant, with pyrophyllite as the diluent:

Weigh 2.000 grams of the powder into a small beaker. [For dusts containing 10% of 2,4-dinitroanisole, such as is recommended by Gould (*5*), about 0.400 gram suffices.] Stir the sample with four or five portions of acetone, decanting each time through a Gooch crucible that contains an asbestos mat and is held in an all-glass Gooch funnel. With care, the solution may be filtered directly into a 100-ml. volumetric flask, if a large enough filtering bell jar is used. Continue to wash with acetone until the volume is nearly 100 ml. and then make up to volume and mix. The solution should be perfectly clear and will have a yellow color due to the pyrethrum oleoresin and other constituents. Take a 10.00-ml. and a 15.00-ml. aliquot, and add 5.00 ml. of acetone to the 10.00-ml. aliquot. Prepare comparison standards containing 2, 4, and 6 mg. of pure 2,4-dinitroanisole and dilute each to 15.00 ml. with acetone. These standards are conveniently prepared from a standard solution containing 40 mg. of 2,4-dinitroanisole per 100 ml. of acetone. Add 5.00 ml. of 0.5% aqueous potassium cyanide to each of the solutions, mix, let stand for one hour, and measure the color in a photometer, using acetone as the blank. An Aminco photometer, type F, using photometer test tubes and a No. 58 yellow filter (wave length of maximum transmission at about 580 millimicrons) is suitable. It was found by experiment that if a No. 58 filter is used there is no interference from the other constituents in the amounts in which they are present in the insecticide dust, even though they contribute a yellow color to the acetone solution.

The results for the standards may be plotted as per cent transmission against concentration on semilogarithmic paper, or as log $\left(\frac{100}{\%\ \text{transmission}}\right)$ against concentration on ordinary graph paper. The concentration of 2,4-dinitroanisole in the unknown may then be read off this graph. The color follows Beer's law, as shown in Figure 1.

Acetone was used as the solvent in order to obtain a rapid and complete solution of the constituents of the powder without having to resort to a Soxhlet or other extractor. However, potassium cyanide is not soluble in acetone, and a 0.5% aqueous solution of this reagent had to be used. The amount of water thus added to the acetone solutions was found to be sufficient to keep the potassium cyanide in solution without precipitating any of the dissolved organic substances.

As an example of the precision to be expected, a commercial sample of dust supposed to contain 2% of 2,4-dinitroanisole plus

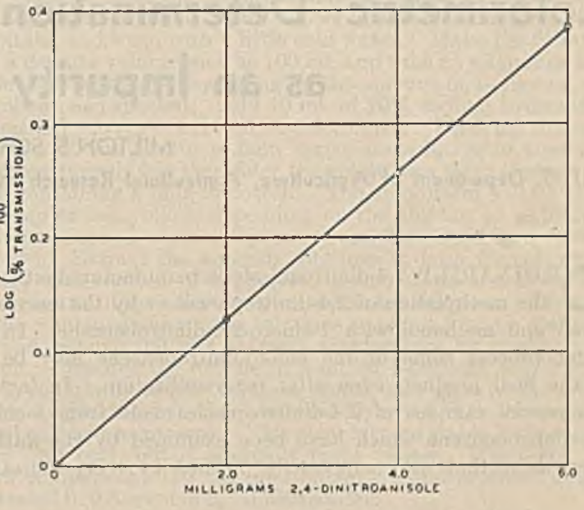


Figure 1. Determination of 2,4-Dinitroanisole Using Potassium Cyanate as the Reagent

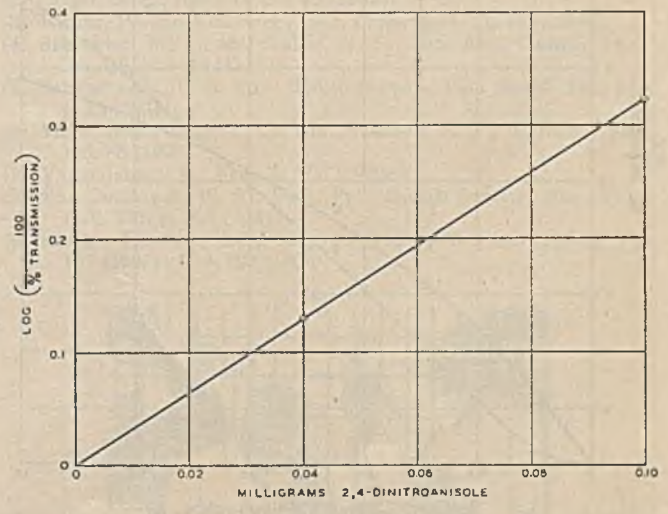


Figure 2. Determination of 2,4-Dinitroanisole Using Acetone and Alkali

the other constituents named above, when analyzed by the proposed method gave, as an average of 10 determinations, 2.17% with an average deviation of 0.05 and a maximum deviation of 0.12% when the 10-ml. aliquots were used, and 2.11% with an average deviation of 0.04 and a maximum deviation of 0.11% with the 15-ml. aliquots.

A more sensitive color reaction took place when 25 ml. of an acetone solution of 2,4-dinitroanisole were shaken with 5 ml. of concentrated sodium hydroxide solution (about 35%), with which it is immiscible. After the solution has been shaken for several minutes in a glass-stoppered cylinder and has stood for 30 minutes, a beautiful violet color develops in the acetone layer. The acetone may be decanted into a photometer tube and the color measured photometrically (a No. 58 filter on the Aminco photometer, type F, was suitable).

Some data to illustrate the sensitivity of the method are plotted in Figure 2. The test was found to be too sensitive to obtain concordant results in the analysis of dusts containing as much as 2% of 2,4-dinitroanisole, possibly because of the greater effect of interferences on such a sensitive reaction. However, this method would certainly be useful where very small amounts of 2,4-dinitroanisole had to be determined. This reaction is similar to that described for the analysis of *m*-dinitrobenzene (*7*). 1-Chloro-2,4-dinitrobenzene, which sometimes occurs as an impurity in 2,4-dinitroanisole, also gives this color reaction. One of the interferences which must be scrupulously avoided is the presence of even traces of sulfur, such as contamination from the sulfur in rubber stoppers. Sulfur destroys the violet color, producing a greenish coloration instead.

LITERATURE CITED

(1) Anger, V., *Mikrochim. Acta*, 2, 2 (1937).
(2) Anon., *Soap Sanit. Chemicals*, 18 (11), 105 (1942).
(3) Beilstein, "Handbuch der organischen Chemie", Aufl. 4, Bd. 15, p. 58, Berlin, Julius Springer, 1932.
(4) Feigl, F., "Qualitative Analysis by Spot Tests, Inorganic and Organic Applications", p. 270, New York, Nordemann Publishing Co., 1939.
(5) Gould, G. E., *Soap Sanit. Chemicals*, 19 (8), 90 (1943).
(6) Schechter, M. S., and Haller, H. L., IND. ENG. CHEM., ANAL. ED., 16, 326 (1944).
(7) Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis", Vol. 2, p. 5, New York, D. Van Nostrand Co., 1937.

Colorimetric Determination of 1-Chloro-2,4-dinitrobenzene as an Impurity in 2,4-Dinitroanisole

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ORDINARILY 2,4-dinitroanisole is manufactured either by the methylation of 2,4-dinitrophenol or by the reaction of alkali and methanol with 1-chloro-2,4-dinitrobenzene. In the latter process some of the chlorodinitrobenzene may be left in the final product, even after recrystallization. In fact, all commercial samples of 2,4-dinitroanisole made from 1-chloro-2,4-dinitrobenzene which have been examined by the authors, even those that were supposedly purified by recrystallization, when analyzed by the colorimetric method outlined below proved to contain about 0.5% of 1-chloro-2,4-dinitrobenzene. Procedures for determining 1-chloro-2,4-dinitrobenzene in 2,4-dinitroanisole based on the conversion of the chlorine to chloride by heating in alkaline solution and gravimetric or titrimetric determination of the chloride are unsuitable for small concentrations of the chlorodinitrobenzene, since a large sample has to be used and a correction also has to be made for inorganic chloride derived from salt left in the compound in the process of manufacture.

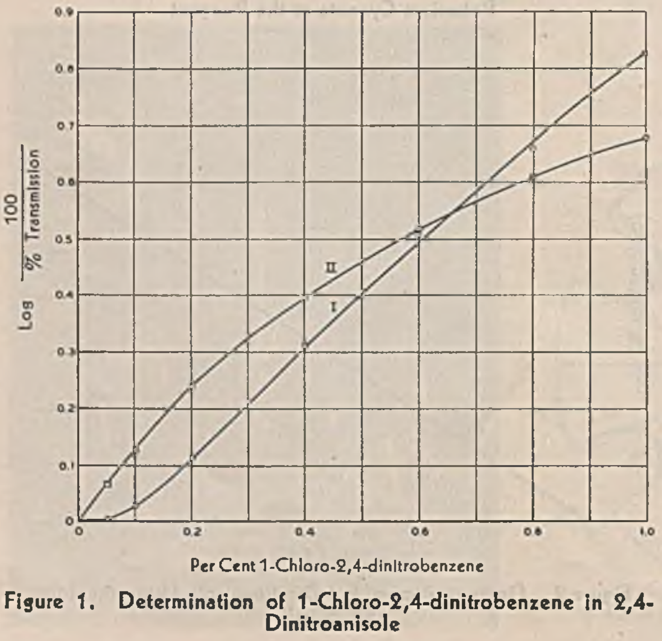
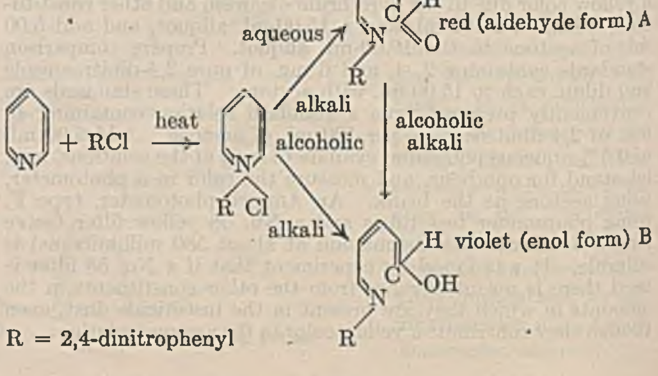


Figure 1. Determination of 1-Chloro-2,4-dinitrobenzene in 2,4-Dinitroanisole

2,4-Dinitroanisole is used as an insecticide (*1*, *2*), and a method for its analysis in insecticidal powders is described (*4*). Since 1-chloro-2,4-dinitrobenzene is a powerful skin irritant and repeated contacts may cause hypersensitization (*5*, *8*), it is desirable to have a sensitive colorimetric method of analysis for this compound in dinitroanisole.

The procedure developed is based on the Vongerichten reaction (*7*, *9*):



R = 2,4-dinitrophenyl

This reaction was first used in the detection of pyridine using 1-chloro-2,4-dinitrobenzene as a reagent (*7*) and has also been used more recently in the determination of nicotinic acid and its amide (*3*, *6*), but it has never been applied to the determination of 1-chloro-2,4-dinitrobenzene. It is very specific, since neither *o*- nor *p*-nitrochlorobenzene gives the reaction. Quinoline does not react and therefore cannot be used instead of pyridine.

Since commercial samples of 2,4-dinitroanisole made from 1-chloro-2,4-dinitrobenzene contain about 0.5% of the latter, the following procedure was developed for amounts of this order, though the method can be made more or less sensitive as desired by using different-sized samples or aliquots. Standards made from pure 2,4-dinitroanisole to which known amounts of 1-chloro-2,4-dinitrobenzene are added and heated with pyridine must be prepared, for two reasons: (1) The 2,4-dinitroanisole is partly converted to 2,4-dinitrophenol, thus contributing a yellow color to the solutions; and (2) the amount of color produced by heating 1-chloro-2,4-dinitrobenzene with pyridine in the presence of much 2,4-dinitroanisole is considerably less than when no 2,4-dinitroanisole is present. Pure 2,4-dinitroanisole used in the standards of comparison may be prepared by recrystallizing from ethanol the product prepared by the methylation of 2,4-dinitrophenol.

PROCEDURE

Place 0.500 gram of each sample in a photometer test tube that has been marked for a capacity of 25 ml. For standards of comparison, use pure 2,4-dinitroanisole (free of 1-chloro-2,4-dinitrobenzene) in the following amounts: 0.500, 0.500, 0.499, 0.498, 0.497, 0.496, and 0.495 gram. Weigh accurately 50 mg. of 1-chloro-2,4-dinitrobenzene into a 50-ml. volumetric flask. From a buret add 5.00 ml. of colorless pyridine to each of the samples to be analyzed, and to the standard comparison tubes add, in order, 5.00, 5.00, 4.00, 3.00, 2.00, 1.00, and 0 ml. Immediately make the 1-chloro-2,4-dinitrobenzene up to 50.00 ml. with pyridine, mix thoroughly, and add to the standard tubes, in order, 0, 0, 1.00, 2.00, 3.00, 4.00, and 5.00 ml. of this standard solution. Since this solution will darken in a short time, it should be made fresh for each analysis and used immediately. Swirl each test tube until the solution is homogeneous, and heat all the tubes in a boiling-water bath for 30 minutes. Cool, make up to 25 ml. by adding ethanol, mix thoroughly by swirling, and measure the color in a photometer using a No. 58 color filter (one having its wave length of maximum transmission at about 580 millimicrons; an Aminco photometer, type F, and appropriate photometer test tubes were used). The standards containing 0.500 gram of 2,4-dinitroanisole and no 1-chloro-2,4-dinitrobenzene are used as blanks to balance the photometer at 100% transmission. This gives reading I. The red color is presumably due to the presence of compound A.

With a pipet place 1.00 ml. of each of the foregoing solutions in another set of photometer tubes, make up to 25 ml. with ethanol, add 1.00 ml. of colorless 2% ethanolic sodium hydroxide solution, mix thoroughly by swirling, stopper with corks, and measure the color of this set of solutions in the photometer using a No. 58 filter. This gives reading II. The color is presumably due to the presence of compound B. Because of the yellow color of 2,4-dinitrophenol, the solutions appear red rather than the pure violet given by compound B. This reaction with alkali is far more sensitive than the red color given by reading I, and therefore interference from colored impurities will be much less. If the concentration of 1-chloro-2,4-dinitrobenzene in 2,4-dinitroanisole is low, an aliquot greater than 1.00 ml. should be used; if it is very low, the standards of comparison should be prepared with appropriately smaller concentrations of 1-chloro-2,4-dinitrobenzene, and aliquots greater than 1.00 ml. may also be used for reading II to increase the sensitivity.

The results may be plotted on semilogarithmic paper as per cent transmission against per cent concentration of 1-chloro-2,4-dinitrobenzene or on ordinary graph paper as $\log\left(\frac{100}{\%\ \text{transmission}}\right)$ against per cent concentration. The curves are illustrated in Figure 1. The per cent of 1-chloro-2,4-dinitrobenzene in the unknown may be read from the graph.

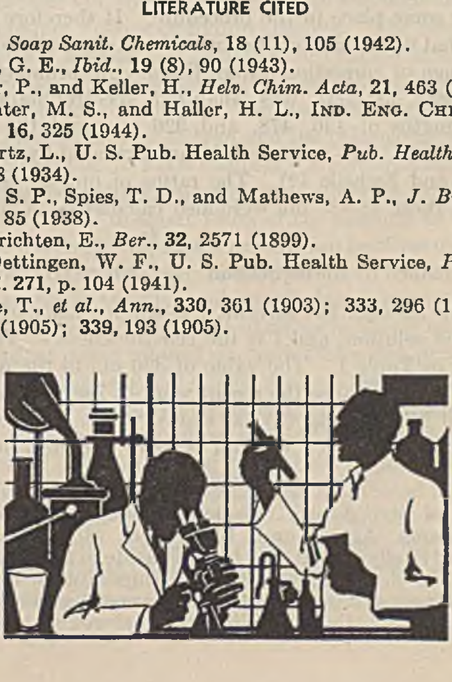
The concentration read from the standard curve using reading I will usually agree with that read from the second curve using reading II. However, some commercial samples known to contain no 1-chloro-2,4-dinitrobenzene appeared to contain a small amount when reading I was used but gave 0% when reading II was used. Since this was probably due to the presence of a small amount of colored impurity, reading II should be relied on when the sample is suspected of containing any colored impurities, which usually can be detected by visual comparison of the color of the original sample with that of the pure 2,4-dinitroanisole. The use of both readings serves as a check and may indicate the presence of colored impurities (other than 1-chloro-2,4-dinitrobenzene). If desired, reading I may be omitted altogether and the samples may be heated with pyridine in ordinary Pyrex test tubes, followed by dilution to the 25-ml. mark, and the placing of 1-ml. aliquots in photometer test tubes for reading II. With some experience, the number of standards to be prepared may be cut down, especially where the approximate concentration of 1-chloro-2,4-dinitrobenzene is known, but the order of operations should be carried out exactly as described.

A qualitative test for 1-chloro-2,4-dinitrobenzene in 2,4-dinitroanisole has also been developed, which enables the characteristic violet color of compound B to be seen without serious interference from the yellow color of 2,4-dinitroanisole and 2,4-dinitrophenol.

Heat 0.5 gram of the material with 2 ml. of pyridine in a boiling-water or steam bath for 20 to 30 minutes. Cool, add water in small amounts until the 2,4-dinitroanisole begins to crystallize, and then dilute to about 30 ml. Cool in an ice bath, filter the precipitate, and wash with a little cold water. Make the filtrate up to a definite volume such as 100 ml. and take an aliquot or all of it for the next step, depending on the amount of 1-chloro-2,4-dinitrobenzene expected. Add 10 ml. of 10% sodium hydroxide solution and extract with 10 ml. of chloroform. Wash the chloroform with 50 ml. of 2% sodium carbonate solution in another separatory funnel, and then filter the chloroform layer through a funnel containing a plug of cotton. The chloroform will be colored more or less yellow, depending on the amount of 1-chloro-2,4-dinitrobenzene originally present, and this itself is a fairly good test. Extract the aqueous solutions in both funnels successively with another 10-ml. portion of chloroform and, if necessary, repeat until the chloroform washings are colorless. Evaporate the combined chloroform solutions to about 1 ml. on a water bath and remove the rest at room temperature by applying a vacuum. Dissolve the residue in 2 ml. of 1-butanol, add 2 ml. of 10% sodium hydroxide solution, shake, and observe the red-violet color produced in the 1-butanol layer if any 1-chloro-2,4-dinitrobenzene was present. This color is more stable if the solution is kept cold, but it gradually turns yellow. If a blank is run for comparison, 0.01 mg. of 1-chloro-2,4-dinitrobenzene can be detected in 0.5 gram of 2,4-dinitroanisole.

LITERATURE CITED

(1) Anon., *Soap Sanit. Chemicals*, 18 (11), 105 (1942).
(2) Gould, G. E., *Ibid.*, 19 (8), 90 (1943).
(3) Karrer, P., and Keller, H., *Helv. Chim. Acta*, 21, 463 (1938).
(4) Schechter, M. S., and Haller, H. L., Ind. Eng. Chem., Anal. Ed., 16, 325 (1944).
(5) Schwartz, L., U. S. Pub. Health Service, *Pub. Health Bull.* 215, p. 18 (1934).
(6) Vilter, S. P., Spies, T. D., and Mathews, A. P., *J. Biol. Chem.*, 125, 85 (1938).
(7) Vongerichten, E., *Ber.*, 32, 2571 (1899).
(8) Von Oettingen, W. F., U. S. Pub. Health Service, *Pub. Health Bull.* 271, p. 104 (1941).
(9) Zincke, T., *et al.*, *Ann.*, 330, 361 (1903); 333, 296 (1904); 338, 107 (1905); 339, 193 (1905).



Effects of Beta-Carotene Isomerization on Its Absorption at 326 Millimicrons

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THE importance of the influence of the carotenoid pigments upon the absorption at 326 mμ is well known to workers who are attempting to estimate vitamin A concentrations by spectrophotometric methods. The usual procedure is to measure the absorption due to carotene at 450 mμ and use a certain percentage of this value as the correction in the ultraviolet for vitamin A determination. Considerable discrepancy exists in these correction values as reported in the literature. Gillam (*4*) reports a factor of 6.5%, Steenbock (*1*) 10%, McNicholas (*5*) 5%, and Peterson (*8*) values ranging from 5 to 8.3%.

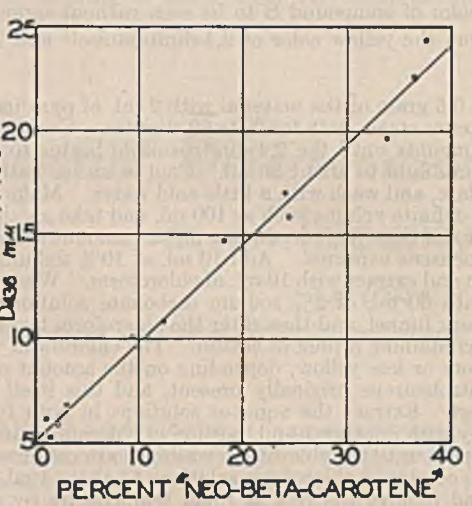

Figure 1. Relation between Optical Density Ratios and Calculated Per Cent Isomerization of β-Carotene

Recent studies on the carotenoids (*2*, *10*) have shown that heat is one of the factors responsible for their isomerization. All the methods in general use for vitamin A determination require heating at some place in the procedure. It therefore appeared probable that isomerization phenomena were partially responsible for the range of correction values listed. Accordingly, a series of β-carotene extracts was analyzed spectrophotometrically at wave lengths of 436, 478, and 326 mμ, and the per cent isomerization to "neo-β-carotene" was calculated by the method of Beadle and Zscheile (*2*). The ratios of optical densities at 326 mμ to those at 436 mμ were also calculated. (The optical density is defined by the expression $\frac{\log_{10}\frac{I_0}{I}}{l}$ where I_0 is the intensity of radiation through the solvent, I is the intensity of radiation through the solution, and l is the cell thickness.) The results are shown in Table I. The value of 326 mμ in the ultraviolet has been chosen because the recent work of Zscheile and Henry (*11*) and of Morgareidge (*7*) has shown this to be closer to the absorption maximum of vitamin A than the previously used 328 mμ.

A series of pure β-carotene samples (obtained from Dr. Salmon, Alabama Agricultural Experiment Station) dissolved in redistilled Skellysolve B, had been set aside in tightly stoppered test tubes, in the dark, at different temperatures, in order to study the kinetics of isomerization to the neo-β-carotene reported by Beadle and Zscheile (*2*). When the analyses of these samples were made for the per cent of isomerization to neo-β-carotene the optical density at 326 mμ was also determined.

The carotene was extracted from the alfalfa in a Waring Blendor with an alcohol–Skellysolve B mixture. The extract was filtered, washed with water, extracted three times with Skellysolve B, concentrated to approximately 60 ml., dried with sodium sulfate, and adsorbed on a column of 2 parts of Hyflo Super-Cel and 1 part of magnesia (Micron brand No. 2641). The carotene was separated from the xanthophylls and chlorophylls by elution with a 4% acetone–Skellysolve B solution. This is, essentially, the method of Moore and Ely (*6*), as modified by Wall and Kelley (*9*). This fraction, no doubt, contained a small percentage of α-carotene. Since acetone exhibits considerable absorption at 326 mμ, it was removed from the eluted carotene solution by washing with water. The purified extract was then dried over anhydrous sodium sulfate before making absorption measurements.

Figure 1 shows that a straight-line relationship exists between the extent of β-carotene isomerization and the calculated optical density ratios; and, therefore, explains the apparently anomalous correction values which have been reported. The values obtained in this study include the range of corrections previously reported. It would appear that the density ratio for pure β-carotene is about 5.0% in Skellysolve B. Estimating from the data given by Zechmeister and Polgár (*10*), the value is about 6% in hexane. The equation of the line in Figure 1 is:

$$\frac{D_{326\ m\mu}}{D_{436\ m\mu}} \times 100 = 5.0 + 0.480 \times \%\ \text{"neo-}\beta\text{-carotene"}$$

Care in the use of reported correction values is necessary. The shift in absorption maxima in various solvents is well known. The type of instrument on which the calibration is made is also of importance. Such factors as slit width and scattered radiation will also undoubtedly influence correction values. The data presented here were taken on the Beckman (*3*) spectrophotometer, using slit widths of 0.02 mm. at 478 mμ, 0.04 mm. at 436 mμ, and 0.34 mm. at 326 mμ.

SUMMARY

The isomerization of β-carotene is at least partially responsible for the wide range of correction values reported for vitamin A analysis in the ultraviolet. The correction required at 326 mμ for β-carotene in Skellysolve B has been calculated on the basis of data taken on the Beckman spectrophotometer and shown to be a linear function of the per cent isomerization.

Table I. Effect of β-Carotene Isomerization on Absorption at 326 Mμ

Sample	Optical Density 436 mμ	Optical Density 478 mμ	Optical Density 326 mμ	"Neo-β-Carotene", %	$\frac{D_{326}}{D_{436}} \times 100$
β-Carotene					
Sample 1	0.730	0.781	0.109	18.3	14.9
Sample 2	0.692	0.762	0.075	12.5	10.8
Sample 3	0.611	0.704	0.036	2.2	5.9
Sample 4	0.597	0.690	0.031	1.5	5.2
Sample 5	0.988	1.030	0.156	24.5	15.8
Sample 6	0.900	0.898	0.176	33.8	19.6
Sample 7	0.678	0.779	0.048	3.0	7.1
Sample 8	0.641	0.744	0.040	1.0	6.2
Alfalfa leaf extract	0.805	0.842	0.138	24.0	17.1
Alfalfa leaf extract	0.256	0.286	0.026	9.4	10.1
Alfalfa leaf extract (refluxed 30 hours)	1.293	1.267	0.316	37.5	24.4
Alfalfa leaf extract (refluxed 30 hours)	0.825	0.811	0.187	36.5	22.7

LITERATURE CITED

(1) Baumann, C. A., Steenbock, H., Beeson, W. M., and Rupel, I. W., *J. Biol. Chem.*, 105, 167 (1934).
(2) Beadle, B. W., and Zscheile, F. P., *Ibid.*, 144, 21 (1942).
(3) Cary, H. H., and Beckman, A. O., *J. Optical Soc. Am.*, 31, 682 (1941).
(4) Gillam, A. E., *Biochem. J.*, 28, 79 (1934).
(5) McNicholas, H. J., *Bur. Standards J. Research*, 7, 171 (1931).
(6) Moore, L. A., and Ely, R., Ind. Eng. Chem., Anal. Ed., 13, 600 (1941).
(7) Morgareidge, K., *Ibid.*, 14, 700 (1942).
(8) Peterson, W. J., private communication.
(9) Wall, M. E., and Kelley, E. G., Ind. Eng. Chem., Anal. Ed., 15, 18 (1943).
(10) Zechmeister, L., and Polgár, A., *J. Am. Chem. Soc.*, 65, 1522 (1943).
(11) Zscheile, F. P., and Henry, R. L., Ind. Eng. Chem., Anal. Ed., 14, 422 (1942).

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Apparatus for Rapid Polarographic Analysis

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A VARIETY of different types of cells, each of which has its merits, has been proposed for polarographic analysis (*3*). Fundamentally, these all fall into two categories; (1) those in which a quiet pool of mercury in direct contact with the solution being analyzed constitutes the second electrode, which were recommended originally by Heyrovský and much used in the earlier work with the dropping electrode, and (2) those in which a saturated calomel, or other nonpolarizable reference electrode, is used as the second electrode. For reasons already discussed (*3*) cells of the latter type, such as that described by Lingane and Laitinen (*5*), are preferable for general use, particularly in research studies when the polarographic behavior of a substance is being investigated for the first time. However, for more or less routine analyses of substances of well-known polarographic characteristics cells of the first type often are more convenient. The cell shown in Figure 1 has proved to be very useful for a variety of analyses.

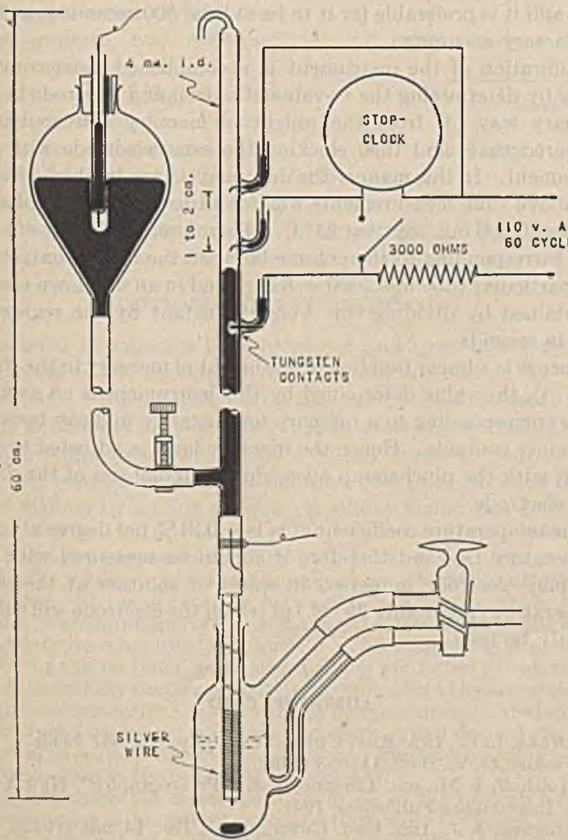

Figure 1. Polarographic Cell

SIMPLIFIED POLAROGRAPHIC CELL

In this simple cell the inconvenient classical mercury pool anode has been replaced by a silver–silver chloride anode, which consists of No. 22 silver wire wound as a tight cylinder directly on the dropping electrode capillary, as shown, with its free end spiraled up to the rubber connecting tube where it is held in place by a wrapping of copper wire. The silver wire cylinder is about 2 cm. long, and its lower end extends to within about 3 or 4 mm. from the tip of the dropping electrode. To ensure a reproducible potential, it is advisable to deposit electrolytically a thin coating of silver chloride on the silver electrode before use. The apparent area of the electrode is about 5 sq. cm., which is amply large to prevent appreciable polarization. As a matter of fact, the area of the electrode immersed in the solution may be as small as 1 sq. cm. without significant polarization occurring with currents of the usual magnitude.

This silver–silver chloride electrode may be employed whenever the solution investigated contains chloride ion, and when it does not contain substances which will dissolve silver chloride (metathesis of the silver chloride to a more insoluble salt is permissible). For example, it may be used with any of the common supporting electrolytes containing alkali or alkaline earth halides, hydrochloric acid, acidic, neutral, or basic tartrate solutions containing chloride ion, sodium hydroxide, in solutions of the tetraalkylammonium halides or hydroxides, etc. The electrode may not be used in ammoniacal solutions, in cyanide solutions, or in general whenever the solution contains substances that form very stable complex ions with silver, because in such cases the silver chloride coating will be dissolved and the polarogram will show a diffusion current of the silver complex. A safe criterion that may be applied in doubtful cases consists of adding a drop or two of 0.1 N silver nitrate to about 10 cc. of the solution to be investigated, and if a precipitate forms (it need not be silver chloride) the silver chloride electrode may be used safely.

The potential of the silver–silver chloride electrode in any particular medium may be determined either by direct measurement against the saturated calomel electrode (for which purpose an H-cell with saturated calomel anode, *5*, is convenient), or by comparing the apparent half-wave potential of some substance as determined with the silver–silver chloride anode with the known value referred to the saturated calomel electrode. The potential of the silver–silver chloride electrode is subtracted algebraically from observed half-wave potentials to refer the latter to the standard saturated calomel electrode. In any given chloride-containing medium the potential of the silver–silver chloride electrode is 0.046 volt more negative than that of a calomel electrode in the same solution.

The cell is provided with two gas-inlet tubes, the lower of which is constructed of capillary tubing to facilitate the formation of small gas bubbles and thus provide a large contact surface between the gas and the solution. Nitrogen or hydrogen is first passed very rapidly through the lower inlet tube to free the solution from dissolved oxygen, and then it is passed at a slower rate over the surface of the solution by means of the upper inlet tube during the recording of a polarogram.

This cell is convenient because it requires only a small volume of solution (3 to 7 cc.), but more importantly because it permits very rapid removal of dissolved air from the solution. This latter advantage is demonstrated by the polarograms in Figure 2.

In this experiment, 5 cc. of a 0.465 millimolar solution of cadmium ion in 0.4 *M* sodium tartrate, 0.1 *M* sodium hydrogen tartrate, 0.1 *M* sodium chloride, and 0.005% gelatin, were used. Curve *a* is a polarogram of the solution before removal of dissolved air, and it shows a large wave of oxygen prior to the cadmium wave. Curve *b* was recorded after a very rapid stream of pure nitrogen was passed through the solution for only 1 minute, and it is seen that in this short time about 90% of the oxygen was removed. Curve *c* was recorded after a rapid stream of nitrogen was passed for a total of 3 minutes, and curve *d* was obtained after a slower flow of nitrogen had been maintained for an hour longer. The fact that there is no significant difference between curves *c* and *d* shows that removal of dissolved oxygen was complete after only 3 minutes. The practical advantage of being able to remove oxygen this quickly is obvious.

AUTOMATIC DETERMINATION OF RATE OF MERCURY FLOW FROM DROPPING ELECTRODE

The stop-clock circuit sketched in Figure 1 determines automatically the rate of mercury flow, *m*, from the dropping electrode, which datum is required in applications of the Ilkovič equation (*3*), and especially for the use of diffusion current constants in practical analyses (*4*). The operational principle of this device is essentially the same as that employed by Feskov (*2*) and Drake (*1*) for automatic measurements with gas effusiometers—namely, that the flow of a conducting liquid through a tube past fixed metallic contacts automatically starts and stops an electric stop clock, which thus registers the time required to empty or fill the volume between the contacts.

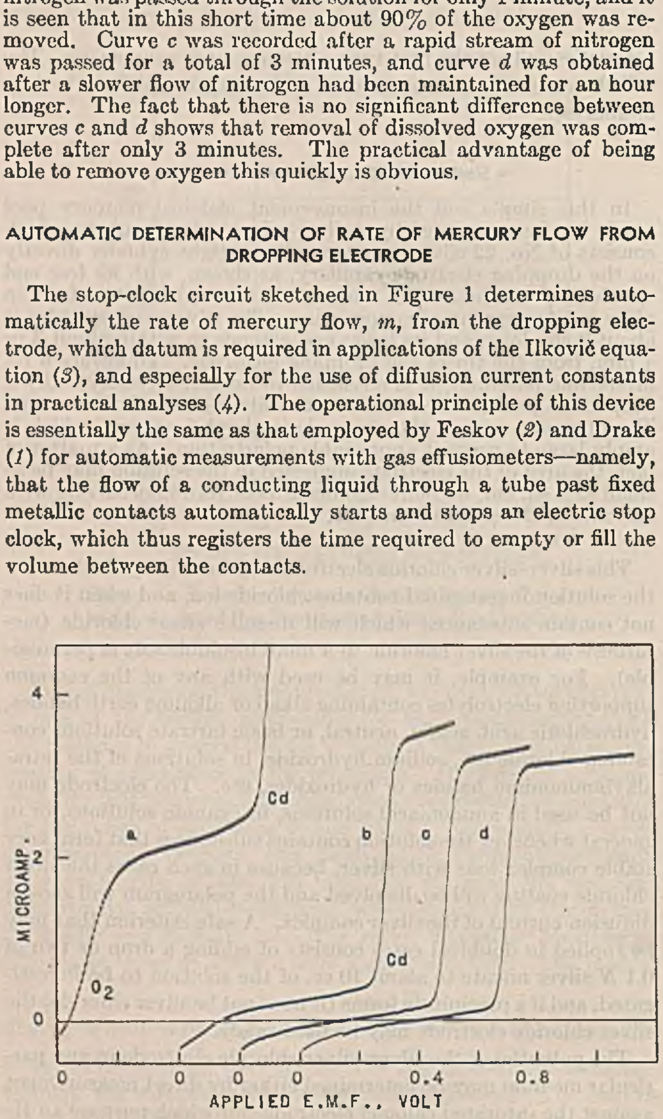

Figure 2. Polarograms

Referring to Figure 1, three tungsten contact points are sealed into the stand tube above the dropping electrode; the two lower contacts complete the circuit through the clock, while the uppermost short-circuits the clock and prevents it from running. The stand tube is constructed from Pyrex tubing 4 mm. inside diameter. The two upper contacts are placed between 1 and 2 cm. apart, and the lower contact is sealed in at any convenient point below the middle contact. To minimize the tendency for the mercury to adhere to the contacts, they should be cleaned carefully, filed to a fine point, bent downward as shown, and located as exactly as possible in the center of the tube.

A 3000-ohm resistance was placed in series with the clock to minimize sparking at the contacts. This resistance should be as large as operation of the clock will permit, and its magnitude will depend on the characteristics of the clock that is used. The author used a precision stop clock manufactured by the H. C. Thompson Clock Co., Bristol, Conn., but an ordinary inexpensive clock which will start and stop without more than 1-second lag or coast, and which will allow the use of a series resistance of at least 1000 ohms, should be equally satisfactory. The switch shown in Figure 1 is provided to permit ordinary use of the clock for other measurements.

A measurement is started by raising the mercury reservoir until the mercury level is a few millimeters above the upper contact. The screw clamp on the rubber tube connecting the mercury reservoir with the stand tube is then closed tightly, the stop clock is set to zero, and the apparatus is left to itself. When the mercury level falls below the upper contact the short-circuit is broken and the clock starts. Then when the mercury level leaves the middle contact the circuit through the clock is opened and it stops. Thus, the clock registers the time of flow of that weight of mercury that is equivalent to the volume between the two upper contacts, and *m* is obtained by dividing this previously determined weight in milligrams by the registered time in seconds. By merely opening the screw clamp to reset the mercury level, the device is readied for another measurement.

The precision with which this device measures *m* is demonstrated by the following successive readings obtained with the same dropping electrode: 505, 506, 510, 507, 509, and 508 seconds. The average deviation of these values from the mean (508 seconds) is ±2 seconds, or ±0.4% and the largest discrepancy between any two readings is 5 seconds, or 1%. Since polarographic diffusion currents are measurable with an accuracy of about ±1% at best under practical analytical conditions, and since the diffusion current is a function of the two-thirds power of *m*, it is evident that this instrument is amply accurate for general use. By placing the contacts closer together and/or using a narrower tube the time of measurement could be shortened, but since the measurement is made automatically the time is not important, and it is preferable for it to be at least 500 seconds to ensure satisfactory accuracy.

Calibration of the instrument is accomplished most conveniently by determining the *m*-value of a dropping electrode in the ordinary way (*3*) from the weight of mercury delivered in a measured time, and then clocking the same electrode with the instrument. In this manner the dropping electrode which yielded the above time measurements was found to have an *m*-value of 4.056 ± 0.006 mg. $sec.^{-1}$ at 25° C. Therefore, the weight of mercury corresponding to the volume between the upper contacts of this particular tube was 2060 ± 8 mg., and in an unknown case *m* is obtained by dividing this weight constant by the registered time in seconds.

Since *m* is a linear function of the height of mercury in the stand tube (*3*), the value determined by this instrument is an average value corresponding to a mercury level exactly midway between the upper contacts. Hence the mercury level is adjusted to this point, with the pinchclamp open, during actual use of the dropping electrode.

The temperature coefficient of *m* is +0.31% per degree at room temperature (*4*), and therefore it should be measured with the dropping electrode immersed in water or solution at the same temperature (preferably 25° C.) at which the electrode will subsequently be used.

LITERATURE CITED

(1) Drake, L. C., Ind. Eng. Chem., Anal. Ed., 15, 647 1943).
(2) Feskov, G. V., *Ibid.*, 11, 653 (1939).
(3) Kolthoff, I. M., and Lingane, J. J., "Polarography", New York, Interscience Publishers, 1941.
(4) Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 14, 655 (1942); 15, 583 (1943).
(5) Lingane, J. J., and Laitinen, H. A., *Ibid.*, 11, 504 (1939).

Fluorocolorimetric Determination of Blended Oils and Oil in Oil-Water Emulsions

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IN THE past few years the use of fluorescence in both qualitative and quantitative analyses has advanced rapidly. Many photoelectric and fluorescent instruments and techniques have been developed and are now available to the analyst. The application of this principle to analysis has speeded up and made more accurate the determination of many elements and compounds.

The author of this article was called upon to determine the concentration of sulfurized cutting oils blended with straight mineral oil used as a cutting coolant and also the oil content of oil-water emulsions.

The only method available for cutting oils was by means of viscosity, a slow and messy procedure. It was necessary to make up definite concentrations of the blended oils and determine viscosities on these standards, after which the viscosities of the samples themselves were determined; such a procedure, while perhaps accurate, was certainly time-consuming.

In the case of the oil-water emulsions, it was found necessary to break the emulsion by the use of large quantities of sulfuric acid and then measure, by volume, the amount of oil in the samples. Both methods were very slow, and the latter was inaccurate.

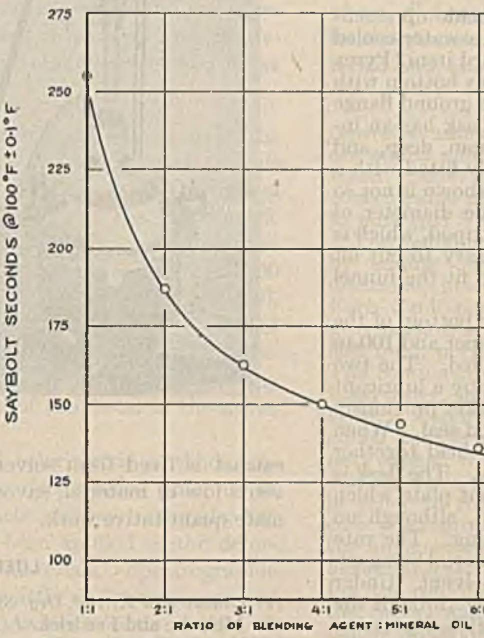

Figure 1. Viscosity of Cutting Oil

DETERMINATIONS BY FLUORESCENCE

In order to improve the procedures and speed them up, use was made of the phenomenon of fluorescence excited by ultraviolet rays. Determinations by this means could be made in as many minutes as the older ones took in hours and were applicable to all oils and waxes which exhibited any degree of fluorescence. Oils and waxes which did not fluoresce could be estimated in the same manner by adding suitable oil-soluble fluorescent dyes.

Ultraviolet rays were supplied by a bank of four 2-watt argon bulbs, the visible rays being filtered out by a Wratten ultraviolet ray filter. Strips of blotting paper, 0.6 × 3.75 cm. (0.25 × 1.5 inches), were impregnated with standard samples of the oils made up to definite concentrations, and these, because of the fluorescent nature of the oil itself, produced a sharp gradation of colors. It was then an easy matter to match the samples to these standards. As the concentrations of the various blends can be related graphically to the viscosity, it is only necessary, when desired, to refer to an appropriate curve to express the fluorescent-colorimetric determination in terms of Saybolt seconds.

To determine the concentrations of oil in the oil-water emulsions, samples of known oil concentrations were prepared and the unknown sample was colorimetrically compared with them. The standards could be used indefinitely, and did not deteriorate over long periods of time.

EXTRACTION METHOD

Many emulsions are subject to contamination that might interfere with the visual colorimetric method and lead to erroneous results. In order to remove the interfering parts of the sample, the following extraction method was developed:

Two milliliters of the sample were placed in a large stoppered test tube and 10 ml. of ether added. This was well shaken, and 25 ml. of a saturated solution of sodium chloride were added to break the emulsion.

A small portion of the ether layer, now containing all the oil in the sample, was placed in stoppered glass tubes 0.47 cm. ($^3/_{16}$ inch) in diameter. It was not necessary to measure the volume of this portion of the sample, as each tube was of equal size and all held the same volume.

Standards treated in exactly the same manner were prepared and colorimetric comparisons made. It was necessary to prepare only one set and seal them well in order to prevent evaporation of the ether, as these could be used indefinitely.

Very close estimation of the total oil content in emulsions could be made by this method, as any error caused by evaporation of the ether was negligible and no measurable trace of oil remained in the aqueous layer. Determination of oil in oil emulsions could be performed, by visual matching, to ±0.1% (12.5 parts in 10,000).

In the case of blended oils, all samples when checked colorimetrically with viscosity, showed a difference of only ±2 Saybolt seconds. Figure 1 shows the relationship of Saybolt seconds to composition of blended oils in terms of ratios—i.e., the proportions of blending agent to mineral oil. This difference brings a maximum error of only 3% at the lower end of the graph and much less at the higher end. As the usual ratio of blending agent to mineral oil lies about the center, the error is reduced proportionately. The blended oils referred to do not contain water; they are not emulsions.

In the estimation of emulsions by means of the ether-extraction method, smaller samples gave a much sharper color gradation.

This principle was also applied to determine the efficiency of oil removal when metal parts were cleaned and washed by various methods. A trace of oil not visible to the naked eye became apparent when excited by ultraviolet rays.

ACKNOWLEDGMENT

The author must express his gratitude to Albert W. Bull, without whose assistance and criticism this method could not have been developed.

A Versatile Continuous Laboratory Extractor

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IN CONNECTION with a project carried out in this laboratory, it was necessary to extract a fairly large quantity of various crude materials with organic solvents, such as ether, acetone, methanol, and benzene. It was desired to make the extractions approximately quantitative. The ordinary size of Soxhlet extractor does not have the capacity required, while large all-glass Soxhlet extractors are expensive. The extractors of Clarke and Kirner (*1*) and Tanner (*3*) were considered not rapid enough and subject to loss of solvent vapor, respectively.

An improved extractor constructed from apparatus found in the laboratory possesses certain unique advantages.

As shown in the photograph, the extractor is made up essentially of a distilling flask, a Büchner funnel, and a water-cooled condenser. The distilling flask, which is a standard item (Pyrex Catalog 3480), consists of two parts: a heavy Pyrex bottom with a wide ground rim, and a Pyrex dome with a wide ground flange and an opening at the top. The bottom of the flask has an inside diameter of approximately 165 mm., is 105 mm. deep, and has a capacity of 2000 ml. The dome is preferably fitted with a standard taper joint at the top, although the one shown is not so constructed. The Büchner funnel has an outside diameter of 106 mm. and is supported in the flask on a small tripod, which is easily made from wire or glass rod. It is necessary to cut off about 3 cm. of the stem of the funnel in order to fit the funnel into the flask.

About 300 to 500 ml. of solvent are put into the bottom of the flask. The funnel is fitted with a sheet of filter paper and 100 to 200 grams of the material to be extracted are added. The two parts of the flask are sealed by a rubber gasket or by a lubricant unaffected by organic solvents (*2*). A Thiokol gasket previously extracted with the solvent to be used makes a good seal. When a gasket is used, the two sections of the flask are held together by three Hoffman clamps placed around the flange. The flask is heated by a thermostatically controlled electric hot plate which may for safety be covered with an asbestos pad, although no breakage has been encountered with direct heating. The rate of heating is so adjusted that the surface of the material being extracted is at all times covered with a thin layer of solvent. Under these conditions there is a constant flow of solvent through the material, thereby preventing restricted flow through a depression caused by the drip of the condensate.

If the material being extracted is very porous, the use of more than one sheet of dense filter paper will hold up the solvent sufficiently to keep the material covered with solvent.

After the extraction is complete, the funnel and tripod are removed, a distilling head is connected to the flask, and the condenser is arranged for distillation to remove the solvent. When all the solvent has been removed, the apparatus is dismantled, and the bottom of the flask is placed in an oven or desiccator in order to dry the extract. The large surface presented by the bottom of the flask facilitates drying, particularly with viscous liquid extracts.

When used in the organic chemical laboratory, the extractor possesses the unique advantage of permitting the following sequence of operations to be carried out in the same apparatus: the crude material is collected by filtration in the Büchner funnel; the funnel is transferred to the extraction flask and the crude material is extracted; and the extract is freed from solvent and dried. Such continuity prevents loss of material, saves time, and makes possible approximate quantitative work.

LITERATURE CITED

(1) Clarke and Kirner, *Org. Syntheses*, 2, 49 (1922).
(2) Meloche and Fredrick, *J. Am. Chem. Soc.*, 54, 3264 (1932).
(3) Tanner, Ind. Eng. Chem., Anal. Ed., 4, 397 (1932).

A Support for Flasks on Steam and Water Baths

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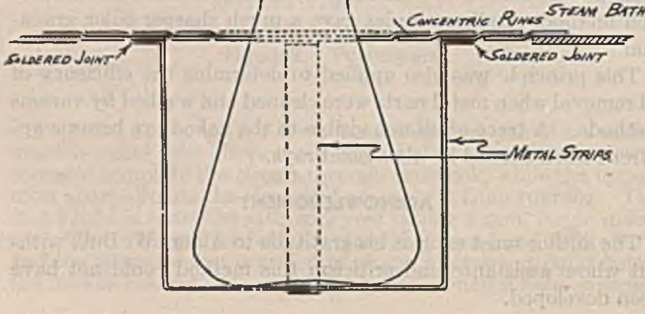
THE refluxing and distillation of solvents in flasks on steam baths are often rather slow, but can be considerably speeded up by lowering the flasks into the bath so that a greater part of the surface is exposed to the steam. The concentric rings which ordinarily form the covers of steam baths allow no more than the bottom half of round flasks and only the flat bottom of Erlenmeyer flasks to be exposed to the steam, unless the flasks are supported by a buret clamp or some other means.



A simple attachment to the covers is shown in the accompanying illustration. It consists of two strips of sheet metal bent into a U-shape as shown, and soldered to the lower part of the bottom surface of the concentric ring, having an inside diameter larger than that of the flask to be supported. The two U-shaped strips are soldered to the ring at right angles to each other, so that they form a rack to support the flask.

The depth of the sides of the U-shaped strips is such that when the flask is in position the next smallest ring or set of rings may be dropped into place over the neck of the flask and will fit closely around the narrow upper portion of the flask and also to the other rings.

The greater portion of the flask is enclosed by the steam bath and covers and is exposed effectively to the steam, without the necessity of outside supports. The covers serve as a seal around the upper portion of the flask and no other packing is required to stop escape of steam from the system.

Determination of Cadmium in Biological Material

Spectrographic, Polarographic, and Colorimetric Methods

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Reliable spectrographic, polarographic, and colorimetric methods for the determination of cadmium in biological material are described. In each method cadmium is first separated from the bulk of the wet-ashed matrix by extraction with di-β-naphthylthiocarbazone (or dithizone) in chloroform.

As little as 0.4 microgram of cadmium may be determined spectrographically. This method is the most specific and the most rapid when many samples are analyzed routinely. The polarographic method is the most convenient for the analysis of occasional samples and is capable of detecting 1.5 to 500 micrograms or more per 3 ml. of solution. Its specificity is excellent. The colorimetric method is the most sensitive, but it is laborious and time-consuming, and requires careful attention to details if contamination by zinc is to be avoided. Cadmium is separated from lead and zinc by an extraction with dithizone solution from 5% sodium hydroxide solution. Entrained zinc, lead, and bismuth are then removed by washing the extract with water. Loss of cadmium to the wash water is prevented by adding an excess of dithizone solution to the cadmium dithizonate extract. The cadmium is estimated colorimetrically from a mixed color phase, di-β-naphthylthiocarbazone in chloroform being employed for this purpose. Fractions of a microgram of cadmium can be detected and estimated.

DETERMINATION of the quantities of cadmium in the tissues, body fluids, and excreta of experimental animals and exposed human subjects necessitates the use of analytical methods of high sensitivity and specificity. The colorimetric sulfide method in which ultraviolet intensification is employed (*8*) lacks sensitivity. A sensitivity of detection of 1/2,500,000 has been claimed for it (*8*), but Prodan (*15*), using the method, failed to detect cadmium in 62- to 117-gram samples of blood from cats killed immediately at the termination of feeding experiments with cadmium salts. This was particularly striking since he reported high concentrations of the metal in the urine, kidneys, and liver of these animals.

Polarographic, spectrographic, and colorimetric methods employing dithizone have been used to detect small amounts of cadmium in various industrial products and raw materials, but apparently these methods have not been applied to the determination of cadmium in biological materials. Spectrographic detection was found possible with as little as 0.4 microgram of cadmium in the direct current arc (*4*), while as little as 0.5 to 1 microgram per milliliter of solution can be detected with the polarograph if instruments are employed with which it is possible to eliminate or reduce galvanometer oscillations (*12*). Fischer (*9*) claims for the dithizone method a sensitivity of detection of 0.01 microgram of cadmium in nonferrous alloys, and Sandell (*16*) has applied Fischer's method to the analysis of igneous rock containing 10^{-5}% cadmium. Sensitive methods for the detection of traces of cadmium have also been reported by Mahr (*13*) and by Dwyer (*7*), but these methods cannot be used for quantitative determination of the element.

This paper, therefore, concerns itself with the modifications and details necessary to adapt spectrographic, polarographic, and di-β-naphthylthiocarbazone or diphenylthiocarbazone (dithizone) methods to the determination of cadmium in biological material in any range of concentration likely to be encountered in such material.

PROCEDURES

PREPARATION OF SAMPLES AND INITIAL CONCENTRATION OF CADMIUM. The sample, 50 to 100 ml. of urine, 5 to 20 grams of tissue, dried feces, blood, or other material, is wet-ashed by a sulfuric acid–nitric acid mixture in an open beaker, Kjeldahl flask, or closed digestion system such as has been used for arsenic analysis (*10*). The digest is evaporated to fumes of sulfur trioxide, any char occurring meanwhile being destroyed by repeated addition of small portions of nitric and perchloric acids. When ashing is complete, the cooled sample is rinsed into a clean 125-ml. graduated Squibb-type separatory funnel. Fifteen milliliters of ammonium citrate solution (400 grams of citric acid in 600 ml. of water made alkaline to phenol red with concentrated ammonia and diluted to 1000 ml. with distilled water) are added and the volume is made up to 50 ml. with distilled water. After the addition of 2 drops of phenol red indicator, concentrated ammonia is added until the indicator just changes to pink (pH 8.3).

The cadmium, zinc, lead, and other metals are then extracted by adding 5-ml. portions of di-β-naphthylthiocarbazone (or dithizone) in chloroform (200 mg. in 1000 ml. of chloroform). Each 5-ml. portion is removed to a second funnel before the next portion is added, and the extraction is continued until the last 5-ml. portion added shows no change in its original color. The combined chloroform extract is shaken with 50 ml. of distilled water, and is then removed to another funnel. The aqueous layer is shaken with 5 ml. of clear chloroform and this too is added to the chloroform extract. The chloroform extract is next shaken with 50 ml. of 0.2 N hydrochloric acid and is discarded, while the aqueous layer is washed with pure chloroform in order to remove entrained di-β-naphthylthiocarbazone. In case polarographic or spectrographic estimation is to be made, the aqueous layer is then transferred quantitatively to a small beaker and is allowed to evaporate to dryness on the hot plate. For the colorimetric method, the aqueous portion is retained in the funnel and the procedure described below under "Colorimetric Method" is followed.

SPECTROGRAPHIC METHOD. To the dried residue in the beaker, 1 ml. of a salt buffer solution (1% solution of disodium acid phosphate, sodium chloride, or urine salt stock, *3*, containing 10 mg. of molybdenum as sodium molybdate per 100 ml.) is added, and 0.2 ml. of the resulting solution is placed in a crater (3 × 10 mm.) drilled in a 2.5-cm. (1-inch) length of 0.78-cm. ($^5/_{16}$-inch) graphite rod. The rod is dried in an oven and is then used as the lower positive electrode of a direct current arc, the upper electrode consisting of a 3.75-cm. (1.5-inch) length of rod, one end of which is turned to a point in a pencil sharpener. The arc is operated for 2 minutes at 10 amperes from a 110-volt direct current line, and the spectrum is photographed on an Eastman No. 33 plate at setting 4 of the large quartz Littrow spectrograph. Each analytical spectrum is obtained with a rotating 5-step sector (factor 2) set before the slit of the spectrograph. The developed and dried plates are then photometered and partial H and D curves are plotted for the cadmium line at 3261 Å., and for the molybdenum (internal standard) line at 3209 Å. The log exposure separation between the two curves at T = 0.50 (D = 0.30) is then obtained and the concentration of cadmium is read from a predetermined calibration curve derived from spectrograms of known amounts of cadmium in 1-ml. portions of the salt buffer (*4*). This technique is satisfactory for the determination of 5 to 200 micrograms of cadmium in 1 ml. of the salt buffer.

For the determination of 2 to 5 micrograms of cadmium per milliliter of buffer solution, corrections for plate background must be made. The technique for this procedure, involving intensity ratios, has been described in an earlier paper (*5*). In this low range, the cadmium line in the step representing the maximum exposure and the molybdenum line in the third step of each stepped-spectrogram, are employed.

The more widely used ratio procedure (log ICd/IMo) with plate calibration has also been employed in some of this work. With this method also it was found advisable to employ the 5-step sector in each analytical spectrum, in order to extend the analytical range. With the maximum exposure step the range of analysis was found to be only 2 to 50 micrograms of cadmium per milliliter of buffer solution, but when the next lower exposure step was used, the analytical range was increased to 2 to 150 micrograms of cadmium. Background corrections should be made for the entire range. The serious disturbance caused by this factor is illustrated in Figure 1, where the cadmium calibration curves are shown for the uncorrected densitometric ratios, and also for the ratios obtained following correction for background according to the method of Pierce and Nachtrieb (*14*).

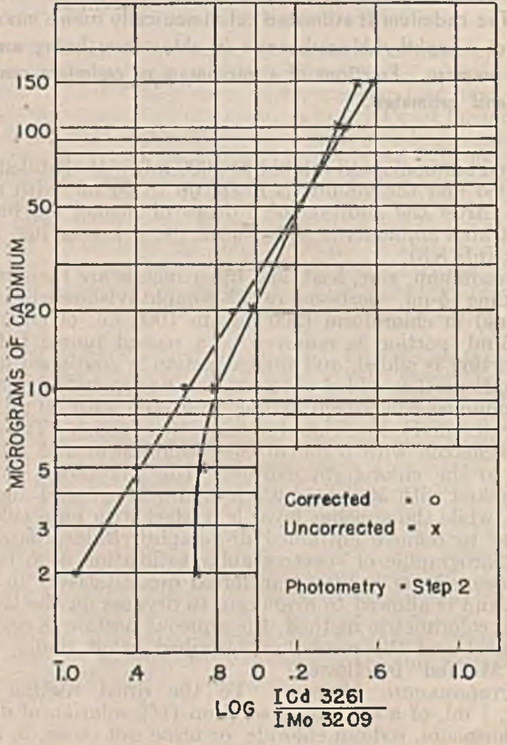

Figure 1. Effect of Background in Spectrographic Calibration Curves and Curve Obtained by Correction for This Effect

Polarographic Method. To the dry residue in the beaker are added 3 ml. of a solution containing 0.1 *N* potassium chloride and 0.1 *N* hydrochloric acid. The solution is transferred to a polarograph cell and after oxygen has been removed by bubbling nitrogen gas through it for 5 minutes, the solution is electrolyzed cathodically from −0.5 to −0.9 volt. The cadmium diffusion wave appears at −0.7 volt (empirical on Leeds & Northrup Electro-Chemograph) and it can be evaluated from a calibration curve made by obtaining the diffusion currents of known amounts of cadmium in 0.2 *N* hydrochloric acid exactly as was done with the samples. The polarograms are obtained at a constant temperature and a uniform rate of fall of mercury drops. By calibrating for several galvanometer sensitivities it is possible to determine 0.002 to 0.5 mg. or more of cadmium in 3 ml. of solution.

Colorimetric Method. To the 50 ml. of 0.2 *N* hydrochloric acid containing the cadmium and other metals (particularly lead and zinc) there are added 5 cc. of a 25% sodium tartrate solution and 20 ml. of sodium hydroxide solution (25 grams of sodium hydroxide per 100 ml. of solution), and the volume is adjusted to 100 ml. with distilled water. The cadmium is extracted by adding 5-ml. portions of dithizone in chloroform (10 micrograms of dithizone per milliliter). Extraction is continued until the last portion of dithizone solution added gives a colorless chloroform phase, each portion being transferred to a second separatory funnel containing 5 ml. of dithizone solution (100 micrograms per milliliter of chloroform) before the next is added. The dithizone extract is now washed with 50 ml. of distilled water and the cadmium is finally shaken into 50 ml. of 0.2 *N* zinc-free hydrochloric acid (made by absorbing, in triple distilled water, hydrogen chloride liberated by the addition of concentrated sulfuric acid to reagent grade hydrochloric acid, *2*).

Colorimetric Estimation. The acid extract, containing only cadmium, is now made alkaline by adding 50 ml. of zinc-free ammonia. (The zinc-free ammonia is obtained by diluting 50 ml. of concentrated ammonia, specific gravity 0.9, to 1000 ml. with distilled water and shaking it with 10-ml. portions of di-β-naphthylthiocarbazone solution, 20 micrograms per milliliter, until no change of color occurs in the last portion added. Entrained di-β-naphthylthiocarbazone must be removed completely by washing the dilute ammonia with pure chloroform until the last wash is colorless.) Five milliliters of a standard solution of di-β-naphthylthiocarbazone in chloroform (20 micrograms per milliliter) are now added and the mixture is shaken for one minute. After the phases have separated completely, a portion of the chloroform phase is diluted fivefold with pure chloroform; a 2.5-cm. cell is filled with the diluted solution and its transmittancy or density is obtained at 540 mμ with any suitable photometer.

The amount of cadmium present is then determined from a working curve prepared by treating known amounts of cadmium in 50-ml. portions of 0.2 *N* zinc-free hydrochloric acid exactly as was done with the sample. It is convenient to prepare working curves for two ranges of concentration—0 to 5 and 0 to 50 micrograms. In the latter case the strength of the standard extraction solution is increased so that each milliliter of chloroform contains 200 micrograms of di-β-naphthylthiocarbazone. Photometry in the 0 to 50-microgram range is carried out with a 1-cm. cell and the solution used is obtained by diluting the mixed color twentyfold with pure chloroform. (Weak standard di-β-naphthylthiocarbazone solutions must be stabilized unless they are made up just before use. The stabilization technique described by Bambach and Burkey, *1*, for standard dithizone solutions may be employed.)

DISCUSSION

In preparing samples for analysis, it is advisable to employ a wet-ashing technique. The dry-ashing method at 500° C. has proved unsatisfactory whenever deflagration occurs and whenever samples containing more than 10 micrograms of cadmium are low in their total ash content. Some improvement in recovery is obtained if ash-aid material (Na_2HPO_4) is added to "bulk" the ash. However, if too much is added, samples are not burned out cleanly and losses occur when the ash is again treated with nitric acid, and reignited. The magnitude of the losses which occur in the dry-ashing technique under a number of conditions is illustrated in Table I.

Although dithizone may be used throughout except for the purification of ammonia, di-β-naphthylthiocarbazone (*2*, *11*) has been used for the initial extraction of cadmium as well as for the final extraction in the colorimetric procedure. Extraction with this reagent is more rapid than with dithizone because, in con-

Table I. Cadmium Recovery Following Dry-Ashing

Cadmium Added *Micrograms*	Blood Used *Grams*	Na_2HPO_4 Added *Gram*	Cadmium Recovered *Micrograms*
	Urine (100-ml. portions)		
2			2.3, 2.4
10			9.5, 9.3
200			200, 202
	Blood		
3	5	...	3, 3
10	5	...	9.5, 9.5
50	5	...	42, 42
50	5	0.1	47
50	5	0.5	30, 42[a]
50	10	...	48
100	5	...	76
100	5	0.1	92
100	5	0.5	82, 82[a]

[a] These samples ashed cleanly only after a reignition following treatment with nitric acid.

trast to dithizone, di-β-naphthylthiocarbazone and its metal complexes are insoluble in the alkaline aqueous phase and therefore fewer extractions are required (particularly at higher pH values) to remove the metal complexes completely. This insolubility is disadvantageous, however, in the step of the colorimetric procedure in which the cadmium is separated from the zinc and lead by extraction from the strongly alkaline aqueous phase, since all metals forming complexes with di-β-naphthylthiocarbazone are also extracted. For this isolation, therefore, dithizone must be used. Di-β-naphthylthiocarbazone is again used in the final colorimetric step in which only pure cadmium is present, since its insolubility eliminates the need for a strict control of pH in obtaining a stable and reproducible zero point. Dithizone partitions more readily between the chloroform and alkaline aqueous phases, and a strict control of pH is required to obtain reproducible results.

The colorimetric method, although the most sensitive (as little as 0.01 microgram of cadmium can be detected, *9*), is attended by a number of difficulties which are eliminated or reduced only by careful attention to detail. The greatest danger lies in the fact that it is difficult to separate cadmium completely from the zinc which is entrained with the cadmium dithizonate. Fischer (*9*), recognizing this difficulty, advised washing the cadmium dithizonate with a 2% solution of sodium hydroxide. The authors have found that while this treatment is effective in removing zinc, it also results in a loss of cadmium (1 to 5 micrograms), especially when less than 20 micrograms of cadmium is present. The same loss was found to occur if distilled water was substituted for the alkali, but not if the cadmium dithizonate was stabilized by the presence of excess dithizone. It is for this reason that the dithizone extracts from the 5% alkali are run immediately into a separatory funnel containing 5 ml. of the strong dithizone solution. The wash water is made sufficiently alkaline by removal of sodium hydroxide entrained in the chloroform extract, to extract all the zinc, but only a portion of the excess dithizone. The final washed chloroform phase must contain some excess of dithizone in order to prevent loss of cadmium, and the analyst must use his judgment in determining the proper amount of strong dithizone to add in order to make certain that some remains in the chloroform phase. This is especially true when larger amounts of alkali are entrained as a consequence of increasing the number of dithizone extractions in order to make certain that all of the cadmium has been extracted.

Sandell (*16*) has stated that when nickel is present in the strongly alkaline phase it is slowly extracted by dithizone. It is the authors' opinion, however, that interference on the part of nickel is due chiefly to its oxidative action on weak dithizone solutions. This oxidation may be readily recognized by the fact that instead of the colorless chloroform obtained when cadmium extraction is complete one obtains a yellow shade which is due to oxidized dithizone. In such cases even though the chloroform phase does not become colorless when all the cadmium has been extracted, completeness of extraction may be assumed if the yellow tinge persists in the chloroform phase. That a complete separation of cadmium from zinc and nickel was attained by the authors' method of extraction and washing, was proved by the polarographic examination of the acid extract of the washed cadmium dithizonate–dithizone phase.

This is illustrated in Figure 2, in which *A* represents a sample of 10 micrograms of cadmium to which 100 micrograms each of zinc and nickel were added. Extractions with dithizone were then made following the addition of 1.25 grams of sodium tartrate, 5 grams of sodium hydroxide, and adjustment of the volume to 100 ml. *B* represents a comparison polarogram obtained with the evaporated residue of a hydrochloric acid solution to which 10 micrograms of cadmium and 2 micrograms each of nickel and zinc were added. Separation of the nickel and zinc diffusion waves was accomplished by electrolyzing the residues following their solution in 3 ml. of a solution containing 0.1 *N* ammonium acetate and 0.025 *N* potassium thiocyanate.

Lead and bismuth are the only other metals which may be extracted with cadmium and zinc and carried along to the step in which the cadmium is isolated. Like zinc, however, lead and bismuth are not extracted by dithizone from strongly alkaline solutions and therefore they are removed along with the zinc in the extraction and washing step. Cobalt, nickel, copper, mercury, and silver originally present in the sample are extracted initially, but all except possibly traces of copper and nickel remain behind in the chloroform phase when the latter is shaken with the 0.2 *N* hydrochloric acid in preparing the extract for separation of the cadmium from zinc and lead. The small amounts of copper and nickel that may be carried to the cadmium-isolation step are not extracted by dithizone from the 5% sodium hydroxide solution.

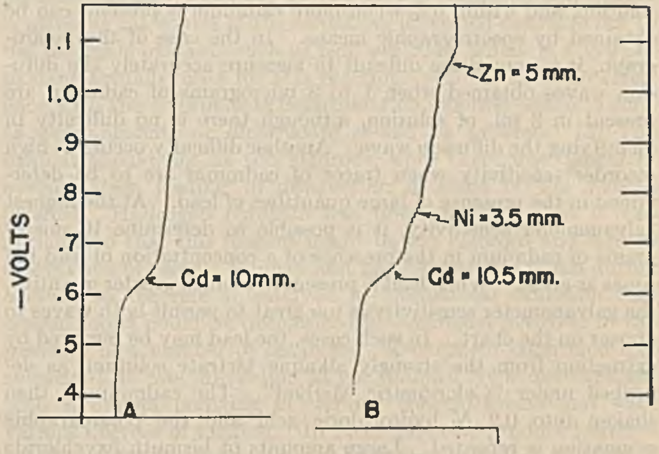

Figure 2. Polarograms Demonstrating Removal of Interfering Zinc and Nickel in Colorimetric Determination of Cadmium

In developing the colorimetric method it was noted that when the dithizone solution made from Eastman dithizone was used in the cadmium-separation step, it imparted a pink color to the chloroform even in the absence of cadmium. This was found to be due to the presence of semicarbazone which, however, was easily removed by purifying the dithizone according to the procedure described by Cowling and Miller (*6*). It was also observed, in confirmation of Sandell's finding (*16*), that weak cadmium dithizonate solution (as well as weak dithizone solution) was so unstable that the colors obtained could not be used directly for photometric purposes. This fact forced the authors to lengthen the colorimetric procedure considerably by introducing the mixed-color photometric step, for only in the presence of excess di-β-naphthylthiocarbazone (or dithizone) is sufficient stability obtained to permit the reliable estimation of small amounts of cadmium dithizonate by photometric means.

If reliable results are to be obtained with the colorimetric method, great care must be taken to ensure cleanliness of the extraction apparatus, pipets, and other containers used in making the final dilution for photometric reading. If this is not done, zinc present as surface contamination will also give a color which is read as cadmium. If the glassware is properly cleaned by repeated rinsing with dilute nitric acid and distilled water, it is possible to estimate quantities of cadmium in the 0- to 5-microgram range with a sensitivity of ±0.1 microgram, and in the 0- to 50-microgram range with a sensitivity of ±1 microgram.

The spectrographic and polarographic methods are satisfactory from the standpoint of specificity, sensitivity, and reproducibility (see Table II). Of the two, the spectrographic method is somewhat the more sensitive, and no difficulty is encountered in detecting even 1 microgram of cadmium when the residue of the 0.2 *N* hydrochloric acid extraction is taken up in 0.5 ml. of the buffer salt solution. Results that are accurate within ±1 microgram in the range of 0 to 10 microgram per milliliter buffer

Table II. Comparison of Results Obtained with Spectrographic, Polarographic, and Colorimetric Methods

(Recoveries of cadmium added to 100-ml. portions of urine)

Cadium Added	Cadmium Recovered: Spectrographic method	Cadmium Recovered: Polarographic method	Cadmium Recovered: Colorimetric method
Micrograms		*Micrograms*	
0	1.0	2	1.2
1	2.5	....	2.2
2	3.0	3.5	3.2
5	7	6.5	6
10	11	12	11[a]
50	48	50	48[a]

[a] Measured on 0–50 γ range.

solution, and within 5% when more cadmium is present, can be obtained by spectrographic means. In the case of the polarograph, it is sometimes difficult to measure accurately the diffusion waves obtained when 1 to 3 micrograms of cadmium are present in 3 ml. of solution, although there is no difficulty in identifying the diffusion wave. Another difficulty occurs at high recorder sensitivity when traces of cadmium are to be determined in the presence of large quantities of lead. At the highest galvanometer sensitivity, it is possible to determine 10 micrograms of cadmium in the presence of a concentration of lead ten times as great. When lead is present in a much greater quantity, the galvanometer sensitivity is too great to permit both waves to appear on the chart. In such cases, the lead may be removed by extraction from the strongly alkaline tartrate solution, as described under "Colorimetric Method". The cadmium is then shaken into 0.2 *N* hydrochloric acid and the polarographic estimation is repeated. Large amounts of bismuth oxychloride also interfere polarographically, but this interference may be eliminated by filtration and re-evaporation of the filtrate to dryness. The interference by bismuth oxychloride may also be eliminated by a re-extraction of the cadmium with dithizone as mentioned above for lead. Other metals such as nickel, cobalt, and zinc give diffusion waves above that of cadmium and consequently do not interfere.

It will be noted from Table II, in which the recoveries by the three methods are compared, that cadmium was detected in the samples to which no cadmium had been added. From some of the data in Table I, it seemed likely that the considerable quantity of cadmium present in the blank was due to its presence in the reagents. This was proved by analysis of large volumes of sulfuric and nitric acids, for it was found that two thirds of the blank was due to the 10 ml. of sulfuric acid, and the rest to the approximately 50 ml. of nitric acid used in each digestion.

In the matter of the choice of one of these methods for routine use, the authors have found that the polarographic method is the most convenient, particularly when only occasional samples are to be run. The spectrographic method, in their opinion, offers the most rapid and economical means of analysis, if large numbers of samples are to be handled daily. The colorimetric method, while the most sensitive, is the most laborious and time-consuming, but provides a reliable means for determination of cadmium when polarographic or spectrographic equipment is not available.

LITERATURE CITED

(1) Bambach, K., and Burkey, R. E., Ind. Eng. Chem., Anal. Ed., 14, 904 (1942).
(2) Cholak, J., Hubbard, D. M., and Burkey, R. E., *Ibid.* 15, 754 (1943).
(3) Cholak, J., and Story, R. V., *Ibid.*, 10, 619 (1938).
(4) Cholak, J., and Story, R. V., *J. Optical Soc. Am.*, 31, 730 (1941).
(5) *Ibid.*, 32, 502 (1942).
(6) Cowling, H., and Miller, E. J., Ind. Eng. Chem., Anal. Ed., 13, 145 (1941).
(7) Dwyer, F. P., *Australian Chem. Inst. J. Proc.*, 4, 26–34 (1937).
(8) Fairhall, L. T., and Prodan, L., *J. Am. Chem. Soc.*, 53, 1321 (1931).
(9) Fischer, H., *Angew. Chem.*, 50, 919–38 (1937).
(10) Hubbard, D. M., Ind. Eng. Chem., Anal. Ed., 13, 915 (1941).
(11) Hubbard, D. M., and Scott, E. W., *J. Am. Chem. Soc.*, 65, 2390 (1943).
(12) Lingane, J. J., and Kerlinger, H., Ind. Eng. Chem., Anal. Ed., 12, 750 (1940).
(13) Mahr, C., *Mikrochim. Acta*, III, 300 (1938).
(14) Pierce, W. C., and Nachtrieb, N. H., Ind. Eng. Chem., Anal. Ed., 13, 774 (1941).
(15) Prodan, L., *J. Ind. Hyg.*, 14, 132 (1932); 14, 174 (1932).
(16) Sandell, E. B., Ind. Eng. Chem., Anal. Ed., 11, 364 (1939).

Spectrophotometric Determination of Leuco Crystal Violet after Oxidation with Benzoyl Peroxide

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A method is reported for determining leuco crystal violet by oxidizing with benzoyl peroxide and measuring, by means of the spectrophotometer, the intensity of the color formed. The method has a precision represented by a standard deviation for a single value of ±0.25% of the total leuco crystal violet. The effect of impurities upon the accuracy is discussed.

ONE method described in the literature for the production of crystal violet involves the initial preparation of leuco crystal violet, *p,p′,p″*-methenyltris-(*N,N*-dimethylaniline), followed by oxidation to the finished product. The proper control of the oxidation necessitates a knowledge of the content of the leuco form. As far as the authors know, no method of determining this compound has been published; previous to the development of the method reported here leuco crystal violet had been determined merely by ascertaining the amount of material insoluble in a solution which was about neutral after the acid-insoluble constituents had been removed. Obviously, this method is not specific for the leuco crystal violet, so that it became desirable to find a more satisfactory method. Since the colorless leuco crystal violet is converted to the colored form by oxidation, the possibility of utilizing this behavior as the basis of a colorimetric method was considered.

After a consideration of oxidants, benzoyl peroxide was chosen. A study was then made of the optimum conditions of temperature, time, and concentration for color formation with this oxidant. The detailed method of analysis is given below, followed by a discussion of the experiments which determined the conditions of analysis.

METHOD OF ANALYSIS

Apparatus. Most of the color measurements were made using a modified automatically recording Hardy spectrophotometer (*2, 3, 4*). Calibrated cells, approximately 1 cm. in length, were used. This spectrophotometer plots the spectral curve as log log $1/T$ against a logarithmic function of the wave length, referred to as the octaval and measured in constant resolution units (c.r.u.).

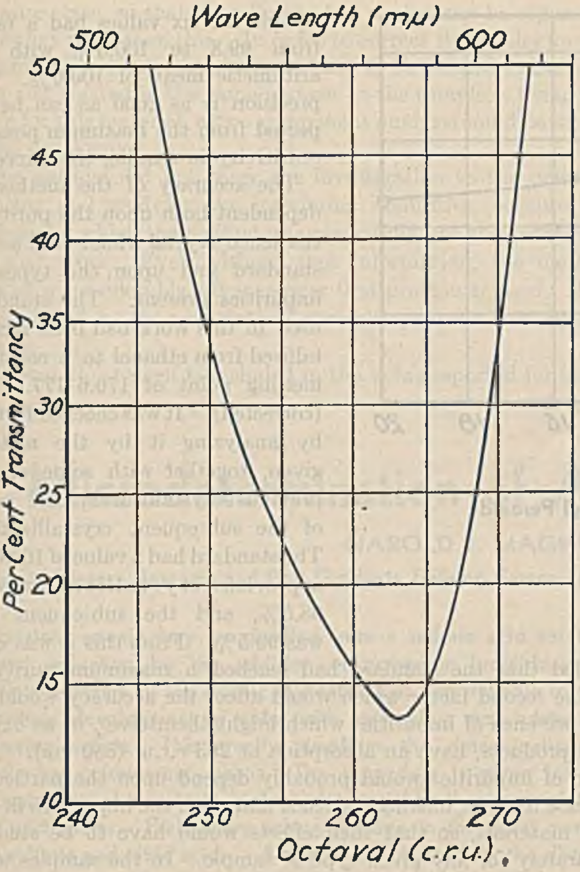

Figure 1. Standard Curve from Oxidation of Recrystallized Leuco Crystal Violet

Octaval (c.r.u.) = 332 log λ (mμ) − 655

This latter function can be converted to the more familiar wave-length scale by the equation:

$$\text{Octaval (c.r.u.)} = 332 \log \lambda\ (\text{m}\mu) - 655$$

In order to facilitate the interpretation of these curves, a wave-length scale in terms of millimicrons is shown at the top of Figures 1 and 3.

It should be possible to make the color measurements for this determination with considerable precision with any one of several filter photometers now available commercially. With this type of instrument, a filter transmitting in the range 525 to 625 mμ should be used. The instrument must be calibrated, using a leuco sample of known purity.

Reagents. Glacial acetic acid, which must be as free as possible from turbidity and colored impurities.

Benzoyl peroxide solution, 0.250 gram of C.P. benzoyl peroxide, dissolved and diluted to 100 ml. in glacial acetic acid in a volumetric flask. The solution may be kept for a few days in the dark without obvious deterioration, but must be discarded when it develops a yellow color.

Caution. Benzoyl peroxide must not be ground nor exposed to heat because it is said to explode under those conditions.

Preparation of Sample and Development of Color. The size of the sample taken for analysis depends upon the leuco crystal violet content. A sample of a weight to contain 0.15 to 0.23 gram of real leuco crystal violet is dissolved and diluted to 100 ml. in a volumetric flask with glacial acetic acid. A 10-ml. aliquot is again diluted to 100 ml. Ten milliliters of this dilution, representing 1.5 to 2.3 mg. of real leuco crystal violet, are transferred to a test tube (approximately 18 × 150 mm.), and 5 ml. of the benzoyl peroxide solution are added. The tube is rotated to mix its contents, immersed in a briskly boiling water bath for exactly 4.5 minutes to develop the color, then transferred immediately to an ice bath and shaken for about one minute to reduce to about room temperature as rapidly as possible (to prevent overoxidation). Too long cooling is avoided in order to prevent the acetic acid from freezing.

Measurement of Color Intensity and Calculations. The colored solution which is formed is too dark for direct measurement. Five milliliters are diluted, immediately after cooling, to 100 ml. in a volumetric flask with glacial acetic acid. The color intensity of this solution is measured within a period of not more than one hour. The transmittancy is measured at 263 c.r.u. (580 mμ) and the amount of leuco is calculated from the following equation:

$$\text{Leuco content (\%)} = \frac{-22.87 \log_{10} T}{\text{length of cell (cm.)} \times \text{wt. of sample (grams)}}$$

In this equation T is the transmittancy expressed as a decimal. The sample must be diluted as directed in this paper for this equation to hold. Figure 1, the curve upon which this equation is based, was obtained with a 0.2000-gram sample of purified leuco crystal violet after indicated dilutions.

COLOR REACTION

Choice of Oxidant. In choosing the proper oxidant, at least three criteria had to be kept in mind. (1) For manipulative convenience, as well, possibly, as for speed of oxidation and ease of controlling the course of the oxidation, it seemed desirable not to use insoluble oxidants such as lead peroxide, which is a type of oxidant actually used for this reaction. (2) To avoid interference with the colorimetric determination, colored oxidants such as permanganate or dichromate should be avoided. (3) The oxidant should not be too vigorous, since there was danger of overoxidation leading to destruction of some of the colored product. Hydrogen peroxide was first suggested, but it was anticipated that this reagent might be too vigorous and lead to destruction of color. Ellinger and Landsberger (*1*) found during a study of the role of catalysis in biochemical oxidation that crystal violet could be decolorized by hydrogen peroxide in the presence of a number of catalysts. Experiment confirmed this suspicion; it was impossible to get uniform color development with hydrogen peroxide in various concentrations and with various degrees of heating. In fact, the color produced always faded rapidly and often was completely destroyed to yield a colorless solution.

Benzoyl peroxide was then studied. This reagent seems to be a less vigorous oxidant than hydrogen peroxide; it is colorless; and it is soluble in glacial acetic acid, in which both leuco crystal violet and crystal violet itself are also soluble. Furthermore, even under extreme conditions of time and temperature, benzoyl peroxide did not cause sufficient overoxidation to destroy the color completely; at most, a brownish-red coloration was produced by some breakdown of the desired blue color.

Optimum Conditions for Oxidation. A study of optimum conditions for using this oxidant showed that by proper adjustment of the concentrations and relative proportions of reductant and oxidant, the time of reaction, and the temperature, a well-controlled oxidation to the violet color could be achieved.

A satisfactory heating time is one which causes a maximum development of color with the least possible decomposition of the oxidized form. This, of course, varies with the temperature. All work was done in a boiling water bath. In attempting to establish the optimum time some determinations were made with heating times varying from 3 to 11 minutes, and all other conditions unchanged. The intensity (absorption peak) of the purple color increased to a maximum, then decreased with longer heating periods. This effect is shown in curves 1, 2, and 3 of Figure 2, curve 1 illustrating the oxidation of purified leuco, and curves 2 and 3 illustrating the oxidation of two commercial samples. Curves representing samples heated for different lengths of time showed another and somewhat different effect in the blue region of the spectrum (Figure 3). The intensity of absorption in this region increased with the time of heating even after the intensity at the absorption peak had actually passed its maximum. This effect is probably due to some decomposition of the oxidized form.

The concentration of benzoyl peroxide and sample size are closely related, since their relative proportions affect the rate of oxidation. Curve 1 of Figure 2 shows the analysis of purified leuco using 12.5 mg. of benzoyl peroxide (as described in the method), curve 4 half that amount, and curve 5 twice that amount. The 12.5 mg. of benzoyl peroxide were selected as the

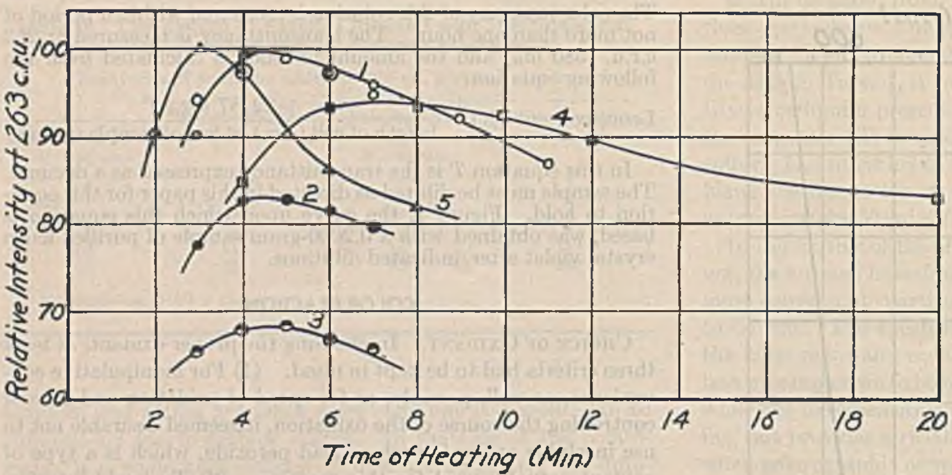

Figure 2. Effect of Time of Heating and Concentration of Benzoyl Peroxide

1, 4, 5. Recrystallized samples
2, 3. Commercial samples
1, 2, 3. 12.5 mg. of benzoyl peroxide per 15 ml.
4. 6.25 mg. of benzoyl peroxide per 15 ml.
5. 25.0 mg. of benzoyl peroxide per 15 ml.

optimum concentration (for 2 mg. of leuco) because the lower concentration failed to give sufficient color development while the higher concentration, although giving a similar maximum color, required too close an adjustment of the heating period with the possibility of missing the optimum time.

Cutting down the sample size has an effect similar to increasing the benzoyl peroxide concentration. The sample size must be adjusted to contain about 2 mg. of real leuco in order to maintain approximately the same peroxide-leuco ratio used and found to be optimum for the standard. Various weights of a commercial sample which had less than 50% of leuco was analyzed. The values found varied with the sample size as follows:

Sample Size, mg.	Leuco Found in Sample, %
2	39
3	42
4	43

Characteristics and Stability of Color. The color obtained conforms to Beer's law over the range 50 to 100% in strength at the maximum of the absorption band. Below 50% strength, there is a small negative deviation, which at 25% strength amounts to about 4% of the leuco present. This deviation would not affect an actual analysis, however, since the size of the sample is adjusted so that about 2 mg. of the leuco crystal violet are oxidized.

On aging, the solution gradually becomes weaker at a rate of about 0.5% strength per hour, so that the spectral curve should be determined within one hour after the preparation of the solution.

The color obtained is not affected by irradiation. Exposure of the solution for 3 minutes at a distance of 1 inch from a 100-watt electric light bulb does not affect the curve in any way.

The temperature at which the color is measured does not affect the strength obtained to an extent greater than that which may be accounted for by the thermal expansion of the solvent. No effect was obtained for the range in temperature (25° to 31° C.) in which the color measurements were made.

PRECISION AND ACCURACY

From twelve separate complete determinations including all the steps of the method (six determinations on each of two samples), a value for the standard deviation of a single value from the mean was calculated as ±0.25 part per 100 of leuco crystal violet. For one sample six values had a range from 84.5 to 85.2% with an arithmetic mean of 84.9%; for the other sample the six values had a range from 99.8 to 100.5% with an arithmetic mean of 100.0%. The precision is as good as can be expected from the maximum possible sensitivity in reading the curves.

The accuracy of the method is dependent both upon the purity of the leuco crystal violet used as the standard and upon the types of impurities present. The standard used in this work had been recrystallized from ethanol to a constant melting point of 176.6–177.6° C. (corrected). It was checked further by analyzing it by the method given, together with some of the previous crystallization and some of the subsequent crystallization. The standard had a value of 100.0%, a previous crystallization was 98.5%, and the subsequent one was 99.5%. From this it was concluded that the standard had reached a maximum purity.

The second factor which would affect the accuracy would be the presence of impurities which might themselves, or as oxidation products, have an absorption at 263 c.r.u. (580 mμ). The type of impurities would probably depend upon the particular process used for making the leuco and upon the impurities in the raw materials, so that their effects would have to be studied separately for any given type of sample. In the samples with which the authors worked there seemed to be two general classes of impurities—one which absorbed in the region of 210 to 240 c.r.u. (400 to 450 mμ), which would not interfere with the method; and another class which absorbed in the same spectral region as the oxidized leuco crystal violet, the peak of the absorption band being about 265 c.r.u. (588 mμ) against 263 c.r.u. (580 mμ) for the pure leuco crystal violet. This material was not isolated in

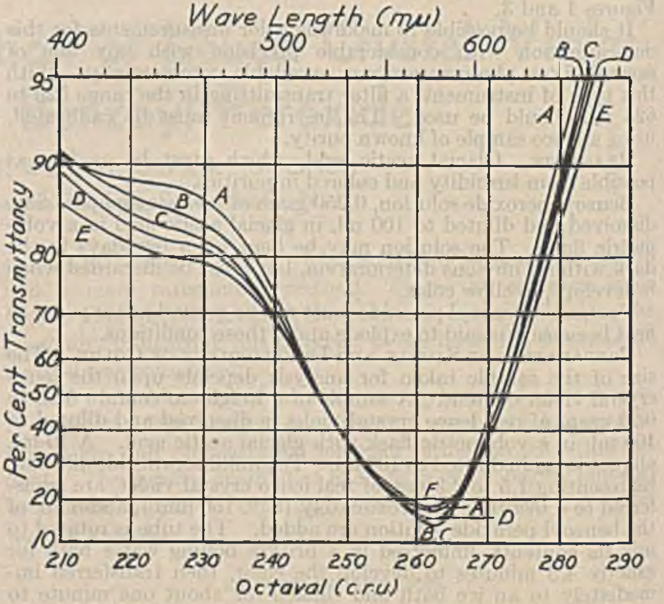

Figure 3. Variation of Transmission Curves with Variation in Heating Time

Octaval (c.r.u.) — 332 log λ (mμ) — 655

A. 3 minutes
B. 4 minutes
C. 5 minutes
D. 7 minutes
E. 11 minutes

the pure state, so that actually the two peaks may be separated somewhat more than this. In order to correct the results for the presence of this impurity, it would have to be isolated in the pure form and treated in the same manner as the sample. Using the curve for this material, a two-component analysis could be set up in the usual way.

The authors did not carry the investigation to the point of isolating and studying the interfering impurities, because the purpose for which the method was needed did not necessitate doing that work. Even without that information, the method marked a considerable advance over that previously used. The values found by the new method were always lower than by the old one.

Crystal violet itself is included in the value reported for leuco crystal violet, but its presence can be corrected for after determining crystal violet separately without oxidation.

ACKNOWLEDGMENTS

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LITERATURE CITED

(1) Ellinger, P., and Landsberger, M., *Klin. Wochschr.*, 2, 966–9 (1923).
(2) Shurcliff, W. A., *J. Optical Soc. Am.*, 32, 229–33 (1942).
(3) Stearns, E. I., IND. ENG. CHEM., ANAL. ED., 14, 568–9 (1942).
(4) Stearns, E. I., *J. Optical Soc. Am.*, 33, 27–30 (1943).

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Microdetermination of Arsenic in Biological Materials

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Pentavalent arsenic may be distilled from a sulfuric acid solution without reduction by the addition of potassium bromide. The distillate contains all the arsenic in pentavalent form suitable for the immediate development of color with ammonium molybdate and hydrazine sulfate. This greatly simplifies the determination of arsenic by colorimetric means. The procedure is given for the determination of arsenic in biological material in the range of 1 to 100 micrograms. Preliminary ashing is done in the usual manner with sulfuric and nitric acids. A special still is used for the distillation to give a small volume of distillate in which the molybdenum blue color is developed by adding the color reagents directly to the distillate. Antimony does not interfere. Large amounts of phosphorus may interfere, but can be removed by special treatment.

METHODS for the determination of arsenic have depended on separation of the arsenic from other metals, either by the evolution of arsine or by the distillation of the arsenic as the trichloride. The most satisfactory colorimetric determinations of small amounts of arsenic have depended on the formation of molybdenum blue, a procedure which has been used by a large number of workers (*1–5*). For this colorimetric procedure the arsenic must be present in pentavalent form, and it is necessary to treat the separated arsenic with some oxidizing agent. Nitric acid has been most commonly used, but this has had several disadvantages. Since the nitrate ion interferes with the color reaction, all traces of the nitric acid must be removed by heating; this must be carefully controlled to prevent losses of arsenic. In addition, considerable time is lost in this step when large numbers of arsenic determinations are done.

The method described here is based on the finding that pentavalent arsenic may be distilled as such to give a distillate which contains the arsenic in pentavalent form, without the use of oxidizing agents. Under these conditions the molybdenum blue color may be developed directly on the distillate without further treatment. This modification has given more reliable and consistent results than could be obtained by the method previously described (Chaney and Magnuson, *1*), and is more rapid than other published methods. Twenty to thirty determinations can be done each day with no difficulty. The method is most useful in the range of 1 to 100 micrograms of arsenic. While it has been used for the determination of arsenic in biological materials, it could be adapted to other uses.

CHEMICALS

All chemicals should be of the best reagent grade. The reagent grade of sulfuric acid (Merck) has been found more satisfactory than some lots of special arsenic-free grades. Sulfuric acid, concentrated. Nitric acid, concentrated. Perchloric acid, 60% Potassium bromide. Ammonium molybdate. Hydrazine sulfate.

REAGENTS

In working with small amounts of arsenic the authors have made up reagents fresh daily to avoid contamination and possible decomposition. They have not determined the keeping qualities of these reagents.

Potassium bromide, 30% solution in distilled water.

Molybdate color reagent. Add 10 cc. of concentrated sulfuric acid to 40 cc. of distilled water, cool, add 1.0 gram of ammonium molybdate, and dilute to 100 cc.

Hydrazine sulfate, 0.05% solution in distilled water.

Standard pentavalent arsenic solution. Dissolve 1.5 grams of arsenic pentoxide in 100 cc. of *N* sodium hydroxide, add 600 cc. of distilled water, neutralize with 100 cc. of *N* hydrochloric acid, and dilute to 1000 cc. Place three 25-cc. aliquots in glass-stoppered flasks and add 25 cc. of concentrated hydrochloric acid and 50 cc. of 10% potassium iodide to each. Make simultaneous blank determinations in triplicate. Allow the flasks to stand in the dark for 2 hours, then titrate the free iodine with 0.1 *N* sodium thiosulfate. One cubic centimeter of 0.1 *N* sodium thiosulfate is equivalent to 3.75 mg. of arsenic.

Make appropriate dilutions from the stock solution to give 10 and 50 micrograms of arsenic per cc. This pentavalent arsenic solution remains unchanged for months.

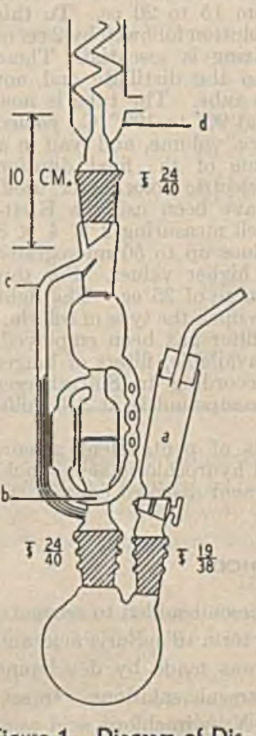

Figure 1. Diagram of Distilling Apparatus

APPARATUS

Round-bottomed two-necked, distilling flasks of 250-cc. capacity, with 24/40 ₮ center joint and 19/38 ₮ side joint.

Dropping funnel, 19/38 ₮ joint to fit 250-cc. distilling flask.

Graham reflux condenser, coil-type, 200 mm. in length with 24/40 ₮ joint at either end.

Special still, now available commercially from the Scientific Glass Apparatus Co., Catalog No. M-1586 (Figure 1).

Heater, 350-watt Cenco hot cone. Hot plate. Photoelectric colorimeter. Test tubes graduated at 25 or 35 cc. Erlenmeyer flasks.

Table I. Recoveries from Reagents

Arsenic Added *Micrograms*	Arsenic Found *Micrograms*	Maximum Error %
0	0, 0, 0, 0.1, 0.1	..
1	1.1, 1.1	10
2	2.1, 2.2, 2.0, 2.1	10
3	3.2, 3.2, 2.9, 2.8	7
4	3.9, 3.9, 4.0	3
5	5.0, 4.9, 5.0, 5.0	2
6	6.1, 6.2	3
8	8.1	1
10	9.9, 9.9	1
20	19.9, 19.6	2
30	29.6, 29.6	1
40	39.0, 38.4	4
50	49.3, 49.8	1

PROCEDURE

The sample is digested in Erlenmeyer flasks, using 5 cc. of sulfuric acid and excess nitric acid as recommended by Morris and Calvery *(4)*. Care should be taken to maintain an excess of nitric acid until all organic matter is destroyed. A few drops of perchloric acid will speed the final stages of the digestion. When the digest is colorless and has cooled, it is transferred to a two-necked distilling flask using two or three 5-cc. quantities of water as a wash. The solution is then heated on the hot cone heater until strong fumes of sulfuric acid appear, in order to remove traces of nitric acid.

Distillation. Five cubic centimeters of water are added to the cooled sulfuric acid digest, and 2 cc. of 30% potassium bromide are put in the dropping funnel (*a*, Figure 1), which is then connected to the outer neck of the distilling flask. The distilling head is connected to the center neck and the flask placed on the already hot Hot Cone heater. The flask should rest on the largest removable ring of the heater. When boiling has started and steam has begun to condense in the trap, *b*, 3 cc. of distilled water are added through the top of the still, and the condenser is put in place so that the condensed vapor will drip down the capillary tube, *c*. The potassium bromide is now blown in through the dropping funnel followed by 2 cc. of water as a wash. The distillation is continued for 4 minutes from the time the potassium bromide is blown in; then the still is disconnected from the flask and condenser and the distillate poured out through the top of the still into the test tube in which the color is to be developed. The trap is rinsed two or three times with 2 cc. of water and these rinses are added to the tube. The still itself is rinsed thoroughly with distilled water, and is ready for use again. No further cleaning is necessary.

Color Development. The amount of solution in the color tubes following the rinses will be from 15 to 20 cc. To this are then added 2 cc. of the molybdate solution followed by 2 cc. of the hydrazine sulfate. Thorough mixing is essential. These solutions should be added directly to the distillate and not allowed to run down the sides of the tube. The tube is now heated for 10 minutes in a water bath at 90° to 100° C., cooled in cold water, brought to a 25- or 35-cc. volume, and read in a photoelectric colorimeter. The volume of the final dilution will depend upon the type of photoelectric colorimeter used. For the present work the authors have been using a Klett-Summerson instrument employing a cell measuring 2 × 4 × 8 cm. The 4-cm. length is used for values up to 50 micrograms of arsenic and the 2-cm. length for higher values. For this cell the authors have used a final volume of 35 cc. The light filter to be used depends to some degree upon the type of colorimeter. With the Klett a 690-millicron filter has been employed. Where other types of photocells are available, filters of longer wave lengths may be employed. According to Sultzaberger *(6)*, the maximum absorption of the compound is at 840 millimicrons.

In setting up undistilled standards of pentavalent arsenic for color development, 3 cc. of normal hydrochloric acid should be added to allow for the amount of acid distilled over in the unknowns.

TESTS OF THE METHOD

Shown in Table I are recoveries of arsenic added to reagents. The arsenic was added in pentavalent form to sulfuric acid and then distilled. The reference curve was made by developing the color directly on the pentavalent arsenic solutions. In setting up these standard curves 3 cc. of *N* hydrochloric acid were added to the solution in the color tube before the molybdate was added. With 1 to 3 micrograms of arsenic the recoveries were within 10% of the true values, and above this level all recoveries were within 5%. Blank values which range from 0 to 0.2 microgram were subtracted from the recoveries in each instance.

In Table II are shown recoveries of arsenic from whole blood. Known amounts of arsenic were added to 5 cc. of whole blood, digested, and distilled. Blank values were subtracted from the recoveries. Recoveries at the 1-microgram level were within 10%, and above this level were within 5%.

DISCUSSION

In the course of developing the method, the interesting finding has been made that, contrary to general belief, pentavalent arsenic can be distilled from a mixture of sulfuric acid and potassium bromide and that the distillate contains the arsenic in pentavalent form. This has been shown in two different ways. First, the arsenomolybdate color does not develop unless the arsenic is present in pentavalent form. In the distillates as obtained by the method here described, the color develops without any preliminary oxidation of the arsenic.

Table II. Recoveries from Whole Blood

Arsenic Added *Micrograms*	Arsenic Found *Micrograms*	Maximum Error %
0	0.3, 0.3	..
1	1.1, 1.1	10
5	5.0, 5.0, 5.0, 5.1, 5.1, 5.0	2
10	10.1, 9.5, 9.7, 9.5	5
20	19.7, 19.3, 20.0, 19.8	4
40	40.0	0
50	50.2, 50.2, 49.8, 49.8	1
100	100, 102	2

In the second place, arsenic in the distillate does not titrate as trivalent arsenic with iodine, but does titrate as pentavalent arsenic with iodide. Distillates containing 1- to 5-mg. quantities of arsenic were obtained by pooling a number of distillates from the microstill. A number of distillations were also done using a round-bottomed flask connected to a Fresenius flask by a glass tube. Water was used in the Fresenius flask to catch the distillate. Using either method of distillation it was found that if pentavalent arsenic were added to the sulfuric acid before distilling, no trivalent arsenic could be recovered in the distillate, and 95 to 100% could be titrated as pentavalent arsenic.

When the arsenic was added to the sulfuric acid in trivalent form before distillation, 23 to 30% could be titrated in the distillate as trivalent arsenic and the remainder as pentavalent arsenic.

Titration of Trivalent Arsenic *(6)*. The distillate was titrated with 0.01 *N* iodine in the presence of excess sodium bicarbonate. A blank was run simultaneously.

Titration of Pentavalent Arsenic *(6)*. Concentrated hydrochloric acid was added to the solution to give a final concentration of approximately 6 *N*, and 5 cc. of 10% potassium iodide were then added. At the end of 2 hours the free iodine was titrated with 0.01 *N* sodium thiosulfate. Blanks were run at the same time and subtracted from the final readings.

The authors have not identified the form in which the arsenic is distilled in the present method. Since the arsenic is present in the digest and in the distillate in pentavalent form, it is probably distilled in the form of an unstable arsenic pentabromide which decomposes on passing through the water in the trap.

The authors have used various types of simple distillation apparatus for determining 50-microgram quantities of arsenic, but recoveries have in no case been comparable to those obtained with the microstill. For large quantities of arsenic the microstill was not necessary.

THE REAGENT BLANK. Certain lots of sulfuric acid have given difficulty with a reagent blank which is apparently not due to arsenic and is of significance only on determinations below 3 micrograms. With such lots the blank is irregular, and recoveries below 3 micrograms are correspondingly erratic. However, recoveries above this level are perfectly regular, and give no indication of the presence of the blank. Furthermore, if to such distilled blanks one adds pentavalent arsenic in excess of 3 micrograms, color develops only in an amount proportional to the added arsenic, and the interfering blank is not observed. The authors have been unable to identify this interfering substance, which is found only in certain lots of sulfuric acid. The most satisfactory sulfuric acid has been the regular reagent grade rather than some of the "arsenic-free" grades.

A "pseudo blank" may also appear if the molybdate solution is added down the sides of the test tube rather than directly to the distillate; the molybdate may decompose on the sides of the hot tube and result in a blue color.

INTERFERING SUBSTANCES. During the distillation process complete separation from phosphorus is accomplished except for a mechanical carry-over of approximately 1 part in 100,000. Thus, if one adds 0.1 gram of phosphate to the digest, about 1 microgram will appear in the distillate. The importance of this phosphorus interference will obviously depend on the relative amounts of phosphorus and arsenic in the digest. In most biologic work it becomes important only when large amounts of urine, or specimens of nervous tissue or bone are to be analyzed. In such cases, phosphorus interference may be eliminated by pouring first distillate into a second distilling flask, adding 2 to 3 cc. of concentrated nitric acid and 5 cc. of concentrated sulfuric acid, taking down to strong fumes of sulfuric acid, then redistilling.

Antimony does not interfere with the determination.

RATE OF DISTILLATION AND LIMITS OF ACID TOLERANCE. The rate of distillation of the arsenic under the heating conditions described depends upon the amounts of sulfuric acid and water present. The 4-minute distillation time will allow complete recovery of the arsenic unless the loss in sulfuric acid volume during digestion has been more than 40%.

The amount of hydrobromic acid distilled in the 4-minute period varies between 2.5 and 4.0 milliequivalents. Using the color solutions as described there is no significant difference in the color intensity in the range between 1.0 and 5.0 milliequivalents. There is thus an adequate margin of safety with respect to acidity.

SUMMARY

A rapid method for the determination of small amounts of arsenic in biological material is described in which the arsenic distillate is obtained in pentavalent form. This distillate can be used without further treatment for the final colorimetric determination with ammonium molybdate. The method is rapid, and has given results comparable in accuracy to other published methods for microdetermination of arsenic.

LITERATURE CITED

(1) Chaney, A. L., and Magnuson, H. J., IND. ENG. CHEM., ANAL. ED., 12, 691 (1940).
(2) Hubbard, D. M., *Ibid.*, 13, 915 (1941).
(3) Maechling, E. H., and Flinn, F. B., *J. Lab. Clin. Med.*, 15, 779 (1930).
(4) Morris, H. J., and Calvery, H. O., IND. ENG. CHEM., ANAL. ED., 9, 447 (1937).
(5) Scott, W. W., "Standard Methods of Chemical Analysis", 5th ed., pp. 99, 115, New York, D. Van Nostrand Co., 1939.
(6) Sultzaberger, J. A., IND. ENG. CHEM., ANAL. ED., 15, 408 (1943).

Determination of Nitric Oxide Using Solid Reagents

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SMITH and Leighton (*5*) have described a micromethod for the determination of nitric oxide in mixtures of hydrogen or nitrogen which consists in a modification of the macromethod of Baudisch and Klinger (*1*). Their procedure is based on the oxidation of nitric oxide by the addition of oxygen and the rapid absorption of the resulting oxides of nitrogen by a moist potassium hydroxide bead. The method is indirect, because the amount of oxygen required is variable and consequently the amount of hydrogen or nitrogen in the original mixture must be calculated by analyzing for residual hydrogen after removing all the remaining oxygen by combustion with an excess of hydrogen (a known volume of hydrogen being added if necessary). A further disadvantage is the possibility of contaminating the mercury surface through the presence of the oxides of nitrogen.

The present method is an adaptation of that of Divers (*3*), who found that alkaline sodium sulfite solution readily absorbed nitric oxide with the formation of sodium hyponitrososulfate. Further work by Moser and Herzner (*4*) showed that the reagent was superior to ferrous sulfate in its capacity for absorbing nitric oxide but the rate of absorption was somewhat less.

A pellet of potassium hydroxide is ground in a mortar and sodium sulfite crystals ($Na_2SO_3.7H_2O$) are added till a thick paste is formed. No water is required, as the mixture becomes moist. The paste is then formed into a bead on a platinum loop and if sufficient sodium sulfite has been added very little drying is necessary. If the bead is thoroughly dried no absorption takes place, but aside from this the moisture content does not appear to be critical. When placed in the gas containing nitric oxide absorption is complete in 5 to 10 minutes.

Table I is indicative of the accuracy obtainable by this method, using the Blacet-Leighton apparatus (*2*).

Table I. Determination of Nitric Oxide

Determination	Volume of Sample *Cu. mm.*	Nitric Oxide Theoretical %	Nitric Oxide Determined %	Difference %
		Nitric oxide-hydrogen mixtures		
1	41.68	0.0	0.2	−0.2
2	47.17	13.4	13.5	−0.1
3	51.32	21.6	1.4	0.2
4	65.11	38.4	38.6	−0.2
5	81.18	50.2	50.0	0.2
6	60.83	66.6	66.2	0.4
7	49.12	80.4	80.0	0.4
				Av. 0.3
		Nitric oxide–ethylene mixtures		
1	41.97	0.0	0.2	−0.2
2	45.79	8.8	8.4	0.4
3	51.81	19.4	19.0	0.4
4	64.73	35.4	35.0	0.4
5	83.56	49.8	49.7	0.1
6	62.85	65.8	65.0	0.8
				Av. 0.4

In contrast to the method of Smith and Leighton, the present method can be used in the presence of combustible gases other than hydrogen, and very satisfactory results have been obtained in the presence of acetylene as well as ethylene and hydrogen.

LITERATURE CITED

(1) Baudisch, O., and Klinger, G., *Ber.*, 45, 3231 (1912).
(2) Blacet, F. E., and Leighton, P. A., IND. ENG. CHEM., ANAL. ED., 3, 266 (1931).
(3) Divers, E., *J. Chem. Soc.*, 75, 82 (1899).
(4) Moser, L., and Herzner, R., *Z. anal. Chem.*, 64, 81 (1924).
(5) Smith, R. N., and Leighton, P. A., IND. ENG. CHEM., ANAL. ED., 14, 758 (1942).

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Colorimetric Determination of Traces of Osmium

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THE work here described was undertaken to develop a colorimetric method for determining minute amounts of osmium after volatilization as the tetroxide, with special reference to the determination of the element in meteoric iron. Goldschmidt and Peters (*3*) and I. and W. Noddack (*4*) have determined the abundance of the platinum metals in meteorites by spectrographic methods. From these studies it appears that the average osmium content of the nickel-iron phase of meteorites lies somewhere in the range 3 to 10 parts per million. This order of magnitude is such that osmium can be determined successfully colorimetrically by making use of the sensitive thiourea reaction discovered by Chugaev (*1*), after isolation of the tetroxide by distillation from a 1- to 2-gram sample.

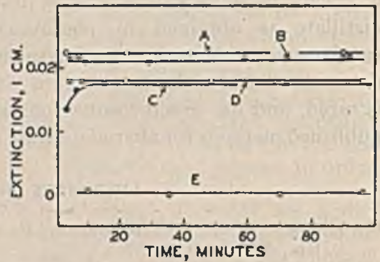

Figure 1. Color Intensity of Osmium-Thiourea Solutions as a Function of the Time of Standing after Addition of Thiourea

Green filter, Cenco No. 2

A. 1.47 p.p.m. of Os as OsO_4 in a solution 2 *N* in HCl and containing 0.2% thiourea; room temperature (27° C.)

B. As in *A* except 4 *N* HCl

C. As in *A* except 6 *N* HCl

D. 0.5 ml. of OsO_4 solution containing 0.0368 mg. of Os treated with 10 ml. of 6 *N* HCl saturated with SO_2 and allowed to stand at room temperature for 20 minutes; 0.5 ml. of 10% thiourea solution then added and whole diluted to 25 ml. with water.

E. 2.0 p.p.m. of Os as chloroosmate in 2 *N* HCl and 0.2% thiourea solution at room temperature.

The procedure ordinarily used for the distillation of decigram (*2*) and milligram-centigram (*6*) quantities of osmium tetroxide involves passage of a stream of air through the boiling nitric acid solution and absorption of the tetroxide in several receivers of dilute hydrochloric acid saturated with sulfur dioxide; the solution is then evaporated with hydrochloric acid and osmium precipitated hydrolytically as the hydrous dioxide.

This procedure has been modified for the present purpose. Distillation is made by boiling without passage of air through the solution. Hydrochloric-sulfurous acid is retained as the absorbing solution, but the latter is not evaporated after the distillation, because this results in serious losses of osmium. The osmium in the hydrochloric acid–sulfur dioxide solution reacts readily with thiourea to form the red complex, which is stated (*1*) to have the composition $[Os(NH_2CSNH_2)_6]Cl_3.H_2O$ in the solid state. Since concentration of the absorbing solution by evaporation after the distillation is not admissible, the volume of the distillate must be kept as small as possible to avoid undue loss in sensitivity. Fortunately, osmium tetroxide is readily volatilized, so that boiling off one fifth of the original solution gives a quantitative expulsion of small amounts of osmium. In one experiment, 140 ml. of solution containing 12 micrograms of osmium were distilled according to the procedure described below, and it was found that approximately 70% of the osmium was present in the first 10 ml. of distillate collected and 30% in the second 10-ml. portion; no osmium was detectable in the third 10 ml. of distillate. Usually the solution to be distilled need not have a volume greater than 50 ml., so that only 10 ml. of distillate need be collected. A single portion of hydrochloric acid–sulfur dioxide absorbing solution having a volume of 10 ml. (or even 5 ml.) suffices for satisfactory collection of osmium tetroxide (Table I).

The volume of the final solution in which the color has been developed can be kept down to 15 to 25 ml. With a photoelectric photometer the limit of detectability of osmium is then 1 or 2 micrograms when a layer of solution 1 cm. thick is examined in green light (a solution containing 1 p.p.m. of osmium gives an extinction of ca. 0.015 in 1-cm. depth with a green filter). The use of a visual colorimetric method is less satisfactory than a photometric method because thiourea gives a yellow color with a sulfur dioxide solution. The formation of this yellow substance is of no importance in a photometric method, since it absorbs green light to a negligible extent (the transmittancy of a blank solution, 1 cm. in thickness, under the conditions recommended below is 99.9% or more with a Cenco No. 2 green filter).

The reaction between thiourea and osmium in the hydrochloric acid–sulfur dioxide solution is rapid even at room temperature and full color intensity is attained in less than 5 minutes. In the preparation of known solutions for the construction of the standard curve, osmium must be added as the tetroxide. Osmium as chloroosmate gives no appreciable color with thiourea at room temperature in hydrochloric acid medium, even after several days' standing. The red color appears only on heating (more rapidly if stannous chloride is added). This behavior indicates that osmium is not present to any extent as chloroosmate in the absorbing solution. The osmium-thiourea color system obeys Beer's law.

When an attempt was made to determine osmium in the presence of metallic iron by dissolving the latter in 5 *N* nitric acid in a distilling flask and then distilling the solution, the results were markedly low. The reason for this was not further investigated, but the evolution of nitric oxide is apparently to blame. The difficulty was avoided by dissolving the iron in sulfuric acid, oxidizing the ferrous salt with potassium permanganate, destroying the excess of permanganate and manganese dioxide with a small amount of ferrous salt, then adding nitric acid, and distilling. The excess permanganate and any higher oxides of manganese must be destroyed, else ruthenium will distill as the tetroxide with osmium and interfere by giving a blue color with thiourea.

APPARATUS

There is required an all-glass distilling apparatus consisting of a round-bottomed flask (provided with an inlet tube for addition of reagents) which is connected by means of a ground-glass joint to a water-cooled condenser. The distilling apparatus used in the present work was essentially the same as that described by Robinson, Dudley, Williams, and Byers (*5*) for distilling selenium and arsenic from soil samples. In this apparatus the thistle tube for addition of reagent solutions is fused into a ground-glass connection, so that it is easy to remove any insoluble material from the flask at the end of the distillation and examine it for osmium. The distilling flask may have a volume of 250 to 500 ml.

Table I. Colorimetric Determination of Osmium after Distillation of Tetroxide

No.	Addition Iron	 Ru^{III}	Os Taken	Os Found
	Gram	γ	γ	γ
1	..	..	7.5	7
2	..	..	18.8	17
3	..	..	37.5	36
4	1	..	7.5	7
5	1	..	18.8	18
6	1	..	37.5	34
7	1	25	18.8	18
8	1	50	18.8	17
9	1	50	18.8	18
10	1	25	3.8	3

SPECIAL SOLUTIONS

Osmium Tetroxide, 0.005% osmium in 0.1 *N* sulfuric acid. This solution is prepared by dilution of a stronger one, which may be obtained as follows: Make a number of scratches with a file on a 0.5-gram ampoule of osmium tetroxide and weigh the ampoule. Drop the ampoule into a glass-stoppered bottle (200 ml.) containing about 50 ml. of water. Break the ampoule by shaking the bottle, and when the osmium tetroxide has dissolved, decant off most of the supernatant liquid into a volumetric flask (250 ml., for example). Rinse the bottle well with successive portions of water and transfer these to the volumetric flask, taking care to leave all the glass fragments in the bottle. Then transfer the glass fragments to a weighed filter crucible and obtain the weight of the whole after drying. The weight of the osmium tetroxide used to prepare the stronger solution is thus obtained by difference.

Thiourea, 10% aqueous solution.

Potassium Permanganate, 5% solution.

Hydrochloric Acid–Sulfur Dioxide Solution, 1 to 1 hydrochloric acid freshly saturated with sulfur dioxide.

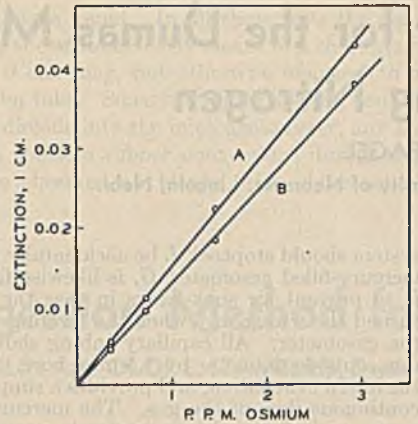

Figure 2. Extinction-Concentration Curves for Osmium Tetroxide–Thiourea Solutions

Green filter, Cenco No. 2

A. Solutions contained 8 ml. of 6 *N* HCl and 0.5 ml. of 10% thiourea in 25 ml., room temperature

B. OsO_4 solutions treated with 10 ml. of 6 *N* HCl saturated with SO_2, allowed to stand 15 minutes at room temperature, 0.5 ml. of 10% thiourea solution added, and whole diluted to 25 ml. with water.

PROCEDURE

The sample solution should have a volume such that when it is ready for distillation, after addition of nitric acid and permanganate, the total volume is less than 50 or 60 ml. Chlorides must be absent, and if permanganate oxidation is necessary the solution should be about 1 *N* in sulfuric acid. Transfer the solution to the distilling flask, and if ferrous iron or other reducing substances are present, add potassium permanganate solution until an excess of a drop is present as indicated by the color change; avoid getting permanganate on the neck of the flask. Next add approximately 50 mg. of ferrous ammonium sulfate hexahydrate to destroy permanganate and higher oxides of manganese. The volume of the solution at this point should be 35 to 40 ml.

Add a few small grains of pumice, connect the flask to the condenser, and heat the solution slowly to near the boiling point to make it certain that higher manganese oxides have been brought completely into solution. Dip the end of the condenser into 10 ml. of hydrochloric acid–sulfur dioxide solution contained in a 100-ml. graduate, the upper half of which has been cut off (a large vial or test tube marked to indicate 20 ml. may be substituted). Add 15 ml. of concentrated nitric acid through the inlet tube of the flask and distill at such a rate that 10 ml. of distillate are collected in 10 to 15 minutes. Transfer the distillate mixture to a 25-ml. volumetric flask, rinsing the condenser and receiver with a few milliliters of water, add 0.50 ml. of thiourea solution, and make up to the mark with water. Determine the transmittancy of the solution after 5 minutes (longer standing does no harm), using green light. In constructing the standard curve add 0, 25, and 50 micrograms of osmium as the tetroxide to distillates obtained from osmium-free nitric acid mixtures as already described.

If the amount of osmium is likely to be less than 10 micrograms, use 5 ml. of hydrochloric acid–sulfur dioxide solution contained in a 25-ml. graduate for collecting 10 ml. of the distillate. Add 0.3 ml. of thiourea solution, read the volume of the solution in the graduate (which has been checked for accuracy), and determine the transmittancy as described above.

DETERMINATION OF OSMIUM IN METEORIC IRON

The following procedure was used in determining osmium in the Cañon Diablo siderite.

A 1-gram sample was heated near the boiling point with 10 ml. of 6 *N* sulfuric acid in an Erlenmeyer flask until there was practically no further action. The solution was decanted from the unattacked sample and reserved. The remainder of the metal was dissolved in 10 ml. of hot 6 *N* hydrochloric acid. The solution was then treated with 10 ml. of 6 *N* sulfuric acid and evaporated to fumes of sulfuric acid. The evaporation to fumes was repeated after dissolving the salts in water. The residue was then heated with about 10 ml. of water to bring all but a small amount of insoluble material into solution. This solution and the reserved sulfuric acid solution were transferred to the distilling flask and the ferrous iron was oxidized with permanganate. After addition of nitric acid, the solution was distilled and osmium was determined as described above (5 ml. of hydrochloric acid–sulfur dioxide solution were used to collect 10 ml. of distillate).

The small amount of insoluble material remaining in the solution after distillation was collected in a small porous porcelain filter crucible, the bottom of which had been covered with a thin layer of quartz powder to facilitate the subsequent removal of the insoluble material. The collected material was dried by washing with acetone, transferred to a nickel crucible, mixed with 1 gram of sodium peroxide, and heated at low redness for 30 minutes. The melt was extracted with 20 ml. of water and the solution heated near the boiling point to decompose peroxide. The solution was transferred to the distilling flask and treated with 10 ml. of 6 *N* sulfuric acid. Approximately 50 mg. of ferrous ammonium sulfate were added and the solution was heated to destroy nickelic oxide. Nitric acid was then added and the distillation made as already described. No osmium was detected in this distillate.

The osmium content of the Cañon Diablo meteorite thus found is 2.5 p.p.m. Since the method tends to give slightly low results, this value may as well be rounded off to 3 p.p.m. The Noddacks found 3 p.p.m. of osmium in this meteorite, and Goldschmidt and Peters reported an approximate osmium content of 5 p.p.m.

LITERATURE CITED

(1) Chugaev, L. A., *Compt. rend.*, 167, 235 (1918); *Z. anorg. allgem. Chem.*, 148, 65 (1925).

(2) Gilchrist, R., *Bur. Standards J. Research*, 6, 421 (1931).

(3) Goldschmidt, V. M., and Peters, C., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1932, 377.

(4) Noddack, I., and Noddack, W., *Naturwissenschaften*, 18, 757 (1930); *Z. physik. Chem.*, 154A, 207 (1931); *Ibid.*, *Bodenstein-Festband*, 1931, 890; *Svensk Kem. Tid.*, 46, 173 (1934).

(5) Robinson, W. O., Dudley, H. C., Williams, K. T., and Byers H. G., Ind. Eng. Chem., Anal. Ed., 6, 274 (1934).

(6) Russell, J. J., Beamish, F. E., and Seath, J., *Ibid.*, 9, 475 (1937).

A Funnel for Filling Capillaries

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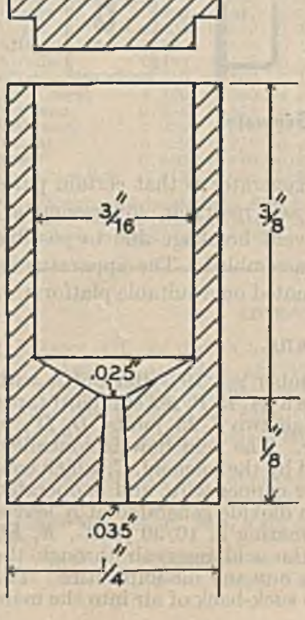
FILLING the capillary tubes used for supporting samples in x-ray diffraction cameras is a tedious and time-consuming procedure. The funnel described and illustrated here greatly simplifies this operation. It is constructed of brass, although other materials could be used.

The dimensions of the taper are determined by the size of the capillaries being filled. Plastic capillaries can be wedged into the tapered hole of the funnel firmly enough to stay in place during the filling operation. Glass capillaries must be held in with a slight pressure of the little finger, with the funnel held between the thumb and forefinger. The ground sample is placed in the funnel, and the top edge of the cap is rubbed with a serrated surface such as the side of a pair of tweezers or a dull file in order to shake the powder down into the capillary. If the hole plugs up, a wire can be used to clear it.



Hygroscopic samples can be dried in the funnel in an oven, broken up with a wire, and introduced into the capillary before they have a chance to pick up moisture.

Carbon Dioxide Generator for the Dumas Method of Determining Nitrogen

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THE all-glass carbon dioxide generators described in the literature (*1–5*) are essentially identical in principle. They differ chiefly in modifications which affect such features as ruggedness, ease of charging and recharging, and control. All are portable and easily supported. Furthermore, their automatic generating feature is desirable. The carbon dioxide produced is claimed to be very pure, but the actual purity obtained is not mentioned by any of the authors.

A different type of generator constructed in this laboratory, shown schematically in Figure 1, appears to have certain advantages over those referred to above: (1) The generating capacity is over six times as large, over 650 liters of gas, exclusive of the amount wasted during the initial evacuation to remove air impurities; (2) the bicarbonate solution is automatically agitated whenever more gas is generated, and therefore stratification is avoided; (3) any traces of residual air in the acid reservoir are effectively swept out whenever the gas is used; (4) no special safety precautions are necessary during the initial evacuation or later operation; (5) since the gasometer (fitted with a flexible glass extension) is an integral part of the generator the two rubber couplings ordinarily used are eliminated from the train.

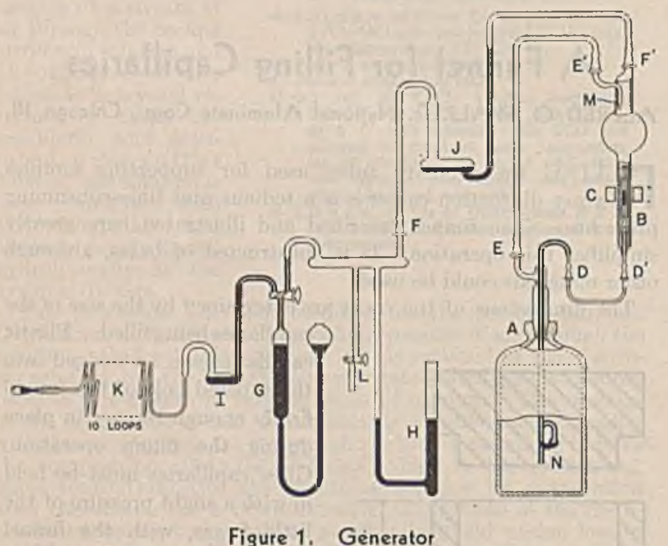

Figure 1. Generator

The chief disadvantage of this generator is that certain parts (particularly the generator bottle, acid reservoir, and gasometer) must be rigidly supported to prevent breakage due to possible misalignment after the parts are assembled. The apparatus is, however, safely portable when mounted on a suitable platform.

APPARATUS

In Figure 1, the generating chamber is a 19.5-liter bottle with the neck accurately ground to take a 34/45 Pyrex standard taper joint, *A*, which is attached through two 7/25 joints, *D*, *D'*, to the 1-liter capacity acid reservoir. The acid flow is controlled by the magnetic valve, *B*, actuated by the solenoid, *C*, which consists of about 700 turns of 22-gage copper wire, and is operated with a 6-volt battery. The carbon dioxide generated at *N* leaves the bottle through the tube terminating in 10/30 joints, *E*, *E'*, then enters the empty space in the acid reservoir through the vertical tube, *M*, where it sweeps out any air impurities. The mercury trap, *J*, prevents possible suck-back of air into the main system should stopcock *L* be accidentally left open. The 100-ml. mercury-filled gasometer, *G*, is likewise fitted with a small trap, *I*, to prevent air suck-backs in case the three-way stopcock is turned the wrong way when the leveling bulb is lowered to refill the gasometer. All capillary tubing shown is approximately 8-mm. outside diameter by 1.5-mm. bore. Stopcock *L* is used for the initial evacuation, and provides a simple means of obtaining a continuous flow of the gas. The mercury-filled manometer, *H*, serves to indicate the approximate pressure in the system and also acts as a safety valve. The helix, *K*, made of 3.5-mm. outside diameter tubing, consists of ten loops each about 22 cm. high by 2.5 cm. wide. This provides lateral flexibility of over 5 cm. without danger of breakage.

The ball and socket acid valve, *B*, is drawn considerably enlarged to show details. The outside diameter of the moving part is 7 mm.; hence the bore of joint *F'* must be slightly larger in order to introduce this part safely into position by means of a wire hook. Special attention is called to the loop-shaped acid delivery tube, *N* (shown enlarged). The trap contains sufficient mercury to seal the capillary tube against back-pressure to a height of about 15 cm.; hence the local pressure produced by the sudden evolution of the carbon dioxide is prevented from accidentally forcing the bicarbonate solution into the acid delivery tube. The wide-angle funnel-shaped opening at the tip prevents the stoppage of the tube caused by the formation of potassium sulfate crystals. The last bubble of carbon dioxide formed during generation always remains in the funnel tip, thereby effectively separating the capillary column of sulfuric acid above from the bicarbonate solution below.

CHARGING AND OPERATION

To charge the generator, 3.2 kg. (7 pounds) of potassium bicarbonate are put into the generator bottle, followed with enough water to give a total volume of about 16.5 liters of solution. After the salt has been dissolved by shaking, a rapid stream of tank carbon dioxide is bubbled through the solution for about 3 hours to remove most of the dissolved air. The acid reservoir is filled with 30 *N* sulfuric acid to a point about 1 cm. below the opening of tube *M*. This solution is likewise treated with tank carbon dioxide. The various removable sections terminating with the standard taper joints are then assembled. Joint *A* is sealed with beeswax, *D*, *D'* with Cenco Plicene cement, and all others with Kronig's glass cement. All joints are securely clamped by means of coil springs of suitable strength. The acid valve is then operated to force most of the air out of the acid line. A vacuum pump is attached to stopcock *L* and the system is evacuated until the difference in mercury level in the manometer is about 30 cm. *L* is then closed and enough gas is generated to re-establish approximately atmospheric pressure. (If any air bubbles remain in the acid line, these can be best removed by operating the acid valve in rapid succession while the system is under reduced pressure.) The evacuation and generation cycle is repeated about 10 times, the pressure is increased until considerable gas blows through the manometer, and the gasometer is filled and completely discharged twice. A rubber tube dipping into a beaker of water is attached to stopcock *L* and the latter is opened to permit about 25 ml. of the gas to escape. More gas is again forced through the manometer and the additional steps are likewise repeated. The apparatus should then be in condition for service.

TEST OF CARBON DIOXIDE PURITY

The generator described above has been used intermittently in this laboratory for over 7 months, and has not been evacuated during this time. Throughout this period, 50- and even 100-ml. samples of the carbon dioxide, tested with the microazotometer, failed to give a readable air blank. On two different days, when the apparatus was in regular use, 500-ml. samples showed 0.002 ml. (4 parts per million) of air impurity in both tests. More recently two additional 500-ml. volumes were tested, the first after the apparatus had stood idle for 3 weeks and the second after an additional 5 weeks. Air impurity blanks of 0.002 and 0.003 ml., respectively, were found. In all these tests the generator was connected to the azotometer by means of a short glass connection which was 9 cm. long, but otherwise identical to a regular micro combustion tube. Since it requires about 1 hour to pass 500 ml. of carbon dioxide into the microazotometer, any air which diffuses through the two rubber connections during this time is included in the observed air blank. Hence the actual purity of the carbon dioxide is probably even higher than the tests indicate.

LITERATURE CITED

(1) Lowe, E. W., and Guthmann, W. S., Ind. Eng. Chem., Anal. Ed., 4, 440 (1932).
(2) Poth, E. J., *Ibid.*, 3, 202 (1931).
(3) *Ibid.*, 11, 518 (1939).
(4) Rauscher, W. H., *Ibid.*, 12, 694 (1940).
(5) Shelberg, E. F., *Ibid.*, 10, 704 (1938).

Rapid Digestion Method for Determination of Phosphorus

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A RAPID quantitative method for the determination of phosphorus is always useful in the analytical laboratory. Perchloric acid either alone or in mixtures with other acids has been used to oxidize organic matter previous to the determination of mineral constituents (*3*, *4*). Work in this laboratory has shown that the presence of molybdenum in a perchloric-sulfuric acid mixture markedly increases the rate of oxidation of organic matter. Most colorimetric methods for the determination of phosphorus are modifications of the Misson (*6*) or Fiske and Subbarow (*2*) methods in which molybdenum is a reagent. The use of molybdenum in small amounts as catalyst proved not to interfere with the quantitative colorimetric determination of phosphorus; hence a rapid method was developed for determining phosphorus by the combined techniques of perchloric-sulfuric acid digestion in the presence of molybdenum followed by colorimetric analyses. Results of phosphorus determinations on feeds digested with perchloric-sulfuric acid mixture in the presence of molybdenum as a catalyst are presented here and compared with results using the official ashing method (*1*).

ANALYTICAL PROCEDURE

Digestion Mixture. Dissolve 30 grams of sodium molybdate in 150 ml. of distilled water, then slowly add 150 ml. of concentrated sulfuric acid to the molybdate solution. Allow this solution to cool and then add 200 ml. of 70 to 72% perchloric acid.

Digestion of Organic Material. Transfer not more than a 500-mg. sample to a dry 100-ml. Kjeldahl flask, and add 5 ml. of the digestion mixture and a few glass beads to prevent bumping. Heat the flask slowly over a microburner. Oxidation will begin in 1 or 2 minutes. At this time the burner may be turned off and the digestion allowed to proceed under its own generation of heat. Wash down any adhering particles on the side of the flask by swirling the flask gently, add 2 ml. of perchloric acid, place the flask back on the burner, and heat until the digestion is complete. Digestion is usually complete within 3 or 4 minutes, and the solution is then clear and no charred material remains. Dilute the digestion mixture to a volume of 100 ml. with distilled water. Filter this solution or let it stand to permit any silica present to settle out. Take a suitable aliquot for the colorimetric determination, and adjust the acidity with perchloric acid to the approximate range of acidity stated in the method used. Since there is a relatively wide acid range in these methods, the approximate adjustment of perchloric acid concentration can easily be made.

The phosphorus was determined by two different colorimetric methods—the development of a blue color by reducing the phosphomolybdate as described by Sherman (*7*) and the development of a yellow color by the formation of a phosphovanadiomolybdate compound by the method of Koenig and Johnson (*5*). The per cent transmission was determined with the Cenco photelometer, using a 420 mμ filter for the yellow color, 600 mμ for the blue color, and a reagent blank as a reference liquid. A standard reference curve was made by plotting values of known amounts of phosphorus against the photelometer readings on semilogarithmic graph paper.

For routine analysis with samples in which the phosphorus range is suitable, the Kjeldahl digestion flask may be calibrated to 100 ml. and the reagents added directly to this flask. By the use of the phosphovanadiomolybdate method, samples containing 0.05 to 0.5% may be determined directly without further dilution. For materials containing less than 0.1% phosphorus and with a 500-mg. sample the reduced phosphomolybdate method (*7*) is more suitable, while for material containing higher amounts of phosphorus the vanadate method (*5*) appears preferable because of the greater stability of the color.

DISCUSSION OF RESULTS

Table I shows good agreement of phosphorus in some typical feeds by the perchloric-sulfuric acid digestion method as compared with the longer ashing method. Values are also given as obtained by two previously published colorimetric procedures. Replicate results by the shorter acid digestion method were always as good as by the ashing method.

Several samples have been digested with perchloric-sulfuric acid in the presence of molybdenum, but no explosions have resulted. With a sample of 500 mg. or less, the reaction proceeds smoothly and a set of six samples can be digested in less than 10 minutes.

Table I. Phosphorus Values

Sample	Ashing			Digestion			
	Blue[a]	Yellow[b]	Average	Blue[a]	Yellow[b]	Average	Difference[c]
	%	%	%	%	%	%	%
Clover chaff	0.094	0.090	0.0940	0.095	0.096	0.0955	+1.6
Beet pulp	0.087	0.088	0.0875	0.087	0.092	0.0895	+2.3
Corn silage	0.234	0.225	0.2295	0.220	0.227	0.2235	−2.6
Range grass	0.060	0.060	0.0600	0.060	0.064	0.0620	+3.3
Barley	0.362	0.357	0.3595	0.362	0.357	0.3595	0.0
Corn	0.306	0.312	0.3090	0.309	0.306	0.3075	−0.5
Alfalfa	0.164	0.168	0.1660	0.167	0.170	0.1685	+1.5
Alfalfa	0.191	0.193	0.1920	0.195	0.200	0.1975	+2.9
Alfalfa	0.110	0.106	0.1080	0.104	0.102	0.1030	−4.6
Meat meal	4.560	4.560	4.5600	4.800	4.800	4.8000	+5.3
Soybean	0.554	0.552	0.5530	0.567	0.555	0.5610	+1.4
Fish meal	2.920	2.970	2.9450	3.070	3.100	3.0350	+3.1
Wheat	0.420	0.419	0.4195	0.417	0.417	0.4170	−0.5
Peas	0.480	0.480	0.4800	0.460	0.468	0.4640	−3.3
Poultry ration	0.815	0.800	0.8075	0.803	0.820	0.8115	+0.5

[a] Phosphomolybdate blue, Sherman method (*7*).
[b] Phosphovanadiomolybdate yellow, Koenig and Johnson (*5*).
[c] Ashing method, basis of 100.

LITERATURE CITED

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 5th ed., p. 133 (1940).
(2) Fiske, C. H., and Subbarow, Y., *J. Biol. Chem.*, 66, 375 (1925).
(3) Gerritz, H. W., Ind. Eng. Chem., Anal. Ed., 7, 116 (1935).
(4) Giesiking, J. E., Snider, H. J., and Getz, C. A., *Ibid.*, 7, 185 (1935).
(5) Koenig, R. A., and Johnson, C. R., *Ibid.*, 14, 155 (1942).
(6) Misson, G., *Chem.-Ztg.*, 32, 633 (1908).
(7) Sherman, M. S., Ind. Eng. Chem., Anal. Ed., 14, 182 (1942).

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All-Glass Midget Impinger Unit

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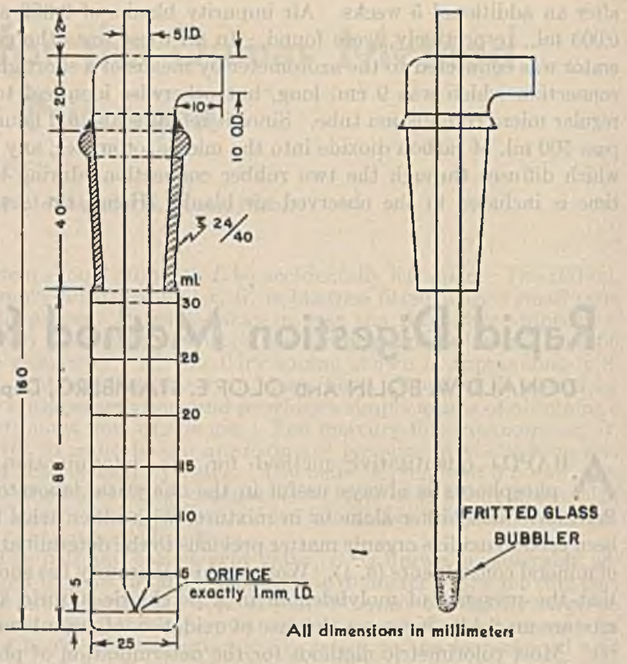
INCREASED use of the midget impinger (*2*) for collecting various atmospheric contaminants has revealed the following disadvantages:

1. The rubber stopper deteriorates through contact with various acids, alkalies, and solvents used as collecting fluids. It is extremely difficult to clean the rubber stopper when slight deterioration has begun. This may result in contamination of the sample. Certain solvents dissolve a color from the stopper, which interferes in colorimetric analysis.
2. The side arm of the impinger flask is sufficiently low to permit drawing over a portion of various alkalies and solvents used as collecting fluids.
3. When the stopper is placed in the flask, an annular groove is formed where the stopper contacts the flask. Air contaminants may settle in this groove and cause subsequent contamination when the sample is transferred in the field.

To eliminate these disadvantages, an all-glass collecting unit (see diagram), similar to the large impinger unit (*1*), has been designed and used satisfactorily during the past year. The all-glass equipment can be cleaned thoroughly. The standard taper permits interchanging of parts without readjusting the position of the impinging orifice, which was necessary in the earlier design. The side arm is 138 mm. above the bottom of the flask, as compared to 103 mm. in the earlier design. This added height reduces the possibility of a draw-over when certain solvents and alkalies are used as collecting fluids. A shoulder around the standard taper stopper covers the groove formed between the stopper and the flask, and prevents the settling of dusty material in the groove where it may contaminate the sample during transfer.



All dimensions in millimeters

For certain purposes, similar all-glass equipment has been designed with a fritted-glass bubbler replacing the impinging orifice. Thus, a single type of unit may be used over a wide range of collecting requirements.

LITERATURE CITED

(1) Greenburg, Leonard, and Bloomfield, J. J., *Public Health Repts.*, 47, 654–75 (March 18, 1932).
(2) Schrenk, H. H., and Feicht, F. L., U. S. Bur. Mines, *Information Circ.* 7076 (June. 1939).

A Simple Titration Rack

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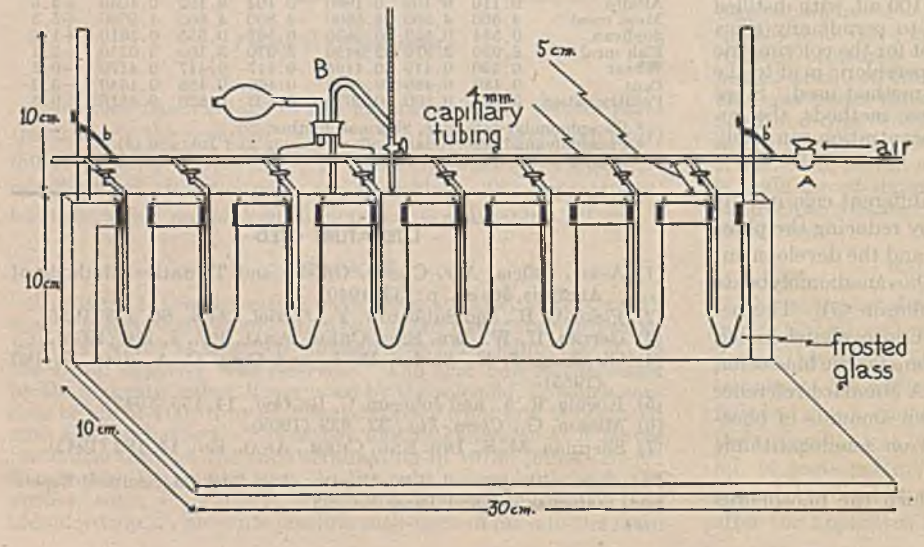
RECENT investigations in this laboratory have involved the use of various semimicrochemical methods of analysis. Such methods often require centrifugation of minute quantities of material in small conical centrifuge tubes, and subsequently a titrimetric determination of this material in the same vessel. However, adequate agitation during the titration is difficult in such containers and the process becomes increasingly tedious when a number of determinations are necessary. In order to obviate this difficulty and to provide a rapid method of analysis, a simple titration rack was designed as illustrated.

The stand consists of a wooden base and frame which support a frosted-glass background. Eight brass spring clips are attached to the frame, so that centrifuge tubes may easily be slipped firmly into position. The glass manifold which serves as an aerating device can then be manipulated into position by means of clamps *b* and *b′*, attached to vertical wooden rods which in turn are supported by the frame.



The rate of air flow is regulated by the control valve, *A*. The small valve above each tube is subsequently opened when the contents are to be titrated. By moving the reagent bottle and attached buret, *B*, consecutively from one tube to the next, a series of eight determinations can be rapidly completed.

ACKNOWLEDGMENT

The author wishes to thank H. Wells for help with the construction of the apparatus.

Improved Apparatus for Use in Chromatography

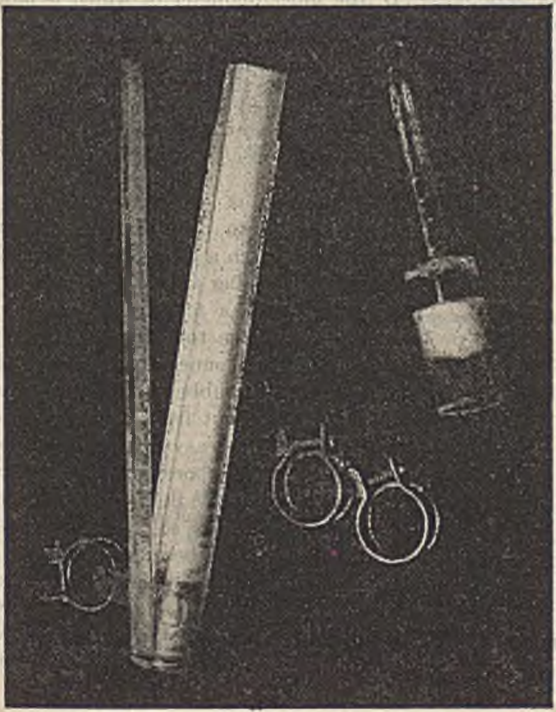
WM. R. CROWELL AND OTTO KÖNIG[1], University of California, Los Angeles, Calif.

IN CHROMATOGRAPHIC work the disadvantage of the inaccessibility of the adsorption column while developing the chromatogram is often realized, especially if a so-called colorless chromatogram is in progress. The development is usually followed by pushing the column of adsorbent out of the tube and brushing solutions of suitable reagents along its surface in order to obtain colored reaction products which indicate the zones of the various adsorbates (*1*, *2*, *3*). In case the chromatogram is not fully developed, the entire run must be repeated. If an ultrachromatogram is developed, the glass of the tube may interfere with the fluorescence phenomenon. In the development of inorganic chromatograms, the developers passed through the adsorbent change entirely by chemical reaction the nature of the components to be resolved.

A tube has been designed which permits one to follow the development of colorless chromatograms by brushing or spotting reagents on the surface of the adsorbent with no loss of time or material, and also to test inorganic chromatograms with traces of reagents, while the bulk of the material remains in the tube in its original state.

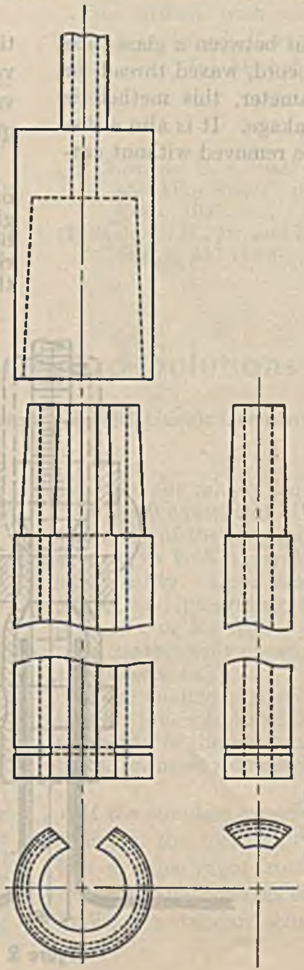
The chief feature of the device is a section cut from a small portion of the circumference of the tube along its entire length, forming a tight-fitting lid in the corresponding lengthwise opening. The earliest tubes were of glass, but later ones were of plastic (Lucite). The latter are limited in their use to chromatograms in which only solvents are used which do not attack the plastic, or where a slight attack and presence of dissolved plastic do not affect the tests—e.g., water, alcohol, and ligroin. Metals also might prove useful in the construction of such tubes.

The tubes used by the authors are 240 mm. long with an inside diameter of 15 mm. They were machined from a 24-mm. round Lucite rod, leaving a wall thickness of 4.5 mm. Two symmetrical cuts converging at an angle of 90 degrees were made along the entire length of the tube to produce an opening 5 mm. wide on the inside and 13 mm. wide on the outside circumference. From a square-shaped Lucite rod a corresponding circular segment was machined fitting smoothly into this opening, and after it was set in the tube the inside was machined perfectly smooth. A short section of the lower end of this two-piece tube was machined so as to reduce its diameter somewhat and produce a slight taper, and an adapter with suction tube, made from Lucite, was fitted into it in such a way that it could not slip entirely up the taper. A clearance of about 15 mm. between the end of the tube and the base of the adapter served as a receptacle for cotton. Near the top of the tube a groove was cut around its circumference and a steel position-tension spring was fitted into it. This made possible an exact replacement of the lid after it was removed. Metal bands with screw and nut hold the tube tightly together.



The adapter is supplied with cotton, the tube is assembled and set into the adapter, the whole apparatus is connected to a suction flask by means of a rubber stopper, the tube is filled in the ordinary way (the authors usually employ slurries of adsorbent in a suitable liquid), and the chromatogram is started. Whenever desired, the apparatus is taken from the flask, the adapter is carefully removed, the metal bands are taken off, and the lid is opened to make the necessary tests. If these indicate incomplete development, the lid is reset and the apparatus reassembled for continued development. Even if particles along the exposed surface are removed with the lid, which needs to be lifted only at one end, the position-tension spring will cause these to return to their original location when the lid is replaced. The minute amounts of reagents used in the spotting or brushing tests do not usually interfere in the continuation of further development. The joints of the lid and tube may be made absolutely tight by winding a strip of scotch tape on the outside surface of the tube. This is recommended for the junction of the tube and the adapter.

Tubes have been opened and reclosed as described several times during chromatographic tests without causing caverns and collapsing of the column, although care must be taken to avoid shocks or injuries to the exposed surface of the adsorbent. It was the experience of the authors that if the lid opening was so large as to expose too much adsorbent surface (one half or even less), the lid could not be reset many times without encountering difficulties due to the formation of cavities and channels as a result of too rapid volatilization of the solvent, as well as failure to replace the lid exactly in its original position.



Tubes of square cross section with one side fitted as a removable lid held by screws have also been used.

ACKNOWLEDGMENT

The authors are greatly indebted to W. Thiele, Baroid Sales Division, National Lead Company, for making the tubes and suggesting improvements, especially the position-tension spring.

LITERATURE CITED

(1) Strain, H. H., "Chromatographic Adsorption Analysis", New York, Interscience Publishers, 1942.

(2) Strain, H. H., Ind. Eng. Chem., Anal. Ed., 14, 245 (1942).

(3) Zechmeister, L., and Cholnoky, L., "Principles and Practice of Chromatography", New York, John Wiley and Sons, 1941.

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[1] Present address, Baroid Sales Division, National Lead Company, Los Angeles, Calif.

NOTES ON ANALYTICAL PROCEDURES

Analysis of *n*-Butane—Isobutane Mixtures by the Density Method

ERNEST SOLOMON, The M. W. Kellogg Company, Jersey City, N. J.

A RECENT paper by Leighton and Heldman (*1*) prompts a brief description of a method that has been employed successfully for several years in this laboratory for the analysis of mixtures of *n*-butane and isobutane. The method is similar to that employed by Leighton and Heldman; however, a description of the apparatus employed may assist other laboratories in assembling a simple and compact analytical unit.

The butane sample, which has been freed of olefins and of lighter and heavier hydrocarbons, is condensed into the inner chamber of a triple-walled Dewar flask. The intermediate chamber, containing liquid propane, is surrounded by an outer evacuated chamber and is further insulated with aluminum foil in which appropriately placed windows have been cut. The temperature of the butane sample is adjusted, by regulating the pressure over the boiling propane, until a small glass float of appropriate density neither rises nor sinks. The pressure over the propane is rapidly adjusted by either applying a pressure of nitrogen or evacuating with a water aspirator through a ballast volume. A small Nichrome heating coil immersed in the propane assists in the rapid attainment of the desired equilibrium temperature; a reflux condenser is provided to return vaporized propane to the intermediate chamber.

It has been found necessary to calibrate for equilibrium flotation temperature with a few known mixtures of *n*- and isobutane since the relationships between isobutane concentration and either propane pressure or sample temperature (expressed as millivolts measured on a multijunction thermocouple immersed in the liquid) are not quite linear. Using calibration charts the method can readily yield results accurate to ±1% in about 15 to 20 minutes from the time the sample is introduced into the sample chamber until the apparatus is ready for the next sample. About 10 ml. of liquid provide a convenient sample for this technique, although there is no reason why this cannot be readily reduced.

LITERATURE CITED

(1) Leighton and Heldman, *J. Am. Chem. Soc.*, 65, 2276 (1943); cf. Randall and Longtin, Ind. Eng. Chem., Anal. Ed., 11, 44 (1939), for generalized discussion of flotation analysis.

Fixing Rubber Connections

HERBERT Z. LITTMAN, Research Department, Palestine Potash, Ltd., Jerusalem, Palestine

IT IS general practice to fasten the joint between a glass tube and a rubber tube by means of a small cord, waxed thread, or copper wire. With tubes of small diameter, this method is troublesome and frequently leads to breakage. It is also a disadvantage that the connection cannot be removed without cutting the wire or cord. In certain cases the following method is very convenient, especially if only a small internal pressure prevails and it is desirable to remove and replace the connection frequently:

Cut a small ring, *A*, from a rubber tube of a diameter equal to or slightly larger than the tube, *B*, which is to be fixed on the glass tube. Lubricate the ring with glycerol and push it on a cork borer sharpener, *C* (Figure 1, movement 1). Then transfer the ring to a cork borer, *D*, the inner diameter of which is larger than the outer diameter of the rubber tube to be fixed (movement 2). Then slip the end of the rubber tube into the cork borer and transfer the rubber ring onto the rubber tube (movement 3). With the aid of glycerol it is now easy to put the rubber tube with its rubber sling upon a glass tube, where it will hold tightly.

The method is especially useful if a thermometer is to be introduced into an apparatus through a glass tube (Figure 2). Here a wide rubber tube which goes over the glass tube has to be used, and consequently it will be too wide for the thermometer. The connection between the thermometer and rubber tube can be made by a rubber ring cut from a heavy-walled rubber tube. It is easy to slip the rubber ring from the cork borer onto the rubber tube. This should be done after the thermometer is in position, so that no force has to be applied to the thermometer.

Anyone trying the method will quickly learn to make the right choice of diameter, wall thickness, and length of the rings, according to the necessary tightness or ease of connecting and removing.

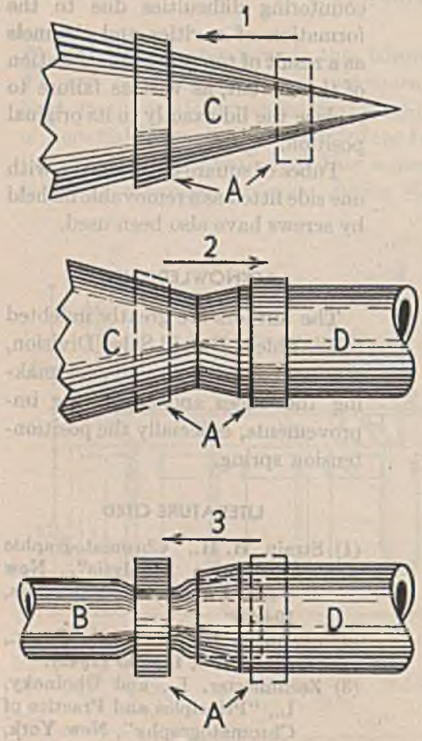


Figure 1

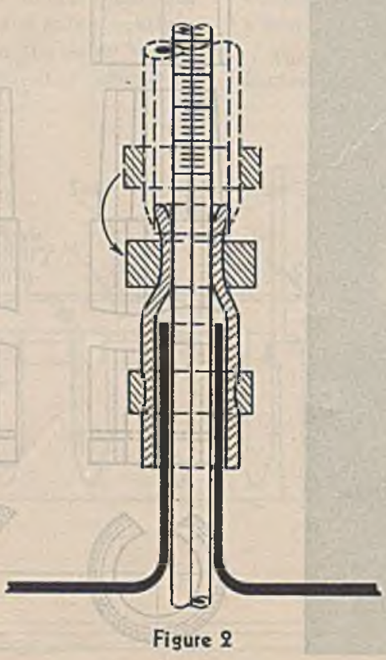


Figure 2

Determination of Sulfur in Brass and Bronze by the Combustion Method

ALBERT C. HOLLER AND JAMES P. YEAGER, United States Metal Products Co., Erie, Pa.

THE authors have successfully applied the well-known high-temperature combustion method of Hale and Muehlberg (*1, 2*) to the determination of sulfur in brass and bronze.

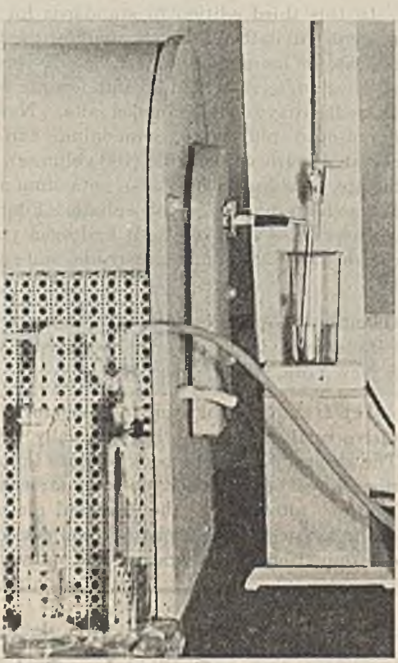


Figure 1

Figure 1 shows the absorption end of the combustion train. A Dietert Varitemp combustion furnace was used for the analyses. The oxygen was purified by passage through concentrated sulfuric acid, 40% potassium hydroxide, and an Ascarite–calcium chloride tube, in order. The exit end of the Zircofrax combustion tube was packed with about 1.25 cm. (0.5 inch) of ignited asbestos and the tube was adjusted in the furnace so that the asbestos packing was heated to redness. Chromium sesquioxide (free of sulfur by ignition in oxygen at 2400° F.) was found to be the only suitable bedding material for use in the combustion boats. Because of the presence of graphite in some of the samples, bromocresol green (pH range 3.8 to 5.4) was used as indicator in the titration of the acid. The sodium hydroxide solution was standardized against a 0.5-gram sample of Bureau of Standards 19c-steel, A.O.H., which contains 0.040% sulfur.

A 0.1- to 1.0-gram sample of drillings which remain on a No. 60 but pass through a No. 20 sieve was taken for analysis. The sample was burned at 2100° F. in a stream of oxygen which passed at the rate of 2 liters per minute. When the combustion was complete (5 or 10 minutes) the acid was titrated with the standard sodium hydroxide solution with the oxygen still on. The combustion was continued for another 5 minutes and if the acid color of the indicator returned, alkali was added until the end point was again reached.

The method was tested on Bureau of Standards samples 124 of ounce metal and 63a of phosphor bronze bearing metal (Table I).

Table I. Determination of Sulfur

Sulfur present %	Sulfur found %	Deviation %
Bureau of Standards Sample 124, Ounce Metal		
0.071	0.072	+0.001
	0.071	±0.000
	0.074	+0.003
	0.070	−0.001
	0.070	−0.001
	0.069	−0.002
	Av. 0.071	±0.0013
Bureau of Standards Sample 63a, Phosphor Bronze Bearing Metal		
0.11[a]	0.097	−0.001
	0.098	±0.000
	0.100	+0.002
	0.097	−0.001
	0.100	+0.002
	0.098	±0.000
	Av. 0.098	±0.001

[a] Provisional analysis.

ACKNOWLEDGMENT

The authors wish to express their deepest appreciation to T. S. Woodward, Carnegie-Illinois Steel Corporation, Youngstown, Ohio, for his helpful comments in connection with this paper.

LITERATURE CITED

(1) Chemists, U. S. Steel Corp., "Sampling and Analysis of Carbon and Alloy Steels", pp. 309–36, New York, Reinhold Publishing Corp., 1938.

(2) Hale, C. H., Jr., and Muehlberg, W. F., IND. ENG. CHEM., ANAL. ED., 8, 317 (1936).

The (Predictable) Concentrating of Standard Solutions Owing to Evaporation

HERMAN A. LIEBHAFSKY, Research Laboratory, General Electric Company, Schenectady, N. Y.

THE author has seen no evaluation of the (predictable) increase in normality caused by the evaporation of water that occurs in a carboy from which a standard solution is being withdrawn and replaced by dry air under the simplest experimental conditions. The problem arose in this laboratory in connection with routine titrations of high precision. In carrying out these titrations, about 40 ml. at a time of carbonate-free sodium hydroxide are forced by means of dry, carbon dioxide–free air from a 15-liter carboy into the buret.

Assume (1) that a carboy of any shape whatever is initially filled with V_1 liters of standard N_1-normal solution, (2) that each portion of solution withdrawn is replaced by dry air, and (3) that the gas space in the carboy becomes saturated with water vapor between withdrawals. Consider the system when the carboy contains an arbitrarily chosen volume, V, of N-normal solution, the solute being nonvolatile. Let 0.024 gram per liter be the water content of saturated air under laboratory conditions. Then, if dV liter of solution has just been withdrawn, 0.024 dV gram (or ml.) of liquid water will be vaporized, and 0.024 $dVN/1000$ equivalent of solute will be left behind to increase the normality of the remaining solution. But this amount of solute is equal to VdN equivalents, where dN is the resulting increase in normality. Upon considering the sign of dV, equating, transposing, and integrating, one now obtains $\ln N_2/N_1 = 2.4(10^{-5}) \times \ln V_1/V_2$, or $\log N_2/N_1 = 2.4(10^{-5}) \log V_1/V_2$. (The subscripts refer to arbitrarily chosen initial and final states; N must increase as V decreases.)

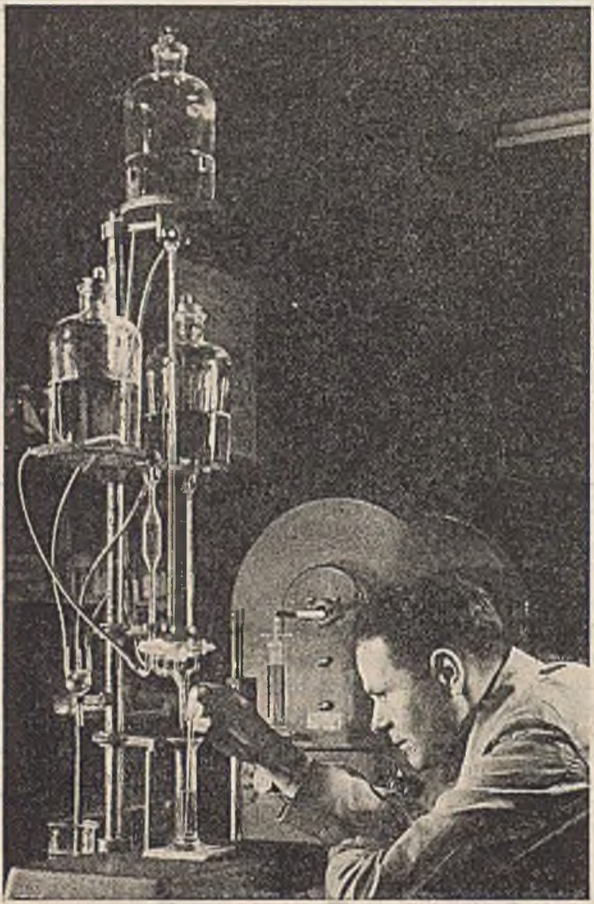
If the volume of solution in a 15-liter carboy is reduced in the manner prescribed to 1.5 ml., $\log N_2 - \log N_1 = 0.0001$, or the normality of the residuum will increase by 0.02%, which is negligible for most volumetric work.

If the simplest experimental conditions do not obtain—if, for example, the room temperature varies markedly, or if there is loss of water vapor from the carboy, as to a drying agent—then unpredictable changes larger than 0.02% may occur in the normality of a standard solution.

NEW EQUIPMENT

Sulfur Determinator

The Harry W. Dietert Co., Detroit, Mich., announces an improved 3-minute sulfur determinator for rapid and accurate sulfur determination of steel, iron, nonferrous metals, and materials such as coal and coke.



Sulfur Determinator

The sample is ignited in a high-temperature furnace in an oxygen atmosphere. The sulfur in the sample is converted to sulfur dioxide gas, which is filtered free of all dust particles by a hot ceramic filter within the furnace combustion tube, then bubbled through an alkaline solution which reduces the alkalinity of this solution. The greater the sulfur content in the sample, the lower the alkalinity of the solution. The alkalinity of the solution is measured by titrating with a standard acid solution.

The sulfur determinator is divided into two units: the measuring burets with 2-liter solution bottles, and a stand and support for holding the solution vessel at the furnace. This arrangement increases the speed with which sulfur determination may be made, since one sample may be in process of combustion while another sample is being titrated. The sulfur percentage is read direct from the buret scale.

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BOOK REVIEWS

AnalaR Standards for Laboratory Chemicals. 3rd ed. 230 pages. British Drug Houses, Ltd., and Hopkin & Williams, Ltd., London, 1944.

In this third edition of standards for more than 200 analytical reagent (AnalaR) chemicals many of the tests have been made more delicate or more definite, particularly those for iron. Tests for impurities in ferric chloride and ferrous sulfate have been entirely altered, as have those for nickel salts. New tests include: ammonium dihydrogen phosphate, ammonium tartrate, cobalt oxide, ethyl acetate, hydrogen peroxide (100 volumes), magnesium acetate, nickel nitrate, perchloric acid (72%), potassium periodate, isopropyl alcohol, and sodium dihydrogen phosphate. Four which appeared in earlier editions have been omitted: hydrogen peroxide (10 volumes), perchloric acid (20%), mercuric oxide, and sodium chloride (fused).

Quantitative Analysis. *Harold Simmons Booth* and *Vivian Richard Damerell.* 2nd ed. 303 pages. McGraw-Hill Book Co., New York, 1944. Price, $2.50.

This is a revision of a text intended for use in the elementary quantitative analysis course that normally follows qualitative analysis. The general plan of the book remains the same, but seven determinations have been added: determination of tin in brass, loss upon ignition, nitrogen by the Kjeldahl method, antimony in stibnite, sulfur in steel, and a chapter on colorimetric analysis, including determinations of manganese and molybdenum.

Ceiling Prices on Laboratory Reagent Specialty Solutions

Manufacturers of laboratory reagent specialty solutions containing U. S. tax-paid ethyl alcohol may add to their present ceiling prices the exact amount of the tax in excess of $4 a proof gallon for the alcohol contained in the solution being sold (Amendment 119 to Revised Supplementary Regulation 14 to General Maximum Price Regulation).

This action, effective April 22, 1944, was taken to correct a condition brought to the attention of OPA by the increased tax on ethyl alcohol which became effective April 1, 1944. Producers of these commercial chemical products, which are solutions of dyes, chemicals, or other substances used for scientific and medical research and clinical laboratory uses, are not refunded taxes paid on ethyl alcohol as are medicinal and drug manufacturers.

When the Revenue Act of November 1, 1942, increased the tax from $4 to $6 per proof gallon on ethyl alcohol, the producers of reagent solutions did not ask for a price adjustment, and assumed that they would be granted a drawback on taxes paid. However, official interpretations of statutes controlling Treasury drawbacks have not permitted recovery of any portion of taxes paid by manufacturers.

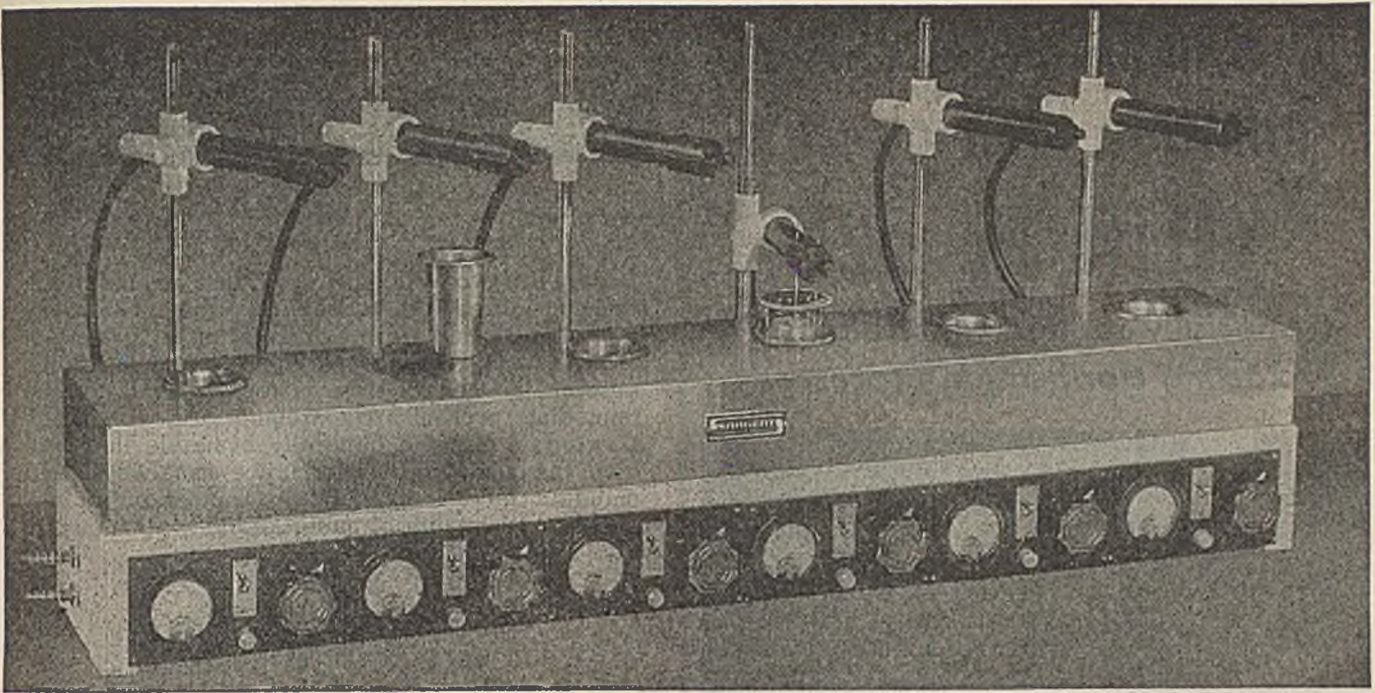
On April 1, 1944, the tax was further increased to $9 a proof gallon, which makes it impossible for manufacturers of reagent solutions to continue production under ceiling prices frozen at March, 1942, high.

Resellers of the solutions may add to their ceiling prices the amount of actual increase resulting to them. The products are sold only to clinics and laboratories, and are not available at retail. Both manufacturers and resellers are required to show the additional charge for the tax as a separate item on invoices.

A.S.T.M. Committee on Metal Powders

A new standing committee, B-9 on Metal Powders and Metal Powder Products, has been organized by the American Society for Testing Materials to undertake formulation of specifications and methods of tests. W. A. Reich, General Electric Co., is chairman, and W. R. Toeplitz, Bound Brook Oil-Less Bearing Co., is secretary.

Three subcommittees have already been organized: Nomenclature and Technical Data, F. N. Rhines, chairman; Metal Powders, D. O. Noel, chairman; Metal Powder Products, R. P. Koehring, chairman.



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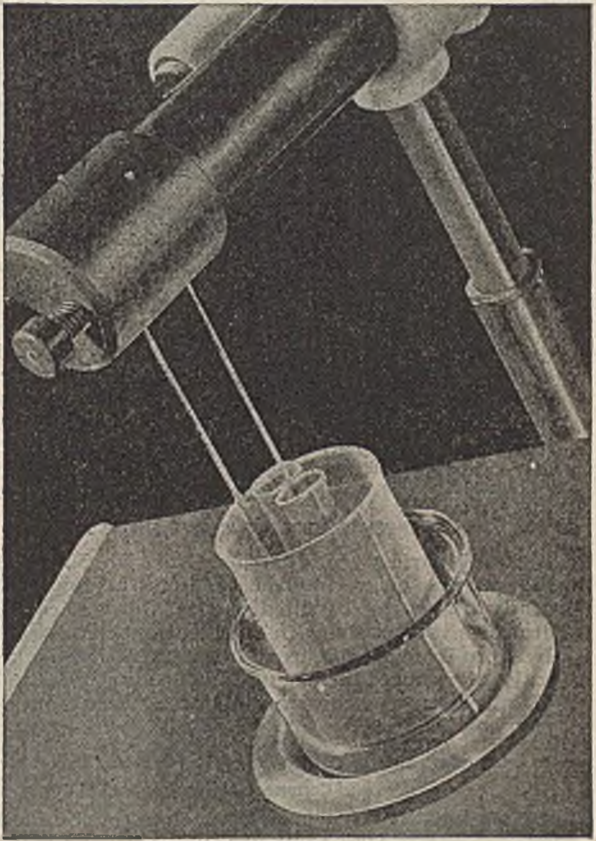

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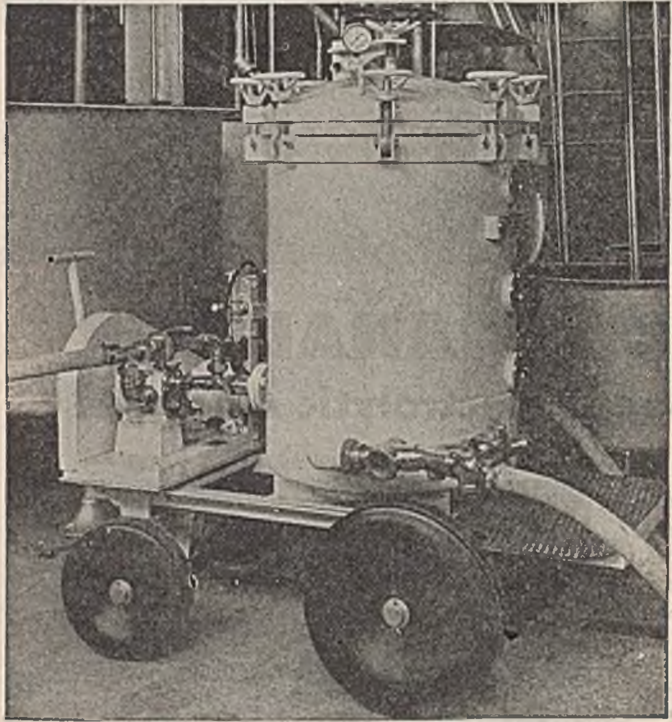


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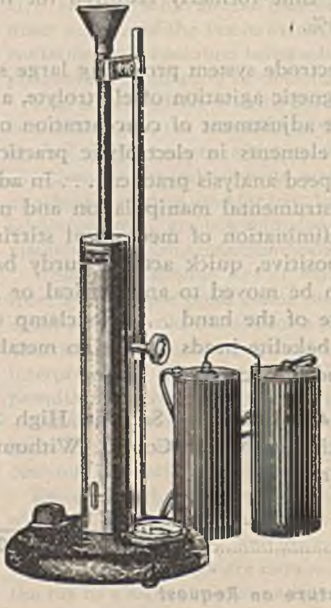

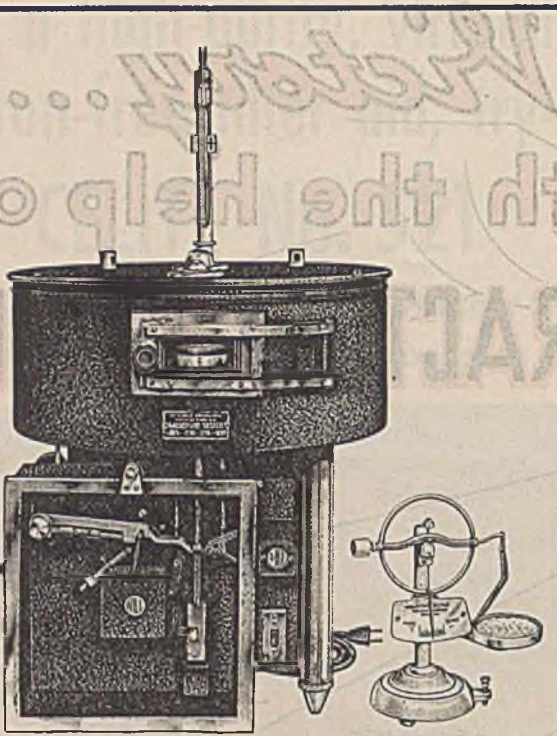

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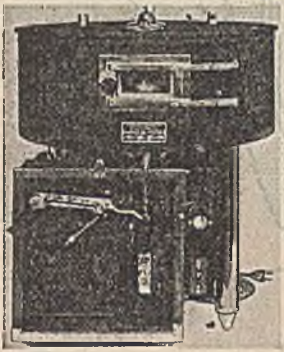

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Numerous figures are used to clarify the presentation, and about 165 tables of selected data appear in the text and appendix. For convenience and utility as a reference work, tables, equations, and subjects are thoroughly cross-referenced. The indexes and glossary of symbols are very extensive.

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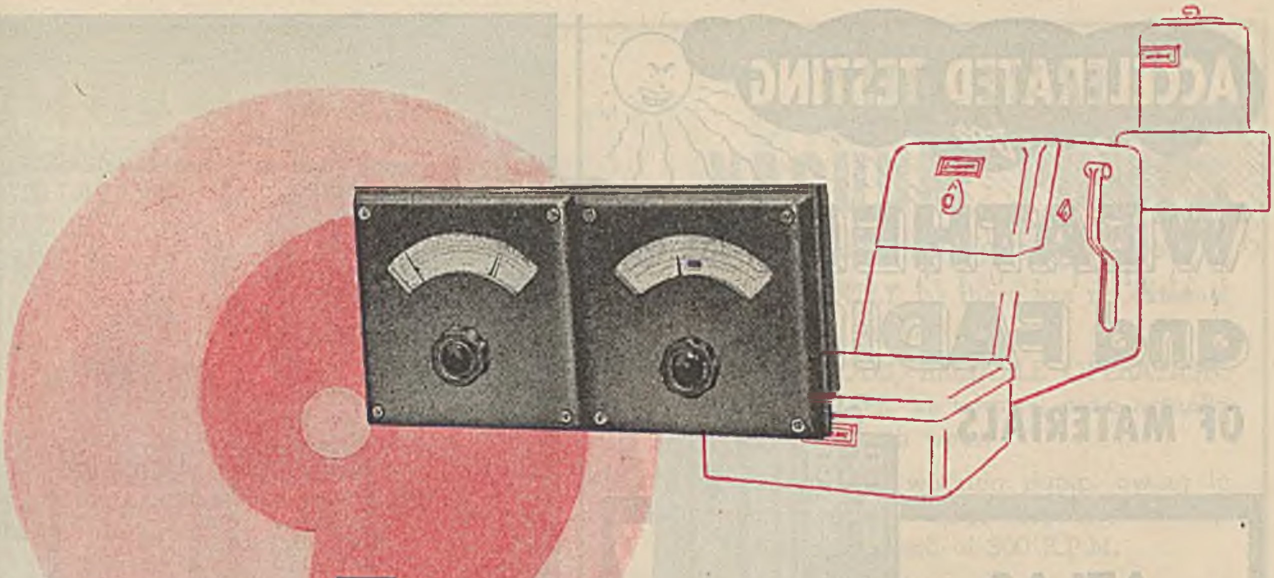

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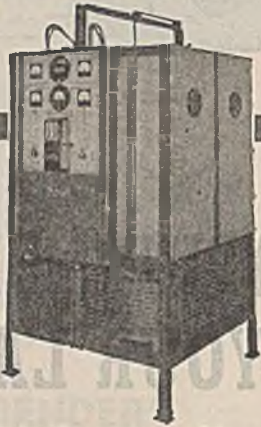


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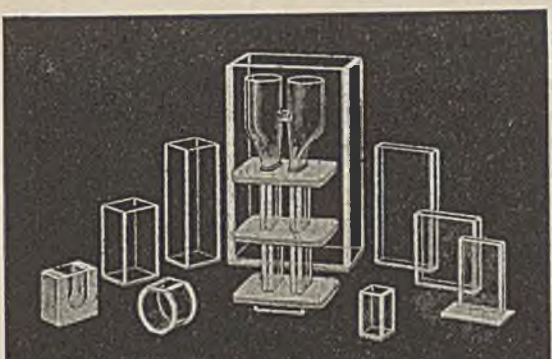

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This new indicator gives accurate results in the titration of most weak acids with strong bases, and is especially suited to the titration of orange- and red-colored solutions in which the phenolphthalein endpoint is impossible to detect. Satisfactory results can be obtained even with extremely dark-colored oils.

The color change is from colorless to deep blue. In the titration of an acid solution with an alkali, the first blue tinge appears at pH 7.5, and at pH 9.1 the change to deep blue is complete.

The new indicator is offered as *Eastman 5488 Ethyl bis-(2,4-Dinitrophenyl) acetate.* Price: 1 gram, $1.00. An abstract of the article by Fehnel and Amstutz, *Ind. Eng. Chem., Anal. Ed., 16,* 53 (1944), describing its properties, will be forwarded upon request. Eastman Kodak Company, *Chemical Sales Division,* Rochester 4, N. Y.

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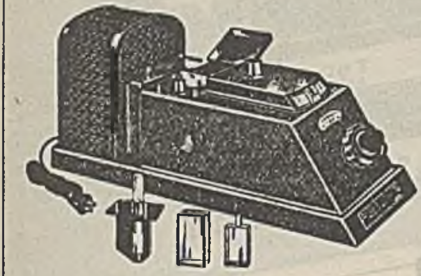

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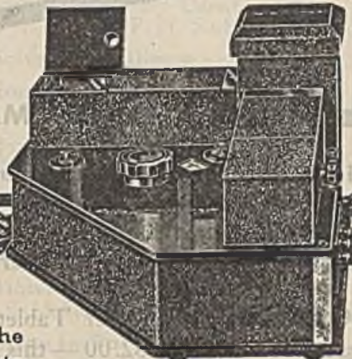

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