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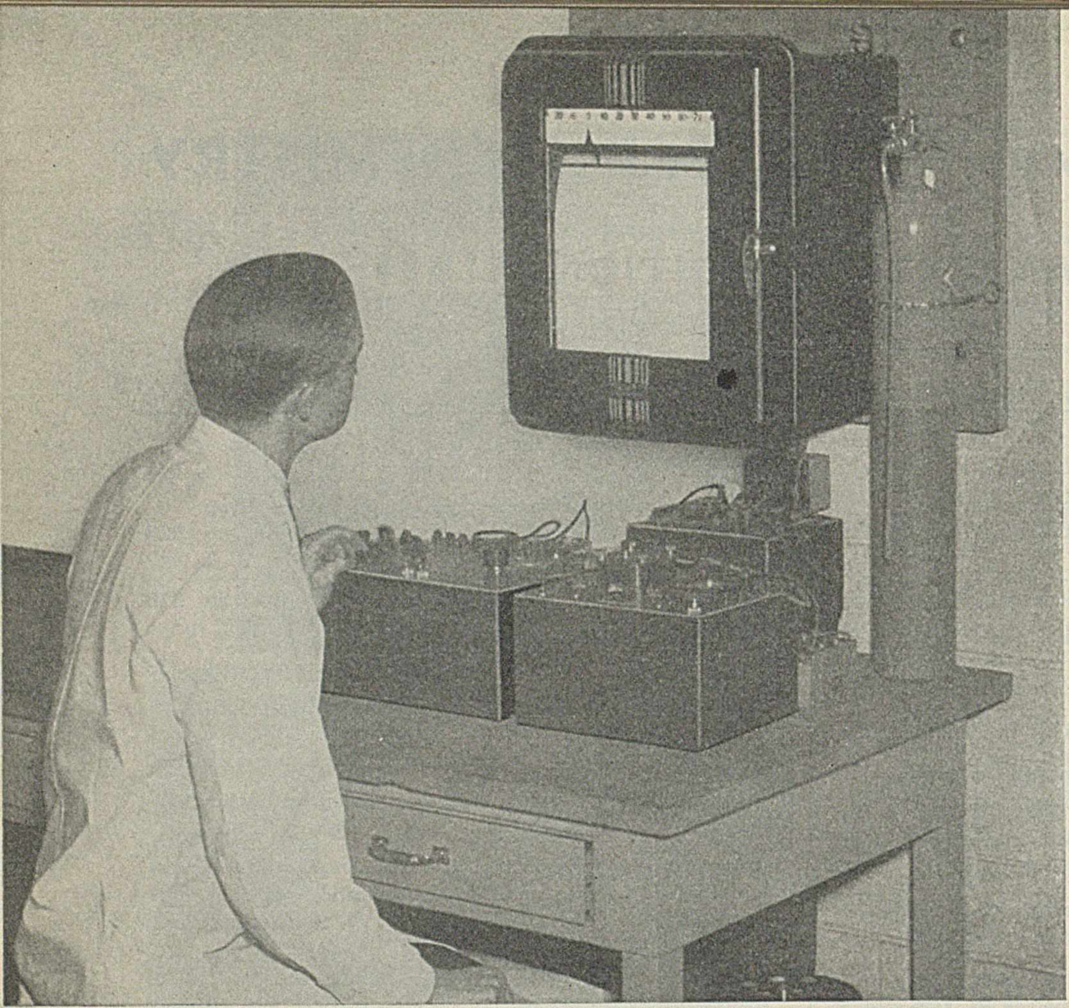

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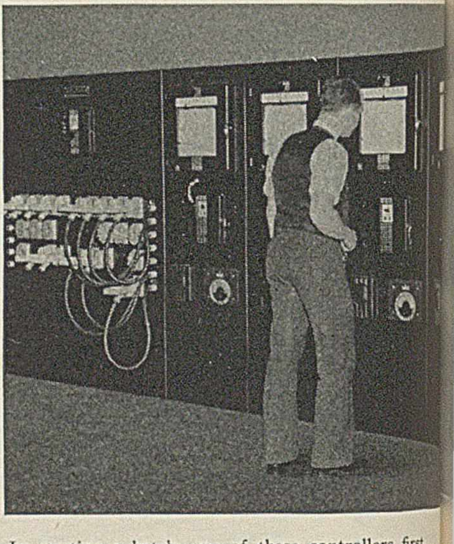

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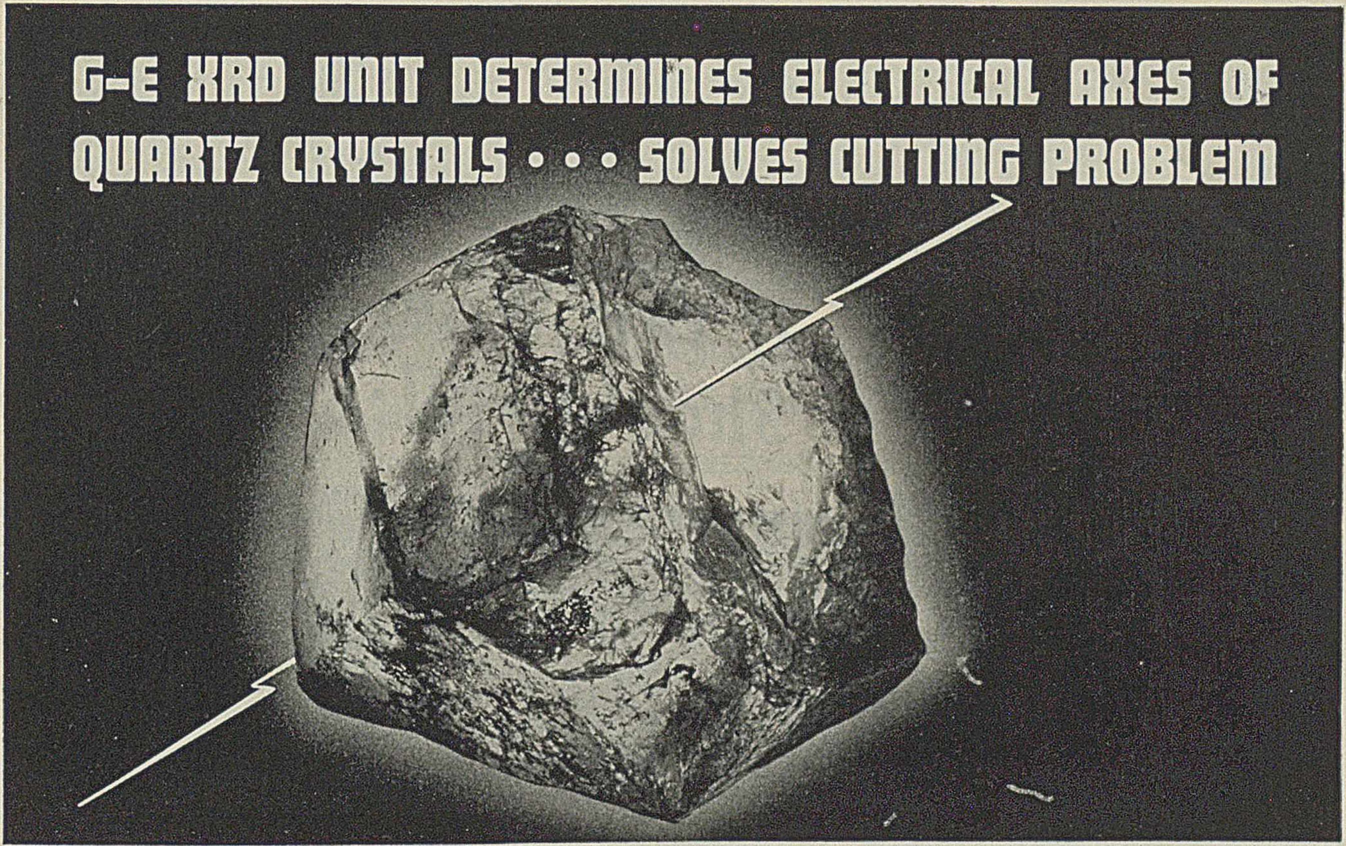

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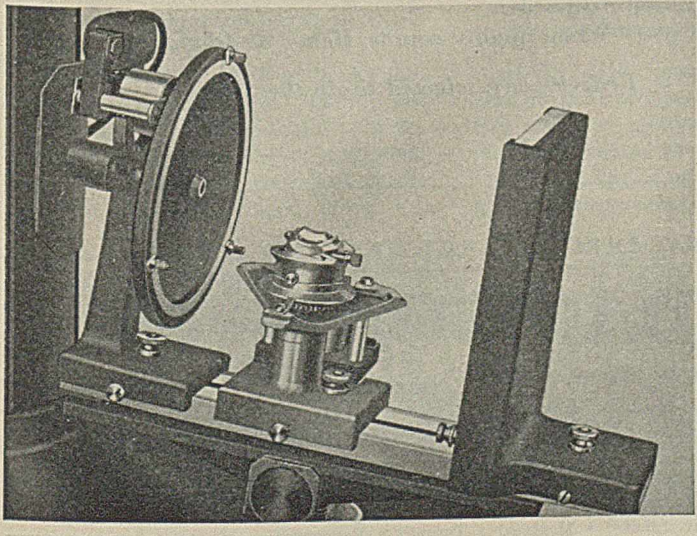

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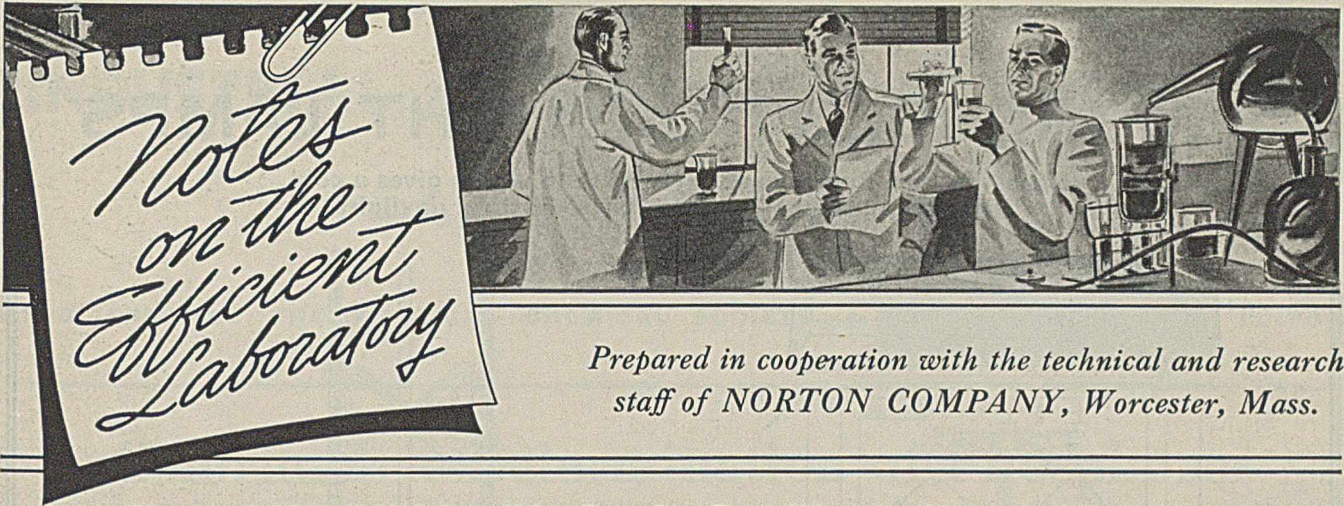

Prepared in cooperation with the technical and research staff of NORTON COMPANY, Worcester, Mass.

Users of ALUNDUM Crucibles Develop Easy Ways to Clean and Restore Porosity

Cleaning Alundum Crucibles

By Philip B. Herman
Osborne-McMillan Elevator Co.
Minneapolis, Minnesota

Users of ALUNDUM crucibles for filtering and subsequent ashing of residues in the crucible have probably noticed that, after a number of such filtrations and ashings, filtering becomes much slower and at times the quantity of liquid being sucked through the crucible is almost negligible. Ashing of the crucible does not seem to improve the situation any.

If the crucible is placed in a bath of concentrated hydrochloric acid for several hours, thoroughly rinsed, and then dried, filtration is improved very much. Possibly minerals from the materials ashed in the crucible, such as animal feeds, have filled the pores of the crucible and hence cut down the rate of filtration. The acid treatment thus dissolves the mineral matter and opens the pores of the crucible again.

It had been the practice in this laboratory to discard ALUNDUM crucibles when they did not filter rapidly. By the above treatment the life of a crucible has been quite a bit prolonged. From "Chemist Analyst," Vol. 30, No. 2.

Restoring the Porosity of Alundum Crucibles

By L. M. Nixon
N. C. Department of Agriculture
Raleigh, N. C.

In routine analytical work where ALUNDUM crucibles are used for filtering or extracting it will be found that the pores of the crucibles gradually become clogged and they filter so slowly that it may be necessary to discard them.

However, by giving them the following treatment when necessary, their porosity can be restored and they can be used indefinitely. First, destroy any organic material that may be present by igniting the crucibles at a dull red heat. Let them cool and place for a few minutes in a boiling 25% solution of NaOH. Wash thoroughly with hot water to remove the NaOH and let them stand immersed for 20-30 minutes in a 1-3 solution of hydrofluoric acid. Wash out thoroughly with hot water and they are again ready for use. If they are not badly clogged, it may not be necessary to boil them in the NaOH solution. From "Chemist Analyst," Vol. 25, No. 1.

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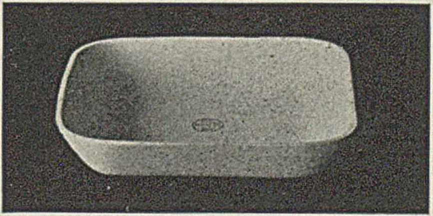

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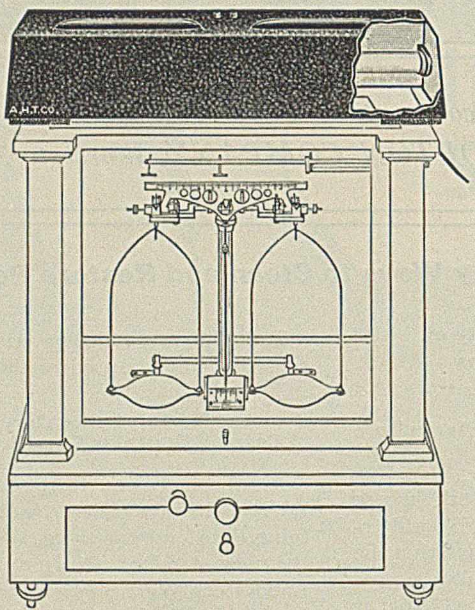

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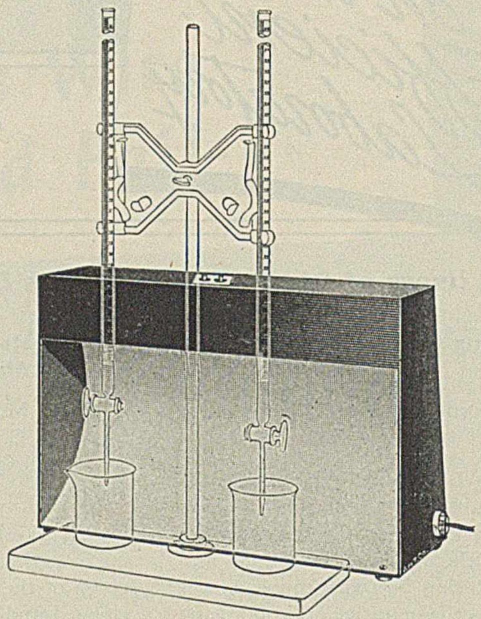

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INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

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Colorimetric Determination of Phosphorus in Iron Ore

E. JOHN CENTER[1] AND HOBART H. WILLARD
University of Michigan, Ann Arbor, Mich.

IRON interferes indirectly with the colorimetric determination of phosphorus. A sample run by the regular procedure but without addition of the final reagent is colorless to the eye, and regardless of the percentage of iron in the sample the transmittance at 450 millimicrons in a Coleman spectrophotometer is the same (distilled water is used as a blank). Curve 2, Figure 1, shows the spectral distribution of such a sample. Curve 1, Figure 1, shows the spectral distribution of a regular sample containing the yellow phosphorus complex [$(NH_4)_3PO_4.NH_4VO_3.16MoO_3$ according to Mission (*1*)].

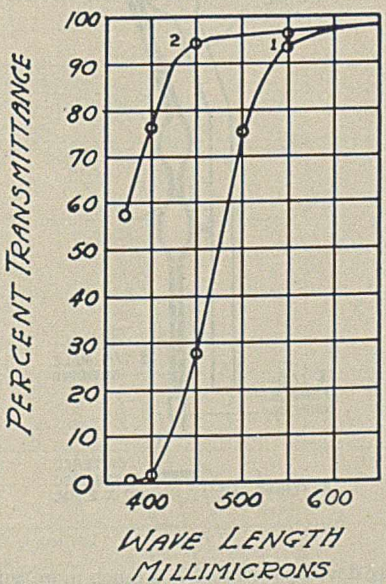

FIGURE 1. TRANSMITTANCE CURVES
1. Color developed
2. Color undeveloped

The proper width of the monochromatic light band (30 millimicrons) is also indicated on this curve, which shows that a narrower slit, 5 or 10 millimicrons, would not be applicable in eliminating fixed iron interference, and is impractical because of the decreased energy output from the spectrophotometer (less light falls on the photoelectric cell) and the critical wave-length setting. Figure 1 also indicates that a larger slit is out of the question. Thus a wave length of 450 millimicrons is employed with a width of 30 millimicrons.

Although the iron interference is constant for varying percentages of iron when the color complex is undeveloped, a marked deviation from the correct phosphorus content is noted when the color is developed and the iron value falls below the 50 per cent mark. In a lean ore or rock (iron below 50 per cent) this phenomenon indicates a low value for the phosphorus content. Figure 2 shows the deviation in the phosphorus value as a function of iron per cent.

For an ordinary iron ore the interference is negligible. If the amount of iron in a sample of lean ore or rock is known, the per cent of phosphorus can be obtained from Figure 2 by adding the correction from the plot to the apparent colorimetric value.

The ammonium phosphovanadomolybdate solution is appreciably sensitive to temperature changes, and, for the most precise analysis, samples must be run at constant temperature. In this work 27° C. is arbitrarily selected as a convenient temperature for seasonal work.

Distilled water does not change appreciably in transmission with temperature changes. Therefore, it can be substituted for the theoretically correct iron blank thus eliminating the necessity of keeping the blank at any definite temperature; moreover, distilled water does not vary in transmission over a period of time whereas a colored, highly acid iron blank must be constantly checked against a standard. The use of a dis-

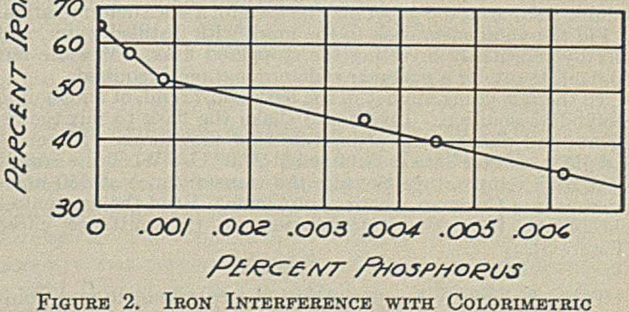

FIGURE 2. IRON INTERFERENCE WITH COLORIMETRIC PHOSPHORUS

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[1] Present address, Battelle Memorial Institute, Columbus, Ohio.

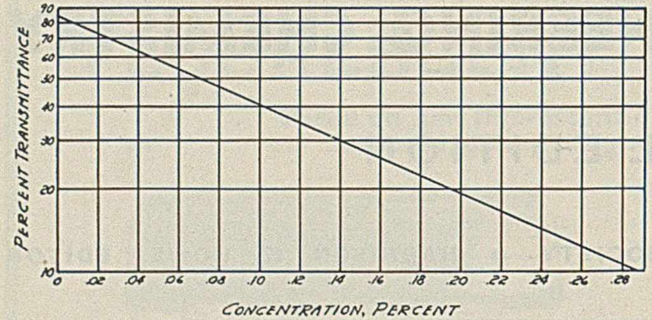


Figure 3. Per Cent Transmittance *vs.* Per Cent Phosphorus

Distilled water used as a blank. Color compared at 27° C.

tilled water blank changes the concentration *vs.* transmittance curve (Figure 3).

For increased accuracy and economy of time the original colorimetric method for phosphorus (*2*) has been slightly modified. A 1-gram sample is used instead of the original 0.5 gram to allow the determination of silica and manganese on the same sample.

Procedure

Weigh out a 1-gram sample of iron ore into a 150-ml. beaker, add approximately 10 ml. of concentrated hydrochloric acid, and heat on a hot plate until the sample is in solution, adding more hydrochloric acid if necessary.

When the ore is in solution add 0.5 ml. of concentrated nitric acid, evaporate the solution to dryness, and carefully bake. Allow the beaker to cool somewhat, add 15.0 ml. of 70 to 72 per cent perchloric acid, and fume on a hot plate until the dark brown ferric solution has changed to a light straw color. The color change requires from 3 to 6 minutes, depending on the temperature of the hot plate. Extreme care should be taken to see that no organic matter contacts the hot fuming perchloric acid.

Allow the sample to cool slightly, add 10.0 ml. of ammonium vanadate solution, place the sample back on the hot plate, and bring it to a boil.

Table I. Determination of Phosphorus

Sample No.	Phosphorus Volumetric %	Phosphorus Colorimetric %
888 GG	0.058	0.058
889 GG	0.066	0.064
7106 GB	0.082	0.081
7107 GB	0.089	0.088
7108 GB	0.093	0.092
866 MB	0.104	0.104
867 MB	0.105	0.105
868 MB	0.129	0.128
869 MB	0.128	0.127
870 MB	0.082	0.082
871 MB	0.099	0.099

Remove the sample from the hot plate and wash the cover glass with a little distilled water; filter into a 100-ml. volumetric flask. Scrub the beaker and wash the contents onto a filter paper. Wash the filter paper five times with distilled water. The insoluble residue on the paper may be used for a silica determination.

Fill the volumetric flask to the mark with distilled water, and mix by repeatedly inverting the stoppered flask. Measure out 50.0 ml. to use for a manganese determination if required.

To the remaining aliquot in the flask add 7.5 ml. of ammonium molybdate solution. Invert and shake the flask to mix the reagents and dissolve the precipitate that first forms. Place the sample in a water bath maintained at 27.0° C. When the sample is at bath temperature measure the transmittance at 450 millimicrons in a Coleman spectrophotometer. Read the per cent of phosphorus from the concentration *vs.* transmittance curve (Figure 3).

Table I shows a comparison of the colorimetric and volumetric methods for determining phosphorus.

Summary

The colorimetric determination of phosphorus in iron ores by the phosphovanadomolybdate method gives results in good agreement with the usual volumetric method. Iron gives a definite measurable interference which is negligible if the ore is above 50 per cent iron. Temperature must be controlled for the most accurate work.

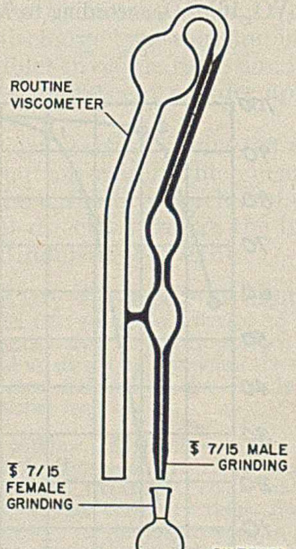
Literature Cited

(1) Mission, G., *Chem.-Ztg.*, 32, 633 (1908).
(2) Willard, H. H., and Center, E. J., Ind. Eng. Chem., Anal. Ed., 13, 81 (1941).

A Filtering Device for Viscosity Tubes

STANFORD J. HETZEL
Sun Oil Company, Norwood, Penna.

CONSIDERABLE difficulty is often encountered in preparing an uncontaminated sample of oil or other liquid for a viscosity determination. A. S. T. M. Designation D-445-39T requires that the sample be filtered through sintered glass or a fine wire screen into a small beaker or bottle. It is somewhat difficult to keep all the apparatus clean and free from solid particles or lint and, unless great care is exercised, the sample may pick up lint from the air before being transferred to the viscometer pipet.



The filtering device illustrated is a much more convenient and rapid means for ensuring an uncontaminated sample for viscosity measurement. It consists of a small interchangeable filtering cap made by sealing a sintered-glass disk 20 mm. in diameter and 2 mm. thick in a glass tube fitted with a standard ₮ 7/15 female joint. A male joint is ground on the end of the capillary arm of the viscometer. With the cap in place the pipet is inverted and immersed in the beaker or wide-mouthed bottle containing the sample, and filled by suction in the usual manner.

Two porosities of sintered-glass disks, medium or coarse, depending on the viscosity of the sample, may be used. The filtering cap holds about 6 to 7 cc. of sample.

Cleaning is accomplished by drawing petroleum ether or benzene through the cap in order to retain any foreign particles on the outside and drying in a stream of air or in an oven.

Colorimetric Determination of Nickel with Ammonia

A Spectrophotometric Study

J. P. MEHLIG, Oregon State College, Corvallis, Ore.

ALTHOUGH it has long been known that nickelous salts in the presence of excess ammonia give a blue to violet colored complex, until recently little has been done toward the development of a colorimetric method for the determination of nickel based upon this reaction. Two methods have been proposed for its determination in steel.

Fieber (*4*) determined it in the filtrate after filtration of the iron precipitate produced by ammonium hydroxide, while Ayres and Smith (*1*) separated the nickel as the dimethylglyoxime salt, decomposed the precipitate with nitric acid, and determined the nickel in the resulting solution. They have stated that as little as 5 p. p. m. of nickel can be detected with certainty when the Yoe (*16*) photoelectric colorimeter is used. The region of highest sensitivity, however, lies between 500 and 1500 p. p. m. The error may amount to as much as about 5 per cent.

The purpose of the work described in this paper was to make a critical study of this method by means of the photoelectric recording spectrophotometer (*10*), with particular attention to the effect of diverse ions upon the color system. Similar studies of other colorimetric methods have recently been made with this instrument (*2, 3, 5, 6, 8, 9, 11, 12, 13*).

Apparatus and Solutions

All spectrophotometric measurements in the present work were made at Purdue University with the self-recording instrument used by the writer in previous investigations (*8, 9*).

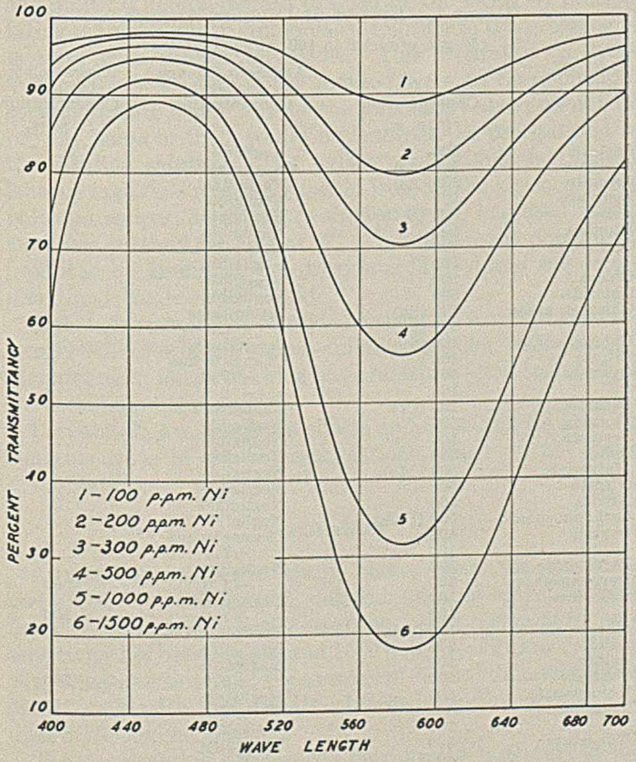


FIGURE 1. TRANSMITTANCY CURVES FOR NICKEL-AMMONIA
100, 200, 300, 500, 1000, and 1500 p. p. m. of nickel in 1.5 *M* ammonium hydroxide. 4.976-cm. cell

A standard stock solution of nickelous nitrate, each milliliter of which contained 10 mg. of nickel, was made by dissolving 20.0133 grams of metallic nickel, of 99.93 per cent purity, in dilute nitric acid and accurately diluting with redistilled water to 2 liters.

Ammonium hydroxide solutions of various concentrations, such as 0.5, 1.5, 3, 4.5, and 6 *M*, were made by suitable dilution of the concentrated solution of specific gravity 0.90.

Standard solutions of the diverse ions were prepared from the chloride, nitrate, or sulfate salts of the cations and from the sodium, potassium, or ammonium salts of the anions. Redistilled water was used in all cases. Each milliliter contained 10 mg. of the ion in question.

To produce the color system 5 ml. of the standard stock solution of nickel in a 100-ml. volumetric flask were just neutralized with 15 *M* ammonium hydroxide, diluted to the mark with 1.5 *M* ammonium hydroxide (*1*), and thoroughly shaken.

The spectral transmission curves were determined for a solution thickness of 4.976 cm. and a spectral band width of 10 mμ. Compensation for the absorption of light by the glass cell and solvent was obtained by placing in the rear beam of light a similar cell filled with 1.5 *M* ammonium hydroxide.

That the color reaction may be reproduced to a high degree of precision is shown by the fact that thirty-one solutions of the nickel-ammonia complex, each containing 500 p. p. m. of nickel and prepared by the above procedure, gave transmittancies at 582 mμ (the peak of the absorption band), the average deviation of which from the mean was 0.15 per cent.

The transmittancy curves for varying amounts of nickel are shown in Figure 1.

Conformity to Beer's Law

Proof that Beer's law is followed by the color system is shown by the straight line which resulted when the logarithms of the observed transmittancies at 582 mμ for six solutions, containing from 100 to 1500 p. p. m. of nickel, were plotted against the respective concentrations. Ayres and Smith (*1*) using the Yoe colorimeter (*16*) reported that the system follows Beer's law up to 600 p. p. m. of nickel.

Effect of Ammonium Hydroxide

Yoe and Crumpler (*16*) have pointed out that ammonia solutions show an appreciable absorption of light in the visual region. It has been shown (*9, 15*) that the concentration of ammonium hydroxide has a pronounced effect upon the color of the copper-ammonia system. A similar result should be expected for the nickel-ammonia system, which to the eye shows a change in hue from blue to violet as the concentration of ammonia increases.

The spectral transmission curves produced by a series of five solutions, each containing 500 p. p. m. of nickel, but made by use of 0.5, 1.5, 3, 4.5, and 6 *M* ammonium hydroxide, were compared. In each case the corresponding concentration of ammonium hydroxide was used in the rear cell. The curves (Figure 2) show that the hue gradually changes as the concentration of the ammonium hydroxide varies. Both the maximum absorption and the wave length of maximum absorption decrease as the concentration increases. Therefore, it is necessary that the concentration chosen for the determination be used throughout in making all the unknown as well as standard solutions which are to be used for comparison. In

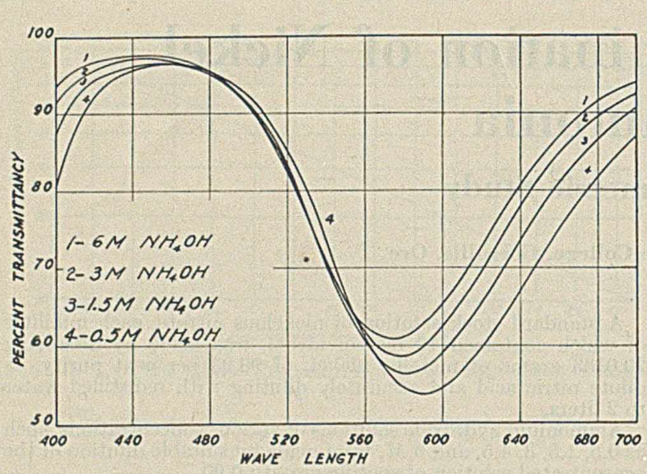


Figure 2. Effect of Concentration of Ammonium Hydroxide

500 p. p. m. of nickel in 0.5, 1.5, 3, and 6 *M* ammonium hydroxide. 4.976-cm. cell

the present work the 1.5 *M* solution used by Ayres and Smith (*1*) was selected. Because of the high concentration of ammonia, no attempt was made to determine pH values.

Stability of the Color

Six solutions, containing 100, 200, 300, 500, 1000, and 1500 p. p. m. of nickel, respectively, in 1.5 *M* ammonium hydroxide, were stored in glass-stoppered Pyrex bottles and allowed to stand in diffuse light. Curves made at intervals for these solutions gave no evidence of fading or other change in color over a period of 4 weeks. Time was not available for a longer testing period. Apparently the color is stable indefinitely. Such marked stability makes possible the use of a series of permanent standards, which must, however, be kept tightly stoppered to prevent loss of ammonia. Any action of the ammonia on the glass to produce turbidity is reduced to a minimum by using Pyrex containers.

Ayres and Smith (*1*) found no change in the color after 150 hours, but did not make tests over a longer time.

Effect of Anions

In the ion interference studies the curve produced by the standard solution containing 500 p. p. m. of nickel in 1.5 *M* ammonium hydroxide was compared with the curve produced by a similar nickel solution containing in addition a known weight of the diverse ion. From the transmittancies at 582 mμ of the standard solution and of each of the other solutions and from the known nickel concentration of the standard solution, the apparent concentration of nickel in each of the solutions containing diverse ions was calculated by the aid of a special color slide rule. The difference between this value and the actual concentration multiplied by 100 and divided by the actual concentration gave the percentage error. The calculation is based upon the formula

$$T_2 = T_1^{\frac{c_2}{c_1}}$$

where T_1 represents the transmittancy, expressed as a decimal, for the solution of concentration c_1 and T_2 the transmittancy for the solution of concentration c_2. In accordance with the practice followed in three former studies by the writer (*8, 9*) and by other workers at Purdue University (*2, 3, 5, 6, 11, 12, 13*) a 2 per cent error was set as the maximum allowable for negligible interference. Although visual methods of color comparison often have a precision of not less than 5 per cent, it was thought advisable to set a lower figure to provide for other possible factors.

When there is a change in hue the curve does not have the same general shape as the standard curve and the point of maximum absorption occurs at a different wave length.

The interfering anions may be divided into four general classes: those, such as cyanide, which form complexes with the nickel ion without a change in hue; those, such as citrate, pyrophosphate, and salicylate, which form complexes with a change in hue; those, such as dichromate, which cause a change in hue because of their own color; and those, such as chlorostannate, chlorostannite, silicate, tungstate, and vanadate, which cause turbidity because of their own hydrolysis or the precipitation of nickel salts.

In Figure 3, curves 2 and 3 show the effects of 500 and 100 p. p. m. of chromium as dichromate ion, curve 4 the effect of 300 p. p. m. of cyanide ion, and curve 5 the effect of 500 p. p. m. of oxalate ion.

The effects of the common anions and their approximate limiting concentrations are listed in Table I.

Effect of Cations

Cobaltous and cupric ions are the only common cations which really interfere. They form soluble, colored ammonia complexes, causing a decided change in hue. In Figure 4, curves 2 and 3 show the effects of 50 and 25 p. p. m. of cobaltous ion and curves 4 and 5 the effects of 50 and 25 p. p. m. of cupric ion. Silver, cadmium, and zinc ions form colorless ammonia complexes which do not interfere. Aluminum, antimonous, barium, beryllium, bismuth, chromic, ferric, ferrous, lead, magnesium (in the absence of ammonium chloride), manganous, mercuric, mercurous, strontium, thorium, uranyl, and zirconium ions precipitate as hydroxides or basic salts in the alkaline solution. These precipitates can

Table I. Effect of Diverse Anions

(50 mg. of nickel in 100 ml. of solution)

Ion	Concentration	Apparent Change in Nickel Concentration	Approximate Limiting Concentration
	P. p. m.	%	*P. p. m.*
Acetate	500	Negligible	...
Arsenate	500 (As)	Negligible	...
Arsenite	500 (As)	Negligible	...
Benzoate	500	Negligible	...
Borate	500 (B_2O_3)	Negligible	...
Bromide	500	Negligible	...
Carbonate	500	Change in hue	
	100	Negligible	150
Chlorate	500	Negligible	...
Chloride	500	Negligible	...
Chlorostannate	500 (Sn)	Precipitates	
	300 (Sn)	+1.9	300
Chlorostannite	100 (Sn)	Precipitates	0
Citrate	100	Change in hue	0
Cyanide	300	−17.8	
	100	− 6.4	0
Dichromate	100 (Cr)	Change in hue	0
Fluoride	500	Negligible	...
Formate	500	Negligible	...
Iodide	500	Negligible	...
Molybdate	500 (Mo)	Negligible	...
Nitrate	500	Negligible	...
Nitrite	500	Negligible	...
Orthophosphate	500 (P_2O_5)	Negligible	...
Oxalate	500	Change in hue	
	100	+7.7	0
Perchlorate	500	Negligible	...
Pyrophosphate	100	−3.0	50
Salicylate	500	Change in hue	
	100	+1.6	100
Silicate	100 (SiO_2)	Precipitates	0
Sulfate	500	Negligible	...
Sulfite	500	Negligible	...
Tartrate	500	+2.0	500
Thiocyanate	500	Negligible	...
Thiosulfate	500	Turbidity	
	200	+2.2	150
Tungstate	500	Turbidity	
	300	+3.0	
	100	Negligible	150
Vanadate	20 (V)	Precipitates	0

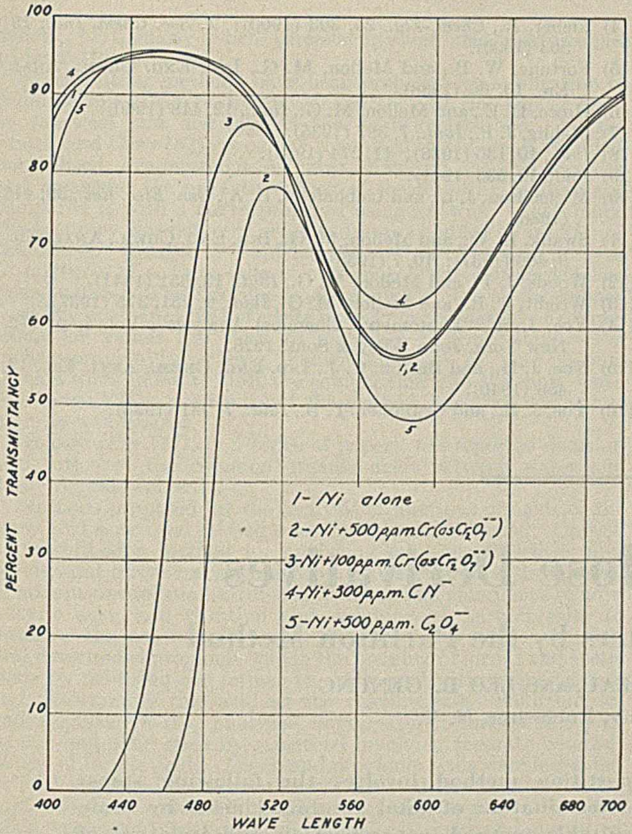


Figure 3. Effect of Anions

500 p. p. m. of nickel with diverse anion in 1.5 *M* ammonium hydroxide. 4.976-cm. cell

be removed by filtration, as was done by Fieber (*4*), but Ayres and Smith (*1*) chose instead to separate the nickel by precipitating it from slightly ammoniacal solution in the presence of tartrate with dimethylglyoxime. This separation is satisfactory for steel, but if the method were to be applied to general testing where any of the ions listed above might be present, some of them would undoubtedly be precipitated in the alkaline solution. The writer recommends for miscellaneous materials relatively low in iron, in the absence of cobalt and copper, a procedure similar to the one used in the ammonia method for copper (*7*, *14*), wherein the precipitate produced by ammonium hydroxide is filtered and the determination is made on the filtrate.

Although ammonium chloride has been shown (*9*, *15*) to intensify the color of the copper-ammonia system, 1000 p. p. m. of ammonium ion as chloride have no effect upon the color of the nickel-ammonia system.

In Table II are listed the effects and approximate limiting concentrations of the common cations which do not cause precipitation.

Summary

A spectrophotometric study shows that the ammonia method for the colorimetric determination of nickel is satisfactory although not highly sensitive. The region of highest sensitivity lies between 500 and 1500 p. p. m. of nickel. While the precision is not high, the average of several determinations agrees well with the results obtained by the gravimetric dimethylglyoxime method.

The Ayres and Smith method need not be restricted to the determination of nickel in steel. However, for miscellaneous materials relatively low in iron it is recommended that any precipitate produced by ammonium hydroxide in the absence of tartrate be filtered and the nickel determined in the filtrate without resorting to the dimethylglyoxime separation.

Table II. Effect of Diverse Cations

(50 mg. of nickel in 100 ml. of solution)

Ion	Concentration *P. p. m.*	Apparent Change in Nickel Concentration	Approximate Limiting Concentration *P. p. m.*
Ammonium	500	Negligible	. . .
Cadmium	500	Negligible	. . .
Calcium	500	Negligible	. . .
Cobaltous	25	Change in hue	0
Cupric	25	Change in hue	0
Lithium	500	Negligible	. . .
Magnesium	200	Negligible[a]	. . .
Potassium	500	Negligible	. . .
Silver	500	Negligible	. . .
Sodium	500	Negligible	. . .
Zinc	500	Negligible	. . .

[a] If ammonium chloride is present.

The concentration of the ammonium hydroxide used for dilution must be carefully controlled because of the ability of the ammonia solution to absorb light. Since the hue varies with the concentration, the same concentration must be used for the standards as for the unknown solutions. A 1.5 *M* solution is recommended.

The color system follows Beer's law.

The color is stable in diffuse light for at least 4 weeks and undoubtedly for a much longer time. The use of a series of permanent standards is therefore possible.

The color reaction may be reproduced to a high degree of precision.

A study of the effect of sixty common ions shows that only a few, especially cobaltous, cupric, cyanide, and dichromate, seriously interfere with the color and that many of the cations

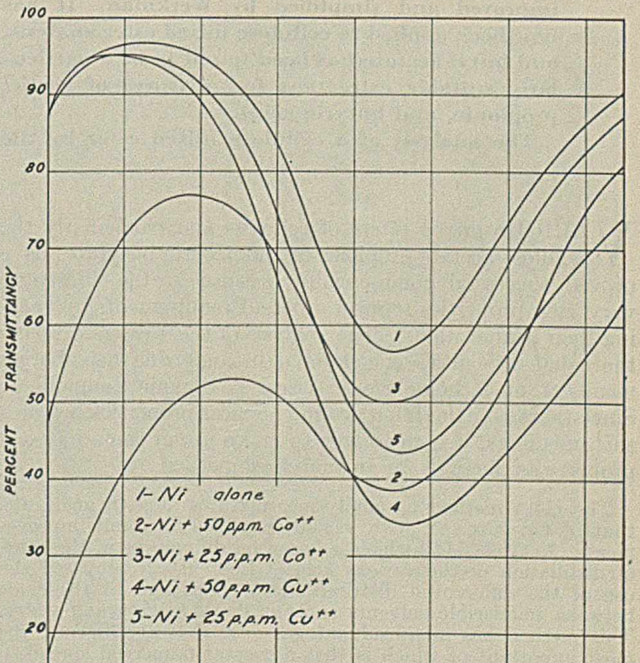


Figure 4. Effect of Cations

500 p. p. m. of nickel with diverse cation in 1.5 *M* ammonium hydroxide. 4.976-cm. cell

cause precipitation or turbidity, but in the course of the determination this latter group would be removed.

Acknowledgments

The writer expresses his sincere appreciation to M. G. Mellon of Purdue University, in whose laboratory this investigation was conducted, and thanks him for the privilege of using the Purdue spectrophotometer. Thanks are also given to R. E. Kitson for his aid in adjusting the spectrophotometer.

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Analysis of Cellulose Derivatives

Analysis of Cellulose Mixed Esters by the Partition Method

CARL J. MALM, GALE F. NADEAU, AND LEO B. GENUNG
Eastman Kodak Company, Rochester, N. Y.

Several methods have been proposed for the determination of the combined acids in mixed esters of cellulose, most of them based on some physical property of the acids. The differential partition (or distribution) of the acids between immiscible solvents has proved to be a satisfactory and practical means for determining the composition of mixtures of acids. This principle was utilized by Behrens and the manipulation was improved and simplified by Werkman. It has now been applied to cellulose mixed ester analysis, and butyl acetate has been found to be a particularly suitable extractant for mixtures of acetic, propionic, and butyric acids.

The analysis of a cellulose mixed ester by the partition method involves the following steps: determination of total combined acids by some suitable method, saponification and isolation of these combined acids, determination of the partition coefficients between butyl acetate and water of the acid mixture and also separate measurement of the partition coefficients of each acid present, calculation of the molar ratios of the acids using simultaneous equations, and calculation of the weight per cent of the acids, or combined acyl, from the molar ratios and the total acid content of the ester. Precision, accuracy, and limits of applicability are given. Modifications of the procedure are described for certain higher acyl esters and for nonvolatile acid esters.

VARIOUS mixed esters of cellulose and particularly the cellulose acetate propionates and acetate butyrates have proved successful commercially because of the ability to vary their properties to meet different requirements by varying their compositions. The analysis of these esters presents the usual difficulties encountered in analyzing neighboring members of a homologous series of organic compounds. Since there is little difference in chemical properties between such members, it is necessary to make use of some physical property as the basis for an analytical method.

The older method for analyzing mixtures of such acids was that of Duclaux (*6*), with various modifications and improvements (*7, 14, 28, 32*), which is based on differences in the rates of distillation of the various acids. Behrens (*2*) proposed the use of the differential distribution (or partition) of the acids between immiscible solvents such as diethyl ether and water. This method has many advantages over that of Duclaux, the most important of which is that a greater numerical spread in values may be obtained. Behrens titrated the acid present in each phase and calculated his results algebraically using simultaneous equations. He showed that mixtures of as many as five acids could be analyzed with reasonable accuracy by measuring partitions under several different sets of conditions. The acids studied were acetic, propionic, butyric, valeric, caproic, succinic, lactic, glycolic, malic, citric, and tartaric.

Werkman successfully applied this principle to two-component mixtures using isopropyl ether (*29*), diethyl ether (*30*), and isoamyl ether (*31*). Calculations were made by graphical methods. Osburn and Werkman (*18*) extended the procedure to mixtures of acetic, propionic, and butyric acids and developed nomograms to simplify the calculation. Later (*19*) they modified the procedure to include formic acid and to indicate the presence of other acids such as lactic and pyruvic. Fuchs (*8*) has systematically studied the indirect methods of analysis, including application of the partition method to mixtures of the lower aliphatic acids.

Yackel, Staud, and Gray (*34*) applied the procedure of Werkman to cellulose esters by saponifying the esters by the modified Eberstadt method (*16*), removing the alcohol by evaporation, acidifying with phosphoric acid, and steam-distilling. The acid distillates were extracted with diethyl ether. Steam-distillation of propionic and butyric acids is not very satisfactory from an analytical standpoint, so Yackel, Kenyon, and Gray (*33*) modified this procedure by saponifying, removing the alcohol by evaporation, diluting, and exactly neutralizing the alkali with standard hydrochloric acid. The regenerated cellulose was then filtered off, and the filtrate was extracted with diethyl ether by the method of Werkman (*30*). The sodium chloride present was shown to have a negligible effect on the distribution coefficients of the acids.

Malm and Nadeau (*15*) improved these procedures by saponifying the cellulose ester without the use of alcohol and used vacuum-distillation for separating the organic acids from the regenerated cellulose. Normal propyl and butyl acetates were found to have many advantages over the ethers as extracting agents, particularly when three-component acid mixtures are to be analyzed.

Several other methods have been proposed for application to cellulose mixed esters, but in general they do not appear to be so practical and accurate as the partition method. Yackel, Staud, and Gray (*34*) saponified the mixed esters, steam-distilled, neutralized, evaporated to dryness, dissolved the sodium salts, and measured the refractive index of the resulting solution and compared it with a curve prepared using knowns. They found the accuracy was not very great and were troubled by interfering impurities. Tanghe (*25*) applied the method of thermal analysis to mixtures of sodium salts of two acids isolated from cellulose mixed esters. The freezing or congealing points as determined from the cooling curves of melts gave some indication of composition for values less than 25 mole per cent propionyl. For higher propionyl contents, known amounts of pure sodium acetate were added to shift the composition into the more sensitive range. The sensitivity of the method, however, was not so high as was desired.

Kolossowsky (*11*), in a series of papers, has reported distribution ratios of the common organic acids between water and many organic solvents.

Methods proposed for the analysis of mixtures of acids of the fatty acid series and related acids include the following: Crowell (*4*) described a method for analyzing mixtures of acetic, propionic, and butyric acids based on the extraction with kerosene of an aqueous solution saturated with calcium chloride to remove butyric acid, and titration and weighing of barium salts to measure the amount of acetic and propionic acids. McNair (*13*) determined propionic acid in the presence of formic and acetic acids by oxidizing the former to oxalic acid with permanganate and determining this acid as the calcium salt. Sukhanovskiĭ and Roginskaya (*24*) analyzed mixtures of formic, acetic, propionic, and oleic acids by a method involving separate determination of formic acid. Acetic and propionic acids were measured as lead salts and by special extraction and fusion steps; oleic acid was then obtained by difference. Lecoq (*12*) steam-distilled acetic and butyric acids from lactic acid and measured the amounts of these volatile acids either from the differential solubilities of their barium salts in ethyl alcohol or by converting the mixed barium salts to barium sulfate. Vinogradov and Ostroumova (*27*) determined propionic and butyric acids in acetic acid by stepwise neutralization with hydrochloric acid of a solution of the sodium salts of the acids. After each neutralization, the mixtures were extracted with ether and the acids in the ether layers were converted to their sodium salts. Addition of ferric chloride resulted in precipitates or colors from which the amounts of propionic and butyric acids could be estimated.

Tasman (*26*) estimated formic, acetic, and propionic acids in bacteriological nutritive media by steam-distilling the acids, measuring formic acid separately by the reduction of mercuric chloride to mercurous chloride, and destroying formic acid in another portion of the distillate by oxidizing with acid dichromate. The resulting mixture of acetic and propionic acids was then distilled in fractions, the distillates were neutralized, concentrated, and combined, and after acidification a "half distillation" value was measured, from which the relative proportions of the acids were found by comparison with a standard curve. Klinc (*10*) determined butyric acid in the presence of formic, acetic, propionic, and lactic acids by controlled oxidation to acetone using hydrogen peroxide. The acetone formed was measured by precipitating with an alkaline mercuric cyanide–silver nitrate mixture. Bekhtereva and Ierusalimskiĭ (*3*) analyzed mixed acids obtained in a butyl alcohol–acetone fermentation. Mixtures of acetic and butyric acids were analyzed by measuring formic acid by the reduction of mercuric chloride, butyric acid by the colorimetric method of Peterson and Fred (*20*), and acetic acid by difference.

Qualitative methods for the identification of organic acids of the homologous fatty acid series include the following: Agulhon (*1*) identified these acids by observing colors formed in solvent layers when ferric or cupric salt solutions of the acids were extracted with certain organic solvents. Dyer (*7*) modified and improved the method of Agulhon. Denigès (*5*) formed characteristic crystals by treating the acids with cholesterol and examining them microscopically. Musicant and Kaszuba (*17*) identified propionic acid in the presence of acetic and butyric acids by microscopic examination of their mercurous salts. Schicktanz, Steele, and Blaisdell (*21*) analyzed mixtures of formic, acetic, propionic, *n*- and isobutyric acids qualitatively and semiquantitatively by a method based on azeotropic distillations with benzene and toluene.

Procedure

The procedure given has been found satisfactory from a practical standpoint, and involves the following steps:

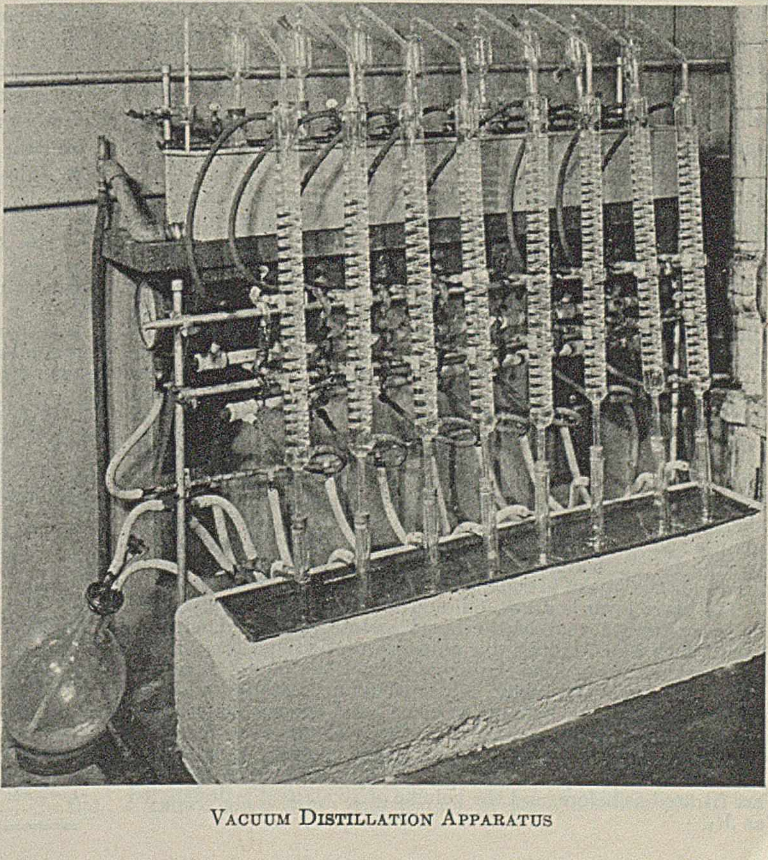
1. An analysis to determine the total combined acids present.
2. Saponification and isolation of the combined acids.
3. Determination of the partition coefficients between butyl acetate and water of the acid mixture and separate measurement of the partition coefficients of each acid present.
4. Calculation of the molar ratios of the acids using simultaneous equations.
5. Calculation of the weight per cent of the acids (or combined acyl) from the molar ratios and the total acid content of the ester.

Special Apparatus and Reagents. Constant-temperature bath or oven at 40° C.

Vacuum-distillation apparatus, each consisting of a 500-ml. round-bottomed flask fitted with a rubber stopper carrying a capillary inlet tube and Kjeldahl distillation head, which is in turn connected to a vertical condenser, the lower end of which reaches within 7.5 cm. (3 inches) of the bottom of a 500-ml. sidearm distillation flask used as the receiver. Efficient condensers, preferably of the spiral type, are recommended. The distillation flasks are heated in a water bath, and the receivers are cooled in a brine bath or with ice and salt at about 0° C.

Phosphoric acid solution, 1 molar.

Butyl acetate must be free from water to ensure good keeping quality and must be free from acidity to give accurate results. As much as 5 per cent of butyl alcohol can be tolerated. When commercial butyl acetate is used, it must be neutralized with sodium carbonate, dried over calcium chloride, and then carefully distilled. The distillate should be tested for freedom from acidity by mixing 50 ml. of butyl acetate with 50 ml. of carbon dioxide–free distilled water and titrating with 0.1 *N* sodium hydroxide solution. If a pure grade of butyl acetate is avail-



Vacuum Distillation Apparatus

able, it should be shaken with solid sodium carbonate and sodium sulfate. After settling and decanting, it is ready for use. This material may be analyzed for its water (*23*) and butyl alcohol (*22*) contents by the methods described by Smith and Bryant.

Pure samples of the acids in the ester to be analyzed.

Determination of Total Acyl Content. The total acyl content may be determined by one of the methods described by Genung and Mallatt (*9*). The modified Eberstadt method should be used if applicable; otherwise, the alcoholic alkali method should be employed. The alkali consumed is calculated as per cent acetyl (equivalent weight 43). The result is actually an "apparent acetyl" value, and is a measure of the total acyl content of the ester.

Isolation of a Mixture of Acids. Duplicate 3.0-gram samples (not especially dried) are heated with 100 ml. of 0.5 *N* sodium hydroxide solution in stoppered 500-ml. round-bottomed Pyrex flasks in a water bath or oven at 40° C. for 48 to 72 hours. Enough molar phosphoric acid solution (about 50 ml.) is added to each flask to form monosodium phosphate, which liberates the organic acids from their sodium salts. The flasks are connected to the Kjeldahl heads, the distillation apparatus is assembled, and the solutions are vacuum-distilled to dryness, allowing a small stream of air bubbles to enter if necessary to avoid bumping. Twenty-five milliliters of distilled water are added to the residue in each flask and the vacuum-distillation is again taken to dryness. This operation is repeated with second 25-ml. portions of distilled water. The conditions of the distillation must be such that no phosphate ion is carried over into the distillate.

In this operation, it is not necessary to work with quantitative accuracy, but it is necessary to obtain water solutions of the acids in the same ratio as they occur in the ester. The distillate is diluted to about 250 ml. with carbon dioxide-free distilled water which, in the majority of cases, automatically adjusts the acidity of the distillate to 0.08 to 0.12 *N*, the range desired for subsequent extractions.

Many modifications of the distillation apparatus might be used. The apparatus described, however, is simple, it may be assembled from ordinary laboratory equipment, and it has been proved by long use to be satisfactory and practical.

Determination of Molar Ratio of Acids. The following procedure is based on the distribution of the various acids and the unknown acid mixture between water and *n*-butyl acetate. The ratios are first determined for the individual acids using samples of known high purity. From these values and the partition ratio of the mixture, the molar ratio can be calculated.

The distribution ratios of the known acids are determined as follows. The case of acetic, propionic, and butyric acids is used in the following discussion:

The calculated amounts of the pure acids (1.43 ml. of acetic, 1.87 ml. of propionic, and 2.30 ml. of butyric acid) are each diluted to 250 ml. to give approximately 0.1 *N* solutions. A 25-ml. portion of each acid solution is titrated with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator. The volume of alkali in each case is designated as M. Thirty milliliters of acid solution and 15 ml. of butyl acetate are transferred to a small separatory funnel, using accurate pipets or burets, the mixture is shaken thoroughly, and the two layers are allowed to separate. The conditions of shaking are not critical, but they must be standardized by each operator. It is recommended that the shaking be continued for 2 minutes at about 100 strokes per minute and that the funnel be held in such a way as to minimize heating by the hand. Several minutes' standing should be allowed for the layers to separate.

The lower layer is drawn off, and the upper layer is discarded or saved for recovery of the butyl acetate. A 25-ml. pipet is rinsed with 2 or 3 ml. of this aqueous solution and then 25 ml. are pipetted into a clean flask containing 25 or 50 ml. of carbon dioxide-free distilled water. This solution is titrated with 0.1 *N* sodium hydroxide solution as before, and the volume of alkali in each case is designated as M_1. Other 30-ml. portions of the acid solutions are extracted in the same manner, using in this case 60 ml. of butyl acetate, 25-ml. portions of the aqueous layers are titrated as before, and the volume of alkali used is designated as M_2.

The following ratios are then calculated for each acid:

$$\frac{M_1}{M} = k_1 \qquad \frac{M_2}{M} = k_2$$

The distribution ratios, or partition coefficients, thus determined represent the fraction of the acid remaining in the water layer under the conditions specified. Numerical values are thus obtained for the following partition coefficients:

k_1, acetic acid with 15 ml. of *n*-butyl acetate
k_2, propionic acid with 15 ml. of *n*-butyl acetate
k_3, butyric acid with 15 ml. of *n*-butyl acetate
k_4, acetic acid with 60 ml. of *n*-butyl acetate
k_5, propionic acid with 60 ml. of *n*-butyl acetate
k_6, butyric acid with 60 ml. of *n*-butyl acetate

These values must be determined by each operator for every new supply of butyl acetate. The numerical values will vary with the butyl alcohol content of the butyl acetate and with the individual technique of the operator.

Before continuing the analysis, the extraction technique and the partition coefficients should be checked by preparing and analyzing an acid mixture of known composition.

Convenient weights of the three acids are thoroughly mixed in a flask and 1.75 to 2 ml. of the mixture are diluted to 250 ml. to give an approximately 0.1 *N* solution, the exact molar composition of which is calculated from the weights of the acids. A 25-ml. portion is titrated, the titer is designated as M, and 30-ml. portions are extracted with 15 and 60 ml., respectively, of butyl acetate and are titrated using exactly the same technique previously employed.

The following percentage coefficients are then calculated:

$$\frac{M_1 \times 100}{M} = K_1 \qquad \frac{M_2 \times 100}{M} = K_2$$

In this case the K values are expressed as percentage partition coefficients rather than as ratios. The composition of the known acid mixture is then calculated from these data, using Equations 6, 7, and 1 as described below. If the result agrees satisfactorily with the known composition of the mixture, the coefficients and the equation are ready for use. If the agreement is poor, the individual partition coefficients should be rechecked and the mixture reanalyzed until satisfactory results are obtained. This may involve a considerable amount of work for a new operator, but when the extraction technique has been standardized, acceptable results can usually be obtained in the first attempt.

The distillates may then be analyzed by the procedure described above. 25-ml. portions are titrated, the volumes of alkali are designated as M, 30-ml. portions are extracted and titrated as before, and the titration from the 15-ml. extraction is designated as M_1 and from the 60-ml. extraction as M_2. The percentage partition coefficients, K_1 and K_2, are calculated as in the case of the known acid.

Calculations. *Case of a Mixture of Three Acids.* In order to evaluate three unknowns, three simultaneous

Table I. Partition Coefficients of Various Acids

Acid	k_1, 15 Ml. of Butyl Acetate, 30 Ml. of Water	k_2, 60 Ml. of Butyl Acetate, 30 Ml. of Water
Formic	0.885	0.660
Acetic	0.851	0.589
Propionic	0.592	0.263
n-Butyric	0.288	0.093
Isobutyric	0.280	0.090
n-Valeric	0.124	0.040
n-Caproic	0.036 (0.04 *N* solution used)	0.013
Crotonic	0.350	0.121
Methoxyacetic	0.920	0.752
Chloroacetic	0.532	0.233
Levulinic	0.869	0.624

Table II. Analyses of Acid Mixtures of Known Composition

Acid	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken
	Mole per cent									
Acetic	90.1	90.6	88.2	88.4	61.5	61.5	46.5	46.6	9.5	9.9
Propionic	5.1	4.8	4.1	4.6	29.3	29.2	32.9	33.0	46.7	46.0
Butyric	4.8	4.6	7.7	7.0	9.2	9.3	20.6	20.4	43.8	44.1

Acid	Found	Taken	Acid	Found	Taken
	Mole per cent			*Mole per cent*	
Formic	41.0	40.8	Acetic	77.1	76.8
Butyric	59.0	59.2	Caproic	22.9	23.2
Acetic	65.2	65.1	Acetic	21.7	21.6
Propionic	34.8	34.9	Chloroacetic	78.3	78.4
Acetic	37.1	37.2	Butyric	26.1	26.4
Butyric	62.9	62.8	Caproic	73.9	73.6
Acetic	77.0	76.8			
Crotonic	23.0	23.2			

algebraic equations involving the three unknown quantities are necessary. In the case of a ternary acid mixture, the sum of the mole percentages of the acids present represents the total acidity or 100 per cent. If A, P, and B represent mole percentages of acetic, propionic, and butyric acids, respectively, the first equation becomes:

$$A + P + B = 100 \tag{1}$$

The second and third equations are:

$$Ak_1 + Pk_2 + Bk_3 = K_1 \tag{2}$$

$$Ak_4 + Pk_5 + Bk_6 = K_2 \tag{3}$$

Note that k_1, k_2, k_3, k_4, k_5, and k_6 are known and refer to the pure individual acids, whereas K_1 and K_2 refer to the ternary mixture. By solving these equations for P, the following expressions may be derived:

$$P = \frac{\dfrac{K_1 - 100k_1}{k_3 - k_1} - \dfrac{K_2 - 100k_4}{k_6 - k_4}}{\dfrac{k_2 - k_1}{k_3 - k_1} - \dfrac{k_5 - k_4}{k_6 - k_4}} \tag{4}$$

$$B = \frac{K_2 - 100k_4 - P(k_5 - k_4)}{k_6 - k_4} \tag{5}$$

Typical values for the partition coefficients of the acids are:

$k_1 = 0.852$
$k_2 = 0.587$
$k_3 = 0.282$
$k_4 = 0.586$
$k_5 = 0.261$
$k_6 = 0.091$

When these values are substituted in Equations 4 and 5, they simplify to the following forms:

$$P = 10.5\ (58.6 - K_2) - 9.14\ (85.2 - K_1) \tag{6}$$

$$B = 2.02\ (58.6 - K_2) - 0.656P \tag{7}$$

The above constants and numerical values in the equations are typical, but the exact values should be determined by each analyst, using his own reagents and the best pure acids available. These constants must be checked from time to time, particularly when new reagent solutions are put in use.

The mole percentages of acid are converted to weight per cent acyl as follows:

$$A \times \text{per cent apparent acetyl} = \text{weight per cent acetyl} \tag{8}$$

$$P \times \text{per cent apparent acetyl} \times 57/43 = \text{weight per cent propionyl} \tag{9}$$

$$B \times \text{per cent apparent acetyl} \times 71/43 = \text{weight per cent butyryl} \tag{10}$$

Case of Two Acids. When it is known that only two acids are present, the manipulation and calculation may be simplified considerably. Only two simultaneous equations and only one set of partition coefficients are then required. In the case of a cellulose acetate butyrate, using the above terminology, the necessary equations are

$$A + B = 100 \tag{11}$$

$$Ak_1 + Bk_3 = K_1 \tag{12}$$

These equations, when solved, become

$$B = \frac{K_1 - 100\ k_1}{k_3 - k_1} \tag{13}$$

$$A = 100 - B \tag{14}$$

When the numerical values for k are substituted in Equation 13, it simplifies to the form:

$$B = 1.75\ (85.2 - K_1) \tag{15}$$

A similar equation can also be derived using the other set of constants:

$$B = \frac{K_2 - 100\ k_4}{k_6 - k_4} \tag{16}$$

Limits of Applicability

The procedure as described above is satisfactory for the analysis of cellulose acetate propionates and cellulose acetate butyrates having propionyl and/or butyryl contents less than about 35 to 40 per cent. The limit cannot be drawn more closely than this because the physical condition of the sample to be saponified is an important variable.

This principle can also be applied to the analysis of other volatile water-soluble acid esters of cellulose. The accuracy obtained depends upon the difference in the numerical values of the partition coefficients. Typical partition coefficients for a series of such acids are given in Table I. These values are comparable, for they were determined using one particular sample of butyl acetate which contained 0.04 per cent water and 1.81 per cent butyl alcohol, but such coefficients would vary with different operators and different reagents.

Analysis of Known Mixtures

When acid mixtures of known composition are analyzed, results such as those given in Table II are readily attainable.

Acid mixtures of known composition were distilled in the usual way to check the completeness of distillation, and analysis of the distillates gave the following results:

Acid	Found	Taken
	Mole per cent	
Acetic	56.9	57.0
Propionic	29.4	29.7
Butyric	13.7	13.3
Acetic	62.3	62.0
Propionic	28.3	28.6
Butyric	9.4	9.4

A known acid was also distilled and analyzed in the same way, except that 1.5 grams of cotton linters were present in the distillation flask during the distillation, which approximately duplicates the condition normally encountered.

Acid	Found	Taken
	Mole per cent	
Acetic	15.6	16.0
Propionic	30.6	30.6
Butyric	53.8	53.4

The effect of the saponification was measured by heating 1.5 grams of cotton linters and about 2 ml. of an acid mixture of known composition with 100 ml. of 0.5 N alkali at 40° C. for 3 days, then acidifying with phosphoric acid, distilling, and analyzing by the usual procedure. The results were as follows:

Acid	Found	Taken
	Mole per cent	
Acetic	15.6	16.0
Propionic	30.6	30.6
Butyric	53.8	53.4

These experiments show that no appreciable errors are introduced at any stage in the manipulation. This conclusion is supported by the fact that when cellulose acetate is analyzed, practically 100 mole per cent acetic acid is found. Qualitative tests on the distillates show negligible amounts or no phosphoric or formic acid to be present.

Precision and Accuracy

Examination of the data on known solutions indicates that accuracy within ±0.4 mole per cent is usually attained. In cellulose esters containing approximately 50 per cent acyl, the accuracy is thus about ±0.2 per cent acyl. The precision is better, and is usually within ±0.2 mole per cent or ±0.1 weight per cent acyl.

Procedure for Mixed Esters of High Propionyl or Butyryl Content

In the case of cellulose acetate propionates and acetate butyrates having more than 35 to 40 per cent propionyl and/or butyryl, the apparent acetyl content must be determined by the alcoholic alkali procedure (*9*) or an equivalent method, and the saponification and isolation of the mixed acids are carried out as follows:

Duplicate samples of approximately 3.0 grams (not especially dried) are weighed into 500-ml. round-bottomed flasks. Approximately 100 ml. of methyl or ethyl alcohol and 100 ml. of 0.5 *N* sodium hydroxide solution are added to each flask. The saponification is then conducted at room temperature for 48 to 72 hours, except in cases where this treatment is not vigorous enough. In some cases, it will be necessary to conduct the saponification at 40° C. for 48 to 72 hours. The flasks are then connected to distillation apparatus and the alcohol is removed by vacuum-distillation. After distilling to dryness, the vacuum is released, the condenser and receiver are rinsed down, and the distillate is discarded. The required amount of phosphoric acid and 100 ml. of distilled water are added to each flask, and the apparatus is reassembled. The distillation, extractions, and calculations are then carried on as described above. It is necessary to remove all the alcohol by the first distillation, or the partition constants and the results will be in error.

Small amounts of formic acid are formed when cellulose is heated in the presence of alkali. This effect can be reduced and the accuracy of the above procedure can be slightly improved when desired by filtering off the regenerated cellulose before removing the alcohol by vacuum-distillation.

This method is applicable to the analysis of volatile water-soluble acids which include acetic, propionic, butyric, and valeric acids. Caproic and higher acids cannot be analyzed by this exact procedure, because of their lower solubility in water and their poorer volatility. However, the procedure can be modified to include caproic by using more dilute solutions such as 0.04 *N*.

The precision and accuracy are slightly poorer when alcohol must be used, for the conditions of saponification are more vigorous, and the distillation to remove alcohol is made on the alkaline solution. As a result, measurable amounts of formic acid are formed, which cause the apparent acetic acid results to be high, and propionic or butyric results to be low. On the other hand, any alcohol which is not removed by the first distillation and is carried with the acids in the second distillation produces an error in the opposite direction. The accuracy is also affected by errors in the total acyl analysis. A precision of ±0.4 mole per cent or about ±0.2 weight per cent acyl is usually attained. The average accuracy is of the order of ±1 mole per cent or ±0.5 weight per cent acyl.

Procedure for Nonvolatile, Water-Soluble Acid Esters

The saponification is conducted as described above. If alcohol is used, it must first be removed by evaporating or distilling to dryness. Distilled water is added if necessary to restore the original volume, and then standard hydrochloric acid is added to neutralize exactly all the alkali present. The regenerated cellulose is removed by filtration, is washed well, and the volume of the filtrate is adjusted to 200 to 250 ml. This filtrate differs from the distillates obtained in the other procedures in that it contains sodium chloride equivalent to the amount of alkali originally taken. Partition ratios may be determined on this filtrate by the above-described procedure with the difference that the coefficients for the known acids must be determined using 0.1 *N* solutions of the acids containing the same sodium chloride concentration as the filtrates.

Partition coefficients of the known acids between butyl acetate and water are appreciably lowered by sodium chloride, whereas Yackel, Kenyon, and Gray (*33*) found that it has little effect on the coefficients for diethyl ether and water.

This method is particularly adapted to the analysis of esters of water-soluble volatile or nonvolatile acids. The accuracy obtainable depends upon the exactness of the neutralization of sodium hydroxide with hydrochloric acid and also upon the numerical difference between the distribution coefficients of the acids involved.

TABLE III. EFFECT OF BUTYL ALCOHOL CONTENT ON PARTITION COEFFICIENTS

	Butyl Acetate Sample						
	1	2	3	4	5	6	7
Butyl alcohol (*22*), %	0.87	1.30	1.90	2.09	2.42	5.10	8.80
Water (*23*), %	0.17	0.03	0.00	0.03	0.02	0.06	0.10
k_1	0.857	0.855	0.852	0.849	0.847	0.825	0.793
k_2	0.601	0.598	0.587	0.589	0.584	0.551	0.513
k_3	0.294	0.293	0.282	0.288	0.282	0.260	0.234
k_4	0.602	0.597	0.586	0.584	0.576	0.531	0.472
k_5	0.275	0.271	0.261	0.261	0.255	0.227	0.194
k_6	0.098	0.096	0.091	0.092	0.089	0.079	0.067

Effect of Variables

EFFECT OF BUTYL ALCOHOL CONTENT OF BUTYL ACETATE. The butyl alcohol content of the butyl acetate has an appreciable effect on the numerical values of the partition coefficients (*k*) for acetic, propionic, and butyric acids, as shown in Table III.

Other variables, such as the technique of the operator, may affect these numerical values, so it is not practical to use *k* values based on the butyl alcohol content as found by analysis.

Butyl acetate samples 1 and 7 have too high water contents to keep well, and sample 7 also has too much butyl alcohol to be satisfactory.

EFFECT OF TEMPERATURE OF EXTRACTION. The temperature at which the extractions are carried out in connection with the determination of the partition coefficients has a small effect on the numerical values obtained. It is small enough, however, not to cause trouble if the partition coefficients for the known acids (*k* values) are measured at approximately the same room temperature at which the analysis is run. Accurate results on known acid mixtures have been obtained at all times and at all room temperatures ordinarily encountered.

EFFECT OF ACID CONCENTRATION. Partition coefficients for the individual acids are measured using 0.1 *N* solutions, but the acidities of the distillates containing the unknown acid mixtures vary at least over the range 0.08 to 0.12 *N*. The effect of such variations was measured by analyzing a known acid mixture at concentrations about 0.060, 0.10, and

Table IV. Effect of Acid Concentration

Ternary Mixture		Acid Concentration 0.06 N	0.10 N	0.12 N
K_1		46.10	46.20	45.85
K_2		21.85	21.70	21.50
Acid	Taken	Found		
	Mole Per Cent			
Acetyl	16.0	17.2	16.5	16.6
Propionyl	30.6	29.8	30.5	29.4
Butyryl	53.4	53.0	53.0	54.0

Table V. Effect of Acid Concentration on Partition Coefficients

Acid	Coefficient	0.06 N	0.10 N	0.12 N
Acetic	k_1	0.846	0.844	0.844
	k_4	0.574	0.573	0.573
Propionic	k_2	0.583	0.579	0.579
	k_5	0.256	0.254	0.252
Butyric	k_3	0.285	0.278	0.273
	k_6	0.092	0.090	0.090

0.12 N, and the results are shown in Table IV. The best agreement between the observed analyses and the amounts taken was obviously obtained with the 0.1 N solution, and poorer results were found using the other solutions.

The six k values for acetic, propionic, and butyric acids were also measured at these same three concentrations (Table V).

It is apparent that the accuracy must suffer as the normality of the test solution deviates from the normality of the known acid solutions used in measuring the partition coefficients. For this reason, it is suggested that the normalities of the distillates be adjusted to within the range of 0.08 to 0.12.

Extractants Tested

Partition coefficients for acetic, propionic, and in some cases butyric acid were measured between water and each of the following organic solvents:

Ethylene dichloride
Propylene dichloride
Carbon tetrachloride

Ethyl ether
Isopropyl ether
Butyl ether
Amyl ether

Benzene
Cyclohexane
Decahydro naphthalene

n-Propyl acetate
n-Butyl acetate
Ethyl *n*-butyrate

Heptane
Pentane
Ligroin

n-Propyl and *n*-butyl acetates were found to give the greatest spread in numerical values for the three acids, and have been selected as the most satisfactory for this purpose.

Summary

The partition (or distribution) method has been found to be practical and satisfactory for the analysis of mixed esters of cellulose, and particularly for cellulose acetate propionates, acetate butyrates, and acetate propionate butyrates.

Details of manipulation are given together with limits of applicability, precision, and accuracy of the method. Necessary variations in the procedure are described for esters of higher acyl content and of nonvolatile acids.

Commercial cellulose acetate propionates and acetate butyrates can be analyzed with a precision of about ±0.1 weight per cent acyl and an accuracy of about ±0.2 weight per cent acyl.

The effects of some of the variables have been measured.

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Correction

In the article on "Determination of Particle Size Distribution" [Ind. Eng. Chem., Anal. Ed., 14, 10 (1942)] several errors occur on page 12.

Column 1, paragraph 4, the last word in the line should be "liquid" instead of "solid".

Column 1, paragraph 8, P_2 in the numerator of the fraction should be ρ_2.

Column 2, Sample Calculation, in the expression for ρ_1 the numerical factor should be 1.0001.

Column 2, the explanation in small type "For 40μ at 20 cm.^{a} t_{40} = 9.75/9 = 1.2 minutes" should be "For 40μ at 20 cm.^{a} t_{10} = 9.75/8 = 1.2 minutes".

W. O. Hinkley

Determination of Strontium in the Presence of Calcium

PAUL B. STEWART AND KENNETH A. KOBE[1], University of Washington, Seattle, Wash.

IN CONNECTION with a phase rule study of the ternary system calcium nitrate–strontium nitrate–water in process in this laboratory an accurate method for the determination of strontium in the presence of calcium was needed. As the system is being studied with the idea that the data gathered may be used as the basis for a fractional crystallization process for preparing pure strontium nitrate from impure or low-grade strontium ores, it was further desired that the analytical procedure be capable of use as a technical method.

TABLE I. SOLUTION OF CALCIUM NITRATE AND STRONTIUM NITRATE IN ACETONE AT ROOM TEMPERATURE

$Ca(NO_3)_2$		$Sr(NO_3)_2$	
Time elapsed, minutes	Salt, gram per ml. of soln.	Time elapsed, minutes	Salt, gram per ml. of soln.
12	0.3118	13	0.0004
25	0.3377	25	0.0007
37	0.3713	57	0.0010
56	0.4189	103	0.0016
78	0.4532		
106	0.4642		

The classical method for the determination of strontium in the presence of calcium is by the extraction of the calcium nitrate from the mixed alkaline earth nitrates with a mixture of absolute alcohol and absolute ether (*1*). These solvents are both expensive and hygroscopic, this latter feature being especially important in many localities. The acetone extraction method of Shreve and co-workers (*2*) seemed to obviate some of these undesirable features. The results claimed for it were substantiated by trial, but only in mixtures containing a calcium to strontium ratio of 3 to 1 or richer in strontium. With increasing proportion of calcium to strontium in the mixture of the salts the method becomes less and less reliable.

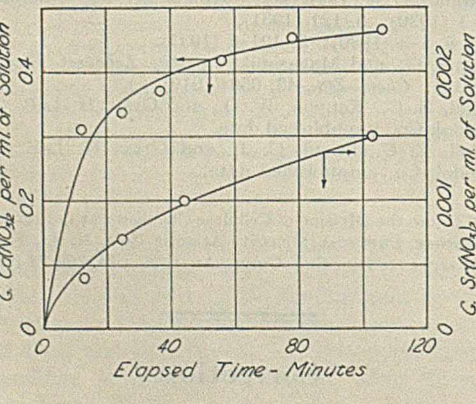

FIGURE 1

As acetone is both cheap and ordinarily readily available, it was decided to attempt to modify the acetone extraction method so that sufficiently accurate results could be obtained. Accordingly, the work of Williams and Briscoe (*3*) was repeated in part, and their finding that calcium nitrate is extremely soluble and strontium nitrate essentially insoluble in acetone at room temperature was confirmed. It was also found that the rate of solution of calcium nitrate in an acetone solution of calcium nitrate was too slow at the end of an hour to make this solution a good solvent. Results of this work are shown in Table I and Figure 1.

Among the variations in procedure tried were varying the length of time with a single extraction, repeated extractions of differing times, ratio of acetone to total salts, and finally a continuous extraction process using Jena sintered-glass filter crucibles in a modified Soxhlet apparatus. None of these gave satisfactory results.

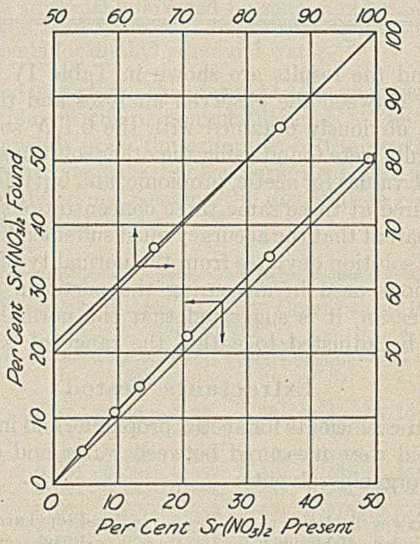

FIGURE 2

It was then decided to standardize a procedure, and to obtain a calibration curve for this method. The variables which it was deemed necessary to control were ratio of solvent to total salts, time of extraction, and manner of extraction. Accordingly, the following procedure was adopted and rigidly followed:

For the analysis of a sample containing other substances than calcium and strontium nitrates it is necessary to isolate these alkaline earth nitrates as in the gravimetric analysis for calcium in limestone. Briefly, this consists of putting the sample in solu-

TABLE II. CALIBRATION OF ANALYTICAL PROCEDURE

	Strontium Nitrate Present							
	%	%	%	%	%	%	%	%
	4.42	9.36	13.24	20.59	33.30	48.84	65.55	85.10
Trial	Strontium Nitrate Found							
	%	%	%	%	%	%	%	%
1	5.00	10.90	14.92	22.52	34.95	49.95	66.55	85.10
2	5.45	9.10[a]	14.67	24.40[a]	36.85[a]	50.45	66.73	85.20
3	5.34	10.70	15.22	21.85	34.90	50.70	66.45	85.10
4	4.46	11.20	14.47	23.75	35.50	50.15	66.25	83.10[a]
5	3.89[a]	11.10	15.41	23.05	34.75	50.40	66.65	85.30
6	4.92	11.50	...	....	....	...	...	....
7	5.32	11.60	...	....	....	...	...	....
8	5.45	10.90	...	....	....	...	...	....
9	4.98	10.50	...	....	....	...	...	....
Av.	5.12	11.05	14.94	22.79	35.02	50.35	66.53	85.20
Av. deviation	0.70	1.69	1.70	2.20	2.72	1.51	0.98	0.10

[a] Not used in average.

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[1] Present address, University of Texas, Austin, Texas.

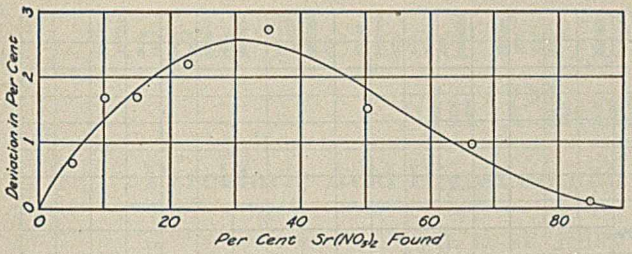

FIGURE 3

tion with hydrochloric acid, after fusing it with sodium carbonate if necessary. The silica is then removed by repeated dehydrations and filtered off, followed by the removal of iron and aluminum as hydroxides by precipitation with ammonium hydroxide. The alkaline earth metals are then precipitated as carbonates with ammonium carbonate and filtered off from the solution. Treatment of the carbonates with nitric acid will then yield the desired solution of the alkaline earth nitrates. This procedure makes no provision for separating barium from strontium and calcium.

The solution, of sufficient size to yield about 1 gram of anhydrous salts, containing the mixed calcium and strontium nitrates, is evaporated on a steam plate for from 12 to 24 hours, and finally dried in an oven at 140° C. for 24 hours. Drying at a lower temperature was found to be too slow, and tests showed no detectable decomposition of the strontium nitrate at this temperature and for this time. Both the evaporation and drying were generally carried out in 40 × 25 mm. weighing bottles with the covers held slightly open for the escape of vapor by a U-shaped wire clip on the top of the bottle. The mixed anhydrous nitrates are then cooled in a desiccator over phosphorus pentoxide (calcium nitrate is an excellent desiccant itself), and weighed. They are then extracted with c. p. acetone, using 4 ml. of acetone per 100 mg. of salts. The salts are transferred to an evaporating dish for the extraction with the extractant acetone, and thoroughly pulverized with a stirring rod, the end of which has been enlarged. During the extraction the contents of the dish are stirred every 8 to 10 minutes, the dish being covered with a watch glass at all other times. At the end of exactly one hour the residue in the dish is filtered off in a No. 3 Jena sintered-glass filter crucible, dried at 140°, and weighed.

Solutions containing known amounts of both alkaline earth nitrates were then prepared, and the foregoing procedure was applied to them. The data in Table II were obtained. These are shown graphically in Figure 2, which shows the values obtained by this analytical procedure compared with the true values. The maximum deviation is in the range of 10 to 60 per cent strontium nitrate. In Figure 3 is plotted the deviation in per cent against the per cent strontium nitrate found in the sample by this analytical method. The deviation is subtracted from the per cent strontium nitrate determined to give the true value.

Although a sample yielding about 1 gram of mixed alkaline earth nitrates was preferred, samples as small as 0.40 gram and up to 3 grams were run by this method. The strontium content of these samples ran from a minimum of 4 to 5 mg. up to practically the entire weight of the sample. In running triplicate samples, almost invariably a pair of values would check to within 5 parts in 1000, based on the original weight of the nitrates. This method has been used on all the analytical work on the phase rule study referred to earlier, and the results have been most satisfactory in that they are thoroughly consistent among themselves.

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Analysis of the Ternary System Ethanol-Methanol-Water

JOHN GRISWOLD AND J. A. DINWIDDIE[1], University of Texas, Austin, Texas

A rapid and accurate physical method of analysis is presented for the ternary system ethanol-methanol-water, which requires the boiling point, refractive index, and specific gravity of the sample. The composition is then read directly from a chart. No assumptions are involved and no adjustment to a definite water concentration is needed.

THIS ternary system is encountered in some antifreeze solutions and certain denatured alcohol formulas and pharmaceutical preparations, although the analysis was developed for use in a study of liquid-vapor equilibrium which will be published later.

Early methods of analysis applied to this system had as their chief purpose the determination of small amounts of methanol in ethyl alcohol and water. Chemical methods of analysis were to oxidize the methanol or subject it to some other chemical reaction, then determine the compound formed.

Leach and Lythgoe (*3*) developed a purely physical analysis for the ternary system, using the specific gravity and refractive index. The method embodied two approximations: that the concentration of total alcohol is a function of gravity only, and that the refractive index is linear with the ratio of the two alcohols. The method is necessarily inexact, and has the disadvantage that the rather inaccessible and not highly accurate Hehner alcohol tables must be used to avoid serious errors.

Lange and Reif (*2*) obtained better accuracy with a similar method, by adjusting the alcohol concentration to 50 per cent by volume, then determining gravity and refractive index.

Williams (*6*) reviewed Leach and Lythgoe's method, and improved upon it by adjusting the sample concentration to 20 per cent by weight of total alcohol before making final gravity and refractometer determinations.

Mortimer (*5*) developed a ternary chart for alcohol concentrations up to 40 per cent by weight in terms of Zeiss refractometer readings, with which the proportion of the two alcohols may be resolved.

Macoun (*4*) improved Lange and Reif's method somewhat by adjusting the sample to a concentration of 40 per cent alcohol by weight. The weight per cent is independent of temperature whereas the volume per cent (used by Lange and Reif) is not. Macoun also prepared a table of alcohol concentration in terms of refractometer readings for values between 39.5 and 40.5 weight per cents of alcohol, and temperatures from 15.6° to

[1] Present address, Humble Oil & Refining Co., Baytown, Texas.

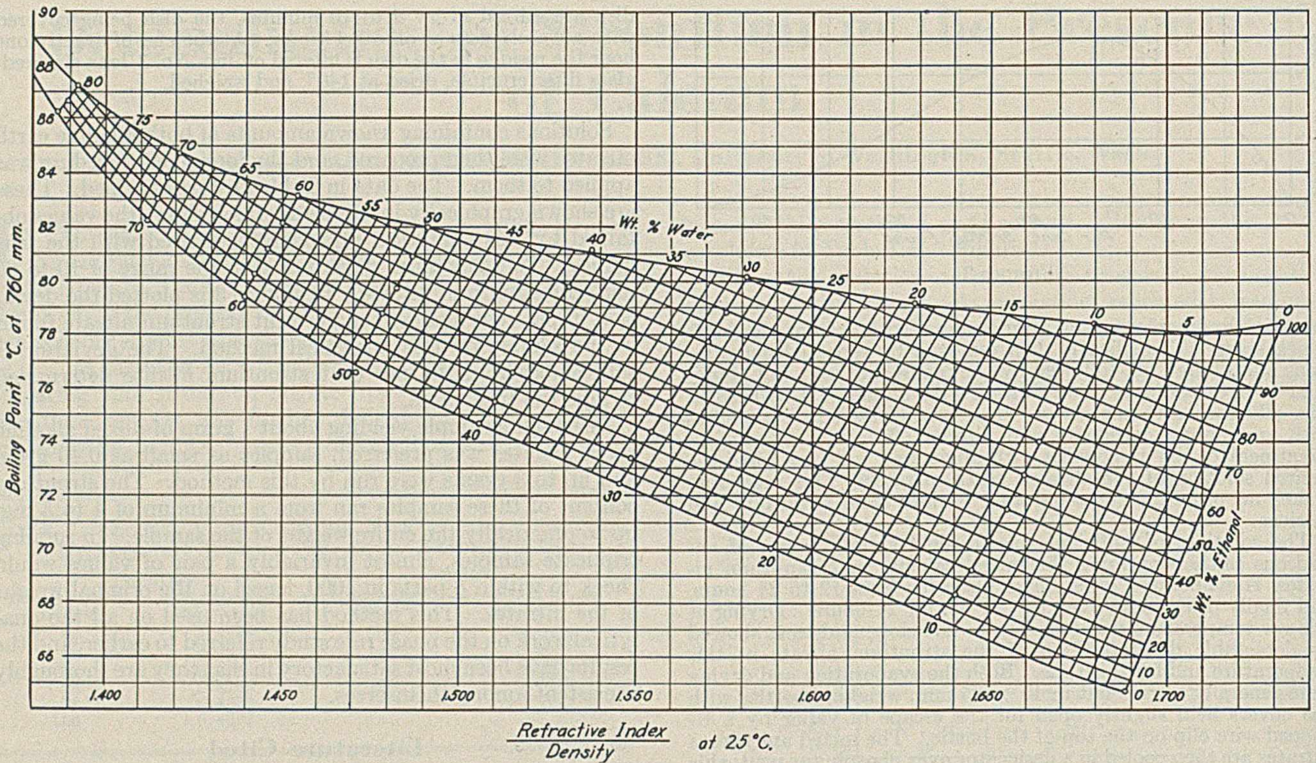

Figure 1. Analysis of Ethanol-Methanol-Water Mixtures

22° C. The relative amounts of the alcohols were computed by the linearity approximation used by Leach and Lythgoe. A footnote to the article is significant:

> At this point the specific gravities of aqueous ethyl alcohol and aqueous methyl alcohol are close together, while their refractive indices lie far apart. Certain errors inherent in this type of determination are therefore greatly reduced.

All the foregoing methods embody the first approximation in that they depend upon gravity alone for the water content, although no brief is held that the gravity is completely independent of the ratio of the two alcohols.

By inclusion of a third physical constant, the boiling point, a method free from approximations was obtained. A series of 56 determinations was made upon prepared samples, systematically varied in composition. The data were then plotted in various ways. The Lorenz-Lorentz relation (which is theoretically inapplicable to mixtures) was tried, but showed no particular promise. The final plot (Figure 1) of boiling point (° C. at 760 mm.) against the refractive index-density ratio at 25° C. (n_d/D_4^{25}) was selected as giving the most uniform spread of and least curvature to the lines of constant composition. Use of the chart is straightforward—the methanol content is obtained by difference. A sample can be analyzed in about 15 minutes' time.

Two unknowns made up by one person and tested by another who had had no previous experience with the method gave the results in Table I. While additional confirmatory determinations would be in order, the method contains no inherent errors and the consistency with which the data on known mixtures fell upon the smooth curves indicate the chart to be accurate to within 0.2 per cent for water and for ethanol. The same degree of accuracy for a determination requires observations of the gravity and refractive index accurate only to the third decimal place with the boiling point accurate to 0.1° C.

To test solutions of composition outside the zone of experimental points on the chart: those containing less than 20 per cent of alcohol may be concentrated by distillation or be enriched by the addition of standardized aqueous alcohol; those containing less than 10 per cent of water may be diluted.

Apparatus and Reagents

Specific gravities were taken at 25° C. as D_4^{25} using a Geissler-type gravity bottle. Refractive indices were determined at 25° C. with an Abbe instrument against the sodium D line. Boiling points were obtained with the conventional Cottrell apparatus and a calibrated Anschutz thermometer. This Cottrell boiler has been used on these same mixtures before (*1*), and it can be made in any laboratory equipped with the usual glass-blowing facilities. The observed boiling points were corrected to 760 mm. by the formula

$$\text{Correction } ° \text{ C.} = \frac{273.1 + t_{\text{obs.}}}{6.0} (2.8808 - \log p_{\text{mm.}})$$

The alcohols were c. p. grade anhydrous methanol and 95 per cent ethanol. They were fractionated through a 3-foot (91.44-cm.) packed column and the heads and tails rejected. Gravity, refractive index, and boiling point determinations on the middle fractions showed no indications of interfering substances. The distilled water for making up the stock solutions was acidified with sulfuric acid, treated with permanganate, and redistilled. Care was taken to keep all solutions in glass-stoppered bottles, and to expose them to the atmosphere as little as possible.

Table I. Analyses of Unknowns

	Sample I		Sample II	
	Taken	Found	Taken	Found
	Wt. %		*Wt. %*	
H_2O	40.7	41.0	10.8	11.8
MeOH	9.6	10.0	49.6	48.5
EtOH	49.7	49.0	39.6	39.7

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Rapid Method for Determining Potassium in Plant Material

Perchloric Acid Digestion and Chloroplatinic Acid Precipitation

J. L. ST. JOHN AND M. C. MIDGLEY
Division of Chemistry, Agricultural Experiment Station, Pullman, Wash.

THE need for a more rapid method for determining potassium in plant material was emphasized by the referee work on ash and the recovery of mineral elements in ash, reported by St. John and Midgley (*11*) and St. John (*10*), which showed that higher ashing temperatures caused an apparent loss of potassium. Methods reported in the literature, involving a number of steps and separations, are somewhat time-consuming and provide more opportunity for loss of potassium.

This laboratory has contributed papers on methods for more rapid oxidation of organic matter, or increased recovery of elements by oxidation with combined nitric, sulfuric, and perchloric acid digestion (*2*, *4*, *5*, *6*). Perchloric acid is increasingly used for this general purpose. Smith (*13*, *14*) has studied perchloric acid and its use in the determination of a number of elements and has presented a method for potassium. Gieseking, Snider, and Getz (*7*) determined potassium and other elements by perchloric acid digestion, followed by the cobaltinitrite method described by Schueler and Thomas (*12*).

Method

A modified method for the determination of potassium has been developed which involves the nitric-perchloric acid digestion of the plant material and chloroplatinic acid precipitation of the potassium, and which eliminates a number of time-consuming steps. Plant products of somewhat widely varying character have been analyzed by this method, presented below, and also by the A. O. A. C. (*1*) method where the plant material is ashed after moistening with sulfuric acid. Temperature was controlled at 600° C. in this work.

Weigh 1 or 2 grams of the sample into a 150-ml. beaker. Add 30 ml. of concentrated nitric acid, cover, and digest over a low flame or on a hot plate until all easily oxidizable organic matter is oxidized. It is occasionally necessary to add a second or third portion of nitric acid. Cool slightly, add 10 ml. of 60 per cent perchloric acid, and continue digestion until the solution is colorless and fumes of perchloric acid begin to appear. Continue heating until all perchloric acid is driven off, taking care to avoid spattering. After fumes cease to appear, place the beaker in a muffle furnace regulated to a temperature of 350° C. and bake for 15 to 30 minutes to remove last traces of acids and any ammonium salts. Remove from the muffle, cool, and transfer the precipitate to a 7-cm. No. 4 Whatman or equivalent filter paper, with a minimum quantity of near-boiling water. The use of a policeman is essential in this transfer. Wash thoroughly with boiling water and collect the filtrate in a 100-ml. beaker, keeping the filtrate to a minimum volume. Evaporate on a steam bath or hot plate to 5 or 10 ml., but not to dryness. Acidify with concentrated hydrochloric acid. Add chloroplatinic acid to precipitate all potassium and sodium according to the A. O. A. C. method for potassium in fertilizers, and wash with 80 per cent alcohol, then with ammonium chloride saturated with potassium chloroplatinate, and finally with 80 per cent alcohol. The results may be checked to determine the presence of any insoluble residue by dissolving the weighed potassium chloroplatinate with near-boiling water, followed by alcohol, drying, cooling, and reweighing.

Discussion

Comparative analyses (Table I) were made of two practical feeding mixtures and of samples of alfalfa, corn, potatoes, soybeans, wheat, and apple juice by the method presented in this paper and the A. O. A. C. sulfuric acid ashing method, using the rapid method for potassium only. Results are calculated in terms of the percentage of the element potassium in the original sample of feed rather than in the ash, and are corrected for insoluble residue.

The data in Table I indicate that satisfactorily consistent results are obtained by the potassium method described in this paper. In general, the agreement among replicates is better than when the results are obtained by the present official method. It is easier to obtain satisfactory agreement by use of the perchloric acid digestion.

The method here described gives a somewhat higher value for potassium in some plant materials than the A. O. A. C. method. With corn, potato, and fruit juice, the percentage of potassium is essentially the same by the two methods. Gieseking, Snider, and Getz (*7*) obtained somewhat lower results (with the A. O. A. C. method) than when using a perchloric acid digestion and cobaltinitrite precipitation.

An interesting and unexpected result is evident from a study of the original data on which the results in Table I are based. In determining potassium in fertilizers, difficulty has been experienced with an insoluble residue which accompanies the chloroplatinate precipitate as reported by Ford (*3*). The authors found an insoluble residue in the potassium precipitate from these samples, when using the A. O. A. C. method. In most cases when utilizing the perchloric digestion method there was no insoluble residue. The amount of insoluble residue was determined in each case by dissolving the soluble

Table I. Potassium in Plant Materials

	Perchloric Acid Digestion %	A. O. A. C. on Ash %
Poultry feed	0.767	0.562
	0.750	0.504
	0.780	0.642
	0.766	0.597
	0.790	0.544
	0.807	
	0.821	
Av.	0.783	0.572
Dairy feed	0.647	0.496
	0.655	0.442
	0.655	0.564
	0.655	
	0.656	
Av.	0.654	0.501
Alfalfa	1.015	0.912
	1.031	0.859
	0.986	0.930
		0.896
		0.820
Av.	1.011	0.883
Corn	0.257	0.258
	0.260	0.253
	0.242	0.264
		0.260
Av.	0.253	0.259
Potato	0.383	0.396
	0.443	0.457
	0.409	0.416
Av.	0.412	0.423
Soybean	2.180	1.866
	2.160	1.798
	2.047	1.843
	2.078	1.678
	2.063	1.862
	2.205	
	2.269	
Av.	2.143	1.809
Wheat	0.305	0.169
	0.310	0.169
	0.300	0.231
	0.310	0.210
		0.246
Av.	0.306	0.205
Apple juice	0.126	...
	0.130	...
	0.130	...
	0.146	...
	0.136	...
Av.	0.134	0.133[a]

[a] The authors extend thanks to A. M. Neubert of this division for this analysis which he is publishing elsewhere.

Table II. Recovery of Potassium

	(1)	(2)	(3)	(4)
	16.5933	16.7007	16.9511	17.0389
	16.5340	16.6395	16.8886	16.9777
	0.0593	0.0612	0.0625	0.0612
Potassium recovered, gram	0.00954	0.00984	0.01005	0.00984

potassium chloroplatinate with hot water and reweighing the crucibles in which the original precipitate had been weighed.

The A. O. A. C. method for plant material does not specify the temperature for ashing and for driving off ammonium salts. However, in using this method, the samples were ashed at 600° C. and the ammonia was driven off at 550° C., since ammonium oxalate is not volatile at 350° C. In the proposed method, ammonium salts were driven off at 350° C., at which temperature both ammonium chloride and nitrate are volatile. Utilization of these controlled temperatures tended to avoid the loss of potassium due to volatilization by localized overheating during ashing or while driving off the ammonia.

The proposed method apparently gives satisfactory results without removal of calcium and other metals. Wiley (*16*) states that a separation of alkali earths, if potassium alone is to be determined, is superfluous since calcium and magnesium chloroplatinate are even more soluble in 90 per cent alcohol than is sodium chloroplatinate. Mellor (*9*) quotes earlier workers to show that calcium chloroplatinate is soluble in alcoholic solution, and a saturated solution contains 53 per cent of the salt. The salt is soluble in ethyl alcohol of specific gravity 0.8035 at 15°, and is decomposed into its component chlorides. Potassium has apparently been satisfactorily determined on soils by the calcium carbonate–ammonium chloride fusion method for many years, without removing calcium.

The method here described is more rapid because of elimination of a number of steps. Nitric-perchloric acid digestion is more rapid than ashing. Digestion is made directly in a beaker, saving a transfer. The time required for evaporations is reduced to a minimum, since there is only one transfer and filtration before precipitation. This filtration requires much less washing than filtering out precipitated iron and aluminum, and evaporation is carried to 10 ml. rather than to dryness. There is no evaporation of a concentrated solution of ammonium salts, since none have been added and thus the difficulty with creeping salts is minimized and considerable time is saved. Any small amount of ammonia present in the original material after digestion is volatilized, and any remaining silica is dehydrated during the baking at 350°. Filtration and washing after baking are much more rapid, and the possibility of potassium loss is reduced in comparison to the method where calcium is separated. With the proposed method, it is easily possible to start and complete the determination of potassium on a set of samples within an 8-hour day.

The somewhat higher results obtained in some cases by the procedure here described than by the A. O. A. C. method are believed to demonstrate the recovery of added potassium from the original sample, since solubility and microscopic examination of the precipitates indicated pure potassium chloroplatinate. Any impurity in the precipitate or any added potassium due to the reagents or procedure should have given higher results in the case of all samples. Further, utilization of the described method with pure salts gives essentially 100 per cent recovery. Data in Table II (1) and (2) are obtained by precipitating the potassium from a solution of potassium chloride containing 0.00996 gram of potassium. To similar aliquots of the same potassium chloride solution there was added a solution of calcium chloride containing about 52 mg. of calcium chloride, equivalent to about the amount present in an average sample of alfalfa. The recovery of potassium is very satisfactory, as shown by (3) and (4), and it is evident that the presence of a comparatively large amount of calcium has not interfered with the complete recovery of potassium; in fact, the amount of potassium recovered is within ±0.1 mg. of the amount in the solution, which is a variation of less than 1 part in 600. A determination of potassium on the calcium chloride solution gave practically negligible results.

The added number of steps in the A. O. A. C. procedure offers greater opportunity for losses. Potassium may be lost during the ashing procedure (*10*, *11*), or by spattering and through the volatilization of potassium salts during ashing (*16*).

It may be advantageous to use a chloroplatinic acid solution made up with hydrochloric acid, as mentioned by Tenery and Anderson (*15*). A large excess of chloroplatinic acid in precipitation is believed essential. The authors have found the chloroplatinic precipitation in hydrochloric acid preferable to precipitation in alcohol as recommended by Smith (*13*).

Caution. Kahane (*8*) and Cook (*2*) have summarized the care that should be taken in digesting with perchloric acid. Thorough digestion with nitric should be completed before the addition of perchloric. No difficulty has been experienced in this laboratory in making hundreds of digestions with perchloric acid.

Summary

A rapid procedure for the determination of potassium in plant material involves a combination of the perchloric acid method of digesting the sample and the familiar chloroplatinic acid precipitation. A number of steps employed in the more commonly used method have been eliminated. In addition to rapidity, ease of manipulation, and ease of obtaining satisfactory agreement of results, the method seems to give better recovery in some instances than the present official method for plant material.

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Correction. In the paper "Rapid Turbidimetric Method for Determination of Sulfates" [Ind. Eng. Chem., Anal. Ed., 14, 119 (1942)] Whatman No. 42 paper should have been mentioned in the procedure, not Whatman No. 12 paper.

J. F. Treon, Jr.

Determining the Fusain Content of Illinois Coals

A Comparison of Chemical and Petrographic Methods

B. C. PARKS, G. W. LAND[1], AND O. W. REES, Illinois State Geological Survey, Urbana, Ill.

THE method commonly referred to as microscopic count or petrographic analysis used for quantitatively determining the different ingredients of banded coal has been standard practice for several years in the coal laboratory of the Illinois State Geological Survey. However, this type of analysis is long and tedious, is subject to personal errors, and does not permit concurrent duplicate determinations. Because of these disadvantages a less time-consuming and less laborious method for determining fusain is desirable. This investigation, therefore, was for the purpose of determining whether the chemical method described by Fuchs, Gauger, Hsiao, and Wright (*2*) would provide values for fusain in sufficiently close agreement with those obtained by the petrographic method to justify its exclusive use.

TABLE I. PETROGRAPHIC ESTIMATION OF FUSAIN CONTENT IN A FINE COAL

$^3/_8$-inch screenings (raw carbon)[a]

Screen Mesh No.	Particle Sizes Retained on Screens *Mm.*	Screening Analysis *Grams*	Screening Analysis *%*
8	+2.36	7.40	3.87
10	−2.36 +1.651	22.10	11.56
14	−1.651+1.17	26.50	13.86
20	−1.17 +8.33	24.40	12.76
28	−8.33 +0.590	21.40	11.19
35	−0.590+0.417	18.30	9.57
48	−0.417+0.300	14.20	7.43
65	−0.300+0.208	10.50	5.49
100	−0.208+0.150	10.10	5.28
150	−0.150+0.104	6.10	3.19
200	−0.104+0.075	6.50	3.40
300	−0.075+0.046	3.30	1.73
Pan	−0.046	20.40	10.67
		191.20	100

[a] Sample from preparation plant of Madison County, Ill., mine.

Petrographic Method

The procedure involves two distinct series of steps after preparation of the sample and riffling a desired amount (approximately 500 grams). In the first step the sample selected by riffling is weighed and separated into size classes by screening through a series of Tyler standard sieves. Twelve sieves generally are used and these are grouped into two nests of six sieves each for convenience in using the Ro-Tap shaker. The sieves range from No. 8 mesh to No. 300 mesh. The size of the openings in the individual sieves decreases in the ratio of the square root of two. The openings of the No. 8 mesh screen are 2.36 mm. square, and of the No. 300 mesh are 0.046 mm. square. The material retained on eleven of the screens, after shaking through the first nest (8- to 35-mesh) for 10 minutes and the second nest (48- to 300-mesh) for 15 minutes, consists of sorted particles, each group having a relatively small size range. In addition to the sized material there are two unsorted batches, the 2.36-mm. material retained on the No. 8 mesh screen and the contents of the pan which passed through the No. 300 mesh screen (Table I).

The essential purpose of the screening is to facilitate the second step of manually separating and counting the component particles. For this work an ore-dressing type of binocular microscope is used.

In the separation and counting of fusain particles use is made of the distinctly different appearance of fusain and of the other constituents. In contrast to particles of the other constituents, fusain particles are flaky and needle-shaped with surface striations and pits often characteristic. These characteristic differences are maintained throughout the entire range of sizes used in the petrographic method of estimation.

In making fusain estimations the number of particles separated and counted in order to arrive at the correct fusain percentage in each size class is dependent upon the frequency of distribution of fusain in the particular class. For the size classes containing less than 10 per cent fusain a count of 2500 particles gave results which could be duplicated within 0.2 per cent by different operators. For size classes which had in excess of 10 per cent fusain good results were obtained by counting as few as 1000 particles in some classes (Table II).

It is obvious that the fusain percentages obtained by separating and counting particles of coal in this manner are not true weight percentages. If all particles in the two separated groups of fusain and nonfusain were spheres of the same size and specific gravity, true weight percentages could be calculated from the count data. It is known, however, that the ingredients of banded coal do not break down into spherical particles and that specific gravity is variable. Notwithstanding this, it was assumed, for practical purposes in obtaining satisfactory results, that every particle of coal separated and counted could be regarded as having the same size and specific gravity. The validity of this assumption was tested by weighing the fusain and nonfusain of ten size classes, cal-

TABLE II. PETROGRAPHIC ESTIMATION OF FUSAIN CONTENT IN A FINE COAL

$^3/_8$-inch screenings, microscopic count

Screen Mesh No.	Particle Sizes Retained *Mm.*	Separation and Count: Fusain	Separation and Count: Nonfusain	Separation and Count: Total	Distribution of Fusain: Fusain and nonfusain *Grams*	Distribution of Fusain: Fusain *Grams*	Distribution of Fusain: %
8	+2.36	104	1700	1804	7.40	0.43	5.76
10	−2.36 +1.651	142	2021	2163	22.10	1.45	6.56
14	−1.651+1.17	151	1950	2101	26.50	1.91	7.19
20	−1.17 +0.833	181	2196	2377	24.40	1.87	7.67
28	−0.833+0.590	210	2348	2558	21.40	1.76	8.21
35	−0.590+0.417	251	2489	2740	18.30	1.68	9.16
48	−0.417+0.300	234	2125	2359	14.20	1.41	9.92
65	−0.300+0.208	333	2584	2917	10.50	1.20	11.42
100	−0.208+0.150	322	2058	2380	10.10	1.30	12.90
150	−0.150+0.104	298	1400	1698	6.10	1.07	17.55
200	−0.104+0.075	264	800	1064	6.50	1.61	24.81
300	−0.075+0.046	408	500	908	3.30	1.48	44.93
Pan	−0.046	560	180	740	20.24	15.44	75.67

Total weight of sample, grams	191.20
Weight of nonfusain, grams	158.59
Weight of fusain, grams	32.61
Content of fusain in sample, %	17.06

TABLE III. COMPARISON OF FUSAIN VALUES BY COUNT AND BY WEIGHT

Microscopic method

Grade Size (Screen Mesh)	Per Cent by Weight	Per Cent by Count
8–10	2.3	2.6
10–14	2.8	2.5
14–20	4.0	3.6
20–28	3.9	3.9
28–35	4.1	3.9
8–10	1.5	2.1
10–14	2.2	1.8
14–20	2.4	2.3
20–28	2.9	2.4
10–14	2.7	2.6

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[1] Present address, Battelle Memorial Institute, Columbus, Ohio.

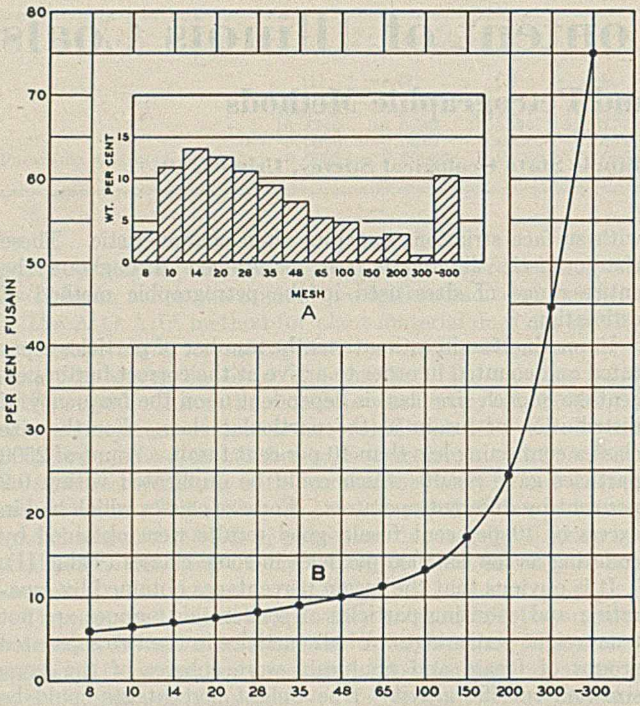

FIGURE 1. DISTRIBUTION OF FUSAIN

A. Histogram showing distribution of coal by weight percentages on screens after Ro-Tap operation of ten minutes for +35-mesh and 15 minutes for −35-mesh screens. Sample same as Table I

B. Direct plot curve showing distribution of fusain by weight percentages in coal retained on screens in *A*

culating true weight percentages, and comparing these with results obtained from count data. The results so obtained are in reasonably close agreement (Table III).

The estimation of fusain by the petrographic method here described is probably subject to unavoidable human errors and is time-consuming. The identification and separation of fusain from nonfusain in the fine sizes are particularly difficult. Eye and muscular fatigue are probably the chief causes of error in identifying, separating, and counting the extremely fine particles. An experienced petrographic observer working carefully can complete an analysis of a coal sample in about one week, and there is no short cut in making a duplicate count. An advantage afforded by petrographic analysis lies in the data obtained with which curves can be drawn showing size frequency distribution of fusain in the sample (Figure 1).

Chemical Method

The chemical method as described by Hsiao and co-authors (*2*) depends upon the relative susceptibility to oxidation of fusain and nonfusain coal material. Briefly, this procedure consists of oxidizing 1-gram portions of −200-mesh coal by boiling in 8 *N* nitric acid for 2-, 3-, and 4-hour periods. After proper washing with sodium hydroxide, hydrochloric acid, and water the residues are dried at 105° C., weighed, and ashed, and the weights of ash are deducted from the weights of oxidation residues. These ash-free residues are then calculated to per cent of moisture- and ash-free coal and plotted against oxidation time. A straight line is drawn through these points (through the last two points if impossible to draw through all points) and extrapolated to cut the zero time axis, and the corresponding residue value is taken as the fusain value. Moisture and ash determinations were made by A. S. T. M. procedures (*1*).

Figure 2 presents curves for three of the samples studied, showing their extrapolation to the zero time axis, as well as a typical oxidation curve (curve *A*) for times from 10 minutes to 4 hours. This curve appears to be made up of two parts, the first or curvilinear portion representing the oxidation of nonfusain coal material and the second flat portion representing the oxidation of the fusain. The curved portion appears to represent a first-order reaction while the flat portion appears to represent a zero-order reaction where extrapolation is easily possible.

Results

Thirteen coal samples were analyzed for fusain content independently by both methods. A comparison was made of the results and certain incidental factors were also observed, such as length of time required for the analyses and the probability of errors. The fusain content of the thirteen samples as determined chemically and microscopically is given in Table IV. The values check reasonably well. In only four of the samples was the difference in the percentage figures more than 2 per cent. In the other nine samples the difference between chemical and microscopic results varied from 0.0 to 1.8 per cent.

TABLE IV. RESULTS OF TESTS

Lab. No.	Moisture in Coal	Ash in Coal	Fusain		
			Chemical method[a]	Petrographic method	Difference
	%	%	%	%	%
C-2336 (1)	5.1	32.2	6.4	6.4	0.0
C-2337 (2)	6.5	24.2	5.4	7.2	+1.8
C-2338 (3)	5.5	41.5	14.2	9.4	−4.8
C-2339 (4)	7.1	25.6	18.0	15.2	−2.8
C-2340 (5)	2.7	18.8	19.0	19.5	+0.5
C-2341 (6)	5.1	24.2	8.5	7.5	−1.0
C-2342 (7)	6.1	19.3	10.1	7.4	−2.7
C-2343 (8)	5.2	11.0	11.5	12.6	+1.2
C-2344 (9)	5.9	23.2	12.8	10.4	−2.4
C-2345 (10)	6.2	19.2	15.9	14.4	−1.5
C-2346 (11)	5.1	10.9	4.2	4.0	−0.2
C-2347 (12)	7.6	13.4	10.9	10.8	−0.1
C-2348 (13)	5.5	9.8	13.8	12.1	−1.7

[a] Moisture- and ash-free basis.

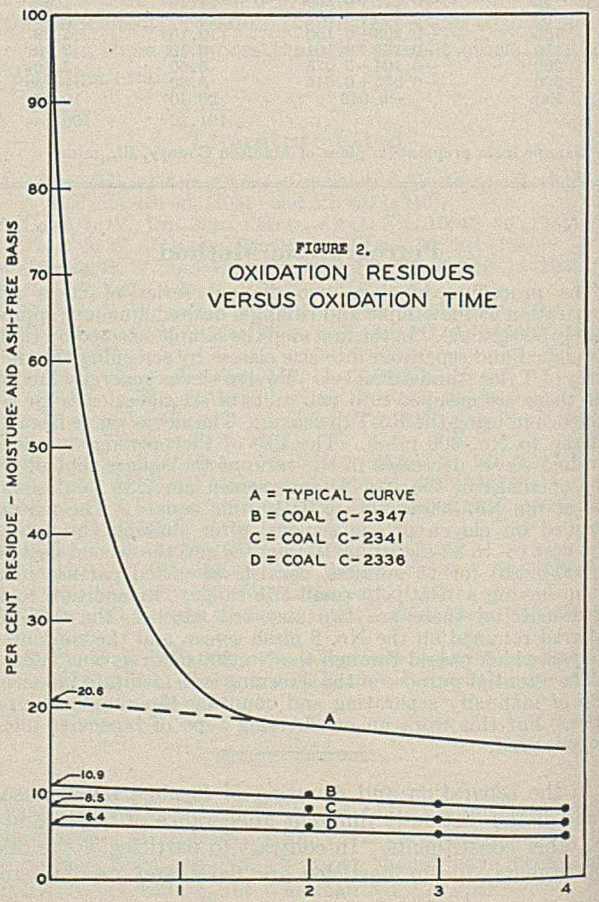

FIGURE 2. OXIDATION RESIDUES VERSUS OXIDATION TIME

The time necessary for conducting the chemical determinations, including duplicate tests of each sample, was 2 days, as compared to 5 to 10 days required for the petrographic estimations.

Certain of the residues from the chemical analyses were saved and examined carefully under the microscope. No organic material other than fusain could be found. The fusain in these residues was unusually easy to identify.

Conclusions

These tests indicate that in the majority of cases practically the same results are obtained by each method. Where different values are obtained, the greater complexity of the petrographic method and its greater dependence on personal judgment seem to favor the results obtained by the oxidation method.

The advantages of using the chemical method as indicated by these tests are summarized as follows: A considerable saving of time is effected. Duplicate analyses can be made simultaneously. There is less liability of human error. The values obtained represent fusain on an ash- and moisture-free weight basis.

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Expected Service Effectiveness of Preservative Treatments Applied to Millwork

A Laboratory Method of Comparison

JOHN B. MELLECKER, 1129 South 18th St., Arlington, Va., AND MERLE W. BAKER, Curtis Companies Incorporated, Clinton, Iowa

A practical laboratory method for evaluating and comparing the effectiveness of various millwork preservatives is described. This method provides moisture for the specimen in the same manner in which most of the moisture is supplied to millwork in service—namely, by condensation.

The specimens are compared either by visual examination of the split specimen or by microscopic examination of sections of the specimens.

CONCENTRATION of effort, during the past five years, on the development of methods for comparing the relative toxicities of various millwork preservative treatments has suggested the need for a technique to evaluate the expected field effectiveness of preservative treatments, particularly with regard to the control of blue stain fungi.

The first step in this direction was made by Hubert (*1*), who in 1938 reported a study on optimum time of immersion of millwork in preservative solutions required to effect a satisfactory treatment. In order to correlate depth of penetration of preservative with the effectiveness for control of fungi, he took 0.125-inch thick sections at various points in the bottom rail of a treated window sash and exposed them to fungi in Kolle flasks. Following this test procedure, the authors' results indicate that most millwork treatments in commercial use have shown adequate control of the important blue strain organisms, particularly when the 0.125-inch sections were taken within 2 inches of the "end" of the rail (where it meets the stile), but sections taken at a greater distance from the end showed less fungus control.

The authors have also noted from observations on window sash in service that where stain occurs, it often appears under the paint coat, suggesting that the stain fungi grew from within the wood rather than from germinating spores on the paint coat. Since present preservative treatments of sash and other millwork are applied as dips rather than by pressure, the wood is not completely impregnated. This fact, coupled with observations on stain development, suggests the desirability of making tests to determine the relative value of commercial preservatives for preventing fungi from growing from the inner untreated portion of the wood through the treated area and on through the paint coats.

Various methods were tested, and as a result of this research the following method is suggested as reliable and practical for testing the relative effectiveness of millwork preservatives.

The Method

In setting up a method in the Curtis Companies Incorporated research laboratory, it seemed desirable to use sections of bottom rails of window sash, treated in accordance with industrial practice, in order to eliminate the artificial character present when used in blocks either completely impregnated or of such shape and so treated that results comparable with those observed in actual field service could not be expected.

In order to carry out further the correlation between laboratory tests and field conditions, all culture media were eliminated. The test specimens themselves provided the medium in the untreated interior portion. Inoculation of the untreated sapwood was accomplished by spraying onto it a spore suspension of the test organism with a small spray atomizer.

A method for providing enclosure, support, and moisture was developed for this work. Adhering to the desirability of a close correlation between the laboratory method and actual service conditions, condensation was employed to provide the specimens with moisture. This was accomplished by chilling the specimen to approximately 45° F., then rapidly raising the relative humidity of the air surrounding the specimen until a heavy condensation was produced on the specimen. (This principle was originally suggested by C. Audrey Richards. Assistance in planning this procedure was also given by Theo. C. Scheffer.)

By performing this operation under identical conditions on all specimens, good control of moisture deposit was obtained. The frequency at which this operation was performed governed the average moisture condition of the specimens.

It is believed that this method has none of the disadvantages, such as overwetting, which is sometimes experienced

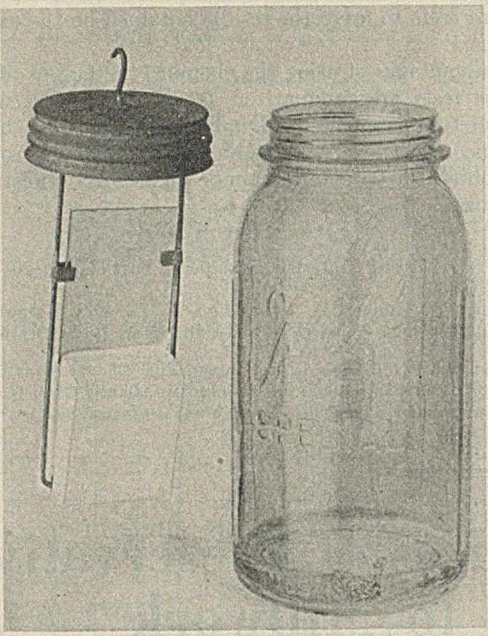

FIGURE 1. METHOD OF SUPPORTING SPECIMEN IN JAR

in the Kolle flask method (*2*) where the specimen receives its moisture by lying near, or in actual contact with, the moisture-bearing substrate. There is also no possibility of conduction of malt or other substances from the culture medium by the fungus mycelia.

Apparatus

No complex or expensive equipment was required. Ordinary wide-mouthed 2-quart glass fruit jars were used, and were modified with a minimum of labor (Figure 1).

The porcelain liners were removed from the lids and to each lid was soldered a support wire shaped at the lower end to fit into a weather-strip groove already in the section of the bottom rail. The wire was of sufficient length to support the specimen at least 1.5 inches above the bottom of the jar. About 0.75 inch of water was placed in each jar.

Three wire trays were constructed to hold 10 jars each. The jars were set in these trays permanently and removed only when the specimen was to be examined.

A water pan sufficiently large to hold one tray and about 6 inches deep was constructed. The tray was supported on brackets about 8 inches from the laboratory bench top and was filled with water to a depth of about 2 inches. Bunsen burners were used to heat this pan and its contents.

The usual incubation facilities were used. Wet incubation was not required. A standard household type of electric refrigerator was used to chill the trays of jars.

Preparation of Test Blocks

The test pieces were obtained from a piece of straight-grained Ponderosa pine sapwood, 1.375 inches × 4 inches × 16 feet, selected from stock according to specifications outlined in the N. D. M. A. standard wood block method (*2*). Liberal use of the benzidine-nitrite indicator assured that no heartwood was present.

After the piece had been machined to the detail of the bottom rail of the sash, thirty-six samples 5 inches long were cut from this piece and a 2.25-inch piece of bottom rail weather strip was stamped into each specimen. For each solution to be evaluated six pieces were prepared: three pieces to be inoculated on unpainted end grain and three pieces to be inoculated on painted end grain. Likewise, two sets of three were run (untreated) for controls.

Treatment of Test Blocks

All solutions were prepared according to manufacturer's directions or the usual industrial procedure.

The eighteen sections 5 inches long to be inoculated on unpainted surfaces were painted with two coats of interior undercoater, on the ends only, before dipping. The eighteen sections to be paint-infected were cut to 2.25-inch lengths and were likewise painted on the ends with two coats of interior undercoater before dipping. After the paint had dried thoroughly, the pieces were given the standard 3-minute immersion in five different preservative solutions. In each case three of the 5-inch pieces and three of the 2.5-inch pieces were treated.

Shortly after treating, 2.25 × 3 inch pieces of glass were glazed in all sections. In the case of the 5-inch pieces the glass was glazed in the center of each piece and the ends were cut off at the edges of the glass, leaving a 2.25-inch piece with unpainted ends to be used for wood infection.

After one week's standing all specimens were painted on the interior side with an interior undercoater diluted 8 parts of paint to 1 part of linseed oil and 1 part of turpentine. The second coat on the interior side was composed of half undercoater and half gloss enamel diluted 8 to 1 with turpentine. The third coat on the interior was straight gloss enamel. The surfaces which would normally be on the outside of the house were painted two coats of an exterior undercoater followed by one coat of gloss white exterior paint. The composition of the paints used in this test is given in Tables I and II.

After standing 2 months more the specimens were sterilized in a sterilizing chamber, using a General Electric germicidal lamp which emits an ultraviolet radiation of 253 Å. (Figure 2). The lamp used was a Type T-8, 15-watt, 110-volt, 60-cycle, which emits 15 to 20 microwatts per square centimeter of 2537 Å. units at 1 meter. The specimens were supported from the fruit jar lids as shown in Figure 1.

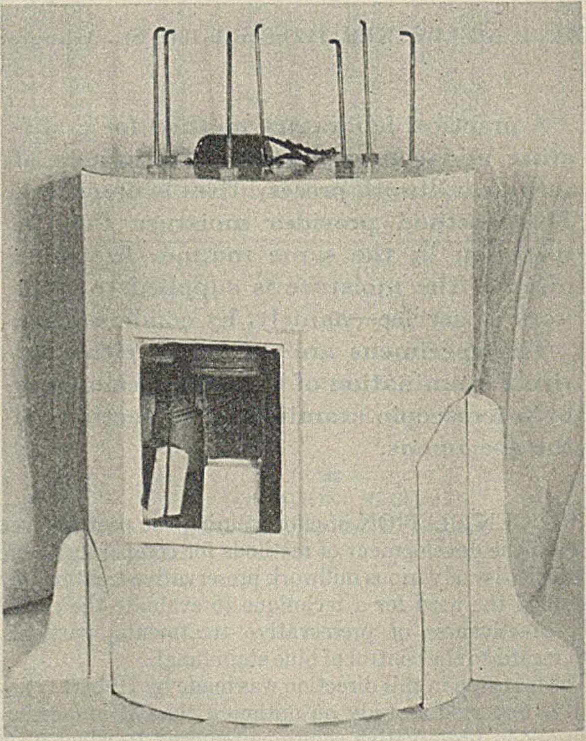

FIGURE 2. ULTRAVIOLET RADIATION STERILIZATION CHAMBER

While the specimens were suspended on the wire, the jar lids and specimens were suspended on the hooks at the lower ends of the rods, seen projecting through the top of the sterilization chamber. During the process of radiation the specimens were raised out of the jars and the rods were turned so each face of each block was exposed to the rays for 20 minutes.

The fruit jars, previously sterilized in an autoclave for 15 minutes at 15 pounds' pressure, with lids loose, were also in the sterilizing chamber during sterilization of the specimens, and at the end of the sterilizing period the specimens were lowered into the jars by means of the rods, which eliminated contamination of the specimens which might have occurred had the chamber been opened and the specimens lowered into the jars by hand.

Inoculation of Test Specimens

Throughout the entire series, *Hormiscium gelatinosum* (F. P. L. 595) was used as the test organism.

Spore suspensions of *Hormiscium gelatinosum* were prepared by shaking small volumes of inoculum in sterile water in a small sterile DeVilbiss throat atomizer. This suspension was then sprayed directly on the surfaces to be inoculated. All specimens were inoculated, on both ends only, in a transfer chamber which was equipped with the germicidal lamp described above. This lamp was not left on during inoculation but was lighted for several minutes before inoculation in order thoroughly to sterilize the air in the chamber.

Incubation and Condensation Cycles

The completely assembled jars were placed in their trays, run immediately through the first condensation cycle, then placed in the incubator overnight. These cycles were performed daily throughout the entire period of the test, except Sundays and holidays.

It was found convenient to place the trays in the refrigerator the first thing each morning, for a period of 2 hours. This was found to be sufficient to give the degree of chilling necessary for a heavy deposit of condensation. Upon removal from the refrigerator, the trays were set in the water pan, where heat was immediately applied. The temperature of the water was raised uniformly, and as rapidly as possible, until actual water drops could be seen standing on the specimens. The tray was then placed in the incubator until the following morning. All specimens were incubated at 79° F.

The condensation cycles were repeated daily until the blue stain had started to grow vigorously and then the cycle was repeated often enough to maintain a standing film of water on the specimens. It was found that a repetition of the cycle every other day provided enough moisture for rapid growth of the fungi after it had started to grow. After 12 weeks of incubation a heavy growth of blue stain was very evident on the untreated controls, so the test was terminated and the specimens were examined.

In this test there was no evidence of any common mold growth, which is common with other means of sterilization, thus testifying to the efficiency of the sterilizing lamp.

Expression of Results

As with all other methods of evaluating resistance to blue staining organisms, the results are expressed qualitatively rather than quantitatively. In this work, however, it was possible to express three classifications of resistance: low, medium, and high. This was possible because the examination was made microscopically, and the criterion was the concentration of mycelia in the cell structure near the paint film relative to the untreated controls. There was so marked a difference between those showing the highest degree of control

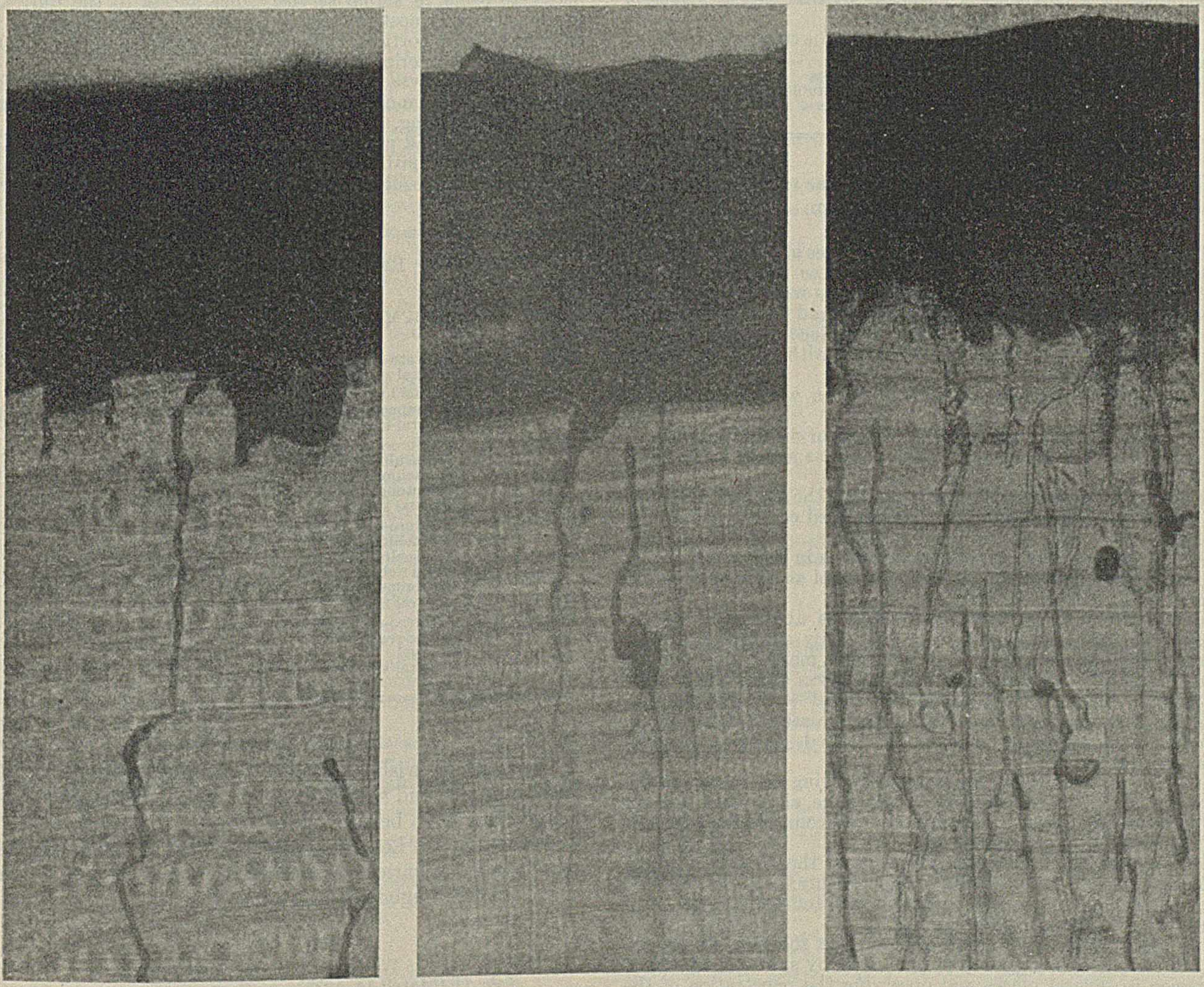

Figure 3. Efficiency of Treating Solution

× 120 photomicrograph of paint film and treated wood section
Left. High efficiency, two blue stain hyphae
Center. Medium efficiency
Right. Low efficiency, indicated by abundance of blue stain hyphae

Table I. Composition of Exterior Paints

Composition of Pigment		% by weight	Composition of Vehicle	% by weight
First and Second Coats—Pigment 64%, Vehicle 36%				
Lead-zinc pigment		30	Linseed oil	64
White lead sulfate	10		Japan drier	15
Zinc oxide	20		Mineral spirits	6
White lead carbonate		36	Turpentine	15
Titanium-magnesium pigment		34		100
		100		
Third Coat—Pigment 65%, Vehicle 35%				
Zinc-lead pigment		45	Linseed oil	89
Basic sulfate white lead	16		Japan drier	11
Zinc oxide	29			
White lead carbonate		18		100
Titanium-magnesium pigment		32		
Titanium dioxide		5		
		100		

Table II. Composition of Interior Paints

Composition of Pigment	% by weight	Composition of Vehicle		% by weight
First Coat—Pigment 65%, Vehicle 35%				
Lithopone	82.0	Linseed oil		10
Zinc oxide	9.0	Varnish		50
Calcium carbonate	4.5	Vegetable oils	22	
Magnesium silicate	4.5	Resins	41	
		Mineral spirits	37	
	100.0	Mineral spirits		40
				100
Second Coat—50% by Volume of First Coat Material, 50% by Volume of Third Coat Material				
Third Coat—Pigment 40%, Vehicle 60%				
Titanium dioxide	33	Varnish		100
Lithopone	67	Resins	20	
		Vegetable oils	31	
	100	Mineral spirits	49	

and the untreated specimens that there was no question about the certainty of the intermediate or medium state.

Each specimen was split radially into pieces about 0.25 to 0.375 inch thick by means of a chisel. Each piece was examined for uniformity of staining. Several small cubes were cut from each specimen selected, so that the paint film would be included. The cubes were placed in boiling water to displace air, and sections were cut with a microtome and examined with a 16-mm. objective × 12 eyepiece.

The degree of staining of each specimen was designated as follows:

+. Very difficult to find any mycelium in the treated layer of wood immediately beneath the paint film, as shown in Figure 3 (left).

++. Moderate growth of mycelium in the treated wood but not nearly so badly infested as the untreated controls (Figure 3, center).

+++. Very heavy growth of mycelium in the treated wood, evidencing no appreciable amount of control as compared to untreated wood (Figure 3, right).

Each individual specimen was rated as above, and all six blocks (for each solution) were evaluated by averaging all plus marks, assigning a value of 1 for each plus mark. The average value for all plus marks for each solution was then calculated—for instance, all six control blocks were rated +++, which gave an average rating of 3.0 and all six blocks treated with 2-chloro-*o* phenylphenol plus water-repellent were rated +, which gave an average rating of 1.0.

It was decided to classify all solutions having an average rating between 2.0 and 3.0 as being low in resistance, all between 1.0 and 2.0 as being medium in resistance, and all from 0 to (and including) 1.0 as being high in resistance.

Since no treatment absolutely prevented the growth of an occasional hypha, no solution had a higher rating than 1.0. On this basis of rating, it was easy to classify each individual method of treatment in one of the three groups.

It is also possible to evaluate the different solutions for the extent of control of the growth of blue stain by splitting the entire specimen in several pieces and observing the penetration of the mycelia into the treated wood. By comparing specimens in this manner, they can be classified into the same general groups as mentioned above.

Results

The treatments tested and the results of the microscopic examination are shown in Table III. These results are based on examination of "wood-inoculated" specimens only. None of the "paint-inoculated" specimens showed enough fungus growth to be evaluated on this basis.

The test proves that combinations of toxics seem to be more effective in preventing the growth of blue stain than either pentachlorophenol or 2-chloro-*o*-phenylphenol used alone.

Probably the most interesting result is that the addition of a water-repellent raises the resistance of a 2-chloro-*o*-phenylphenol solution from low to high. This indicates that the addition of a water-repellent actually increases the value of a toxic solution in preventing the growth of blue stain.

While the method described in this paper may be simplified and made more quantitative, it is believed that it offers a distinct step towards the attainment always worked for in the laboratory: close correlation with actual service experience.

The following features suggest the usefulness of the method:

1. The test specimens are taken from actual window bottom rails.
2. The treatments are applied in the normal way, just as they are used in commercial operations.
3. Treatments, not just treating solutions, are evaluated.
4. The organism most difficult to control by preservative treatment was used for the evaluation.
5. All culture media were eliminated. Infection was produced directly on untreated wood, which appears to be the most likely to occur in actual service, since access to the untreated sapwood core is most frequently gained through checking of the treated exterior portion of the wood and occasionally by damage of the treated exterior portion.
6. Moisture was provided by condensation, which is the manner in which most moisture reaches products in actual service inside a building.
7. This method not only compares one treatment against another, but it furnishes information which aids in determining which treatment will be more completely effective in actual service.

Table III. Results of Microscopic Examination

Degree of Control	Formula of Solution Tested	% by weight	Average Microscopic Rating
Low	2-Chloro-*o*-phenylphenol	5.0	2.67
	Mineral spirits	95.0	
Medium	Pentachlorophenol	5.0	1.5
	Diacetone alcohol	5.0	
	Mineral spirits	90.0	
Medium	2-Chloro-*o*-phenylphenol	2.0	1.5
	Pentachlorophenol	1.5	
	Tetrachlorophenol	1.5	
	Diacetone alcohol	5.0	
	Mineral spirits	90.0	
High	2-Chloro-*o*-phenylphenol	1.5	1.0
	Pentachlorophenol	2.0	
	Tetrachlorophenol	1.0	
	sym-Trichlorophenol	0.5	
	Diacetone alcohol	5.0	
	Mineral spirits	90.0	
High	2-Chloro-*o*-phenylphenol	5.15	1.0
	Water repellent	13.75	
	Pine oil	2.00	
	Mineral spirits	79.10	

Acknowledgment

The authors wish to thank C. Audrey Richards for her helpful advice and suggestions, and Theo. C. Scheffer, whose suggestions have been of much value. The authors are indebted to R. W. Lehman and E. A. Patton for assistance in developing the various features of this method and for helping carry it through to completion.

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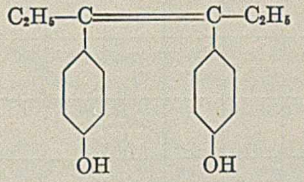
Presented before the N. D. M. A. Preservative Standards Advisory Committee meeting at the Forest Products Laboratory, Madison, Wis.

Colorimetric Determination of Diethylstilbestrol

MANUEL TUBIS, 4860 North 8th St., Philadelphia, Penna.
AND
ALBERT BLOOM, Samet Laboratories, Philadelphia, Penna.

THE universal interest in diethylstilbestrol as a substitute for the naturally occurring estrogens has resulted in the proposal of several methods for its quantitative estimation. Most of the methods (*3*, *4*, *5*, *8*) are not applicable in the presence of the usual tablet compositions. Dechene (*2*) recently applied the "xanthoproteic" reaction to the compound and used this as a basis for a colorimetric method. According to this author, this reaction is not applicable in the presence of any other "phenyl compounds".

In undertaking this investigation, the writers sought a reaction which was specific for one of the functional groups present. As seen from the structural formula, diethylstilbestrol contains two phenolic hydroxyl groups:



Since colorimetric methods for the determination of phenols are well established, the writers applied several of these reactions to the compound and found that the reaction of Folin and Ciocalteu (*6*, *7*) gave the best results. In this reaction the labile complex phosphomolybdic phosphotungstic acids are reduced by the phenolic hydroxyls to give a blue solution of tungstic oxides. It was found that the color produced was stable and readily adaptable to colorimetric or photometric determination and gave a linear relationship over the range of concentrations required. The presence of alcohol, sugars, talc, and fatty acids and their salts did not interfere. Water-soluble colors were eliminated by the technique described below. Figure 1 shows the straight-line graph obtained by plotting the concentrations against the photometer readings. Table I gives data on the extraction of diethylstilbestrol from an artificial mixture. The method was applied to the analysis of commercial tablets and the results are given in Table II.

Experimental

EQUIPMENT. A neutral wedge photometer with a B. & L. Smoke C. glass wedge and filter No. 65 (*1*) was used with a 2.5-cm. (1-inch) cell. A Hellige Duboscq colorimeter was also used.

COLOR REACTION. Diethylstilbestrol (0.2 to 0.8 mg.) in 10 ml. of 30 per cent alcohol contained in a 100-ml. volumetric flask is diluted with 50 ml. of distilled water and 5 ml. of reagent (*7*) are added. After mixing, 15 ml. of 20 per cent sodium carbonate (anhydrous) solution are added and the solution is diluted to the mark with distilled water, mixed, and allowed to stand at room temperature for 1 hour, at which time the color is fully developed. The concentrations are plotted against photometer readings to give a graph, Figure 1, from which the concentration of an unknown solution may be read.

ANALYSIS OF COMPRESSED COLORLESS TABLETS. A number of tablets equivalent to 10 mg. of diethylstilbestrol are weighed and ground. An accurately weighed sample equivalent to approximately 5 mg. of diethylstilbestrol is transferred to a 100-ml. volumetric flask, 30 ml. of alcohol are added, and refluxed on a water bath for 15 minutes. The solution is then cooled and made to volume with distilled water, mixed, and filtered. A 10-ml. aliquot is treated as described above and, at the same time, a standard containing 0.5 mg. of diethylstilbestrol per 10 ml. in 30 per cent alcohol is treated similarly. After 1 hour the colors are compared in a colorimeter. This unknown solution may also be examined photometrically and the concentration derived from the graph.

COLORED TABLETS. The weighed powdered sample, prepared as above, is transferred to a 100-ml. separatory funnel containing 50 ml. of water and extracted with one 20-ml. and three 10-ml. portions of ether. The ether extracts are combined and evaporated. The residue is dissolved in 30 ml. of alcohol, transferred to a 100-ml. volumetric flask, made to the mark with distilled water, and filtered. A 10-ml. aliquot is used for the analysis.

TABLE I. EXTRACTION OF DIETHYLSTILBESTROL FROM A TABLET MIXTURE

Sample[a]	Ether Used	Diethylstilbestrol Present	Diethylstilbestrol Recovered
	Ml.	*Mg.*	*Mg.*
1	20	5	3.4
2	20, 10	5	4.6
3	20, 10, 10	5	4.8
4	20, 10, 10, 10	5	4.6

[a] 1 gram of mixture of starch, lactose, and stearic acid containing diethylstilbestrol.

TABLE II. ANALYSIS OF COMMERCIAL TABLETS OF DIETHYLSTILBESTROL

Tablet	Quantity Recovered Colorimeter[a]	Quantity Recovered Photometer[b]	Quantity Recovered Av.	Labeled Quantity	Difference Found
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
A	0.48	0.49	0.49	0.5	−0.01
B	0.53	0.56	0.55	0.5	0.05
	1.08	1.16	1.12	1.0	0.12
C	0.98	0.99	0.99	1.0	−0.01
D	0.51	0.57	0.54	0.5	0.04

[a] Standard set at 20, average of 5 readings.
[b] Average of 5 readings.

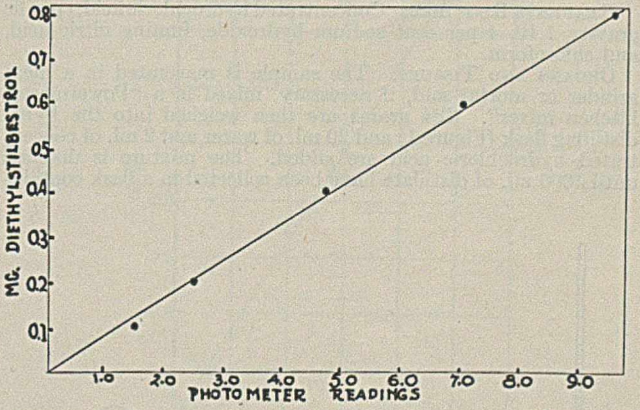


FIGURE 1. TYPICAL GRAPH RELATING WEIGHT OF DIETHYLSTILBESTROL TO PHOTOMETER READINGS

Acknowledgment

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Spectrophotometric Estimation of Pentachlorophenol in Tissues and Water

WILHELM DEICHMANN AND LAWRENCE J. SCHAFER
Kettering Laboratory of Applied Physiology, University of Cincinnati, Cincinnati, Ohio

PENTACHLOROPHENOL is used in industry as an agent for the preservation of wood and wood products. Attention was first called to its toxicity in studies on mice by Bechhold and Ehrlich, in 1906 (*1*). Extensive toxicity studies were carried out by Kehoe, Deichmann, and Kitzmiller in 1939 (*3*), and by Boyd, McGavack, Terranova, and Piccione in 1940 (*2*) and 1941 (*4*).

Extension of the investigation necessitated the development of an analytical method. The procedure reported here utilizes the formation and the spectrophotometric determination of a reddish-yellow pigment formed by the action of fuming nitric acid on pentachlorophenol. The method was found dependable, and of sufficient accuracy to enable the authors to follow this compound through the body and to detect amounts below the harmful levels. Further toxicological studies of this compound will be reported elsewhere.

Method

The following method is suggested for the determination of from 0 to 9 mg. of pentachlorophenol in 10 grams of biological material (except pure fat) and of from 0 to 50 mg. of pentachlorophenol in about 5 ml. of water.

REAGENTS REQUIRED. Concentrated hydrochloric acid, specific gravity 1.19, 4 per cent sodium hydroxide, fuming nitric acid, and chloroform.

ORGANS AND TISSUES. The sample is macerated in a meat grinder or mortar and, if necessary, mixed in a "Powermaster kitchen mixer". Ten grams are then weighed into the Pyrex distilling flask (Figure 1) and 20 ml. of water and 2 ml. of concentrated hydrochloric acid are added. The mixture is distilled until 1000 ml. of distillate have been collected in a flask containing 10 ml. of 4 per cent sodium hydroxide. The distillate is heated over a flame to about 75° C., and then half of this volume is measured into a 1-liter beaker, slowly concentrated on a hot plate to 50 ml., then transferred to a 250-ml. Erlenmeyer and evaporated to about 2 ml. [The other 500 ml. are set aside as a reserve to supply a suitable aliquot, in case the results of the first determination fall beyond the curve (Figure 2).]

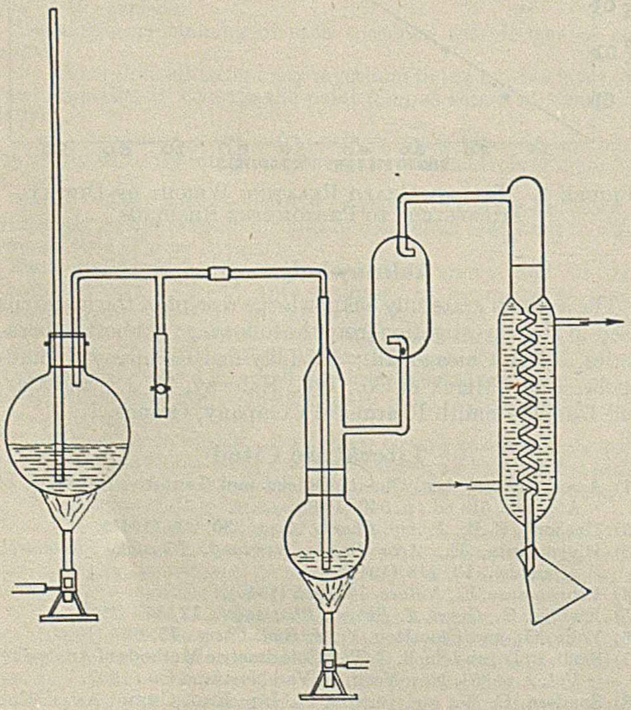

FIGURE 1. DISTILLING APPARATUS

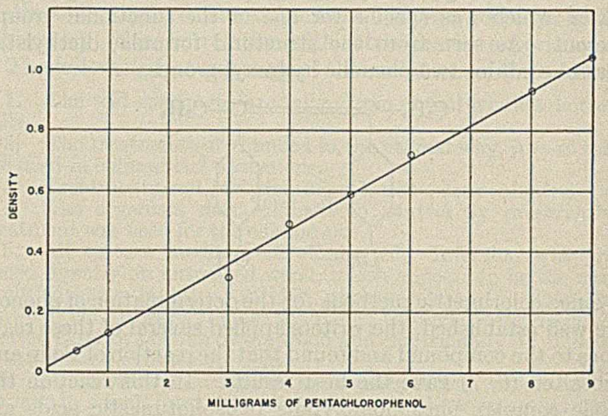

FIGURE 2. RELATIONSHIP BETWEEN DENSITY AND CONCENTRATION, EMPLOYING 10-MM. CELLS

Four milliliters of fuming nitric acid are then slowly added and the precipitate clinging to the bottom of the Erlenmeyer is freed completely with a stirring rod, which is then rinsed with 1 ml. of fuming nitric acid. The solution is placed in ice for 20 minutes and is then washed with about 100 ml. of water into a 250-ml. separatory funnel. The reddish-yellow pigment is extracted with three 8-ml. portions of chloroform, permitting 5 minutes for each separation. The combined chloroform extracts are washed with a single 100-ml. sample of water (to remove water-soluble nitrates) permitting 10 minutes for the separation, then filtered through 2 layers of Whatman No. 1, 9-cm. filter paper wetted with chloroform into a 25-ml. glass-stoppered cylinder. After diluting with chloroform to 25 ml., the concentration is determined by means of standard curves (Figures 2 and 3) using 10-mm. or 4-inch matched Aminco cells and the spectrophotometer at 460 mμ.

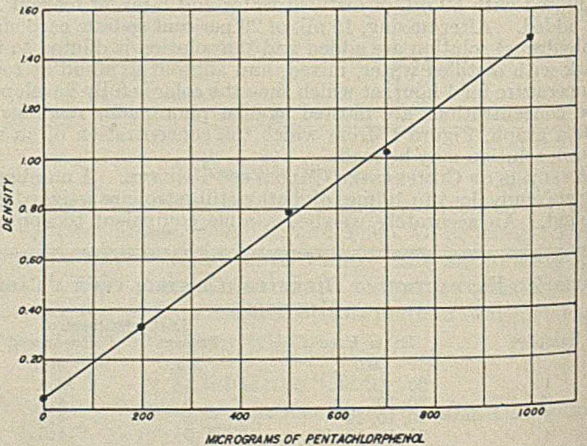

FIGURE 3. RELATIONSHIP BETWEEN DENSITY AND CONCENTRATION EMPLOYING 4-INCH CELLS

Table I. Analyses of Control Blood, Urine, Organs, and Tissues Assumed to Be Free of Pentachlorophenol

Sample	Pentachlorophenol Found *Mg.*	Sample	Pentachlorophenol Found *Mg.*
Rabbit blood, 10 ml.	0	Ground rat, 10 grams	0
	0		0
	0		0.03
	0.02	Beef brain, 10 grams	0
	0		0
	0	Rabbit muscle, 10 grams	0
75 ml.	0	Rabbit liver, 10 grams	0
	0	Rabbit heart, 10 grams	0
100 ml.	0.01	Rabbit kidneys, 10 grams	0.03
	0.01	Human urine, 100 ml.	0.01
Rabbit urine, 10 ml.	0		0.01
	0		0.02
	0		0
	0.01		0
	0		

Figure 4 gives the transmission curve of the pigment formed under these conditions; Figures 2 and 3 give the relationship between density and concentration of pentachlorophenol.

Blood and Urine. Whole blood or urine (10-ml. samples) is distilled directly, after treatment with 20 ml. of water and 2 ml. of hydrochloric acid, but only 300 ml. of distillate are collected in an Erlenmeyer containing 3 ml. of 4 per cent sodium hydroxide. This is evaporated on a hot plate to 20 ml., transferred to a 250-ml. Erlenmeyer, and evaporated to 2 ml. The analysis is then continued as under "Organs and Tissues". In the case of blood, paraffin is added to reduce foaming.

Table II. Recovery of Pentachlorophenol

(Added to 10-ml. samples of blood and urine and to 10-gram samples of organs and tissues)

Added *Mg.*	Recovered *Mg.*	Added *Mg.*	Recovered *Mg.*
Rabbit Blood			
0.03	0.03	0.14	0.12
0.03	0.04	0.14	0.12
0.03	0.025	0.145	0.125
0.06	0.055	2.45	2.50
0.06	0.075	4.54	4.40
0.06	0.055	4.54	4.31
0.11	0.095	6.8	7.0
0.11	0.093	6.8	7.4
0.11	0.10	6.8	6.7
Rabbit Urine (25-ml. samples)		Human Urine	
0.08	0.09	4.54	4.54
0.09	0.09	4.54	4.90
0.09	0.10	5.5	5.0
0.10	0.08	5.5	5.1
0.18	0.19	6.0	6.0
0.18	0.19	6.8	5.4
		6.8	6.9
Ground Rat		9.95	9.6
0.24	0.22	Rabbit Muscle	
0.24	0.21	2.5	2.4
0.24	0.22	5.0	4.9
0.24	0.23	Rabbit Liver	
0.43	0.44		
0.43	0.43	5.0	4.4
1.5	1.4	8.0	8.0
1.5	1.4	8.0	7.6
2.5	2.5	Rabbit Heart	
2.5	2.3		
4.8	4.5	2.5	2.55
Rabbit Lung		4.5	4.0
2.5	2.3	Rabbit Kidneys	
4.8	5.3	2.5	2.4
4.8	5.1	4.5	4.6
Rabbit Fat		Beef Brain	
4.0	2.1	1.5	1.4
4.0	1.9	2.5	2.42
8.0	4.0	2.5	2.38
8.0	3.6	5.0	4.5
		5.0	4.4

Table I gives the values obtained by analyzing samples of normal blood and tissues for pentachlorophenol. Table II indicates the recoveries of pentachlorophenol added to blood, urine, and tissues, respectively.

Water. The steam-distillation is omitted in the absence of other material reacting with nitric acid. A 2–5 ml. sample is pipetted into a 50-ml. Pyrex test tube, and from 3 to 15 ml. of fuming nitric acid are added (depending on the amount of pentachlorophenol in the sample); the whole is then allowed to stand in an ice bath for 20 minutes. From this point the analysis is continued as described above, 10-mm. cells being employed for the spectrophotometric analysis.

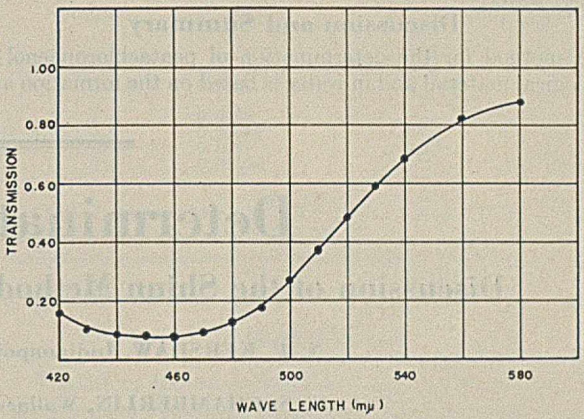

Figure 4. Transmission Curve for Pigment Formed

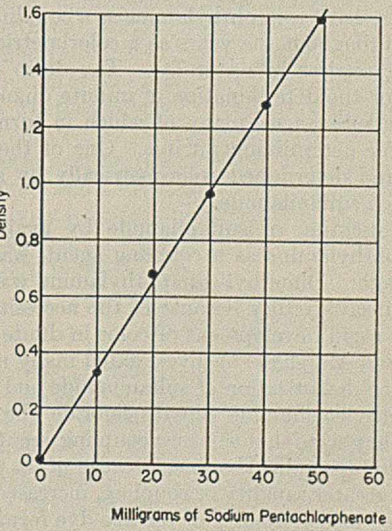

Figure 5. Relationship between Density and Concentration

10-mm. cells employed. Concentration of sodium pentachlorophenate in sample of water is read directly from this graph.

Figure 5 gives the relationship between density and the quantity of pentachlorophenol (in milligrams) present in the original sample. The final estimation can be carried out with a colorimeter by using standard solutions. When 28 mg. of pentachlorophenol as the sodium salt were added to 2-ml. samples of water, the following quantities were recovered: 27.2, 27.4, 28.0, 27.7, 28.0, 28.6, 26.9, 27.7, 28.6, 28.6, and 29.1 mg.

Precautions. It is advisable to read the solutions in the spectrophotometer within 10 minutes; the color is stable, but droplets of water may settle out if the solutions are allowed to stand for longer periods.

Figures 2, 3, and 5 were obtained with the author's photoelectric spectrophotometer and with their equipment; therefore, if accuracy is desired, it is not advisable to use them with other spectrophotometers and cells. It is suggested that other investigators prepare their own figures. The cells, even though they are matched, should not be interchanged and should always be placed in the same position.

It is imperative that any precipitate which may form be loosened completely from the bottom of the Erlenmeyer after the 4 ml. of nitric acid have been added.

Errors will not be introduced if samples go to dryness on the hot plate; the precipitate is brought in solution with about 2 ml. of water.

Discussion and Summary

A method for the determination of pentachlorophenol in biological material and in water is based on the formation and spectrophotometric determination of a reddish-yellow pigment formed by the action of fuming nitric acid on pentachlorophenol.

Substances other than pentachlorophenol may react with nitric acid to form colors which may occasionally give false positive results. In no instance, however, did these errors exceed 0.03 mg. per sample (Table I).

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Determination of Nitrites

Discussion of the Shinn Method As Applied to Examination of Water

N. F. KERSHAW, Indianapolis Water Company, Indianapolis Ind.
AND
N. S. CHAMBERLIN, Wallace & Tiernan Co., Inc., Montclair, N. J.

THE diazotization of sulfanilic acid by the available nitrite in water, using α-naphthylamine as a coupling agent, has continued throughout the years as a colorimetric method for determining nitrites in water (*1*). The diazo reaction has been used for the determination of minute quantities of certain organic substances, many of which in turn could have been used for determining nitrites. One of the compounds diazotized and determined colorimetrically by available nitrite has been sulfanilamide.

The diazotization of sulfanilamide by available nitrite, using α-naphthylamine as a coupling agent, was eliminated some time ago. Dimethyl-α-naphthylamine was next used, but found unsatisfactory because of the necessity of using a catalyst for rapid development of color in dilute solutions.

Bratton and Marshall (*3*) investigated many new coupling agents for the diazotization of sulfanilamide and found *N*-(1-naphthyl)-ethylenediamine dihydrochloride the most satisfactory. They state that this new coupling agent is far better than dimethyl-α-naphthylamine, because of its producibility and purity, greater rapidity of coupling, increased sensitivity, and increased acid solubility of the azo dye formed.

Shinn (*5*) was the first to make use of sulfanilamide and the coupling agent, *N*-(1-naphthyl)-ethylenediamine dihydrochloride, as a means of determining nitrites; in fact, her article was brought to the authors' attention because she had found these reagents far superior to sulfanilic acid and α-naphthylamine. Shinn points out that sulfanilamide is more stable than sulfanilic acid, both in the dry state and in solution; furthermore, it reacts more rapidly in the coupling process. It has been recognized that the coupling of diazotized sulfanilic acid with α-naphthylamine is relatively slow (*2*) and that the color developed must be read within 30 minutes (*1*) because it is so unstable. The authors' experience has shown that, with the standard procedure (*1*), full color development is not reached until 30 minutes' standing with subsequent fading after 30 minutes.

Because of the qualification of the new coupling agent, the use of sulfanilamide, and the resulting improved diazo reaction, it appeared that the use of these two compounds for determining nitrites in water would be worthy of consideration. The Shinn method (*5*) for nitrites was investigated in order to determine its applicability to water because of the need for a more satisfactory method than the standard procedure (*1*).

The Shinn method, as published, prescribes an unknown of no greater volume than 35 ml. which, after the addition of reagents, is diluted to 50 ml. This procedure would be awkward and contrary to best waterworks analytical procedure. Good analytical technique would necessitate the use of 50-ml. or 100-ml. water samples of unknown nitrite content since comparatively few waterworks laboratories have photoelectric colorimeters, but will continue to use for some time to come the Nessler tubes to which they are accustomed. The method emphasizes the increase in sensitivity with decreasing final volumes of the unknown nitrite solution.

As published, the article points out that samples of unknown nitrite content, containing less than 0.0025 mg. of nitrite (NO_2) or 0.000761 mg. of nitrite nitrogen (N) per 50 ml., or 0.050 p. p. m. of nitrite or 0.015 p. p. m. of nitrite nitrogen, gave colors too faint to be read with any reasonable degree of accuracy with a photoelectric colorimeter. If this were the case it would be impossible to apply the method to waterworks practice, since a large portion of the water supplies contain less than 0.015 p. p. m. of nitrite nitrogen. Any method to be given serious consideration must be sensitive to 0.001 p. p. m. of nitrite nitrogen.

Although Shinn recommended that the unknown be limited to 35-ml. volume, it was found by preliminary investigation that like amounts of nitrite nitrogen, treated before dilution, developed less color than when they were diluted to a final volume of 50 ml. before addition of the reagents. The sensitivity of the reagents increased with increasing dilution, and maximum color was not developed until the volume before the addition of the reagents became 40 ml. or more. This fact overcame the first objection to the method.

This led to an intensive study to determine how equivalent amounts of nitrite nitrogen, developed in dilute or concentrated volumes, would give equivalent readings for all amounts of nitrite nitrogen, including those between 0.015 and 0.001 p. p. m. Such a finding would eliminate once and for all the effect of water dilution even in those cases where small amounts of nitrite nitrogen were to be found.

One of the very early developments of the investigation disclosed the necessity of thorough mixing after the addition of each chemical to obtain reliable and consistent results. The ammonium sulfamate was next eliminated, since it had no practical value other than destruction of the excess nitrite in the diazotization reaction, an excess which does not exist in the detection of nitrites in water.

The problem of obtaining equivalent color intensity for equivalent amounts of nitrite nitrogen, by adding reagents to the nitrite in the more concentrated condition as prescribed by Shinn, or in the more dilute condition for use with water, appeared to have a bearing on the pH of the unknown nitrite volume. The acid concentrations, pH, and time for color development were investigated. It was found that equivalent color intensities for equivalent amounts of nitrite nitrogen could be developed by using 2 ml. of 1 to 1 hydrochloric acid in the reaction instead of the prescribed 1 ml.

Because of the fairly large total volume of reagents required some consolidation of the reagents and their volumes was deemed advisable. This was accomplished by using 2 ml. of a 0.5 per cent sulfanilamide solution in 1 to 1 hydrochloric acid, instead of 5 ml. of a 0.2 per cent water solution of sulfanilamide and 1 ml. of 1 to 1 hydrochloric acid. The acid solution had the additional advantage of aiding in the dispersion of the sulfanilamide. When stored in a refrigerator, there is little danger that the sulfanilamide will crystallize out.

By using this modified reagent, the time required for full development of color was found to be 15 minutes, and the color intensity was not only equivalent as developed in both dilute and concentrated volumes for like quantities of nitrite nitrogen, but was of sufficient magnitude in the range of even 0.015 to 0.001 p. p. m. of nitrite nitrogen to give differentiations which were as easily detected as those in the standard method (*1*). An advantage of the Shinn method over the standard method is that the maximum color developed in 15 minutes is more rapid and more stable.

In the Shinn method the nitrite value of the sulfanilamide standard is determined from a nitrite standard in which assayed sodium nitrite is used instead of silver nitrite.

Throughout all the investigational work on the use of the two new reagents, sulfanilamide and *N*-(1-naphthyl)-ethylenediamine dihydrochloride, comparisons were made with Nessler tubes containing nitrite standards prepared from assayed sodium nitrite rather than a sulfanilamide standard which is used in a photoelectric colorimeter and whose nitrite value is determined from a nitrite standard prepared from assayed sodium nitrite. Waterworks people are familiar with the old nitrite standard and from a waterworks practice standpoint it would be out of place to discontinue its use at this time.

The simplicity of the preparation of the nitrite standard from the desiccated reagent grade of sodium nitrite should not be overlooked. This has been thoroughly investigated in the laboratory of the Indianapolis Water Company, and found to be reliable and accurate, eliminating the long and laborious procedure using silver nitrite (*4*).

Table I shows the comparison with the present standard method and gives the quantities required by the Shinn method to obtain good color differentiation. Readings as high as 0.0002 mg. of nitrite nitrogen in 50-ml. Nessler tubes can easily be differentiated in increments of 0.00004 mg. of nitrite nitrogen in 50 ml. and readings as high as 0.0005 mg. of nitrite nitrogen in 50 ml. can easily be differentiated in increments of 0.00005 mg. of nitrite-nitrogen in 50 ml. It is suggested that sodium nitrite solutions of two concentrations be used in making up the standards.

Table I. Preparation of Standard Nitrite Solutions

(Quantities for 50-ml. Nessler tubes)

A. P. H. A. Standard Method Nitrite[a] Solution of 1 Ml. = 0.0005 Mg. of NO_2-N		Nitrite Solution of Shinn Method, 1 to 1000, 0.01 per cent 1 Ml. = Approximately 0.00002 Mg. of NO_2-N	
Standard nitrite soln. *Ml.*	NO_2-N *Mg.*	Standard nitrite soln. *Ml.*	NO_2-N *Mg.*
0.1	0.00005	2.0	0.00004
		4.0	0.00008
0.2	0.00010	6.0	0.00012
		8.0	0.00016
0.4	0.00020	10.0	0.00020
		1 to 1000, 0.1 per cent 1 Ml. = Approximately 0.0002 Mg. of NO_2-N	
0.7	0.00035	1.25	0.00025
		1.5	0.00030
		1.75	0.00035
		2.0	0.0004
1.0	0.0005	2.5	0.0005
1.4	0.0007	3.0	0.0006
1.7	0.00085	3.5	0.0007
2.0	0.001	4.0	0.0008
2.5	0.00125	4.5	0.0009
		5.0	0.0010

[a] Listed as prescribed in (*1*), although closer increments are probably possible.

Modifications

The 50- or 100-ml. unknowns are compared with a series of standards in matched Nessler tubes instead of against a single standard in a photoelectric or Duboscq colorimeter.

Nitrite standards are prepared from assayed sodium nitrite instead of a sulfanilamide standard whose value has been determined from assayed sodium nitrite.

Ammonium sulfamate is eliminated as reagent.

The solution is thoroughly mixed after the addition of each chemical, whether unknown or standard.

Two milliliters of 0.5 per cent sulfanilamide in 1 to 1 hydrochloric acid are used, instead of 5 ml. of 0.2 per cent sulfanilamide and 1 ml of 1 to 1 hydrochloric acid to increase the sensitivity from 0.015 to 0.001 p. p. m. of nitrite nitrogen, thereby making the sensitivity range comparable to the present standard method range.

Conclusions

The method as published is not applicable to waterworks practice, because of lack of sensitivity in the range from 0.015 to 0.001 p. p. m. of nitrite nitrogen. The present limitation of the water sample to 35 ml. or less is awkward and contrary to waterworks practice. The method can be made applicable by certain modifications.

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Correction. In the article on "Assay of Benzaldehyde" [Ind. Eng. Chem., Anal. Ed., 14, 154 (1942)] the reference cited in the 35th line, second column, following the words "bromophenol blue", should be (*6*).

Janet G. Dinkelspiel

Determination of Small Amounts of Iodide in Photographic Developers

R. M. EVANS, W. T. HANSON, JR., AND P. K. GLASOE
Kodak Research Laboratories, Rochester, N. Y.

The method for the determination of iodide in photographic developers which is described involves the precipitation of halides with silver nitrate, followed by the oxidation of the iodide to iodate while it is in the form of silver iodide. The concentration of iodate is then determined polarographically.

This method can be used for the determination of concentration of iodide as small as 1 mg. per liter of potassium iodide. Amounts around 5 mg. per liter can be determined with an accuracy of about 4 per cent.

A STUDY of analytical methods for photographic developers, which has been under way in these laboratories for some time, has given rise to a new method of analysis for iodide in concentrations as small as $6 \times 10^{-6}M$ in the presence of a thousand times the amount of bromide and large amounts of reducing agents. This method involves the chlorine oxidation of the iodide in the form of silver iodide, followed by the polarographic determination of the iodate formed.

Rylich (*2*) first reported the use of the polarograph for the determination of very small amounts of iodate and bromate. He found that concentrations of iodate as small as $1 \times 10^{-6}M$ could be readily determined polarographically. The potential at which iodate is reduced at the dropping mercury electrode depends on the supporting electrolyte and on the pH of the solution. Below pH 7, the potential varies with pH, but above pH 7, the potential changes only slightly with increasing pH, remaining at a value around 1.1 volts against the saturated calomel electrode. The polarographic analysis of iodate is particularly sensitive because of the six-electron change which occurs in its reduction. This results in six times the current and, therefore, six times the sensitivity of a reduction involving a one-electron change.

Method of Analysis

The complete analytical procedure finally developed was as follows:

Take a 100-cc. sample of the developer and add to it 10 cc. of 0.5 *N* potassium bromide and 60 cc. of concentrated sulfuric acid. Pass steam through the solution until the small bubbles which indicate gas evolution disappear. To the hot solution add 100 cc. of water and 25 cc. of 0.5 *N* silver nitrate and pass steam through the solution or boil it for a few seconds to aid in coagulation of the precipitate. Allow the precipitate to settle and pour off the supernatant liquid, leaving the precipitate in the flask. To the precipitate add 50 cc. of 1 to 1 nitric acid and 250 cc. of water, shake, and allow to settle. Pour off the supernatant liquid and repeat this process with two 250-cc. portions of water. To the precipitate, add 50 cc. of fresh chlorine water, heat until the bromine color disappears, filter, and wash the precipitate with two 5-cc. portions of water. Cool the filtrate under the tap. To the filtrate add 1.0 cc. of 5 per cent phenol and 5.0 cc. of 2.0 *N* potassium hydroxide, and dilute to 100 cc. with water. Bubble nitrogen through the solution and electrolyze on the polarograph.

The wave obtained can be measured by any of the standard methods (*1*). The method used to obtain the values given here is illustrated in Figure 1. The ΔI method could also be used. By this method the current readings at -1.0 and -1.4 volts are recorded and the current difference is plotted against potassium iodide concentration.

Experimental

Before the chlorine water is added to oxidize the iodide to iodate, other reducing agents must be removed. In the analysis of photographic developers, this meant that sulfite and developing agents had to be removed. Sulfite was easily removed by acidification, followed by passing steam through the solution, but in order to separate the iodide from the developing agents, it was necessary to precipitate the halide as the silver salt and wash the precipitate thoroughly.

Since some developers contain little or no bromide, it was found necessary to add some bromide in order to get a sufficiently large amount of precipitate to ensure coagulation of the small amount of iodide present. The silver bromide precipitate acts as a collector for the silver iodide.

The precipitate was washed by decantation in order to save time. In this process, it is inevitable that a few particles of precipitate are lost, but since the total amount of precipitate is relatively large, the loss is not detectable in the final result. When the precipitation is carried out as described, the supernatant solution after the first coagulation is turbid, but this solution was always discarded without any attempt to collect the material in suspension. The error was found to be negligible.

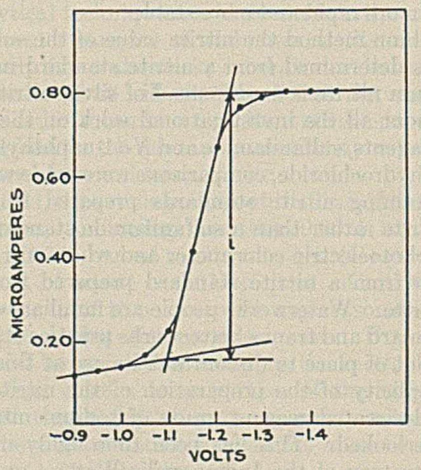

FIGURE 1. METHOD FOR MEASURING WAVE HEIGHT

The precipitate was first washed with nitric acid to aid in the removal of any reducing agent which might be adsorbed to the silver halide. When the nitric acid was omitted, a considerable amount of oxidized material showed up on the polarographic curves as a current at potentials below that of iodate.

In the early experiments on an iodide analysis, it was considered necessary to dissolve the silver halide precipitate before oxidation of the iodide. This caused a great deal of difficulty because the silver thus put into solution had to be re-

Table I. Oxidation of Iodide

Potassium Iodide Added *Mg./l.*	Potassium Iodate Calculated *Mg./l.*	Potassium Iodate Formed *Mg./l.*	Conversion of Iodide to Iodate %
	With Bromine Water		
5	4.3[a]	3.8	88.4
10	8.6	7.6	88.4
15	12.9	11.4	88.4
	With Chlorine Water		
5	4.3	4.3	100
10	8.6	8.5	99
15	12.9	12.9	100

[a] Final volume of solution 150 cc.

moved before a polarographic wave for iodate could be obtained. A very involved method was worked out but the analysis was not practical until it was found that the iodide could be oxidized just as well while it was still in the form of silver iodide.

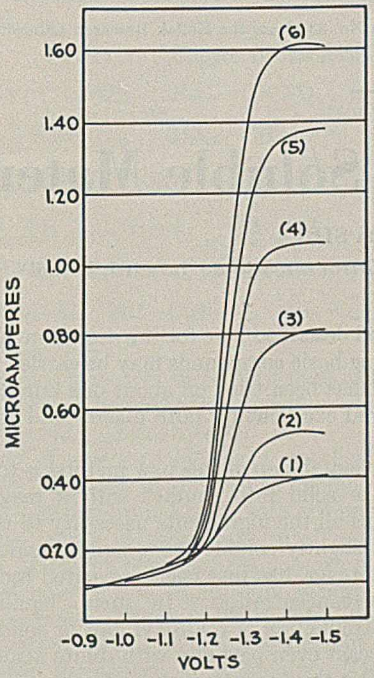

Figure 2. Iodate Waves in 0.1 N KOH at 25° C. for Various Concentrations of Iodide in a Photographic Developer

Concentrations of potassium iodide in mg. per liter: (1) 1.0, (2) 2.0, (3) 4.0, (4) 6.0, (5) 8.0, (6) 10.0. Capillary constants in 0.1 N KOH at $E = -1.40$ volts *vs.* saturated calomel electrode: $h = 63.0$ cm., $t = 3.18$, $m^{2/3}t^{1/6} = 1.45$ mg.$^{2/3}$ sec.$^{-1/2}$

In the first experiments on oxidation of iodide in silver iodide to iodate, bromine water was used as the oxidizing agent. Fairly reproducible results were obtained, but on comparing the polarographic wave heights in the analysis with the wave heights obtained with solutions of iodate in the same salt environment it was found that the amount of iodate obtained from a given amount of iodide was less than the stoichiometric value (Table I). It was presumed that this discrepancy was due to the occlusion of some of the iodide in the mass of silver bromide with which the bromine could not react. Chlorine water should eliminate this difficulty by oxidizing both bromide and iodide and thus penetrate the whole particle. The results obtained with chlorine water confirmed this assumption and Table I shows that the results are quantitative.

In order to ensure complete reaction, the mixture of precipitate and chlorine water is heated until the bromine color disappears. This serves the double purpose of completing the reaction and removing the excess bromine. The fine dispersion of silver chloride which remains is removed by filtration. The use of a kieselguhr filter (made by pouring a suspension of kieselguhr in water over the filter) aids in the clean separation of precipitate and filtrate.

Any excess of bromine or chlorine which may be left is then destroyed by the addition of phenol. The amount of phenol is unimportant as long as it is present in excess. The solution is made approximately 0.1 N with potassium hydroxide in order to have the iodate wave come at a potential of about 1.1 volts.

As in all polarographic work involving reduction, the oxygen in the solution must be removed by bubbling nitrogen through the solution for 5 to 10 minutes. The removal of oxygen is sufficiently complete when the current is small at a potential around −0.7 volt. Before the solution is electrolyzed the temperature should be checked. A 1° C. change in temperature will make about a 2 per cent change in the wave height. For practical purposes, the temperature should be regulated within 0.5° to 1.0° C.

The polarograph used in this work was a Fisher Elecdropode in which a saturated calomel electrode, connected to the electrolysis cell by means of an agar bridge saturated with potassium nitrate, was used rather than the mercury pool. The stream of nitrogen used to drive out the oxygen was passed through a bottle of water to minimize loss of the sample through evaporation.

A calibration curve was made by analyzing samples of developers containing known amounts of iodide. The wave heights were measured, and these values plotted against the concentration of potassium iodide in the developer. Figure 2 shows a set of curves obtained in a calibration and Figure 3 is the calibration curve. Table II gives the results obtained in some typical analyses. Concentrations of around 5 mg. per liter can be determined with an error of approximately 4 per

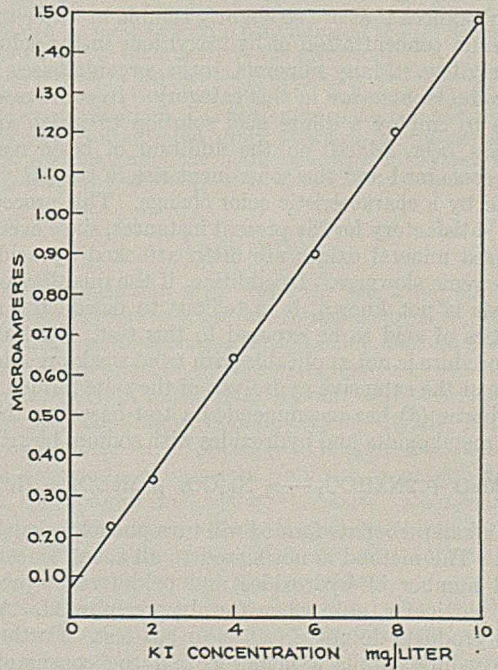

Figure 3. Calibration Curve from Waves in Figure 2

Table II. Oxidation of Iodide

Potassium Iodide Added *Mg./l.*	Potassium Iodide Found *Mg./l.*
2.5	2.6
5.0	5.0
7.5	7.5
10.0	9.9
5.0	4.9
5.0	4.9
5.0	4.8

cent. However, the percentage error increases with decreasing amount of potassium iodide and 1 mg. per liter can be determined with an accuracy of 10 to 12 per cent. Polarographic curves can be obtained with quantities as small as 0.2 mg. per liter. Determinations have been made on various types of developers and in each case the same calibration curve could be used, indicating that variations in the quantities of sulfite, carbonate, bromide, and developing agent were without effect on the test. However, an additional precaution was necessary if thiocyanate was present. Using the above procedure some silver thiocyanate precipitated with the halides, and when the chlorine was added the thiocyanate was oxidized instead of the iodide. The thiocyanate could be removed, however, by steaming the strongly acid solution, letting the hot solution stand for a few minutes, and then steaming the solution again.

Conclusion

Although the method of analysis outlined above has been used only on photographic developers, it should prove useful in any case where it is desired to analyze for iodide in the presence of a thousandfold quantity of bromide and/or such substances as interfere with ordinary iodometric determinations. The final determination of the iodate may be made by one of the usual titration methods if a polarograph is not available.

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Detecting Basicity in Slightly Soluble Materials

FRITZ FEIGL AND CORIOLAN P. J. DA SILVA
Ministerio da Agricultura, Laboratorio Central da Produção Mineral, Rio de Janeiro, Brazil[1]

IT IS often necessary or advantageous to have available a rapid and sure qualitative test for acid-consuming or basic compounds, such as hydroxides, oxides, carbonates, basic salts, or organic bases. When water-soluble compounds are being examined acid-base indicators can be used, and the presence of hydroxyl ions is quickly manifested by characteristic color changes and by the establishing of certain pH values.

The direct use of such indicators is out of the question with basic substances that are so slightly soluble in water that the equilibrium concentration of hydroxyl ions in the solution is extremely low. Many minerals, rocks, organic bases, industrial products, etc., are in this category. In some cases it is feasible to employ a dilute acid solution to which an indicator has been added: on the addition of basic materials acid is consumed and the consequent rise in the pH value is revealed by a characteristic color change. This procedure is seldom satisfactory for the present instances, since even finely pulverized mineral oxides are often attacked by acids only with extreme slowness. In addition, if the quantity of basic materials is not known, it is tedious to decide the minute quantities of acid to be exposed to this test. Furthermore, this procedure is not applicable with most weak organic bases because of the extensive hydrolysis of the salts formed.

Tichborne (*5*) has recommended a test based on the reaction of metal oxides and hydroxides with sodium bicarbonate:

$$\mathrm{MeO} + 2\mathrm{NaHCO_3} \longrightarrow \mathrm{Na_2CO_3} + \mathrm{MeCO_3} + \mathrm{H_2O}$$

Any alkali carbonate formed will turn phenolphthalein deep purple. The method is not suited to all cases, since only a limited number of hydroxides and oxides react promptly, and in particular, only when freshly precipitated. Aged or ignited products do not give a clear-cut test. Furthermore, the procedure entails a filtration and the consumption of considerable quantities of test material.

The method described here for the detection of acid-soluble or acid-binding basic compounds may be carried out well as a spot test. It has been tried on about one hundred materials and has proved excellent for both macro- and microchemical purposes.

The fundamental step of this new method is to bring a test portion of the solid into contact with a reagent solution which contains all the ingredients necessary to the formation of a colored, slightly soluble inner-complex salt, whose precipitation, however, has just been prevented by an adequate hydrogen-ion concentration. In such "equilibrium solutions" the introduction of hydroxyl ions or solid basic materials, which react even partially with dilute acids, is followed immediately by the formation of a colored precipitate. Hydroxides, oxides, carbonates, basic salts, and organic bases respond to this test.

All the organic reagents now in use for the detection or determination of metal ions, by virtue of the formation of slightly soluble inner-complex salts, are acid in character. In many cases the reaction with neutral solutions of the particular metal salts is incomplete, because free acid is produced and this limits the precipitation of the salt. Quantitative precipitation requires buffering, complete neutralization, or often even alkalization, by the addition of ammonia. Alkalization is especially necessary if a reagent must be transformed to an active aci-form. Examples are rubeanic acid, α-nitroso-β-naphthol, etc. Reagents of this type are of no value for the present purpose. Theoretically, detection of acid-soluble basic compounds by the new procedure can be accomplished by means of equilibrium solutions prepared from any of the organic precipitants which give incomplete precipitations because of reversible reactions.

A purely inorganic equilibrium solution is exemplified by the filtrate obtained after the partial precipitation of nickel sulfide by hydrogen sulfide from solutions containing strong mineral acids. Black nickel sulfide appears immediately if these solutions are brought into contact with acid-consuming materials.

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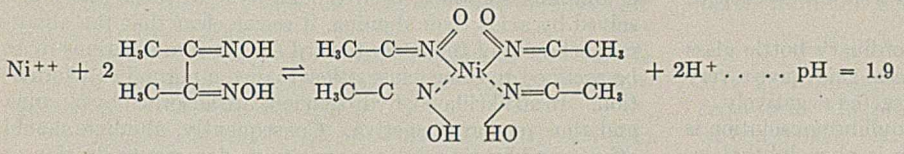
[1] Translated by Ralph E. Oesper, University of Cincinnati.

However, nickel sulfide equilibrium solutions are not recommended because they are unstable and because hydrogen sulfide reacts with many metal compounds.

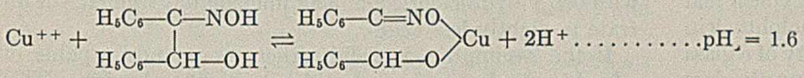
For practical purposes, however, the only suitable organic precipitants are those whose solutions are colorless and which produce colored precipitates. These requirements are well met by dimethylglyoxime, benzoinoxime (cupron), and thioglycolic acid-β-aminonaphthalide (thionalide).

The precipitation of red nickel dimethylglyoxime (*6*), green copper-benzoinoxime (*3*), and brown-black nickel thionalide (*1*) can be represented by the following equations. These reactions are reversible and come to equilibrium, and the precipitation stops as soon as the respective pH is reached.

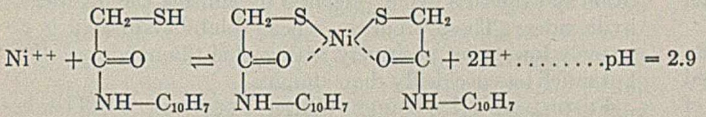
Nickel Dimethylglyoxime



Copper Benzoinoxime



Nickel Thionalide



In the first two instances these pH values were determined electrometrically. The pH of the thionalide equilibrium solution was measured colorimetrically.

Accordingly, if aqueous solutions of nickel salts are treated with alcoholic solutions of dimethylglyoxime or thionalide, or if aqueous cupric solutions react with alcoholic solutions of thionalide (an excess of precipitant in all cases), the clear bright green or bright blue filtrates contain metal ion, reagent, and hydrogen ion in equilibrium corresponding to the foregoing equations. These equilibrium solutions are saturated with respect to the precipitate, a condition that is an advantage from the analytical standpoint. The addition of solids that consume hydrogen ions disturbs the equilibrium, and inner-complex salt, equivalent to the hydrogen ions removed, immediately precipitates. Since this precipitate is highly colored, even traces are easily perceived.

The behavior of slightly soluble basic compounds only is considered here. Patently, solutions of bases (ammonia, etc.) and also salt solutions whose pH is higher than that of the equilibrium solutions will also react. The same will be true of materials that inactivate hydrogen ions by adsorption. Furthermore, metals and alloys that dissolve in dilute acids will also react with equilibrium solutions and cause precipitation of inner-complex salt. The behavior of potassium dichromate and chromate toward nickel dimethylglyoxime equilibrium solution is noteworthy. The former shows no reaction, the latter causes an immediate precipitate. This simple method of detecting the presence of potassium chromate in samples of potassium dichromate will be discussed in a later paper.

The precipitate (red, green, dark brown) is formed on the surface of the basic material and most of it sticks there and so is easy to see. If the sample is colorless, it is possible to detect even traces of basic substances. Since the precipitates are stable, permanent preparations can be made, and basic components, even in mixtures with indifferent materials, can be colored by this process. This method can be used to reveal the presence, and occasionally even the localization, of the basic components of numerous rocks and industrial products, such as cements, pigments, etc.

Organic bases that are only slightly soluble or even insoluble in water, and which consequently do not affect indicators, react nicely toward these equilibrium solutions. It is not even necessary to prepare a solution in alcohol or some other indifferent organic solvent before testing organic preparations as to their basic character or possible content of free bases. The sample is merely placed in one of the equilibrium solutions that contains alcohol, and a color appears if salt-forming basic groups are present. Amphoteric substances whose pH is greater than that of the equilibrium solutions give a positive response to this test. Examples are the aminobenzoic acids, glycine, protein compounds, etc.

Experimental

Reagents (equilibrium solutions). To 50 ml. of a 4 per cent solution of nickel nitrate or copper nitrate add 100 ml. of 1 per cent alcohol solution of dimethylglyoxime, benzoinoxime, or thionalide, warm briefly on the water bath, and filter. If the filtrates are stored in stoppered bottles (neutral glass) they can be preserved for 1 to 2 weeks. The efficacy of the reagent is not impaired if solid reagent separates on standing. Solutions of nickel dimethylglyoxime that remain clear can be prepared by treating a solution of 2.3 grams of hydrated nickel sulfate in 300 ml. of water with 2.8 grams of dimethylglyoxime in 300 ml. of alcohol, and filtering.

Procedure. To a few particles (*circa* 0.5 to 1 mg.) of the finely powdered sample on a white porcelain spot plate, add 1 or 2 drops of equilibrium solution. Mix by means of a fine glass rod or by blowing through a narrow tube. The vulnerability of the sample to the acid in the equilibrium solution determines whether no change is seen, or whether a red (nickel dimethylglyoxime), green (copper benzoinoxime), or dark brown (nickel thionalide) coloration appears at once or after a few minutes. Minute quantities can be tested on a slide, and the development of the color observed under the microscope. Rock and mineral samples can be scraped with a penknife and the resulting powder spot-tested on the main body of the specimen.

The formation of the colored reaction product can be seen well only on colorless substrates. If brown or bright-colored samples are under examination, it is better to make comparative blank tests by substituting a few drops of water for the reagent solution. The formation of the characteristic microcrystals of nickel dimethylglyoxime is easily established if observed under the microscope.

Applications

A positive reaction with each of the three equilibrium solutions was observed with: aluminum hydroxide, aluminum oxide, aluminum phosphate, barium oxide, barium carbonate, beryllium oxide, beryllium carbonate, calcium oxide, calcium carbonate, calcium phosphate, calcium acid phosphate, cadmium oxide, cadmium carbonate, ceric hydroxide, ceric oxide, ferric hydroxide, ferric phosphate, magnesium oxide, magnesium carbonate, magnesium ammonium phosphate, magnesium phosphate, magnesium arsenate, magnesium ammonium arsenate, lead hydroxide, lead oxide, lead carbonate, uranium oxide, ammonium diuranate, zinc carbonate, zinc ammonium phosphate, and zinc phosphate.

A weak reaction was shown by: lead oxide, Pb_3O_4; and mercuric oxide (yellow) stronger than mercuric oxide (red).

No reaction was shown by: bismuth trioxide, ferric oxide (ignited), ferric oxide (Brandt), cobalt oxide, cupric oxide, chromium trioxide, titanium dioxide, magnesium pyrophosphate, uranyl hydrogen phosphate, uranyl pyrophosphate, nor by the acidic oxides: stannic oxide, arsenic trioxide, arsenic pentoxide, molybdenum trioxide tungsten trioxide, vanadium pentoxide, and silica (quartz sand).

The following minerals (mostly from Brazilian sources) gave a positive reaction: malachite, serpentine (magnesite), cerussite, smithsonite, bentonite, fuller's earth (iron-free), pumice, montmorillonite, diabase, and bauxite. (The possibility that alkaline earth oxides might be responsible for the positive reaction of bauxite was eliminated. The reaction was just as strong after the finely powdered specimen was treated with both cold and boiling dilute hydrochloric acid, and then thoroughly washed.) Kieselguhr (84 per cent silica, 13 per cent aluminum oxide, 0.25 per cent ferric oxide) gave a positive reaction, but this failed after the sample was ignited (loss 1.27 per cent). Negative reactions were observed with kaolin and bismuthinite.

Finely pulverized window glass and ordinary bottle glass reacted positively; a good grade of chemical glass gave a very weak test. An excellent ampoule glass reacted negatively.

AMPOULE GLASS. Nickel thionalide equilibrium solution is a more sensitive test for alkalinity than is phenolphthalein. Although nickel dimethylglyoxime equilibrium solution is somewhat less sensitive than the indicator, this may be a real advantage for practical purposes, because the phenolphthalein test is often too delicate when evaluating the quality of a glass with reference to its alkali delivery to water. Ampoule glass of inferior grade can be detected quickly because a little of the powder moistened on a spot plate with 1 to 2 drops of nickel dimethylglyoxime solution shows red at once.

Neutral glass can be tested as to its suitability for ampoule manufacture by comparing the action of a finely powdered sample with that of a pulverized standard glass. Glasses of equal quality develop color of the same intensity, if the grain size of the powders is about the same.

The writers have found that deceptive results are often obtained if the resistance to attack of ampoule glass is tested by the common method of soaking the glass powder for 2 hours in water at 98° C., and then measuring the pH. Even good grades of glass subjected to this treatment sometimes give pH values that may be as high as 8.6. In contrast, large fragments of tubes or ampoules treated with hot water in this manner give pH values that are in accord with the quality of the sample and hence of real value in comparative tests (*2*).

ALUMINUM OXIDE. It is noteworthy that a positive reaction is obtained when any of these equilibrium solutions is brought into contact with aluminum oxide, no matter whether it has been freshly precipitated, aged, or even strongly ignited. The nickel thionalide solution is the most sensitive; a brown color appears almost at once and deepens quickly. The sensitivity of the nickel dimethylglyoxime solution is less, and the copper benzoinoxime solution comes third. This order is observed toward all weakly basic compounds, either inorganic or organic; it is in agreement with the increasing pH values of the three equilibrium solutions.

Analytical application can be made of this behavior of aluminum oxide. The systematic scheme of qualitative analysis always leads to a solution that may contain aluminate. Treatment of this solution with ammonium chloride, or acidification followed by an excess of ammonium hydroxide, will often produce a gelatinous precipitate, a result that seems to establish the presence of aluminum in the original sample. However, this test is far from infallible, because even in the absence of aluminum a gelatinous precipitate may appear. This misleading material is silica, extracted from the glass by strong alkali. Consequently, if only a slight precipitate appears, a confirmatory test for aluminum is imperative. This is no simple matter, as evidenced by the well-known fact that erroneous reporting of the presence of aluminum is one of the most common errors in qualitative analysis. Equilibrium solutions furnish a rapid means of identifying the precipitate as hydrous alumina. The precipitate is washed until the filtrate no longer gives a test for free alkali with equilibrium solution; then it is spot-tested either on the filter or on a porcelain plate with nickel thionalide solution. If aluminum oxide is present, a brown color appears almost immediately and this color deepens on standing.

The weakly acid nickel thionalide solution reacts not only with freshly precipitated alumina, but also with aged or ignited specimens. At first sight, this fact seems incompatible with the known resistance towards acids of aged and particularly of ignited aluminum oxide. In the cold the latter is stable against even concentrated acids. If, in addition, it is recalled that mercuric oxide hardly reacts with the equilibrium solutions, even though it is far more easily dissolved by acids than alumina, it seems clear that the abnormal behavior of the latter toward equilibrium solutions must be ascribed to some cause other than the normal salt formation. In all likelihood, hydrogen ions are adsorbed by alumina and thus rendered inactive. Consequently, alumina should affect equilibrium solutions exactly as does neutralization or buffering. In fact, if alkali-free, ignited alumina is shaken with 0.1 N hydrochloric acid and immediately filtered, the filtrate is slightly less acid.

If the assumption is valid, other compounds capable of adsorbing hydrogen ions should behave like alumina. This conclusion has been substantiated in the cases of zirconium oxide and thorium oxide, prepared by igniting the nitrates or hydroxides. These products, whose solubility in acid is extremely low, react positively with nickel-thionalide solution, but much less decidedly than alumina.

FUSIBLE AND INFUSIBLE WHITE PRECIPITATE. The behavior of the compounds known as fusible and infusible white precipitate is worth special notice. These materials have been given the formulas $HgCl_2.2NH_3$ and $HgNH_2Cl$, respectively. They are white, soluble in acids, show the same reactions, and up to now could be distinguished only by their behavior when heated (fusion and decomposition) and the mercury-chlorine ratio as established by ultimate analysis. However, they behave differently toward nickel dimethylglyoxime solution. $HgCl_2.2NH_3$ reacts in a few seconds, and after several minutes is deep red. In sharp contrast, infusible white precipitate remains completely unchanged even after several hours' contact. This totally different behavior is in agreement with the formulation of these compounds as amino compound and ammoniate, respectively. The latter, as anticipated, shows a strong basic character, in contrast to the amino compound in which the NH_2 group functions as an acid residue. These compounds dissolve in an excess of warm acid, and the fact that both consume equimolar quantities of acid is not in contradiction with their behavior toward the equilibrium solution, since the latter merely reveals the rate of solution, which is conditioned by the character of the compound. This new means of distinguishing fusible and infusible white precipitate made it possible to prove that the latter in contact with ammonium chloride solution even at room temperature is quickly and extensively converted into the fusible salt:

$$HgNH_2Cl + NH_4Cl \rightleftharpoons HgCl_2.2NH_3$$

This conversion was first observed by Kane (*4*) when he treated $HgNH_2Cl$ with boiling ammonium chloride solution.

ORGANIC COMPOUNDS. Care must be exercised in choosing the reagent solution when organic compounds are tested because, for instance, the copper solution should not be used when there is a possibility of the formation of copper double salts with organic bases, or of an oxidation by the cupric content of the reagent.

The following compounds, some of them basic materials not soluble in water, show an immediate positive reaction with the three equilibrium solutions: *p*-aminoacetanilide, *p*-aminophenol, atropine, benzidine, brucine, cinchonine, creatine, creatinine, dicyandiamidine, dimethylaniline, hexamethylenetetramine, naphthylamine (α and β), nicotine, nitron, 8-oxyquinoline, toluidine (*o*, *m*, *p*), phenylhydrazine, tetramethyldiaminodiphenylmethane, and 1,3,4-xylidine.

Comparative tests showed that *m*-aminobenzoic acid reacts very quickly, the para isomer slowly, and the ortho acid practically not at all. Sulfanilic acid does not react, because the acid character predominates in this amphoteric compound. On the other hand, its sodium and barium salts give a positive test immediately. The amide of sulfanilic acid reacts slowly. *m*- and *p*-nitraniline, nitroguanidine, and diphenylamine do not react; they are still acid despite their amino or imino groups.

Glycine and alanine, which are amphoteric and soluble in water, slowly give a rather weak positive test. *p*-Aminoacetophenone behaves similarly.

Egg albumin, keratin (from toothbrush bristles), and hide powder (pH = 5.5) react strongly.

No reaction was shown by caffein, phenylsemicarbazide, *p*-nitrophenylhydrazine, dinitrophenylhydrazine, isatin, and tetramethyldiaminodiphenyl ketone.

FILTER PAPER The constituents of equilibrium solutions are partially separated by capillary action if spots are placed on filter paper. A colored zone surrounds the spot. Nickel dimethylglyoxime solution works best in this kind of experiment. Different types of filter paper behave quite differently. The ring is particularly marked on qualitative papers, while on acid-washed quantitative papers (Schleicher und Schüll 589^2, 589^3) it is exceedingly thin, and on Schleicher und Schüll 590 and 507 the intensity is intermediate. The whole spot is colored on thick absorbent paper, and the red appears first on the back side. The colored zones appear at the places of lowest acidity; the capillaries of the paper obviously hold back hydrogen ions. If neutral litmus paper is spotted with nickel dimethylglyoxime equilibrium solution a red circle is formed that extends beyond the zone of the precipitate. This demonstrates that the precipitation of this salt does not require complete neutralization, but only a decrease in the hydrogen-ion concentration, a conclusion quite in accord with the fact that the salt can be precipitated quantitatively from solutions containing acetic acid.

BICARBONATE SOLUTIONS. The addition of the nickel-equilibrium solution to bicarbonate solutions—e. g., calcium bicarbonate—produces a red precipitate. Hydrogen ion is taken from the equilibrium solution

$$Ca(HCO_3)_2 + 2H^+ \longrightarrow Ca^{++} + 2H_2O + CO_2$$

and an equivalent quantity of nickel dimethylglyoxime separates. The presence of bicarbonate in water containing carbon dioxide can be quickly established by this test. The development of a procedure for the quantitative determination of the temporary (bicarbonate) hardness of waters, based on reactions with equilibrium solutions, is now in progress.

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Potentiometric Determination of Vitamin C

Combined Use of 2,6-Dichlorophenolindophenol and Iodate

J. B. RAMSEY AND E. L. COLICHMAN, University of California at Los Angeles, Los Angeles, Calif.

THAT sodium 2,6-dichlorophenolindophenol is a specific oxidant for ascorbic acid in fruit extracts is generally accepted. Harris and Ray (*5*) have shown this to be true if titration is carried out in acid solution, but not so in the neutral, or nearly neutral, solutions used by Tillmans (*10*). Since the dye is red in the oxidized form in acid solution, it is often difficult or impossible to obtain the end point visually with precision in certain highly pigmented extracts. That the difficulties involved in the colorimetric method may be avoided by electrometric titration has been demonstrated by Kirk and Tressler (*7*).

A serious disadvantage, however, in the use of standard aqueous solutions of the dye is their instability. Frequent standardizations are necessary (*1*). A method which would eliminate this disadvantage and at the same time depend on the specificity of the dye for ascorbic acid seems desirable. Such a method involving the combined use of iodate and the dye has been developed.

Preliminary Experiments

In order to determine the effect of pH on the specificity of iodine as an oxidant for vitamin C, results were obtained with triiodide and with iodate (iodide previously added) on samples of various citrus juices over the pH range 0.3 to 3. The quantity of reducing substances found in these extracts with either of these oxidants was consistently higher, approximately 10 per cent, than that found with the indophenol dye. This is in agreement with the conclusions of previous investigators (*5*, *8*, *9*) so far as the nonspecificity of triiodide is concerned. That iodate, with iodide previously added, should be no more specific than triiodide is to be expected from the fact that in acid solutions iodate and iodide react practically instantaneously to form iodine. In fact, without previous addition of iodide, more iodate was reduced than triiodide by equal volumes of the same fruit juice. All titrations in this investigation were followed electrometrically (to be described later).

Other experiments were carried out to determine whether the dye might act as a selective alternate oxidation-reduction catalyst for the oxidation of ascorbic acid by iodine in citrus juices. Over the pH range 0.3 to 3 no catalytic effect was observed. However, it was noted that iodine did not oxidize the dye (reduced) at an appreciable rate even at those pH's where the oxidation of the dye is thermodynamically possible (*3*). It seemed probable, therefore, that the dye solution could be added to the extracts until the end points corre-

Table I. Typical Potentiometric Data with Grapefruit Juice

With Indophenol Dye			Followed by Iodate, Iodide Previously Added			With Iodate Alone, Iodide Previously Added		
Potentiometer Reading	Potentiometer Increment	Buret, Ml.	Potentiometer Reading	Potentiometer Increment	Buret, Ml.	Potentiometer Reading	Potentiometer Increment	Buret, Ml.
....	....	...	....	....	...	....	....	0.01
....	....	...	....	....	...	0.2317	....	4.01
....	....	0.00	....	....	0.00	0.2356	....	4.06
0.2212	....	8.83	0.2413	....	0.25	0.2373	0.0017	4.11
0.2298	0.0086	8.87	0.2413	....	0.28	0.2556	0.0183	4.16
0.2417	0.0119	8.92	0.2512	0.0099	0.33	0.2757	0.0201	4.20 e. p.
0.2573	0.0156	8.97	0.2752	0.0240	0.37 e. p.	0.2832	0.0075	4.25
0.2763	0.0190	9.02 e. p.	0.2851	0.0099	0.42	0.2912	0.0080	4.30
0.2903	0.0140	9.07	0.2907	0.0056	0.47	0.2953	0.0041	4.35

sponding to the oxidation of the vitamin C were reached, after which the titration could be completed with iodate in the presence of iodide. The total reducing capacity of another equal volume of the citrus juice could then be determined with the standard iodate solution alone. The difference between the equivalents of iodate reduced in the two titrations would thus yield the equivalents of vitamin C present. The determination would therefore be based solely on the standard iodate while making use of the specificity of the dye whose concentration need be known only very approximately.

Procedure and Apparatus

An ordinary student potentiometer, equipped with a reflecting walltype galvanometer with lamp and scale attachment (sensitivity, 0.014 microampere), was used. An agar bridge, saturated with potassium chloride, connected the 200-ml. lipless titration beaker with a saturated calomel half-cell. A platinum wire electrode completed the circuit with the potentiometer setup. Slow uniform stirring was maintained during each titration by means of a mercury-sealed stirrer. By placing the citrus juice in series with the titration beaker, one source of oxygen-free nitrogen served to blanket the juice during the analyses as well as to provide an inert atmosphere during titration, and to force portions of the juice into the pipet.

Procedure Adopted. Ten milliliters of the citrus juice are transferred to the titration beaker and sufficient 2 *N* hydrochloric acid and water are added to make the initial acid concentration of the resulting solution (approximately 100 ml.) between 0.1 and 0.5 *N*. The indophenol dye (Eastman No. P3463) solution, containing 0.5 to 1 mg. per ml., is then added until one drop of the dye solution remains in the oxidized form. Approximately 10 ml. of 0.1 *N* potassium iodide are then added, and the titration is completed with standard 0.01 *N* potassium iodate. The iodate solution must be added dropwise, allowing at least 5 seconds between each drop. Another 10-ml. portion of the citrus juice is titrated with the standard iodate alone at approximately the same acidity and iodide concentration. The main portion of the iodate may be added, in this case, at any convenient rate. Ten-milliliter burets, graduated to 0.05 ml., are used in all iodate titrations.

A simulated fruit juice, containing known quantities of ascorbic acid and glutathione, was used in the development of the above procedure. Equally satisfactory results were obtained at any pH over the range 0.3 to 3. It is somewhat simpler, however, to work at the higher acid concentrations (0.1 to 0.5 *N*) since readily measured volumes (via graduated cylinder) of common acid reagents may be used.

When the main portion of the residual iodate was added too rapidly after the dye end point was attained, more iodate was reduced than that equivalent to the glutathione present. This is due to the fact that the dye (reduced) is oxidized by iodate to a measurable extent, even with iodide present, unless the iodate is added slowly.

The equivalence point is recognized, without plotting titration data, when the largest change in e. m. f. occurs per drop (0.05 ml.) of oxidant solution added. In the titration of pure ascorbic acid solution or citrus juice with the dye, location of the end point with certainty by this procedure necessitates the inert atmosphere.

As is usually the case in potentiometric titrations, it is necessary to go slightly past the end point to be sure that the largest change has been registered. If the approximate volume of the oxidant required is determined by a rapid titration until a color change is noted, then, in the potentiometric determination, oxidant may be added to within several tenths of a milliliter of the approximate end point before recording potentiometric readings (color change not readily observable with dye solution over a week old). When within a few tenths of a milliliter of the end point, an e. m. f. balance is established after each subsequent drop of oxidant added. From 25 to 40 seconds were required for attainment of the maximum e. m. f. reading after addition of each drop. During this time interval, the potentiometer was continually adjusted to maintain zero deflection of the galvanometer, in order to obtain the reading before the drift downward in potential occurred. By this procedure the maximum change in potential per drop added was readily observed. The titration should not be interrupted during the addition of the last few tenths of a milliliter of oxidant; otherwise the drift in potential will make the results unreliable.

The sharpness of the potentiometric end point is assured if the platinum wire electrode is dipped into chromic acid cleaning solution and rinsed with water before each titration.

To illustrate the precision with which the end point can be determined, results of a typical titration on a sample of citrus juice are given in Table I.

Analytical Results

All citrus juices were filtered through a double thickness of cheese cloth. A drop of capryl alcohol was added to each total sample to prevent foaming caused by nitrogen bubbling through. The nitrogen prevented oxidation of the juices during analysis and also kept them uniform.

The results obtained by the combined use of indophenol dye and standard iodate and by the ordinary method, based on standard dye solution, are given in Table II. The dye solution was standardized by the usual procedure, involving the use of a known solution of pure ascorbic acid (Eastman No. 4640), as determined with standard iodate (or triiodide). Standardization was carried out potentiometrically. In every case 10.00 ml. of the citrus juice were used.

Discussion

Certain investigators (*5*, *6*) have reported that the rate of addition of the dye to either pure ascorbic acid solution or to citrus juice is a determining factor. Presumably the titrations were performed in the presence of air. In the inert atmosphere of nitrogen used in this investigation, the volume of dye solution required was found to be independent of the rate of its addition to either of these solutions. This suggests the possibility that in the presence of air the oxidation of ascorbic acid by oxygen may be induced during its oxidation by the dye. This possibility is also indicated by the observations of Harris and Ray (*5*) and of Fujita and Ebihara (*4*) that greater precision is obtained in the ordinary determination with the standard dye solution if the ascorbic acid solution is added to a measured volume of the dye solution. The conditions under which variations in the method of mixing the reductant and oxidant may change the extent of an induced oxidation by oxygen have been described by Bray and Ramsey (*2*, p. 2284).

Table II. Vitamin C Content of Citrus Juices

(Comparison of direct dye titration with dye-iodate method)

Citrus Juice[a]	Orange				Lemon			Grapefruit
	I	II		III	I	II		I
HCl normality	0.25	0.25	0.60	0.25	0.25	0.25	0.50	0.25
Dye normality × 10^3	4.670	5.697	5.697	5.687	5.708	3.146	3.146	4.339
Volume, ml.	11.28	9.89	9.91	9.06	11.12	20.08	20.09	9.09
	11.25	9.90	...	9.08	...	...	...	9.07
Milliequivalents × 10^3, av.	52.60	56.37	56.46	51.58	63.47	63.17	63.20	39.40
Residual iodate, 0.01040 *N*								
Volume, ml.	0.51	0.55	0.55	0.56	0.40	0.42	0.43	0.39
	0.52	0.53	...	0.58	...	...	...	0.37
A. Milliequivalents × 10^3, av.	5.36	5.62	5.72	5.93	4.16	4.37	4.47	3.95
Iodate without dye								
Volume, ml.	5.65	6.00	6.01	5.54	6.56	6.50	6.50	4.18
	5.64	...	...	5.55	...	...	6.51	4.20
B. Milliequivalents × 10^3, av.	58.70	62.40	62.50	57.67	68.22	67.60	67.65	43.58
B minus A	53.34	56.78	56.78	51.74	64.06	63.23	63.18	39.63
Difference from dye titer, %	+1.40	+0.72	+0.57	+0.31	+0.93	+0.09	−0.03	+0.58

[a] Orange I, fresh navel; II, fresh Valencia; III, Valencia after refluxing in air for 0.5 hour. Lemon I, fresh; II, after standing one week out of contact with air (blanketed with nitrogen). Grapefruit, fresh. One milliequivalent of ascorbic acid = 88 mg.

Summary and Conclusions

This potentiometric method for the determination of vitamin C in citrus juices depends upon a stable potassium iodate solution as the only standard oxidant and, at the same time, makes use of the specific oxidation of ascorbic acid by 2,6-dichlorophenolindophenol. Standardization of the unstable dye solution is thereby eliminated.

The results obtained by this method (Table II) are in close agreement with those dependent on direct titration with an accurately standardized dye solution.

The method should be applicable to other biological fluids in which the indophenol dye is a specific oxidant for vitamin C.

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Elimination of the Water Wave in Polarographic Work

At Relatively High Indifferent Electrolyte Concentrations

I. M. KOLTHOFF AND E. F. ORLEMANN

University of Minnesota, Minneapolis, Minn.

IT HAS been found (*1*) that the residual current obtained in relatively concentrated solutions of indifferent electrolytes, like alkali and earth alkali salts, is of the same order of magnitude as that obtained in more dilute solutions, when no electroreducible material is present. However, when a current flows through the cell owing to the reduction of some constituent in the solution, and the concentration of indifferent salt is greater than about 0.5 *M*, an abnormal wave occurs which is due to a reduction of water molecules:

$$H_2O + e \longrightarrow H + OH^-$$

This "water wave" starts at about −0.9 volt (*vs.* saturated calomel electrode), reaches a maximum at about −1.35 volts, and then decreases markedly as the potential is made more negative. This decrease is much larger than corresponds to the effect of the change of the drop time with the potential.

In analytical work the concentration of indifferent electrolyte in the solution is often greater than 0.5 *M*—e. g., in polarographic steel analysis. The occurrence of the water wave in such cases may be the source of large errors or misinterpretations, and should be eliminated, particularly when dealing with mixtures of reducible substances. When the solution contains only one reducible constituent which yields a diffusion current at potentials more positive than −0.9 volt, the water wave appears as a separate wave. On the other hand, when the solution contains a constituent which yields a wave at potentials more negative than −0.9 volt, the water wave overlaps with that of the reducible constituent. Consequently, an apparent diffusion current of the reducible constituent is found which is much larger than the true diffusion current.

In order to illustrate the effect, Figure 1 presents current-voltage curves of 0.0004 *M* zinc chloride in different concentrations of potassium chloride. These curves were obtained some five years ago by C. S. Miller in this laboratory with the manual apparatus at 25.0° using drop times of 1 and 2 seconds. The horizontal portion of curve 1 (in 0.05 *M* potassium chloride) corresponds to the diffusion current of zinc at a drop time of 1 second. Curves 2 and 3 have an abnormal appearance and show maxima. These are not of the same nature as the ordinary maxima which are often observed on current-voltage curves and are due to stirring effects. The maxima on curves 2 and 3 were found at potentials where the water current has a maximum value. The large decrease of the current on curves 2 and 3 after the maximum had been reached is mainly due to a decrease of the water current when the potential is made more negative. However, it is seen that the true diffusion current of zinc has not yet been attained at the potential where the potassium discharge starts. If we measured the "apparent" diffusion current at the

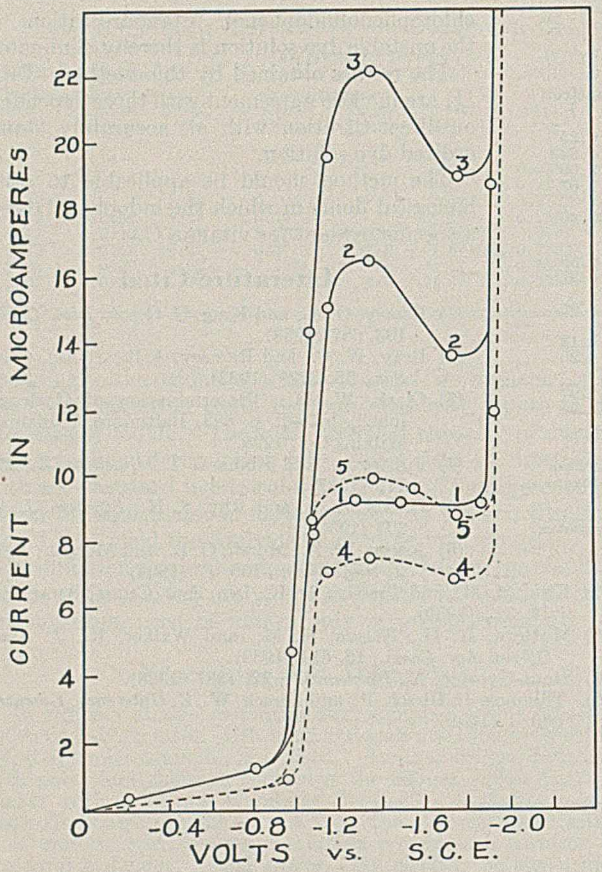

Figure 1. Current-Voltage Curves of 0.0004 *M* Zinc Chloride in Potassium Chloride

Concentration of KCl in curve 1, 0.05 *M*; curve 2, 0.5 *M*; curve 3, 1 *M*; curve 4, 0.5 *M*; curve 5, 1 *M*. Drop time in curves 1, 2, and 3 was 1 second, in curves 4 and 5, 2 seconds

maximum, we would find a value of 16.2 microamperes in 0.5 *N* potassium chloride and of 21.8 in 1 *N* chloride, whereas the true diffusion current is only 9.3 microamperes. The maximum becomes much less pronounced when the drop time is increased, as is evident from curves 4 and 5 in Figure 1. These curves were obtained with a drop time of 2 seconds.

Orlemann and Kolthoff (*1*) found that the water wave is proportional to the total current flowing, that it increases with increasing concentration of indifferent electrolyte in the solution, that it is of the same order of magnitude in solutions of potassium, sodium, and lithium salts, and that the water wave does not occur in solutions of tetraethylammonium chloride. Working with the same capillary the ratio of the water wave (i_{H_2O} at maximum value) to the total current i_t decreases when the pressure of the mercury on the capillary is decreased according to the expression:

$$i_{H_2O}/i_t = kP + \text{constant}$$

For example, in a solution of thallous chloride in 2 *M* potassium chloride they found a ratio of i_{H_2O}/i_t of 0.47 at a pressure of 100 cm. of mercury, of 0.24 at a pressure of 80 cm., and of 0.03 at a pressure of 50 cm. Thus, by working with a very slow-dropping capillary (drop time equal or greater than 5 seconds) the water current can be eliminated. In ordinary polarographic practice such slow-dropping capillaries are seldom used. Fortunately, it has been found possible to eliminate the water current completely by adding 0.01 per cent of gelatin to the solution. The effect of a number of capillary-active substances, including tylose, upon the water wave has been investigated. All the capillary-active substances affected the water wave, but only gelatin eliminated it completely.

Table I. Effect of Water Current in Analysis of Mixtures of Thallium and Zinc at 25° C.

(t = 3.60 seconds at −0.6 volt)

Curve in Figure 2	Concentration of KCl	Gelatin	i_{Tl^+}	$i_{Tl^+} + i_{Zn^{++}}$	$i_{Zn^{++}}$[a]	Error in Zn
	M	%	*Microamp.*	*Microamp.*	*Microamp.*	%
1	0.1	0.01	0	9.30	9.30	..
2	2	0.01	0	9.40	9.40	..
3	2	0	0	12.20	12.20	+30
4	1.0	0	8.00	20.50	11.90	+27
5	1.0	0.01	7.25	16.70	9.45	+ 1

[a] In all solutions concentration of zinc ions was 0.0016 *M* and concentration of thallium ions was of the order of 0.002 *M* in curves 4 and 5.

Therefore, when current-voltage curves are determined with the dropping electrode in solutions whose concentration of indifferent electrolyte is greater than 0.5 *M*, 0.01 per cent of gelatin should be added to eliminate the water current. This addition is especially essential when dealing with mixtures of reducible substances.

In order to illustrate the order of magnitude of the error which can be made when the water current is not eliminated, current-voltage curves of mixtures of thallium and zinc were determined under different conditions. Some of the curves are shown in Figure 2, and analyzed in Table I.

Comparison of curves 1 and 2 (Table I) reveals that the true diffusion current of zinc in 2 *M* potassium chloride is practically the same as in 0.1 *M* chloride. If the water wave was not eliminated in the 2 *M* chloride solution, an apparent diffusion current of zinc was found which was 30 per cent larger than the true diffusion current. Curves 4 and 5 refer

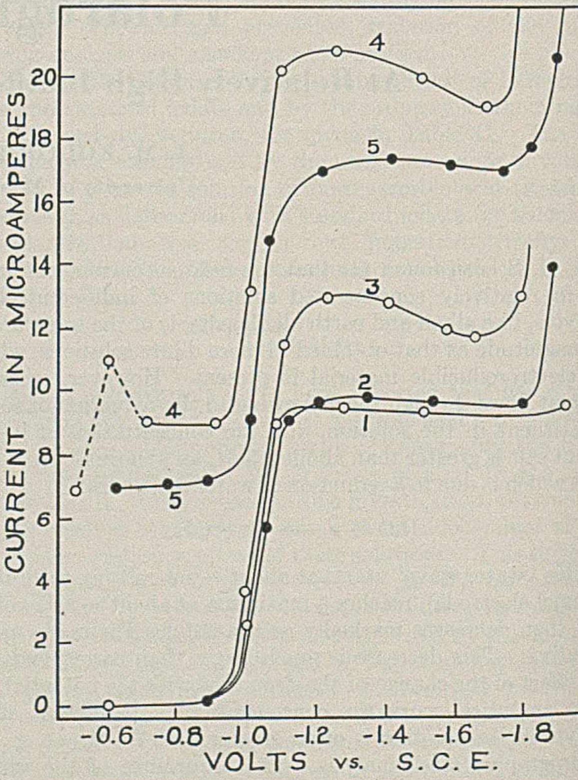

Figure 2. Effect of Gelatin on Water Current in Mixtures of Thallium and Zinc in Potassium Chloride Solutions

Composition of solutions is given in Table I to mixtures of thallium and zinc in only 1 *M* potassium chloride. If the water wave was not eliminated an error of 27 per cent in the zinc wave was found, the error being only 1 per cent in the presence of 0.01 per cent of gelatin. The error in the absence of gelatin would increase with increasing ratio of thallium to zinc, since the water current is proportional to the total current. It would hardly be possible to correct for the water wave by making calibration curves with known mixtures of thallium and zinc in the particular medium. The results in Table I show that such calibration curves are entirely superfluous, if 0.01 per cent of gelatin is added to the solution to be analyzed. The magnitude of the error due to the water wave depends upon the characteristics of the capillary, as mentioned above.

Summary

Large errors may be caused by the occurrence of a water wave in the polarographic analysis of solutions which have a concentration of indifferent electrolyte larger than about 0.5 *M*. The water wave and the abnormalities caused by it are completely eliminated by the addition of 0.01 per cent of gelatin to the solution.

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Specific Gravity of Petroleum Oils by the Falling Drop Method

A. J. HOIBERG, Lion Oil Refining Co., El Dorado, Ark.

A method of densimetry which has shown many advantages in determinations with body fluids has been modified to adapt its use to measurement of the specific gravity of petroleum oils. Operation is rapid and easy, since the procedure depends only on the measurement of the time of fall of a drop of oil in an alcohol-water solution. The specific gravity is then determined by direct conversion of the time of fall from a calibration curve for the solution. This method has been found accurate to within ±0.0010 unit of specific gravity. Since only a few drops of the petroleum fraction are required, the determination may be made on the very small volumes of oils often obtained in analytical distillations or extractions.

OFTEN small volumes of petroleum oils are obtained by extraction or by fractional distillation, especially during the analysis of asphalt and road oil (*2*, *5*, *6*). To understand the nature of these fractions, characterization by physical constants is desired, values for density and refractive index being especially informative (*2*, *7*). Usually but little difficulty is had in obtaining accurate readings of refractive index; however, when only small volumes of oil are available, pycnometer determinations for density are difficult and time-consuming.

A method of densimetry which requires a small volume of fluid and less than a minute's time would be especially valuable. Such a method was described by Barbour and Hamilton (*1*) and later with variations by Guthrie (*3*) and by Kagan (*4*). Although the procedure described was devoted entirely to measurement of body fluids, the principle of the method, "timing the fall of a drop of body fluid of known size, through a definite distance in a mixture nonmiscible with the fluid" (*1*) would generally apply to any liquid.

Modifications of the procedure and equipment to permit the principle to be applied to petroleum oils are described in this paper.

Theory

When a small spherical body moves through a fluid so slowly that the latter flows past it in smooth streamlines, the relative velocity, V, between the body and fluid may be obtained from Stokes' law:

$$V = \frac{gD^2(d_1 - d_2)}{18\mu}$$

where μ is the coefficient of viscosity of the fluid, D the diameter of the sphere, d_1 the density of the sphere, d_2 the density of the fluid, and g the acceleration due to gravity.

V is a constant for a given particle having free movement and, if the distance of fall were fixed, would be inversely proportional to the time of fall of the sphere. Under the conditions of operation of the falling drop method, wherein the distance of fall, 30 cm., the diameter of the drop, D, and the properties of the falling drop solution are constant, V should be directly proportional to the density of the drop, d_1. Actually, over the range covered and with the apparatus described a direct ratio is not obtained, probably because of wall and turbulence effects. However, the results are reproducible as shown by calibration curves, and the accuracy of the measurement is not related to the lack of proportionality.

Equipment

Three glass tubes with a 1.3-cm. bore and 50 cm. long, obtained from a stock of Pyrex boiler gage glass, were marked with lines 30 cm. apart, extending all the way around the tubes, one line being 5 cm. from the end of the tube. Rubber stoppers were inserted to close the ends of the tubes nearest to the lines. As shown by Figure 1, the tubes were mounted in a 2000-ml. cylinder (8 cm. in inside diameter × 48 cm.) by means of a brass plate standing on three 1-cm. legs and with a cap on the top. The three holes fitting the glass tubes in the brass plate and cap were drilled with their centers on the apexes of an equilateral triangle and 3.5 cm. apart. In addition, holes were drilled in the cap for a thermometer, a 250-watt knife-blade heater, and an expansion-type thermoswitch. Copper tubing of 0.3-cm. (0.125-inch) diameter was run down the side of the cylinder to supply air for stirring the water bath. A leveling stand was provided by fastening the base of the cylinder into the case from a Bourdon gage, leveling screws being fastened to the rim of the case. The

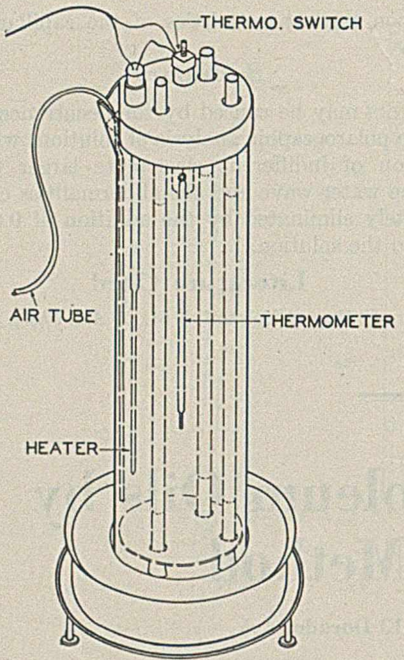

FIGURE 1. FALLING DROP EQUIPMENT

thermometer was suspended so that it could be used as a plumb bob to adjust the falling drop tubes in a vertical position.

A falling drop pipet calibrated to deliver two drops of exactly 0.01-ml. volume each was used to form the drop of petroleum fraction, a Guthrie pipet controller being used to regulate the delivery of the pipet. The time of fall of the drop was measured with an electric timer which could be read to 0.1 second.

Falling Drop Solutions

Solutions of ethyl alcohol and distilled water were mixed to cover the range in specific gravity of the petroleum fractions likely to be run. Before filling the tubes the solutions were heated to boiling under a reflux condenser to dispel any air present; otherwise bubbles collected on the falling drops.

The composition of the solutions used for the determination of the data in Table III and the range of specific gravity for which they could be used are listed in Table I. The range in specific gravity was obtained by referring to a graph similar to Figure 2 constructed for all five solutions and selecting the specific gravities corresponding to the time of fall from 7 to 25 seconds.

Method

After the oil had been drawn into the pipet to the upper mark, a standard drop was formed with the tip of the pipet under the surface of the solution in the tube. A slight jerk upward released the drop. The release was made 5 cm. or higher above the upper mark in the tube to allow a substantially constant velocity to be reached by the drop before the mark was passed. The time required for the drop to fall the 30 cm. between the marks was measured to the nearest 0.1 second by a timer. If the time of fall was not in the range of 7 to 25 seconds, a trial drop was formed in one of the other solutions, trials being repeated until the time of fall came within this range. An additional drop or drops were then released in the selected solution to have determinations agreeing to within 0.2 second.

When viscous oils and waxes were run, the temperature of the water bath was maintained constant at about 71° C. (160° F.) to permit the liquid to be easily expelled from the pipet. The pipet, filled to the upper mark with the sample which had been heated to a fluid condition on a lamp bank, was immersed in the alcohol-water solution to above the upper mark. After holding it thus for 3 to 5 minutes to allow equalization with the temperature of the water bath, the drop was formed and released underneath the surface of the liquid as before.

With such viscous oils, especially if they were resinous, it was difficult to shake the drop from the pipet, the drop sometimes breaking and part remaining on the tip. By rubbing a very small quantity of soap on the tip of the pipet, the interfacial tension was found to be changed so that the drop could be easily formed and released.

The pipet was cleaned of oil with carbon tetrachloride, gas then being blown through the pipet to evaporate the carbon tetrachloride.

Calibration

The falling drop solutions were calibrated by running three oils selected to have times of fall defining the range from 7 to 25 seconds. The specific gravity at 25° C./25° C. of the three oils was determined to within ±0.0005 unit with a 5- or 10-ml. pycnometer. The calibration curve was plotted on semilogarithmic paper as shown by Figure 2, the time of fall being plotted on the logarithmic scale.

After the curve was once established for a particular solution at a given temperature, but one run with a standard oil was necessary to check the calibration. If the concentration of the solution had changed but slightly, the time of fall of this standard oil was used to establish a new calibration curve parallel to the previous curve.

When the determinations were carried out at 71° C. (160° F.) the calibration was checked after each 2 hours of operation to determine if the loss of ethyl alcohol by evaporation had been sufficient to increase noticeably the density of the falling drop solution. The solution was renewed if the run with the standard oil differed markedly from the previous calibration—i. e., by as much as one second in falling time.

Since the coefficient of expansion of petroleum oils may be considered to vary only with specific gravity and not with source, the oils used in calibration need not be from the same crude as the unknown oils. An appreciable error arises in determinations with waxy oils, or with wax, due to the change in volume of wax upon crystallization, but this error may be eliminated by selecting similar waxy oils or waxes as the calibration standards. If the specific gravity data may be reported at temperatures above the crystallization point, calibration curves determined with wax-free oils can be used to determine the density of a hypothetical liquid at 25° C./25° C.; then the National Standard Petroleum Tables can be used to determine the correction needed to obtain the specific gravity at a temperature above the crystallization point.

TABLE I. SOLUTIONS USED

Solution No.	Per Cent Ethyl Alcohol by Volume	Specific Gravity of Solution at 25° C./25° C.	Range in Specific Gravity at 25° C./25° C. for Which Solution Is Suitable
1	98	0.793	0.836–0.877
2	75	0.852	0.873–0.911
3	70	0.865	0.885–0.925
4	60	0.889	0.920–0.950
5	45	0.923	0.953–0.993

Experimental

TEMPERATURE CONTROL. The variations in falling times with a change in temperature of 2.8° C. (5° F.) were determined for oils of known specific gravity. Three alcohol-water solutions representative of the usual concentrations employed were calibrated at normal operating temperatures as shown in Table II. These data, when used to construct a graph similar to Figure 2, show that a 2.8° C. (5° F.) change in temperature shifts the calibration curve by not more than 0.0010 unit in specific gravity. To have data accurate to within 0.0010 unit, the tolerance allowed in the thermostatic control could therefore be ±1.4° C. However, such a wide variation is not permissible if rapid temperature fluctuations occur because convection currents are set up in the alcohol-water solutions. Control within ±0.2° C. is not difficult to obtain and is recommended as desirable to eliminate such currents which interfere with the normal fall of the drop.

Table II. Variation of Falling Drop Time with Change in Temperature of Solutions

Ethyl Alcohol	Temperature		Time of Fall			Specific Gravity at 25° C./25° C. by Pycnometer
			Trial 1	Trial 2	Av.	
% by vol.	*° C.*	*° F.*	*Sec.*	*Sec.*	*Sec.*	
98	28.9	84	10.2	10.3	10.2	0.8520
98	28.9		13.4	13.6	13.5	0.8414
98	28.9		19.1	19.3	19.2	0.8364
98	31.7	89	10.1	10.3	10.2	0.8520
98	31.7		12.9	13.1	13.0	0.8414
98	31.7		18.8	18.9	18.8	0.8364
75	68.3	155	10.4	10.3	10.3	0.8949
75	68.3		11.8	11.9	11.8	0.8873
75	68.3		17.3	17.5	17.4	0.8780
75	71.1	160	10.3	10.4	10.3	0.8949
75	71.1		11.6	11.8	11.7	0.8873
75	71.1		16.7	16.9	16.8	0.8780
40	68.3	155	8.8	8.9	8.8	0.9853
40	68.3		10.3	10.4	10.3	0.9795
40	68.3		16.2	16.4	16.3	0.9666
40	71.1	160	8.6	8.6	8.6	0.9853
40	71.1		10.0	10.1	10.0	0.9795
40	71.1		15.9	16.1	16.0	0.9666

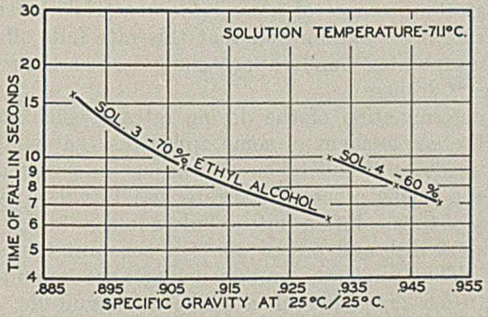

Figure 2. Calibration Curves for Falling Drop Solutions

Comparison with Pycnometer Determinations. The specific gravities at 25° C./25° C. of 37 oils ranging from 0.8364 to 0.9853 were obtained with a 5-ml. pycnometer, duplicate determinations being made which agreed for each oil within 0.0005 unit. The falling times of these oils were determined with solutions which allowed the drop to fall within 7 to 25 seconds, with one exception of 6.3-second time of fall. During the determinations the temperature of the water bath surrounding the falling drop tubes was controlled by the thermostat to within ±0.2° C.

The minimum, an intermediate, and the maximum time of fall for three of the oils run in each solution were plotted as calibration curves on semilogarithmic paper, as illustrated by Figure 2. In all, five different solutions were calibrated, fifteen of the oils being used as standards. The times of fall of the twenty-two remaining oils were converted to specific gravities at 25° C./25° C. by referring to the calibration curves. The pycnometer values were subtracted from the chart values to determine the differences in specific gravity by the two methods, as shown in Table III.

Accuracy

In the group of twenty-two oils, a difference greater than 0.0010 unit was found for four oils, only one determination showing a difference greater than 0.0020 unit. With fourteen oils a difference of 0.0005 unit or less was found. The average difference was 0.0006 unit.

From consideration of this series of runs completed in a routine manner, the accuracy of the method is believed to be within ±0.0010 unit of specific gravity. This is well within the deviation allowable in calculation of characterization factors of complex mixtures, such as petroleum fractions, from density and refractive index.

Range of Application

The lightest oil which could be run would have to be slightly heavier than ethyl alcohol, or with a specific gravity of about 0.79 at 25° C./25° C. If the viscosity is very low, liquids such as kerosene and light gas oil form drops which break off the pipet before the standard drop volume of 0.01 ml. is reached.

The upper range in specific gravity is limited by the oil being too dark for the meniscus in the pipet to be discernable. Viscosity is also a factor, some of the resins recovered from asphalts being light enough in color but too viscous to be handled at the temperature of 71° C., which is about the highest temperature found practicable for operation without excessive evaporation of the ethyl alcohol solutions. The higher alcohols, such as propyl and butyl, cannot be used because of their appreciable solvent power for petroleum fractions at such temperatures.

With the time of fall between 7 and 25 seconds, each solution of alcohol and water has been found suitable for a range of approximately 0.040 unit of specific gravity.

Table III. Comparison of Determinations by Pycnometer and Falling Drop Method

Solution No.	Temperature	Time of Fall			Specific Gravity at 25° C./25° C.		Difference
		Trial 1	Trial 2	Av.	By pycnometer	By time of fall	
	° C.	*Sec.*	*Sec.*	*Sec.*			
1	28.9 (84° F.)	10.3	10.1	10.2	0.8520	Calibration	......
1	28.9	11.6	11.4	11.5	0.8464	Calibration	......
1	28.9	21.5	21.5	21.5	0.8364	Calibration	......
1	28.9	10.9	11.1	11.0	0.8491	0.8484	−0.0007
1	28.9	11.3	11.6	11.5	0.8477	0.8464	−0.0013
1	28.9	14.5	14.3	14.4	0.8415	0.8410	−0.0005
2	71.1 (160° F.)	9.2	9.3	9.2	0.8949	Calibration	......
2	71.1	10.7	10.7	10.7	0.8873	Calibration	......
2	71.1	14.8	15.1	14.9	0.8780	Calibration	......
2	71.1	9.3	9.3	9.3	0.8936	0.8940	+0.0004
2	71.1	9.8	9.9	9.8	0.8895	0.8908	+0.0013
2	71.1	11.5	11.4	11.4	0.8847	0.8849	+0.0002
2	71.1	14.8	15.0	14.9	0.8780	0.8780	0.0000
3	71.1	6.3	6.3	6.3	0.9313	Calibration	......
3	71.1	9.3	9.5	9.4	0.9075	Calibration	......
3	71.1	15.9	16.1	16.0	0.8895	Calibration	......
3	71.1	7.8	7.8	7.8	0.9182	0.9180	−0.0002
3	71.1	8.2	8.3	8.2	0.9150	0.9150	0.0000
3	71.1	10.2	10.5	10.4	0.9033	0.9032	−0.0001
3	71.1	13.8	13.6	13.7	0.8915	0.8940	+0.0025
3	71.1	13.9	13.8	13.8	0.8949	0.8939	−0.0010
4	71.1	6.9	7.0	7.0	0.9497	Calibration	......
4	71.1	8.0	8.2	8.1	0.9421	Calibration	......
4	71.1	10.0	10.0	10.0	0.9313	Calibration	......
4	71.1	8.3	8.5	8.4	0.9398	0.9395	−0.0004
4	71.1	9.0	9.2	9.1	0.9356	0.9358	+0.0002
4	71.1	9.1	9.3	9.2	0.9349	0.9350	+0.0001
4	71.1	9.2	9.2	9.2	0.9341	0.9350	+0.0009
4	71.1	9.6	9.8	9.7	0.9316	0.9330	+0.0014
5	71.1	8.4	8.4	8.4	0.9853	Calibration	......
5	71.1	12.1	12.3	12.2	0.9666	Calibration	......
5	71.1	15.3	15.5	15.4	0.9585	Calibration	......
5	71.1	8.7	8.9	8.8	0.9819	0.9820	+0.0001
5	71.1	9.0	9.2	9.1	0.9795	0.9800	+0.0005
5	71.1	9.1	9.3	9.2	0.9784	0.9794	+0.0010
5	71.1	10.3	10.4	10.4	0.9725	0.9730	+0.0005
5	71.1	13.4	13.6	13.5	0.9622	0.9626	+0.0004

Thanks are due W. E. Garris, Jr., for assistance in the laboratory determinations and in assembly of equipment; and to S. F. Crynes, pathologist at the City Hospital, Springfield, Ohio, for drawing the author's attention to the method and its possibilities in other than clinical determinations.

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Determination of the Drying Rates of Thin Films

GEORGE RIEGER[1] AND C. S. GROVE, JR.[2]
University of Minnesota, Minneapolis, Minn.

An apparatus, which can easily be constructed from equipment available in any laboratory, has been devised for measuring the drying rates of thin films. This apparatus and technique have been applied to a study of thin nitrocellulose films, the maximum dry weight of which was about 0.02 gram; the area was about 13 sq. cm. (2 square inches); the total solvent content was about 300 mg.; and the drying time was about 20 minutes. The drying rates of these selected films have been calculated and the results presented in graphs. The suggested apparatus and technique have been shown to give satisfactory and reproducible results.

IN THE past few years there has been a revival of interest in the evaporation rates of solvents and in the determination of these evaporation rates. Most of this work has been done on pure solvents, and there have been very nearly as many different types of apparatus employed as there have been investigators. Each new development has been in a sense a refinement of older methods in an attempt to obtain an easier operation and a greater reproducibility of results (*1, 5, 6, 8, 10, 11, 12*).

From an over-all viewpoint it has been the endeavor of this investigation to devise an apparatus that will minimize the effects of any local operating conditions and give consistent results. Although these results may not quantitatively be comparable to results obtained on other apparatus, at least they will be relative.

In the case of a pure solvent, the more accurate evaporation measurements show that a plot of the per cent solvent evaporated *vs.* time is a straight line; this means that a pure solvent has a constant evaporation rate. If one or more solvents are introduced into the original solvent and evaporation measurements are made, then the plot of the per cent volatiles evaporated is no longer a straight line. This means that the solution containing two or more solvents does not have a constant evaporation rate.

If instead of another solvent or other solvents, a nonvolatile component be added to the original solvent, it has been shown that the resulting solution again exhibits no constancy of evaporation or drying rate. Bogin and Wampner (*3*), Stewart and Dorsch (*9*), and Durrans and Davidson (*4*) have done much work on the drying rates of solutions of nonvolatiles in volatile solvents. Their published reports indicate that the presence of nonvolatile materials affects the drying rate of a solution and that this rate falls off as the solvent evaporates, finally approaching zero as the resulting mass nears dryness.

The determination of the drying rates of such solutions means the employment of some apparatus that will enable weight readings to be taken at various intervals of time during the drying process. Durrans and Davidson placed a quantity of their solution (nitrocellulose in a suitable solvent) in a shallow dish and passed air of a constant temperature over it. The sample was large enough and the amount evaporated in each time interval of sufficient magnitude, so that any evaporation occurring during the time of weighing probably introduced very little error.

However, the use of a large sample of any appreciable depth means that an actual thin film as ordinarily dealt with in the application of a protective coating is not simulated. Information on the drying rates of any sort of film-forming solutions, it seems, should be obtained when the solution is in the form of a thin film.

The determination of the drying rate of a thin film, however, brings forth difficulties not ordinarily encountered when larger and deeper volumes of solutions are considered. For example, the supporting base or tare on which the film is cast generally constitutes the major portion of the total weight of the whole system. Therefore, a very sensitive weighing de-

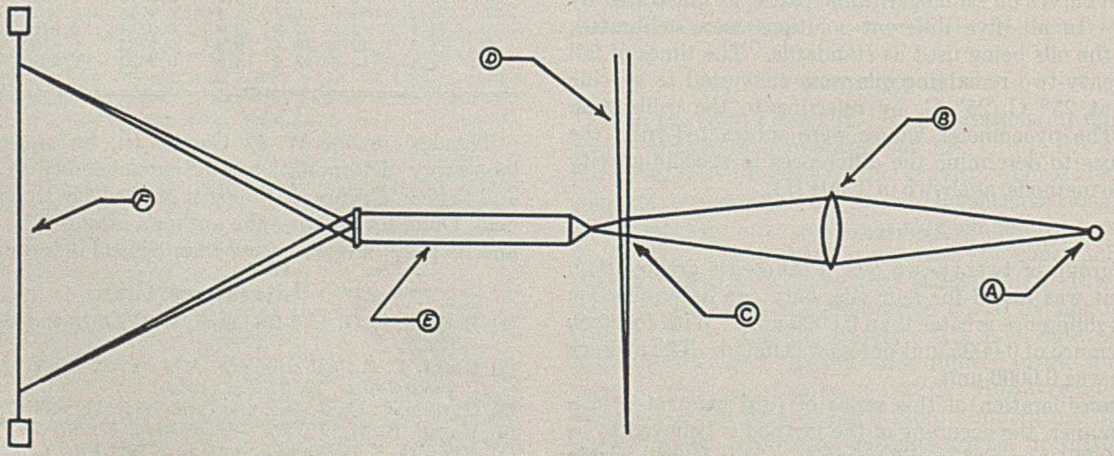

FIGURE 1. OPTICAL SYSTEM

A. Light source
B. Condenser lens
C. Pointer scale
D. Pointer
E. Balance lens
F. Projection screen

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[1] Present address, Ethyl Gasoline Corporation, Baton Rouge, La.

[2] Present address, E. I. du Pont de Nemours & Company, Buffalo, N. Y.

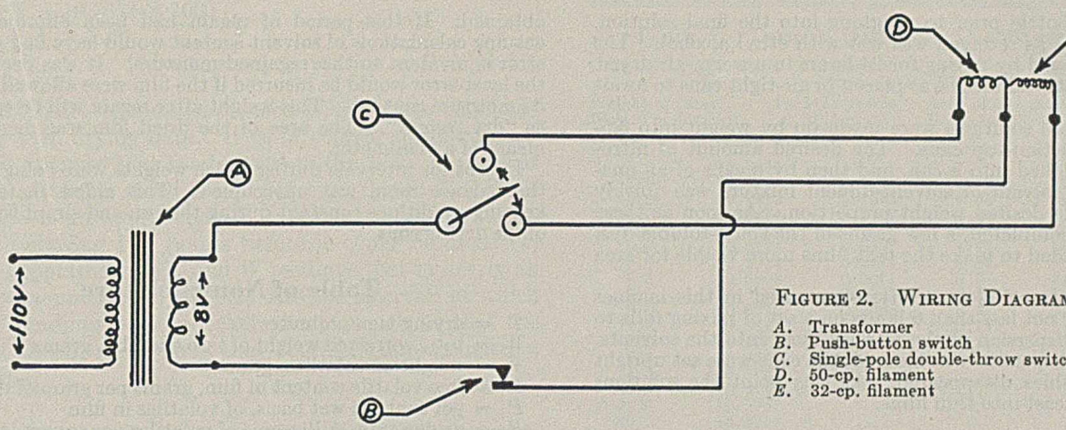


Figure 2. Wiring Diagram

A. Transformer
B. Push-button switch
C. Single-pole double-throw switch
D. 50-cp. filament
E. 32-cp. filament

vice must be used to detect small changes in the weight of the film.

Apparatus

The requirement of sensitivity suggested the use of some standard analytical balance. However, using a chainomatic type of analytical balance, it was found that with very thin films which weighed but a few milligrams and contained fast-evaporating solvents, the balance operator could not keep up with the weight changes with any degree of accuracy. In an attempt to overcome this operational difficulty, the following apparatus was devised for determining the drying rates of thin films.

A Christian Becker (Type 508-A) air-damped analytical balance was used. The distinguishing feature about this balance, which makes it or one similar to it particularly adaptable to a study of the drying rates of thin films, is the scale attached to the pointer. This scale, similar to a microscopic stage micrometer, is ordinarily read by means of a low-power microscope attached to the body of the balance case. It is graduated in milligrams up to 100 mg. on each side of the zero mark. Each milligram is divided into two parts, so that it is possible to estimate to 0.1 mg. weighing with the same accuracy that a rider or chain can be read on the usual type of analytical balance.

The beam is air-damped, which under normal operating conditions prevents overshooting and provides a smooth response to weight changes in the pans. It is possible to read this balance over the range of a 200-mg. change in weight without changing the weights on the pan. The hairline used in conjunction with the pointer scale is an integral part of the eyepiece of the microscope attachment.

Since, in general, it is fatiguing to peer constantly through such a microscope, the objective lens was adjusted so that the scale could be projected onto a screen. In order to project the pointer scale it was necessary to illuminate it with a small concentrated beam of light. The light source employed was a double-filament automobile headlamp bulb having a 32- and a 50-candlepower filament. The 50-candlepower filament was used during operation, while the 32-candlepower filament was kept wired for use in case of failure of the stronger filament. The lens system and wiring diagram are shown in Figures 1 and 2.

The screen was mounted on one edge of the table that supported the balance and was so constructed that it could be swung to one side of the balance while weights were being changed inside the case. The back glass pane of the balance case was removable. This pane was raised slightly and underneath it was fitted a board which held in place a length of rubber tubing connected to an aspirator. Thus the air in the balance was gently exhausted at all times, but not rapidly enough to set up any stray air currents that would disturb the pans. This exhaust system was probably not necessary, since the loss of weight of any sample, which represented the weight of volatiles evaporated into the balance case, was never over 300 mg. This weight, if not removed during the run, would have exerted a negligible vapor pressure compared to that exerted by the solvent in the drying film. Figure 3 is a photograph of the complete assembly.

Besides facilitating reading of the pointer scale, the screen is also useful if the balance is kept in a constant-temperature room. In such a case, a small window may be put in the door of the room, and by placing the push-button switch shown in Figure 2 outside the door, readings may be taken without entering the room. The use of the push-button switch makes it unnecessary for the light to be on except when readings are being taken. Within limits, the scale as projected on the screen may be enlarged to any degree. It is, of course, projected upside down; however, in very little time the operator can become used to reading the inverted scale.

Experimental Procedure

A discussion of the experimental procedure followed during the investigation of some selected nitrocellulose solutions is probably the simplest manner in which to present the technique developed for use with the apparatus just described.

Solvent or solvent-diluent mixtures were made up at 25° C. by use of a 100-ml. buret. The desired portion of one component was thoroughly mixed with the other component and stored in a

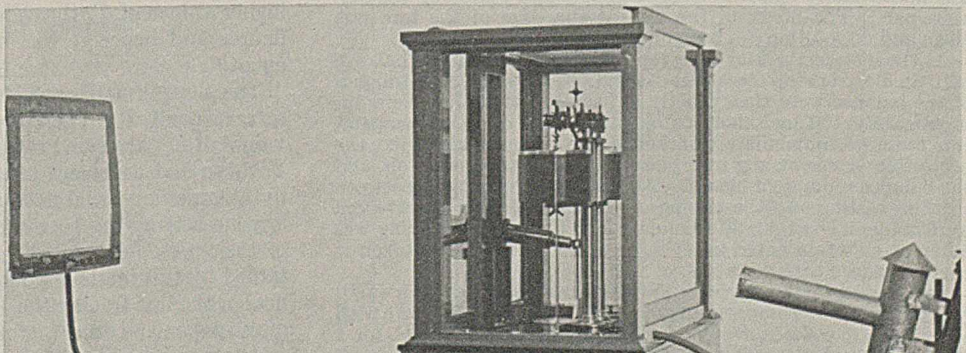


Figure 3. Complete Assembly

stoppered glass bottle prior to weighing into the final solution. The nitrocellulose as received was wet with ethyl alcohol. The alcohol was removed by drying for 24 hours in a warm-air dryer. When dry, the nitrocellulose was placed in air-tight cans to await final formulation.

All nitrocellulose solutions were made up by weight into 0.5-pint standard friction-top cans. The desired amount of nitrocellulose was weighed into a can, and then by means of an analytical pipet the solvent or solvent-diluent mixture was quickly added to give the desired weight proportion. As soon as these operations were completed, a few grains of the spirit-soluble dye, Sudan I, were added to make the cast films more visible for area measurements.

The cans of nitrocellulose solutions prepared in this manner were tumbled for not less than 6 hours on a set of mixing rolls to allow complete dispersion of the nitrocellulose into the solvents. When complete dispersion was assured, the cans were set upright until all air bubbles disappeared. At this point the solutions were ready to be cast into thin films.

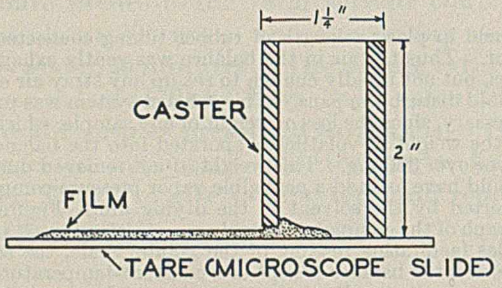


Figure 4. Film Caster

Standard 50- by 70-mm. glass microscope slides were used as supporting bases or tares on which the films were cast. The film caster was made from a 5-cm. (2-inch) length of 3.1-cm. (1.25-inch) thick-walled brass tubing. One end was carefully machined, and a 2.5-cm. (1-inch) casting channel was milled out to a depth of 0.5 mm. (0.02 inch). A schematic drawing of this caster in operation is shown in Figure 4.

The series of operations performed during a drying run may be outlined as follows:

A glass slide or tare was numbered and cleaned and the tare weight obtained. The tare was placed on a clean piece of paper adjacent to the balance, and the film caster was placed on the tare. By use of a short piece of glass tubing, a few milliliters of the solution were placed on the tare area inside the walls of the caster. The caster was immediately drawn over the surface of the tare, excess solution was thrown on the paper, and the tare was immediately removed from the paper and placed on the balance pan. The break in the film at the edge of the tare was clean and no solution ran back on the underside of the tare.

At the instant the film was prepared and placed on the balance pan, an electric stop clock was started. The weights on the pan of the balance were then rapidly adjusted so that they were approximately 100 mg. short of balance. The constant-temperature room was immediately darkened, the balance case closed, the projection screen swung into place, the aspirator turned on, and the balance room door closed. All the above operations between the film casting and the closing of the door of the balance room were made in less than 30 seconds. The first weight reading was taken at a certain noted time; subsequent readings were taken at equally spaced time intervals.

At the end of the drying run, which was marked by a small weight loss over a comparatively long period of time, the tare with the film on it was removed and placed in an oven at 40° C. for 1 hour. Then the sample was allowed to sit in the balance room overnight; after this interval, the final or "dry" weight was determined. This temperature of 40° C. was arbitrarily chosen; the only restriction was that it had to be low enough to prevent decomposition of the film. This had been determined previously by a series of drying tests on a given sample.

It was found that films subjected to this post-drying treatment always lost weight in the oven, and that a portion was regained upon exposure to the atmosphere. It was concluded from this that not only residual solvent but also some moisture was removed in the oven. Upon exposure to the air, this moisture was apparently regained until a constant or equilibrium weight was obtained. If this period of regain had been eliminated, any ensuing calculations of solvent content would have had a positive error equivalent to this regained moisture. It was decided that the least error would be incurred if the film were allowed to regain its moisture content. This weight after regain will be referred to as "dry weight". The area of the dried film was measured by means of a planimeter.

Except for intervals during which weights were being changed, the balance room was unoccupied. This aided materially in keeping conditions constant during the run and simplified control of the drying runs.

Table of Nomenclature

T = drying time, minutes
W = total corrected weight of tare and film, grams
V = weight of volatiles, grams
F = free volatile content of film, grams per gram of dry film
P = per cent, on wet basis, of volatiles in film
R = drying rate, milligrams of volatiles per square inch of dry film per minute

Treatment of Data

After a run was completed, the following original data were at hand: the tare weight of the glass slide; a series of time, T, and weight, W, readings; the final or "dry" weight of the dried film; and the dry film area. The values of weight listed in the tables are the corrected weights, W, at any time, T. These weights are the total weights of the film and tare. By subtracting the tare weight from the final or dry weight, the weight of the dry film is obtained. The weight of the dry film subtracted from any value of W, at time T, gives the weight of the volatiles, V, present in the film at time T.

The weights of the volatiles, V, at any value of T, divided by the weight of the dry film give the grams of solvent per gram of dry film, F, at time T. F is in reality the per cent volatiles in the film on the dry basis divided by 100. It was also desired to obtain the per cent solvent, P, in the film on the wet basis. Such values of P were calculated in two ways:

$$P = 100 \times \frac{F}{1 + F}$$

or,

$$P = 100 \times \frac{V}{V + \text{weight of dry film}}$$

Which of the above equations to use was determined by the accuracy of the values of F. If F were expressed to three or four figures, the first equation was used. However, at higher values of T, the values of F were rounded off to two figures and hence it was more accurate to use the second equation.

The slope of a W *vs.* T curve at any point T is the drying rate at point T. Therefore, one method of calculating the values of R, the drying rate, would have been to draw a W *vs.* T curve and construct tangents at various points. Results by this method could not have been checked very readily by anyone attempting to work with the data later on, because of the "personal element". Then, too, any values of R obtained by this method would have been affected by the thinness of the line tracing the W *vs.* T curve, the accuracy of the graph paper, and other factors not inherent in the original data.

Another method of calculating R values, and the one which was used, was to take T and W readings at regular intervals. If these intervals were short enough so that the portion of the W *vs.* T curve included between them approximated a straight line, the following calculations would be justifiable:

	T *Min.*	W *Grams*	P *%*	Film Area *Sq. in.*
T_1	1.5	10.8179	97.5	2.17
T_2	2.0	10.8003	96.4	..
T_3	2.5	10.7853	95.7	..

$$R = \frac{10.8179 - 10.7853 \times 1000}{1 \times 2.17} =$$
$$15.0 \text{ mg. per sq. in. per min. at } P = 96.4\%$$

Such an illustrated method of calculation is often employed in dealing with drying data. It is, of course, an approximation which assumes that the tangent to the *W vs. T* curve at T_2 is parallel to the chord drawn between T_1 and T_3. Since this method is an approximation, it was necessary to determine the following two points before it could be used: (1) Does the apparatus give *T* and *W* readings that in nearly all cases lie on a smooth curve? (2) Are the intervals at which *T* and *W* readings may be taken short enough so that the portion of the *W vs. T* curve they represent approximates a straight line?

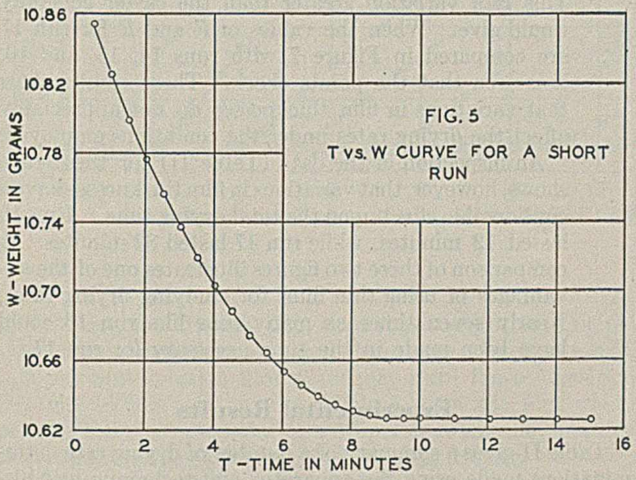


FIG. 5
T vs. W CURVE FOR A SHORT RUN

An inspection of a number of *W vs. T* curves obtained using the apparatus showed these two conditions to be fulfilled. Figure 5 is an example of one of these curves, and represents the data from a run in which the weight and area of the dry film were 15.8 mg. and 13.55 sq. cm. (2.10 square inches), respectively. A consideration of this plot shows that all points lie on a smooth curve, and that approximately straight lines connect these points. Table I presents typical data and calculated results obtained for a drying run on a 5 per cent solution of 20-second nitrocellulose dissolved in ethyl acetate of C. P. grade.

Reproducibility of Results

In his recent book on industrial solvents, Mellan (*7*) lists the following factors as those which influence the rate of evaporation of a solvent from a solution: (1) Temperature of the substance, (2) temperature of the surrounding area, (3) rate of external heat applied, (4) conductivity of heat, (5) specific heat of the substance, (6) latent heat of evaporation, (7) number and type of molecular aggregates, (8) surface tension, (9) presence of dissolved substances, (10) atmospheric pressure, (11) presence of water vapor (humidity), (12) vapor pressure or pressures of the substance or substances under consideration, (13) amount and rate of temperature depression, (14) molecular weight of the substance, (15) method and speed of removal of vapors, (16) depression of vapor pressure, and (17) viscosity.

The factors are, of course, neither equal nor separate in effect, and since the quantitative determination of all is a complex and almost impossible task, it was decided to proceed as follows:

(*a*) Assume some were either constant or negligible; (*b*) maintain others constant; and (*c*) determine the rest quantitatively.

Table I. Typical Data and Calculated Results

(Run 11, 5% solution of 20-second nitrocellulose. Solvent composition, ethyl acetate 100%)

Weight of tare: 10.5473 grams Area of dry film: 3.02 sq. in.
Weight of dry film: 0.0264 gram Room temperature: 23.0° C.

T	*W*	*V*	*F*	*P*	*R*[a]
1.0	10.8847	...	..	..	...
2.0	10.8057	0.2320	8.79	89.7	23.80
3.0	10.7412	0.1675	6.35	86.5	19.60
4.0	10.6874	0.1137	4.30	81.0	16.90
5.0	10.6452	0.0715	2.71	73.0	12.42
6.0	10.6124	0.0387	1.47	59.5	8.90
7.0	10.5914	0.0177	0.67	40.2	5.23
8.0	10.5808	0.0071	0.27	21.2	2.22
9.0	10.5780	0.0043	0.16	14.0	0.60
10.0	10.5772	0.0035	0.13	11.7	0.22
11.0	10.5767	0.0030	0.11	10.2	0.08
12.0	10.5767	...	..	..	...
13.0	10.5764	...	..	..	...
14.0	10.5762	...	..	..	...
15.0	10.5762	...	..	..	...
20.0	10.5757	...	..	..	...
30.0	10.5757	...	..	..	...
Dry	10.5737	...	..	..	...

[a] All values of *R* calculated by 2-minute intervals.

Under (*a*) the following factors can be grouped: (3), (4), (5), (6), (8), (10), (11), (13), (14), and (16). By use of the constant-temperature room and by maintaining the material in the closed cabinet of the balance case, the following may be grouped under (*b*): (1), (2), (12), and (15). By careful formulation of the nitrocellulose solution the following remaining factors fall into group (*c*): (7), (9), and (17).

Of course some of the factors listed in any one group are closely related to factors in the other groups or in the same group; for example, the viscosity (17) of a nitrocellulose solution is a function of the type of nitrocellulose (7) and the amount in solution (9). The vapor pressure of the solution (12) is a function of the temperature of the solution (1), the nature of the solute (7), the amount of solute in solution (9), and the molecular weight of the solute (14).

When one considers all these factors, it is not difficult to understand why such a great deal of effort has been put forth in developing apparatus for the determination of evaporation and drying rates and why results obtained on one apparatus do not agree quantitatively with results obtained on another apparatus. However, it is reasonable to assume that

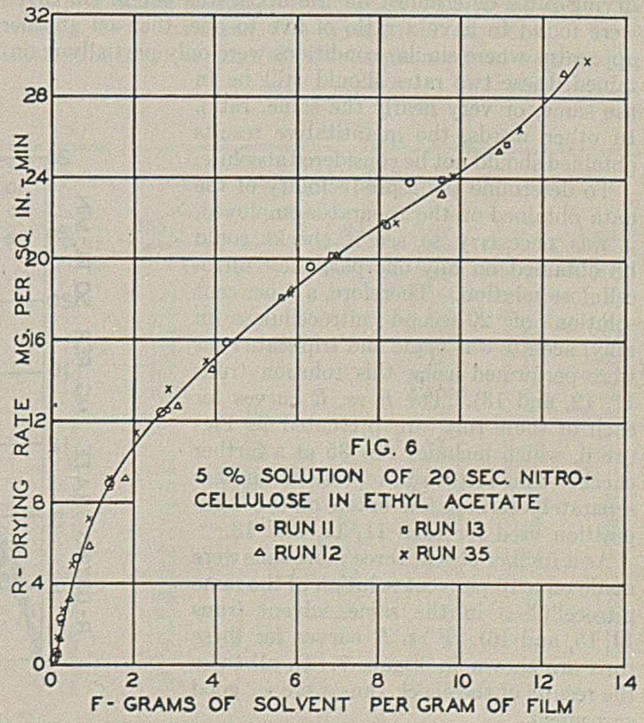


FIG. 6
5 % SOLUTION OF 20 SEC. NITROCELLULOSE IN ETHYL ACETATE

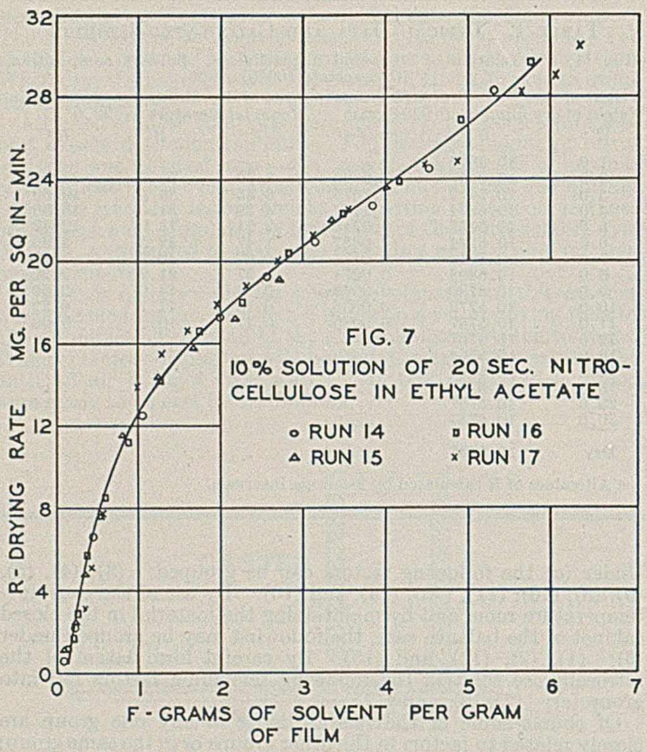


FIG. 7

10% SOLUTION OF 20 SEC. NITROCELLULOSE IN ETHYL ACETATE

results obtained on any one apparatus would have the same interrelation that they would have had had they been determined on another apparatus. This assumption seems to have been borne out to some extent in the data in the literature; hence, the results presented here cannot be compared quantitatively to those obtained by other workers. This means that a drying rate of 15.0 mg. per square inch per minute for a certain solution at a certain per cent solvent concentration could not be reproduced on another apparatus unless all the prevailing conditions and the technique employed were exactly reproduced. However, if two different drying rates determined on the apparatus herein employed were found to have a ratio of five to one, then on another apparatus where similar conditions were only partially maintained, these two rates should still be in the same, or very nearly the same, ratio. In other words, the quantitative results obtained should not be considered absolute.

To determine the reproducibility of the data obtained on the apparatus employed, it was necessary to see if checks could be obtained on any one particular nitrocellulose solution. Therefore, a 5 per cent solution of 20-second nitrocellulose in ethyl acetate was made and triplicate runs were performed using this solution (runs 11, 12, and 13). The *F vs. R* curves for each of these runs are presented in Figure 6, which includes run 35 as a further check. This latter run represents another separately formulated batch of the composition used for runs 11, 12, and 13.

As a further check, three more runs were made on a 10 per cent solution of the same nitrocellulose in the same solvent (runs 14, 15, and 16). *F vs. R* curves for these runs are shown in Figure 7. In all cases the results of the check runs were in good agreement.

In some cases of drying, where diffusion of the volatile component through the drying film controls the rate of evaporation, the thickness of the material affects the rate of drying. The maximum thickness that could be laid down by the caster was 0.5 mm. (0.02 inch), which was the depth of the channel. However, it is generally accepted by users of these film casters that the thickness cast is one-half the channel depth or less. To check the effect of thickness a film was made by literally "piling-on" the same solution as was used for runs 14, 15, and 16. This film was dried and the drying data were plotted as run 17, Figure 7.

From the area and dry film weight, this film was calculated to be 6.04 times as thick as the film in run 15. This is a variation greater than the caster generally would give. When the values of *F* and *R* for run 17 are compared in Figure 7 with runs 14, 15, and 16, it is seen that the points check. These results show that variations in film thicknesses do not appreciably affect the drying rates under the conditions employed.

An inspection of the data (Table II) for these runs shows, however, that variations in film thicknesses have a considerable effect upon the total drying time. Run 16 lasted 12 minutes, while run 17 lasted 82 minutes. A comparison of these two figures illustrates one of the advantages of using thin films for studying drying rates. Nearly seven times as many runs like run 16 could have been made in the time necessary for run 17.

Experimental Results

Table II gives a summary of a number of drying rate determinations made using the apparatus and technique just discussed. These runs are graphically presented in Figures 8 to 12.

A comparison of runs 11, 12, and 13 with runs 14, 15, and 16 indicates that the more concentrated nitrocellulose solutions had the higher drying rates for any given value of *F*. This behavior indicates that the drying rate of a nitrocellulose solution is a function not only of the solvent content of the film after casting, but also of the original solution composition. Such a conclusion is logical, for otherwise, if the drying rate of a solution were a function only of the film's

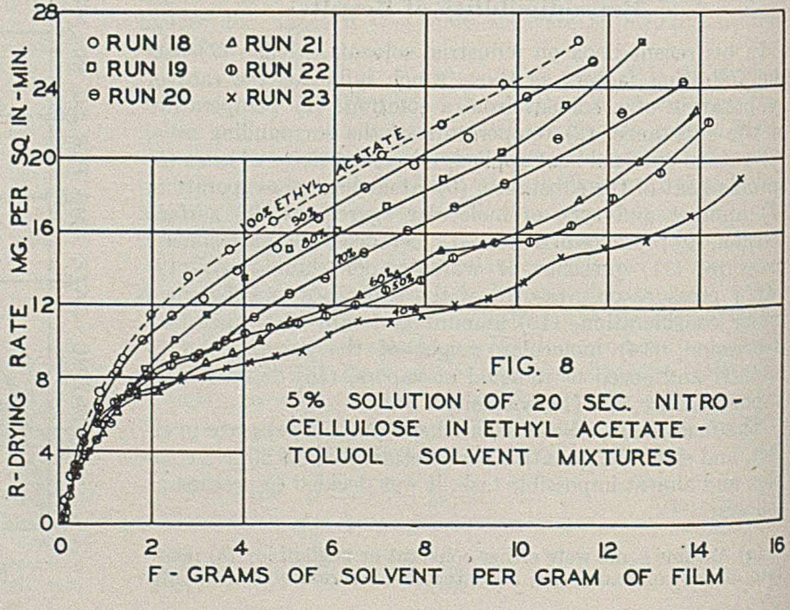
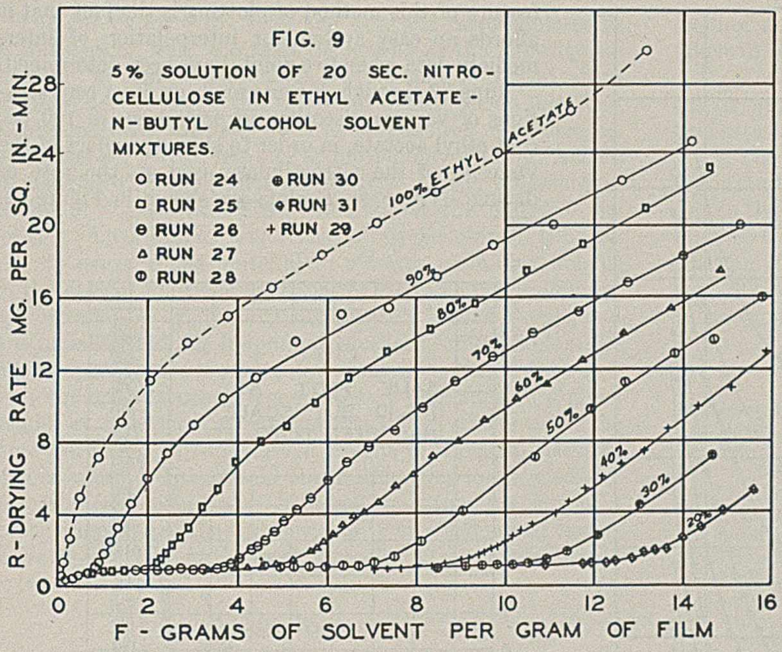


FIG. 8

5% SOLUTION OF 20 SEC. NITROCELLULOSE IN ETHYL ACETATE - TOLUOL SOLVENT MIXTURES



solvent content after casting, then regardless of the original composition all solutions would behave alike. In other words, a 5 per cent solution film would dry until the composition became 10 per cent in nitrocellulose, then the film would assume the characteristics of a 10 per cent solution and dry accordingly. Such a behavior is shown not to exist.

Runs 18 through 23 were made on a 5 per cent solution of 20-second nitrocellulose in solvent mixtures of ethyl acetate and toluene. These runs were made to study the effect upon the drying rate of increasingly greater amounts of nonsolvent or diluent (toluene) in the presence of a solvent (ethyl acetate), and to show the effect of varying two volatiles that had different evaporation rates as determined on the pure solvents. According to Bogin (*2*), ethyl acetate has a rate of 525 compared to *n*-butyl alcohol as a standard of 100, while toluene on the same basis has a rate of 195.

The *F vs. R* curves for each of these runs were plotted and are shown in Figure 8. It is seen that as the composition of the slower evaporating liquid was increased, the rates of drying decreased. The curve for 100 per cent ethyl acetate (run 35) is also shown in Figure 8 for comparison.

The most important feature of this family of curves is the irregularity shown by the lower members. This irregularity is attributed to the fact that these samples blushed to a marked degree. Both the amount of blushing and the irregularity of the curves increased with increasing toluene content. The irregularity of the curves for the blushed samples indicates that when blushing occurs, drying equilibrium is upset in some manner. One explanation would be that the resistance to drying is decreased by the precipitation which causes the blushing. If such were the case, the drying rate would increase momentarily, and the rate would begin falling again until another area blushed and again the rate would increase momentarily. However, as the rate increased owing to blushing, it would at the same time tend to decrease owing to the drop in the solvent content (a decrease in *F*). The combination of these effects would tend to flatten out the drying rate curves at the points of blushing. Examination of the curves (Figure 8) shows no flattening; so this explanation is apparently not valid.

The irregularity in the drying curves of the blushed samples might, however, be explained from another viewpoint which is more acceptable. It may be reasoned that as soon as the film blushed, the blushed area became momentarily useless as an area from which drying could occur. If this were true, the area immediately available for drying would decrease as blushing continued. However, in the calculations of the rate values, the area was taken as the entire area of the dried film, blushed or clear. This use of an area larger than was really available for drying would tend to give rates too low. This means that the *R vs. F* curves would drop momentarily at the points of blushing. By inspection of the curves of Figure 8 this is seen to be the case.

Runs 24 through 31 were made on a 5 per cent solution of 20-second nitrocellulose in solvent mixtures of ethyl acetate and *n*-butyl alcohol. The *R vs. F* curves for this series are shown in Figure 9. The drying rate curve for run 35 is included for comparison.

These runs were made to show the effect of increasingly greater amounts of a very slow-evaporating cosolvent in the presence of a very fast-evaporating solvent. The evaporation rate for *n*-butyl alcohol (*2*), on the basis of *n*-butyl acetate = 100, is 45, as compared to 525 for ethyl acetate. The solvent mixtures for this series consist of two solvents as contrasted to mixtures of a solvent and a nonsolvent (diluent) used in the ethyl acetate–toluene series just discussed.

By inspection of Figure 9 it is seen that as the butyl alcohol content increased, the drying rates decreased. It is interesting to note that all the curves seem to approach a

Table II. Summary of Drying Runs

Run No.	Nitrocellulose Viscosity	Solution Concentration	Solvent Composition Ethyl Acetate	Toluene	Butyl Alcohol	Wt. of Dry Film	Area of Dry Film	Length of Run
	Sec.	Wt. %	% by Volume			Gram	Sq. in.	Min.
11	20	5	100	..	..	0.0264	3.02	11
12	20	5	100	..	..	0.0242	2.85	14
13	20	5	100	..	..	0.0232	2.87	14
14	20	10	100	..	..	0.0420	2.56	17
15	20	10	100	..	..	0.0446	2.68	15
16	20	10	100	..	..	0.0457	2.75	12
17	20	10	100	..	..	0.1004	1.00	82
18	20	5	90	10	..	0.0231	2.67	15
19	20	5	80	20	..	0.0158	2.10	15
20	20	5	70	30	..	0.0212	2.58	15
21	20	5	60	40	..	0.0169	2.16	16
22	20	5	50	50	..	0.0199	2.15	19
23	20	5	40	60	..	0.0187	2.27	17
24	20	5	90	..	10	0.0164	2.26	28
25	20	5	80	..	20	0.0157	2.16	40
26	20	5	70	..	30	0.0179	2.47	60
27	20	5	60	..	40	0.0140	1.92	60
28	20	5	50	..	50	0.0096	1.47	85
29	20	5	40	..	60	0.0139	1.91	100
30	20	5	30	..	70	0.0136	1.98	114
31	20	5	20	..	80	0.0164	2.29	130
32	0.25	5	100	..	..	0.0165	3.16	11
33	0.5	5	100	..	..	0.0173	2.71	13
34	4	5	100	..	..	0.0158	2.13	13
35	20	5	100	..	..	0.0138	1.74	11
36	70	5	100	..	..	0.0171	1.99	11

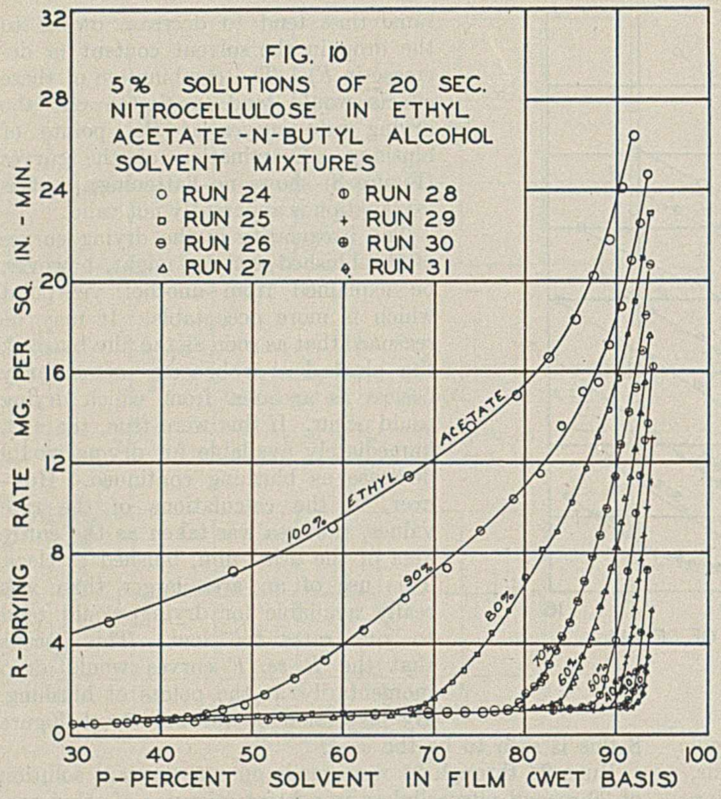


FIG. 10
5% SOLUTIONS OF 20 SEC. NITROCELLULOSE IN ETHYL ACETATE-N-BUTYL ALCOHOL SOLVENT MIXTURES

limiting value of R at about 0.8 mg. per square inch per minute. This leveling off of the drying curves in each case seems to indicate that there was a retention of solvent and that probably the solvent retained was the more slowly evaporating one—i. e., butyl alcohol. The upper portion of the curves, which are all similar, probably is the portion where the composition of the volatiles leaving the films is high in ethyl acetate.

Inspection of the R *vs.* F plots in Figure 9 might be misleading—for instance, in the case of run 24, it might be assumed that at a value of $R = 1$, the film was for all practical purposes dry. However, the same run plotted as P *vs* R shows that at a value of $R = 1$ the film contained very nearly 50 per cent solvent. Figure 10 is a plot of runs 24 through 31 on the basis of P. This gives a more comprehensive picture of the change in solvent content as the films dry.

An inspection of Figure 10 brought forth the interesting possibility that, since the curves were all similar excluding the lower portions, they might all be plotted as straight lines by the selection of proper coordinates. Figure 11 shows the result of such a construction and indicates well that the curves of Figure 10 were similar above the flattened regions.

Mathematically, the curves of Figure 11 state that:

$$f(R) = a + bP$$

where a and b are constants different for each line. This means that some function of the drying rate, R, is a straight-line function of P, the per cent concentration of solvent in the film. This series of curves also shows that:

$$f(R) = a_1 + b_1P,\ f(R) = a_2 + b_2P, \text{ etc.}$$

This indicates that the mechanism of drying for each run is probably the same. Another important feature of this method of plotting is the fact that it affords an easy system for interpolation of intermediate data when two points have been determined.

Runs 32 through 36 were made on 5 per cent solutions of various viscosity nitrocelluloses in 100 per cent ethyl acetate, in order to show the effect of the viscosity of the nitrocellulose used on the rate of drying. The F *vs.* R plots are shown in Figure 12.

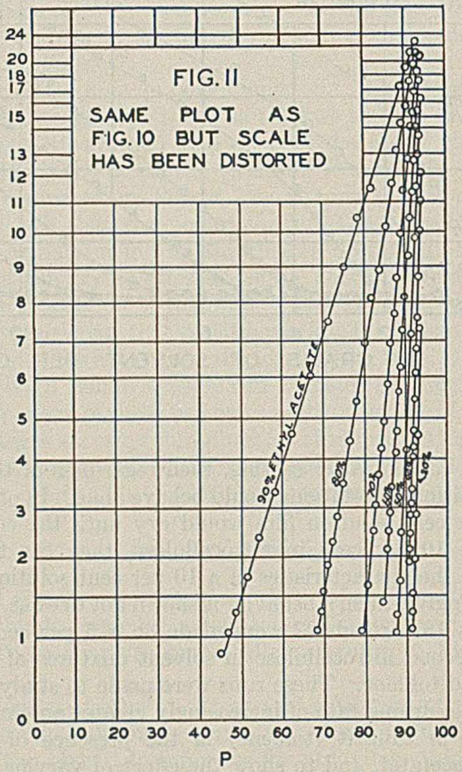


FIG. 11
SAME PLOT AS FIG. 10 BUT SCALE HAS BEEN DISTORTED

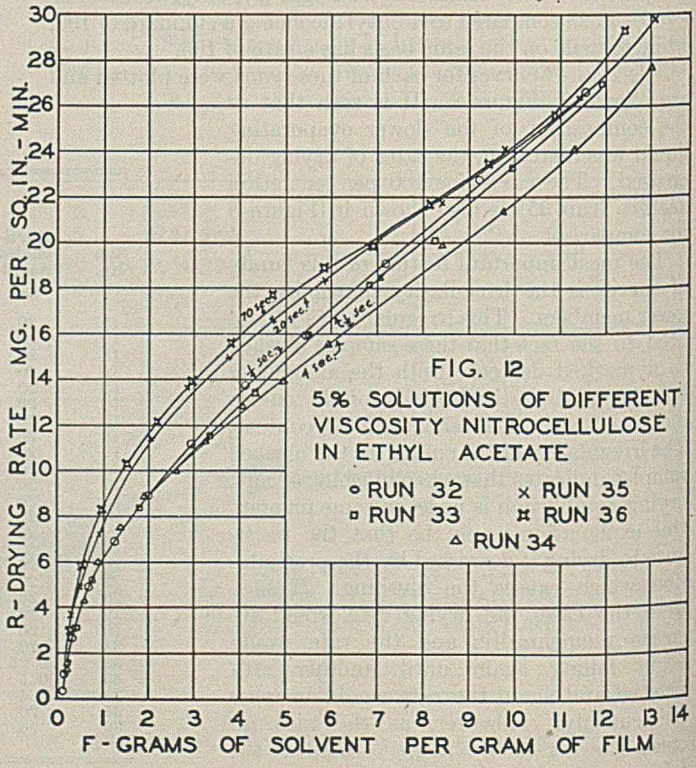


FIG. 12
5% SOLUTIONS OF DIFFERENT VISCOSITY NITROCELLULOSE IN ETHYL ACETATE

The curves for 0.25-, 0.5-, and 4-second nitrocelluloses lie close together, with the rates decreasing as the viscosity increases. However, the curves for 20- and 70-second nitrocellulose do not follow this order but appear above the aforementioned three curves. It is likely that the difference between the curves in Figure 12 is due not only to the differences in viscosities of the solutions, but also to the difference in nature of the nitrocelluloses used to get the different viscosities. To obtain a lower viscosity nitrocellulose, it is necessary to degrade the material to a lower molecular weight. In the case of solutions of the lower viscosity nitrocelluloses, the degradation has been carried out to a greater extent, and it is possible that the individual micelles of nitrocellulose begin to approach true molecular dimensions—i. e., they lose their colloidal nature to some extent. Therefore, in a given weight of a lower viscosity nitrocellulose, there would be more particles than in a given weight of a higher viscosity nitrocellulose. This would mean that the lower viscosity nitrocelluloses would tend to lower the vapor pressure of a solution more than the higher viscosity nitrocelluloses; hence, the rates of drying of the lower viscosity nitrocelluloses would be lower.

Conclusions

1. The apparatus that has been described can very easily be assembled from standard laboratory equipment.
2. The apparatus is particularly adaptable to the investigation of very rapidly drying solutions, and affords a means of studying their behavior when cast into thin films. The operation is simple, direct, and rapid, and the quantities involved are easily handled.
3. In instances where more slowly drying films are studied, the apparatus and technique described afford a means of making numerous drying runs in the time it has formerly taken to make one.
4. The apparatus has, by its proved operation in numerous drying rate determinations, demonstrated the ability to give satisfactorily reproducible results.
5. The apparatus and technique are applicable not only to the study of the drying rates of nitrocellulose solutions, but also to the study of the drying rates of any type of thin film, whether the drying process be purely evaporative, or a combination of evaporation and chemical reaction.
6. The drying rate of a nitrocellulose solution is a function of the type (viscosity) of nitrocellulose in solution.

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Presented by George Rieger as a partial fulfillment of the requirements for the M.S. degree in chemical engineering at the University of Minnesota, 1941.

Construction and Operation of a Polarograph

N. HOWELL FURMAN, CLARK E. BRICKER, AND E. BRUCE WHITESELL[1]
Princeton University, Princeton, N. J.

This paper presents the experience of the authors with a polarograph of conventional design constructed locally from materials normally available in this country. The details of the construction of the instrument and of a modified electrode assembly are given briefly with illustrative material. Some notes on operation are included, together with typical records taken with the instrument.

THE Nejedly model of the Heyrovský-Shitaka polarograph (*1*) has certain advantages in spite of the inconvenience of taking records that have to be developed photographically. Among these are the ability to duplicate the type of record most prevalent in polarographic literature, ability to check and test the various sources of error in the measurements, flexibility of operation, ability to take records with increase or decrease of applied voltage, etc. The instrument also lends itself, in the form here described, to the plotting of curves manually, either roughly during the continual variation of applied voltage, or more accurately by intermittent operation.

At the time when the authors' project was initiated it was not possible to secure an instrument of the standard type with twenty turns of the bridge wire. Owing to the increasing interest in this field of research it was thought that others might profit from the experience here described.

A number of preliminary sketches were prepared and a general statement descriptive of the features desired was drawn up. The determining factors in the design are the amount of resistance desired in the potentiometer wire and the size of the photographic paper. The specifications were for a resistance higher than average—namely, about 30 ohms—and for a paper of rather large size, the final choice being 6 × 9 inches. On the basis of sketches with no exact dimensions, and after a brief inspection of an instrument of the Nejedly type through the courtesy of O. H. Müller at the Cornell University Medical School, New York, W. K. Grove (machinist, Frick Chemical Laboratory) was able to construct, from materials then readily obtainable, an instrument that has given excellent performance over a period of a year. Valuable ideas regarding materials and design were given by H. Boyd (assistant curator, Frick Chemical Laboratory), and numerous original improvements in details of design were made by Mr. Grove as the work progressed.

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[1] Present address, 232 Prospect St., East Orange, N. J.

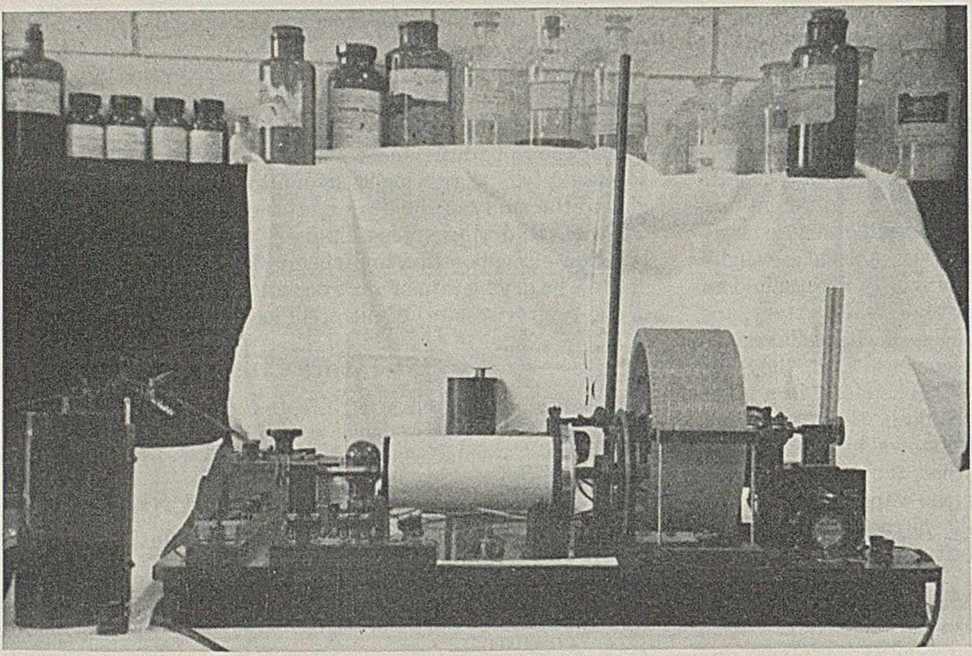

FIGURE 1. GENERAL APPEARANCE OF INSTRUMENT

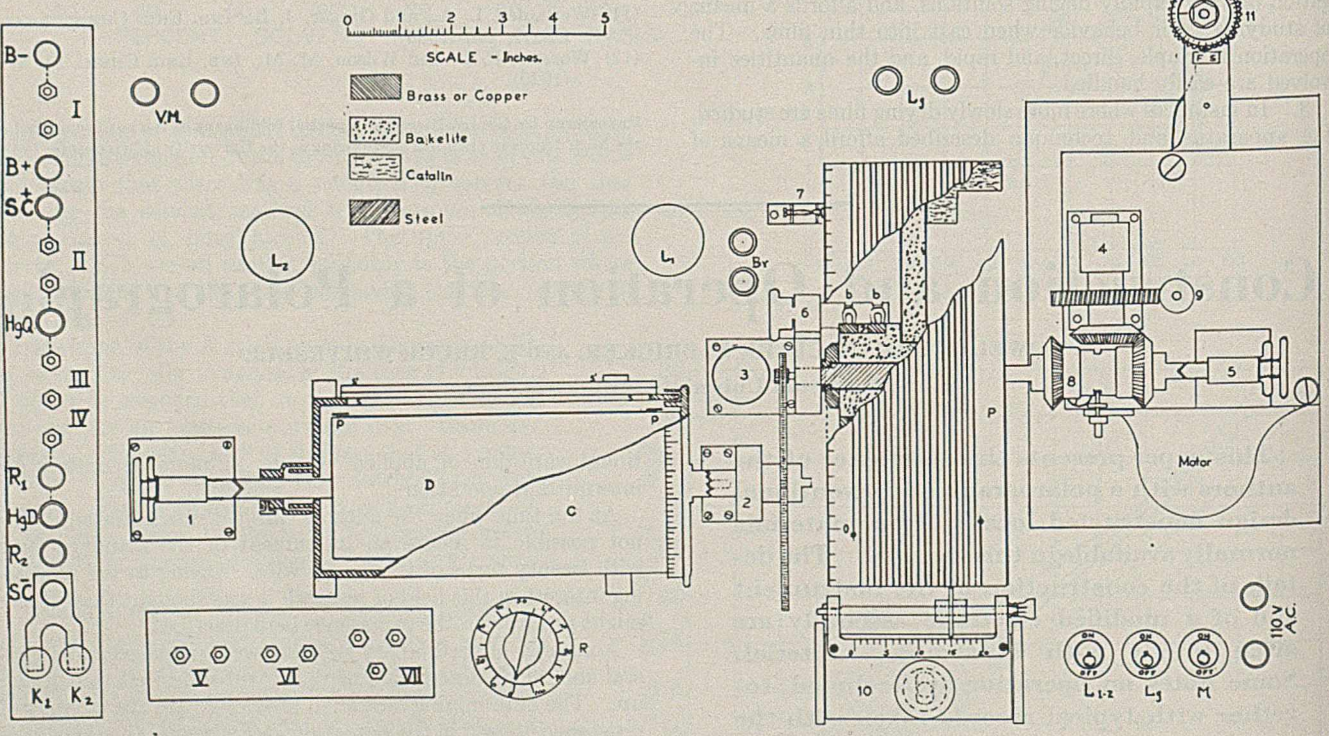

FIGURE 2. PLAN OF POLAROGRAPH

Electrical connections:
- $B-$, $B+$. To 4- or 6-volt cell
- SC^+, SC^-. Standard cell
- *HgQ*, *HgD*. To quiet and dropping mercury electrodes
- R_1, R_2. To shunt and galvanometer
- K_1, K_2. Tapping keys
- *R*. A 100-ohm rheostat
- I. Plug connection to close battery circuit
- II. Connects quiet mercury electrode to battery
- III. For anode potential measurement
- IV. For setting potential against standard cell
- V, VI. To short 16-ohm resistances ahead of or after potentiometer wire
- VII. Reversing device to make dropping electrode either anode or cathode
- *Br*. Binding posts to brushes
- L_1, L_2. Ordinate lamps
- L_g. Posts to galvanometer lamp
- *V. M.* Binding posts to voltmeter
- *M*. Switch for motor
- Lamp switches are near motor switch, lower right.

Mechanical features:
- 1, 2, 3, 4, 5. Bearings for camera drum, potentiometer wheel, and driving gears
- 6. Holder of Catalin for brushes *b*, *b*
- 7. Contact device for ordinate lamps, L_1, L_2
- 8. Reversing gears
- 9. Worm drive
- 10. Support for potentiometer contact wheel
- 11. Speed regulator for motor
- *C*. Camera
- *D*. Drum for photographic paper
- *P*. Potentiometer drum
- *b*, *b*. Brushes, multiple bearing surfaces
- *p*, *p*. Pins to hold thin metal strip that fastens bromide paper
- *s*, *s*. Slit of camera
- *s'*, *s'*. Adjustable jaws of slit

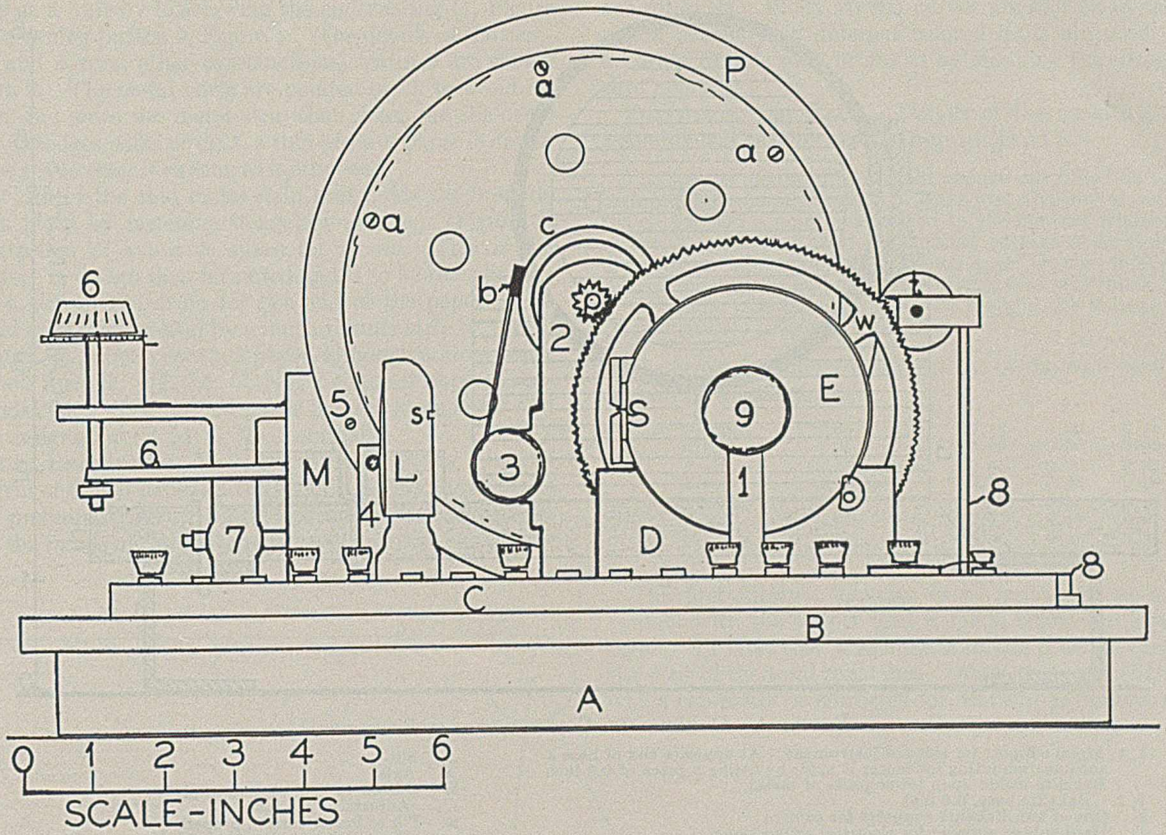

Figure 3. Elevation of Instrument

A. Base formed of Bakelite strips at end and of iron pieces at sides
B. Bakelite floor
C. Hard-rubber strip with binding posts, etc.
D. Bakelite camera support
E. Camera
L. Ordinate lamp and housing
M. Motor housing
P. Potentiometer drum
S. Camera slit
a, *a*, *a*. Screws to hold Catalin drum fast to Bakelite disk
b. Brush with multiple contact
c. Copper commutator ring
s. Slit in housing of ordintae lamp
t. Contact wheel to potentiometer wire
w. Spur gear to drive camera drum
1. Camera bearing
2. Potentiometer bearing
3. Brush holder
4. Contact for ordinate lamps
5. Screw that operates 4
6, 6. Speed regulator
7. Bearing of motor
8, 8. Base of support for contact wheel

Plan and Materials

The general appearance of the instrument is indicated in Figure 1. The finish of the instrument is, in the main, black. The drum, brush holder, and other Catalin parts are red. The brass gears are unpainted, but the remaining exposed metal is painted. The camera is at left; paper on drum as for manual recording.

The plan of the instrument, drawn to scale, is shown in Figure 2. The more or less standardized relative arrangement of parts has been followed, but the choice of a high resistance and a large record has made the instrument rather larger than others of similar type (26.75 × 16 inches maximum height 10.25 inches).

The parts, other than small items of hardware and odds and ends of rod of brass and steel that are apt to be found in a well-equipped machine shop, were as follows:

Bearings, thrust type, to be used at points 2 and 3, Figure 2.

Gears, miter [3 for reversing gear (8, Figure 2) Boston, Mass., Gear Works].

Gear, brass spur wheel, 48 pitch, 0.125-inch face, 5 inches, with 240 teeth to turn camera drum (Philadelphia Gear Works).

Lamps for ordinates, 7-watt, with Bakelite housings (F. W. Woolworth & Co.).

Pinion rod, 12 teeth, for potentiometer axle (near 3, Figure 2, Philadelphia Gear Works).

Motor, Majestic, phonograph type, 20 watts (0.2 ampere at 100 to 110 volts) with speed regulator.

The following materials were especially purchased and needed to be cut, machined, or mounted:

Bakelite for base and substage motor mount (16 × 36 inches, 0.5 inch thick).

Bakelite rod, 2 inches round, 3 inches long, for potentiometer axle.

Brass rod, 4 inches round, 0.75 inch long, to form end of camera drum with scale.

Brass tube, 3.5 inches round, 0.125-inch wall, 7.25 inches long, for camera.

Brass tube, 2.75 inches round, 3 inch wall, 7 inches long, for camera drum.

Catalin cylinder 4 inches long, 1.25-inch wall, 8.25-inch diameter, for potentiometer.

Catalin rod, 2 inches round, 0.375 inch long, for commutator spacer.

Catalin rod, 0.563-inch diameter, 1.375 inches long, for brush holder.

Copper tubing, 2 inch diamter, 1.88-inch wall, for commutator rings.

Manganin wire, No. 24 B. & S. gage, 45 feet, for potentiometer (33 ohms).

Hard rubber for binding posts, plug sockets, and tapping key mounting, 2 × 24 × 0.5 inch.

Steel drill rod, 0.5 inch, 20 inches long for axles.

The elevation of the instrument from the camera end is shown in Figure 3.

The Camera. The camera and drum and a light trap attached to the axle at the left of the camera (Figure 2) are de-

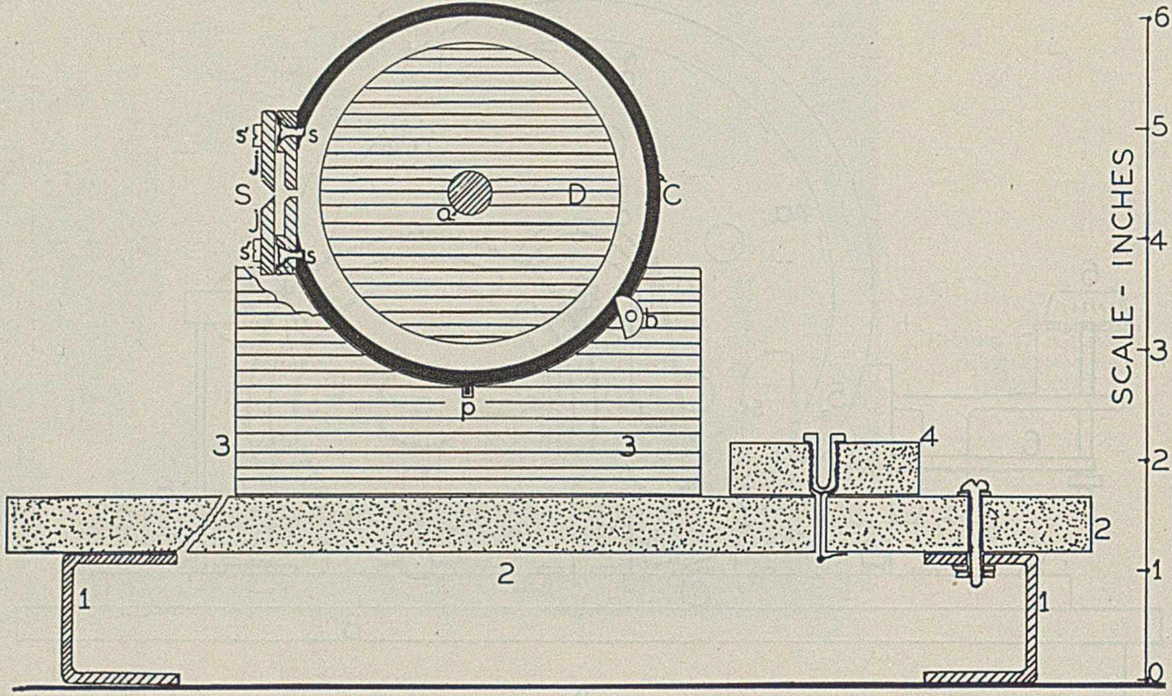

FIGURE 4. CAMERA AND CONSTRUCTIONAL FEATURES

1, 1. Metal support for sides of instrument. At opposite end of base a substage mounting for motor is made by fitting a piece of 0.5-inch Bakelite inside upon lower parts of metal
2, 2. Bakelite base, 0.5 inch
3. One of two Bakelite supports for camera
4. Hard-rubber support for electrical connections
C. Camera
D. Camera drum
S. Slit
a. Axle
b. Button to hold camera in place
j, j. Adjustable slit jaws
p. Pin to locate camera properly
s, s. Two of eight screws to hold slit to camera
s′, s′. Two of four screws for adjusting jaws of slit

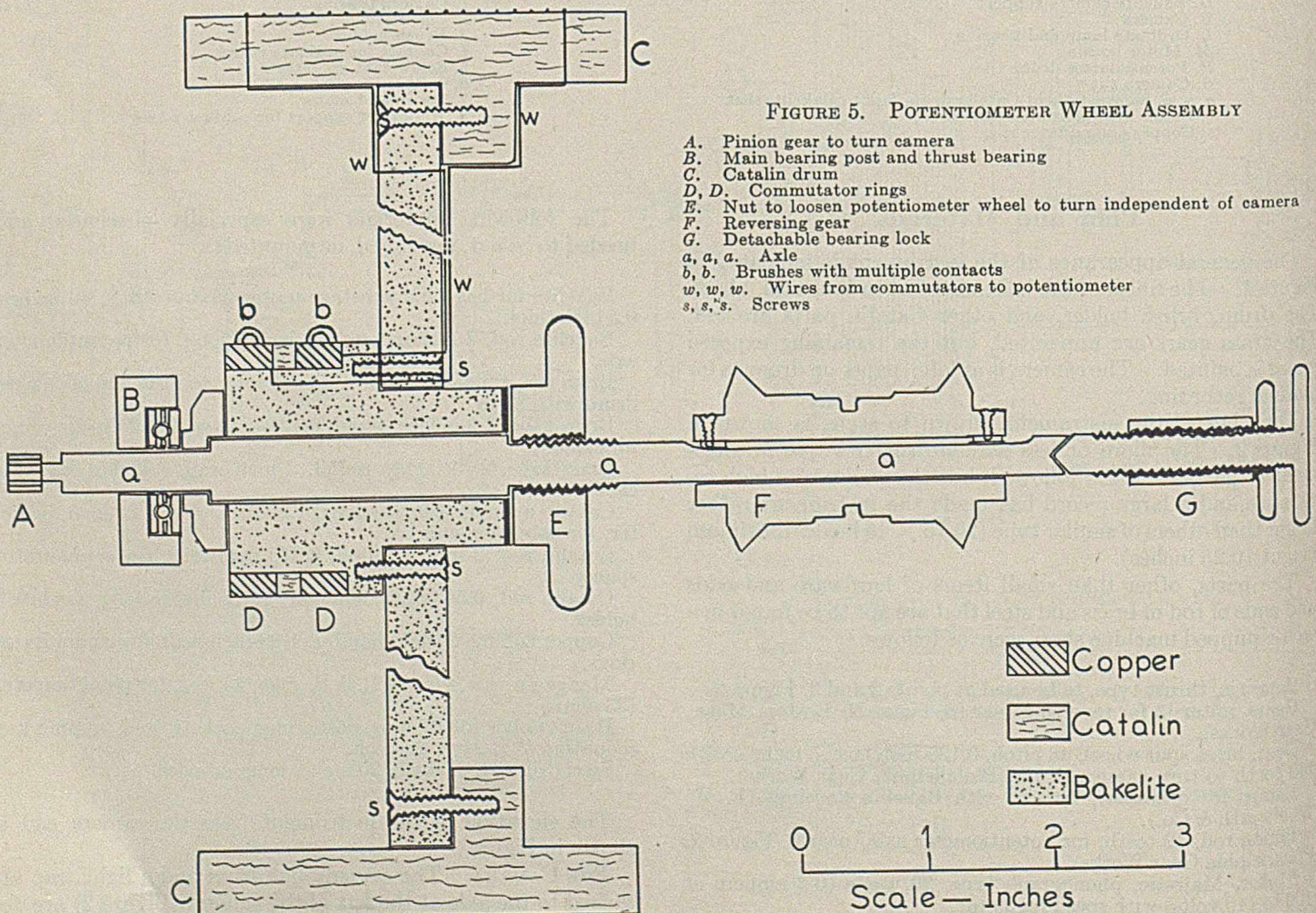

FIGURE 5. POTENTIOMETER WHEEL ASSEMBLY

A. Pinion gear to turn camera
B. Main bearing post and thrust bearing
C. Catalin drum
D, D. Commutator rings
E. Nut to loosen potentiometer wheel to turn independent of camera
F. Reversing gear
G. Detachable bearing lock
a, a, a. Axle
b, b. Brushes with multiple contacts
w, w, w. Wires from commutators to potentiometer
s, s, s. Screws

tachable as a unit by unscrewing the end bearing (1, Figure 2) and loosening button *b*, Figure 4. The details of the camera slit and several other constructional features are shown in Figure 2. The metal parts are painted black to avoid reflections, and since the metal strip that closes the slit occasionally dislodges paint or dust, a thin piece of paper is drawn along the slit to clear it as soon as it is opened.

The width of the thin metal strip that holds the bromide paper in place by fastening it against pins *p,p* (Figure 2) represents loss of available space for record. This is the chief defect in design thus far noted and is to be remedied by cutting a slot in the drum for one end of the paper. The other end may then be held by a much thinner strip or a wire.

The authors prefer a contrast paper, although normal paper gives good records. [P. M. C. No. 2 contrast paper, Eastman Kodak Co. The normal paper has the same letter and number designation (P. M. C. No. 2 normal).]

MANUAL RECORDING. With the camera housing removed and a strip of 6-inch paper on the drum it is very easy to take a rough preliminary record with the drum moving by putting dots on the image of the galvanometer filament at equal voltage intervals. When several curves are plotted in the same region pencils with different colored leads are used. More accurate records may be taken by stopping the drum to record points.

POTENTIOMETER DRUM. Details of the construction and assembly will be evident from Figures 2 and 5.

The wire is mounted in a slight groove machined on at 0.125-inch pitch per turn. A scale of 100 equal divisions is marked on the drum, and a pointer attached to the contact wheel support makes it possible to read the applied voltage accurately. The divisions are approximately 0.25 inch apart, so that interpolation is very reliable. The uniformity of the wire was tested relative to the whole wire taken as unity by reading the voltage at turn 20, then at turn 1, then at turn 20, etc.

The errors for the various fractions of the wire were, in per cent of the total length:

Fraction	0.05	0.10	0.15	0.20	0.25
Error	+0.05	−0.03	+0.04	−0.06	−0.08
Fraction	0.55	0.60	0.65	0.70	0.75
Error	−0.10	−0.07	−0.12	−0.06	−0.08
Fraction	0.30	0.35	0.40	0.45	0.50
Error	−0.07	−0.07	−0.11	−0.10	−0.07
Fraction	0.80	0.85	0.90	0.95	1.00
Error	−0.07	−0.01	−0.03	−0.07	Std.

The first interval includes extra resistance, because the contact with the copper lead is made below the face of the drum. In fact, this resistance is of the order of about 0.08 per cent of the total resistance. Aside from this slight error, which can easily be corrected for, the wire is uniform; this is

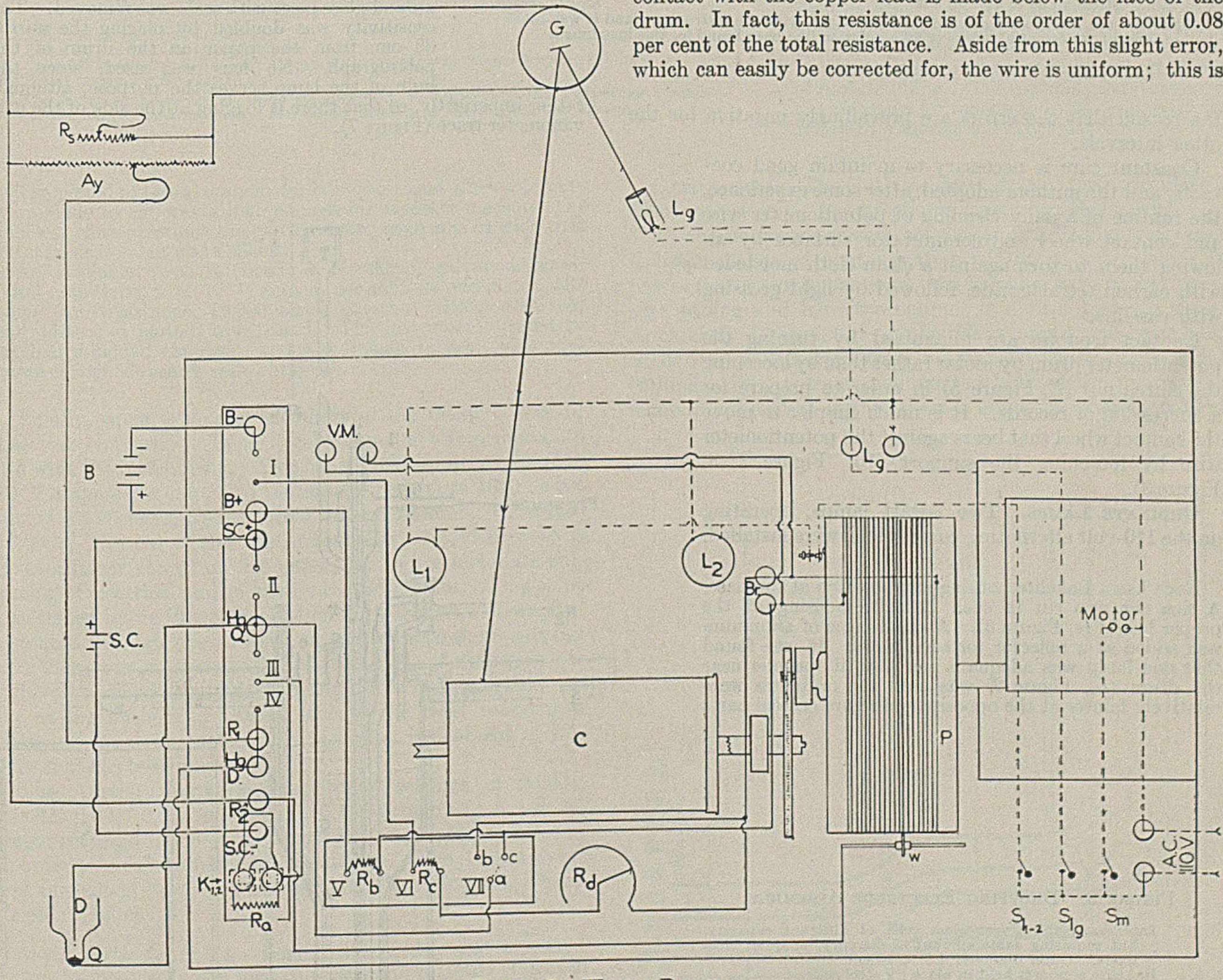

FIGURE 6. WIRING DIAGRAM

Binding post connections and plug connections I to VII are as listed for Figure 2.

G.	Galvanometer
Ay.	Ayrton shunt, 10,000 ohms total resistance
R_s.	Shunt resistance (4-dial 10,000-ohm box used for convenience)
B.	Battery
S. C.	Standard cell
D.	Dropping electrode
Q.	Quiet electrode
R_a.	10,000-ohm protective resistance
R_b.	16 ohms
R_c.	16 ohms
VII, *a—c.*	Connection for dropping cathode; *a—b* for dropping anode
R_d.	100-ohm rheostat

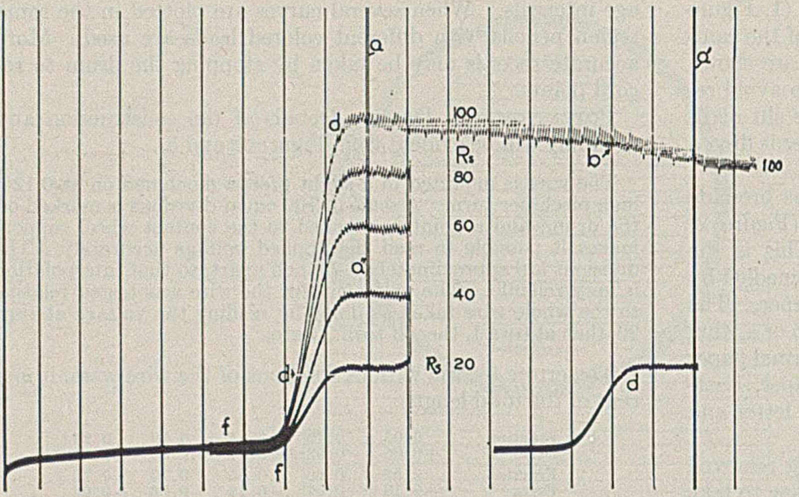

Figure 7. Record Taken with Portable 2420-d Galvanometer

0.001 M cadmium chloride in 0.1 M KCl solution, at various sensitivities
f. Fogging due to imperfect lens action of lamp bulb
a, *a'*. Ordinates put on with decreasing e. m. f. *a"* ordinate next to *a* is masked off at bottom
b. Undesirably wide galvanometer record at increased sensitivity
d, *d*, *d*. Streaks due to dirt on slit
This was the first polarogram one observer took with the instrument, and it was taken before some of the essential points of manipulation had been found for this instrument

the reason that the errors are prevailingly negative for the other intervals.

Constant care is necessary to maintain good contacts, and the authors adopted, after some experience, the routine of a daily cleaning of potentiometer wire and contact wheel and commutator surfaces by allowing them to turn against a clean cloth moistened with carbon tetrachloride, followed by light greasing with vaseline.

Contact troubles are minimized by turning the potentiometer drum by motor rather than by loosening the clutch nut (E, Figure 5) in order to prepare for a succession of records. It is much simpler to move the contact wheel that bears against the potentiometer wire by loosening the support (10, Figure 2; 8, Figure 3).

Ordinate Lamps. Two 7-watt lamps, operating on the 110-volt alternating current line, were installed.

Each has a Bakelite housing and a switch at the base. A fine slit was cut in each Bakelite housing at the proper height (s, Figure 3). A small piece of aluminum was added as a reflector for each lamp. It was found that one lamp was adequate and that if the one near the drum (L_1, Figure 2) was used the ordinates were relatively fainter at the opposite end where critical parts of the records are apt to be located (Figures 9 and 10). There is a slight play in the gear mechanism, so that ordinates are flashed on in the direction in which records are taken, and in general only once for any part of the paper. In putting on a series of exposures, the critical ordinates are flashed on when the particular curve to which they apply is being taken. If ordinates are put on in both directions on a single sheet of paper, part of one series is masked off by covering a part of the slit (Figure 7, ordinate a'').

Electrical Circuits, Galvanometer, Shunt, and Galvanometer Lamp. The general wiring diagram is shown in Figure 6. The alternating current circuits are shown in dotted lines.

Galvanometer. Preliminary Experiments. At low sensitivities a portable box type of galvanometer (Leeds & Northrup 2420-d of rated current sensitivity 5 × 10^{-8} ampere per mm. on glass scale 18 cm. from mirror, 310 ohms coil resistance, external critical damping resistance 2000 ohms, and a 3-second period) gave satisfactory records. The lamp was remounted with provision for adjusting the focus and the ground-glass piece with scale was removed. The sensitivity was doubled by placing the mirror 36 cm. from the paper on the drum of the polarograph. No lens was used, since the bulb of the lamp serves the purpose, although rather imperfectly, so that there is fogging at the side of the galvanometer trace (Figure 7).

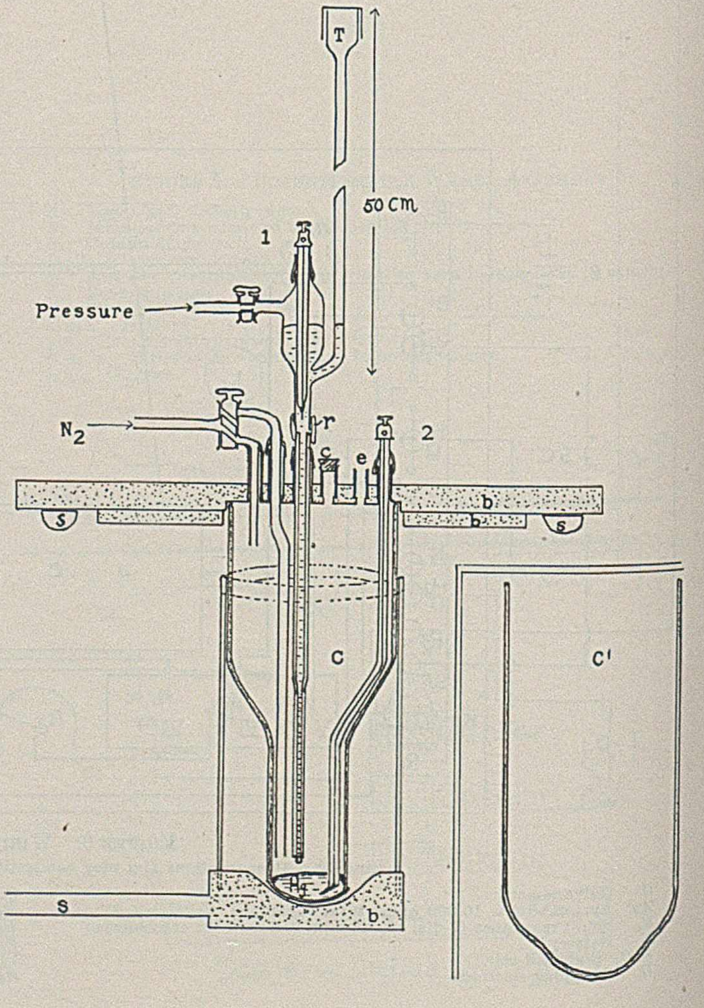

Figure 8. Dropping Electrode Assembly

C, *C'*. Interchangeable Pyrex glass cells of different capacity, but requiring same amount of mercury for quiet electrode. Outer diameter 4.5 × 10 cm.
b, *b*, *b*. Bakelite supports held in place by steel rods
s, *s*, *s*. Steel supports leading to heavy ring stand with two upright rods
1. Dropping electrode arrangement, with tube T, pressure inlet and electrode connection. Connected to capillary by r
2. Connection to quiet electrode
N_2. Washed nitrogen led either through or above solution
c. For introduction of microburet or pipet
e. Outlet for nitrogen and for introduction of side arm of half-ce for potential measurements

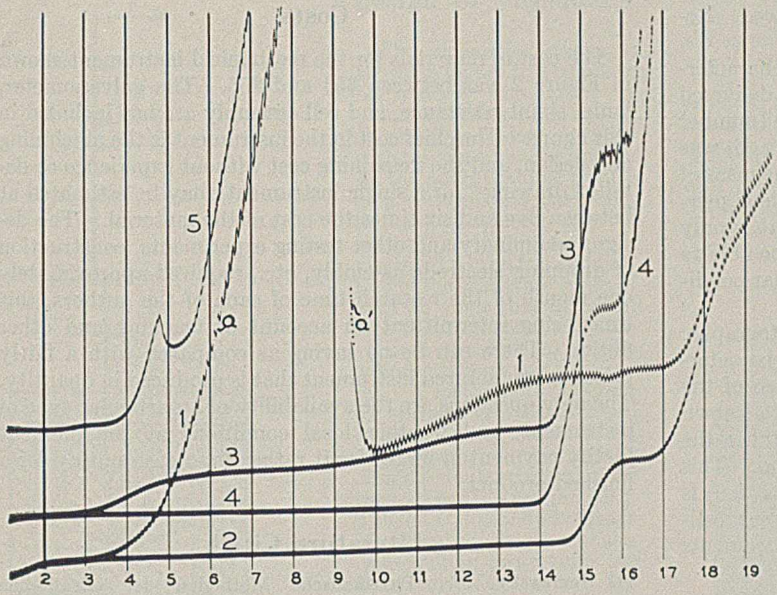

Figure 9. Maxima Due to Air or Other Causes

1. Effect of oxygen, maximum a, a'
2. Same as 1 after removal of oxygen
3. With air present and 4 are for same solution. Air was removed before taking 4
5. Small maximum not due to air

The instrument follows all these changes very well, although the descending branch, a', of the oxygen maximum on 1 can barely be seen on the original photograph.

The period of this glavanometer is so short that when attempts were made to get waves high enough for accurate measurement at lower concentrations the galvanometer trace was so wide that exact measurement was difficult.

An available Type R (Leeds & Northrup) galvanometer of rated sensitivity 9×10^{-11} ampere per mm. at one meter, 582 ohms' coil resistance, 19,000 ohms' external critical damping, and 14-second period, was tested. The instrument tended to lag badly behind the drum and was tedious to use; with adequate care good records were obtained.

Finally, upon advice of members of the research staff of Leeds & Northrup a Type P galvanometer was acquired to use with the instrument. This has a rated sensitivity of 9×10^{-10} ampere per mm. at 1 meter, coil resistance 1060 ohms, period 14 seconds, and external critical damping resistance 10,000. The use of this instrument was advised because it gives a linear record on flat paper, through a fortunate balancing of electrical and geometric characteristics. This point was tested by finding the variation of deflection with applied potential through known resistances at various shunt settings and there was no systematic trend in units of deflection per millivolt applied at any point along the recording drum. As far as the authors are aware, this is the most economical choice of a galvanometer for a recording instrument of this type that has been made.

The Ayrton shunt had sensitivity settings of 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, and 1. A few selected settings of the other shunt, R_s (Figure 6), were found in order to give intermediate sensitivities. The Ayrton shunt was one made by the Shallcross Manufacturing Co., Philadelphia, Penna.

Galvanometer Lamp. An economical assembly sold as a light source for photocells was used as a source of material (Herbach and Rademann Co., Philadelphia, Pennsylvania). This was made into a transformer unit, and the lens and a galvanometer lamp (0.5 ampere at 3.5 to 4.0 volts) were mounted in a locally made housing with concentric brass tubes for focusing.

Dropping Electrode and Accessories. The authors have modified somewhat the conventional assemblies to produce an arrangement with interchangeable cells that should be easy to thermostat, although they have not done so. The cells have widely different capacities, so that volumes of 1 to 2 or 90 to 100 ml. may be handled, the latter being convenient when it is desired to run a series of experiments with substances added between polarograms. The assembly is shown diagrammatically in Figure 8. The pressure head is believed to be the design of the research staff of Leeds & Northrup, although similar general assemblies have been described by others (*2*, p. 242).

The various tubes led through the Bakelite mounting pass through short pieces of wider glass tube that are cemented with methyl methacrylate polymer applied in solution. These tubes fit in holes bored about three-fourths of the way through the Bakelite. The cells are held in place by stout wires mounted in the Bakelite support shown at the bottom of the diagram, and soldered to a metal collar that holds the cell rather rigidly in upright position. In this way damage to capillary and other tubes is avoided. The tubes that pass down through the Bakelite are fastened to the supporting tubes by short pieces of rubber tubing. The assembly is rather easy to take down for repairs and was designed to be suitable for measurements or titrations.

Capillaries. The authors have drawn their capillaries following closely the directions given by Heyrovský (*1*). With the mercury pressure head as shown in Figure 8 there is little chance of contamination of the mercury, since it passes through only one joint that is sealed with rubber pressure tubing and here the contact is almost glass to glass. Apparently the useful life of a capillary might well be as long as it can be protected from mechanical shock or chemical etching. The reservoir holding the bulk of the mercury is made broad enough so that there is almost no change in level

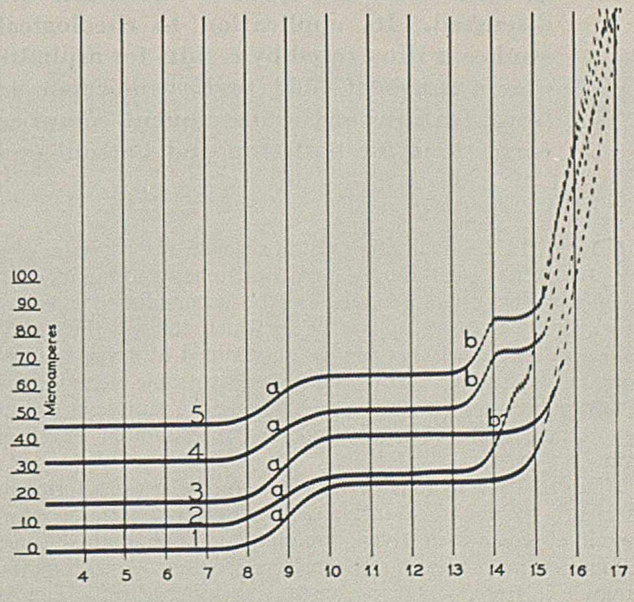

Figure 10. Typical Performance, Succession of Waves

Inflections at a, a, a correspond to maleic acid; at b, b, b are due to phthalic acid.
In 1 and 3 no phthalic acid is present.

in tube T (Figure 8) while a single curve is being traced. Readjustment of level is made when needed.

CAPILLARY CONSTANT. The simple method of characterizing a capillary by weighing the amount of mercury delivered in air at measured mercury pressure in a given time (number of drops and drop time noted) as described by Müller (*3*) was used. The constant $k = P/m$ is found by noting the mass of mercury delivered per second, in milligrams at various mercury pressures in centimeters. Then for solutions it is only necessary to note P and the drop time in order to be able to calculate $m^{2/3}t^{1/6}$ for the capillary under the particular conditions.

CURRENT. The number of millimeters on the photographic record that corresponds to 1 microampere can best be determined by noting with a resistance in series, in place of the mercury electrode cells, the deflection produced by a known applied e. m. f. Then with a second known resistance the e. m. f. that will produce the same deflection is found. This method, described by Kolthoff and Lingane (*2*, pp. 227–9) is exceedingly simple and checks well with the current estimated from the rated characteristics of the instruments (within 1 per cent for this galvanometer).

Typical Performance

Figures 9 and 10 are typical polarograms taken with the instrument. Ones rather heavily exposed were selected in order to reproduce well.

Costs

The cost of materials for the mechanical instrument shown in Figure 2 was between $54 and $55. The galvanometer, lamp, shunt resistance, and cell assembly are not included in this figure. The chief cost in the instrument is the machining and design, and the machining cost without experience or detailed drawings, for a single instrument, may be estimated at between five and six times the cost of the material. The design, preliminary and other testing experiments, construction of dropping electrode assembly, etc., required approximately one month of the research time of each of the authors, this time being intermittent on account of teaching and other duties. There can be no saving as compared with a fairly priced manufactured instrument that is produced in quantity. The only questions are the availability of a particular type of instrument, and whether local conditions at the moment justify payment in wages for it rather than cash outlay for a finished product.

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Rotary Viscometer for Determination of High Consistencies

R. N. TRAXLER, J. W. ROMBERG, AND H. E. SCHWEYER
The Texas Company, Port Neches, Texas

The design, construction, and operation of a new rotating cylinder viscometer are discussed. Its application to rheological studies is illustrated by results for asphalts over a range of 0.001 to 1000 megapoises. Novel features of the instrument comprise corrections for both top and bottom end effects and a special design whereby the viscosity is measured at a constant mean rate of shear. The apparatus is particularly adaptable for measurement of equilibrium consistency, and studies of complex flow and the elastic properties of materials having relatively high viscosities.

COMPLETE evaluation of the rheological properties of a material possessing a high consistency and manifesting complex flow characteristics can be accomplished satisfactorily only with an apparatus in which the rate of shear–shearing stress relation can be determined at several different rates of shear. To evaluate a thixotropic material the instrument must be capable of shearing the sample at a constant rate in the same direction for an unlimited length of time.

The rotating cylinder viscometer, in the various forms in which it has found extensive application, fulfills the requirement of shear in a given direction for an unlimited time. However, most rotating viscometers are designed so that the sample is tested under a constant shearing stress. This is not satisfactory for evaluating the consistencies of materials manifesting thixotropy because, as the structure within the sample is destroyed by the mechanical working, a progressive decrease in consistency occurs with a concomitant increase in rate of shear under the constant applied shearing force. Thus, with the usual type of rotating viscometer, it is difficult to compare the consistencies of different complex (non-Newtonian) liquids at the same rate of shear.

Csagoly (*3*) proposed a rotating cylinder viscometer operating at a constant rate of shear for use in the study of the flow properties of asphalts having viscosities of 0.5 to 50 poises. However, his apparatus was not rugged enough to permit testing the asphalts at service temperatures where the consistencies are greater than one million poises (one megapoise). In the instrument described below, Csagoly's design has been improved and amplified to give a viscometer of rugged construction and simple operation capable of measuring an extremely wide range of consistencies—e. g., 0.001 to 1000 megapoises. In addition, a smaller sample (about 20 ml.) is required for test.

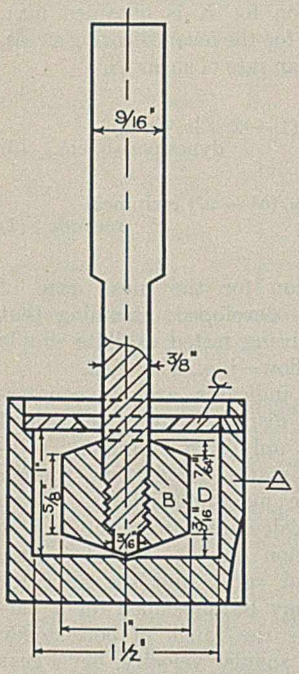


Figure 1. Dimensional Sketch of Rotor and Stator

Design of Viscometer

The viscometer proper is shown in Figure 1. The space, *D*, between the rotor, *A* (outer chamber), and stator, *B* (inner cylinder), is filled with the material to be tested. As the outer chamber rotates at a constant angular velocity, the torque required to prevent *B* from rotating is measured. The top and bottom of the stator are cones of such an angle that the mean rate of shear is essentially the same at the ends as in the cylindrical part of the annulus. A method of correcting for end effects was developed by Mooney and Ewart (*5*) for the bottom; in the present design a similar correction for the top has also been included. The lid, *C*, has the advantage of preventing elastic asphalts from pulling away from the inner cylinder under the shearing action. The viscometer proper is fabricated from rolled brass except for the shaft which is of stainless steel. The brass surface of *B* and the inner surface of *A* are knurled in order to minimize slippage at the metal-liquid interface when materials of high consistency are being tested.

Figures 2 and 3 show the complete assembly. The outer cylinder of the viscometer proper (rotor *A*) is centered in the water bath, *E*, by means of a chuck in which the rotor makes a sliding fit. The double-walled water bath, *E*, is mounted on turntable *F* which contains a gear reducer. This is driven by a constant-speed motor, *H*, connected through a gear reducer, *I*, and a series of gears, *G*, capable of being shifted readily in order to obtain different angular velocities for the rotor.

B is connected by the friction coupling, *J*, to the vertical rod, *K*. A pair of bevel gears, *L*, transmit the torque to the horizontal shaft, *M*, and the indicator lever, *N*. The torque required to keep the stator from rotating varies, depending on the consistency of the material being tested and the rate of shear employed. A range of torque is covered by using weights of various sizes at different distances from the center of *M*. A wide range of consistency may be measured conveniently by using different pairs of bevel gears, *L*, of different gear ratios, by using a single pair of bevel gears and a variable series of driving gears, *G*, or by a combination of both arrangements. Scale *O* is calibrated to measure the deflection of the indicator which is directly proportional to the consistency. The indicator arm is a brass rod and is counterbalanced as shown. Shafts *K* and *M* are supported by ball bearings. The apparatus is mounted on a reinforced iron plate, and the upper assembly is supported by 2.5-cm. (1-inch) angle irons. Temperature of the water in *E* may be controlled by a suitable thermostatic arrangement.

Operation

In making a consistency determination on a material such as asphalt, rotor *A* and stator *B* are heated well above the softening point of the sample before the latter is poured into the viscometer. In practice a special holder (Figure 4) is used to fix the rotor and stator in proper alignment during the heating and filling operations. The annular space, *D*, is filled with the sample which has been heated until fluid. If the rotor lid, *C*, is put on immediately, the asphalt may pull away from some part of the stator as it cools and contracts. To prevent this the viscometer is filled almost to the top and allowed to cool to approximately the test temperature. A small additional amount of hot material is then poured into the viscometer and the hot lid put in place. Any excess of the sample comes out at the clearance between the stator shaft and rotor lid and is removed with a small spatula.

Since most asphalts harden rapidly with time (*6*, *8*), it is essential that evaluations of such materials be made at the same age if values are to be compared. Normally, a determination on an asphalt is started at one hour after pouring. The viscometer should be in the constant-temperature bath for at least 20 minutes of this hour. The gears are selected to give the rate of shear desired, the necessary weight is located at the proper position on the indicator arm, *N*, and the motor is started. As the outer cylinder rotates the indicator arm moves upward until a torque

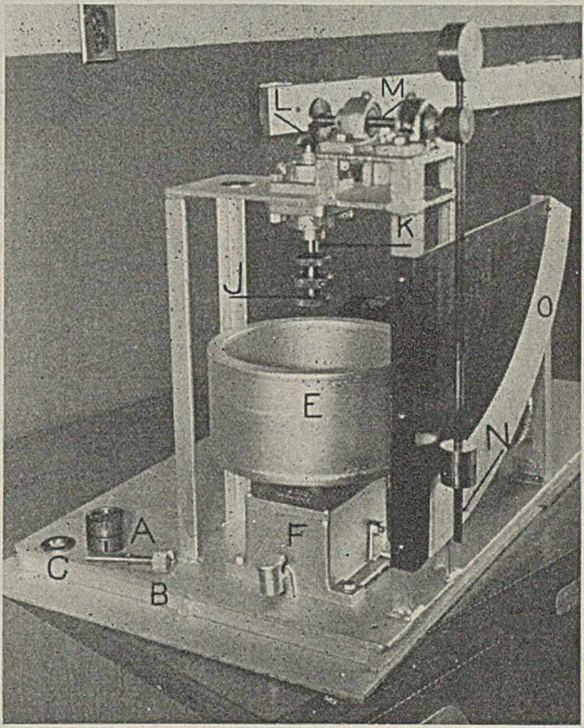


Figure 2. Rotary Viscometer Assembly

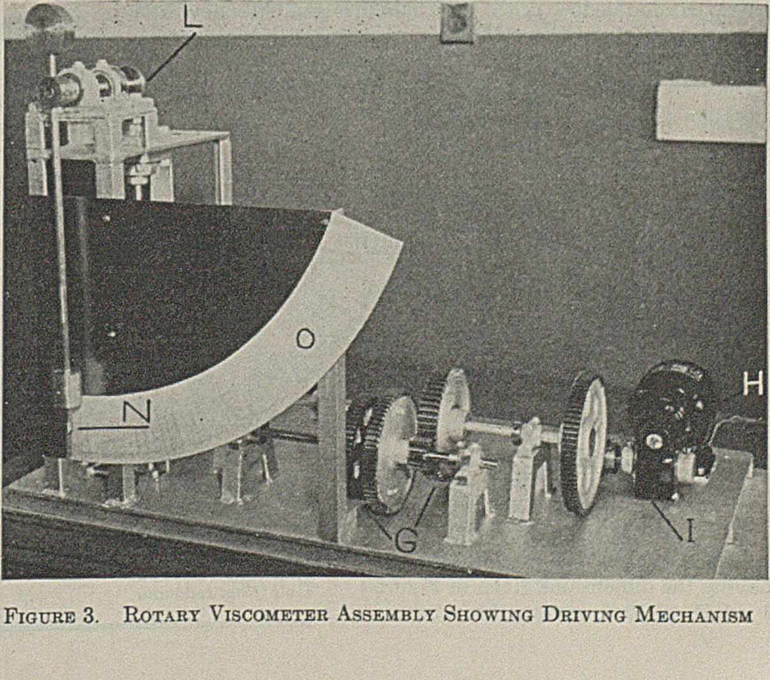


Figure 3. Rotary Viscometer Assembly Showing Driving Mechanism

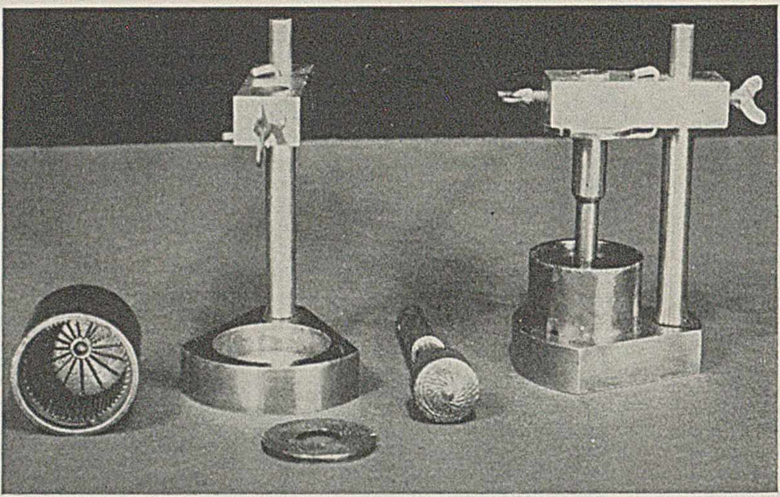


Figure 4. Alignment Device for Holding Viscometer during Filling

sufficient to prevent the stator from moving is attained. The time required to make a determination, after the sample has been poured and brought to a constant temperature, will vary, depending on the nature and consistency of the material and the rate of shear employed. For asphalts having viscosities of 0.001 to 10 megapoises from 5 to 40 minutes will be required.

Calculations

The viscosity or consistency is calculated by the equation:

$$\eta = K(T/\omega) \qquad (1)$$

where η = viscosity or consistency, poises
T = torque required to prevent the stator from turning, dyne-centimeters
ω = angular velocity of rotor, radians per second
K = a constant determined by the dimensions of the viscometer, cm.$^{-3}$

Mooney and Ewart have developed the equations for evaluating the constant, K, for a rotating viscometer having an inner cylinder with one conical end. For an instrument with both ends of the inner cylinder conical, the equations for evaluating K are the same except that the correction for end effect is doubled. With this modification Mooney and Ewart's equation becomes

$$K = (b^2 - a^2)/[4\pi h_0 a^2 b^2(1 + 2r_0/3h_0 \sin \theta_0)] \qquad (2)$$

where a = radius of inner cylinder, cm.
b = radius of outer cylinder, cm.

$$r_0 = [2a^2b^2/(a^2 + b^2)]^{\frac{1}{2}} \qquad (3)$$

$$\theta_0 = (\alpha + \beta)/2 \qquad (4)$$

where α = angle of cone of inner cylinder (69°)
β = angle of cone of outer cylinder (90°)

$$h_0 = h_c + (b - a) \times (1 - \cos \theta_0)/\sin \theta_0 \qquad (5)$$

where h_0 = mean length of sample
h_c = length of cylindrical section of inner cylinder

The value of K for an instrument having the dimensions given in Figure 1 is 8.79×10^{-3}.

The equation for K is obtained from the equations for the mean shearing stress, F, and the mean rate of shear, S.

$$F = T/[2\pi r_0^2 h_0(1 + 2r_0/3h_0 \sin \theta_0)] \text{ dynes per sq. cm.} \qquad (6)$$

$$S = (a^2 + b^2)\omega/(b^2 - a^2) \text{ reciprocal seconds} \qquad (7)$$

The equation for the mean rate of shear, S, was developed, assuming that the material being tested exhibits simple (Newtonian) flow—i. e., $\eta = F/S$.

Since the indicator arm is counterbalanced, the displacement of the added weight is the only torque resisting rotation of the stator (neglecting friction which can be made negligible). Thus, T is easily calculated from the weight and its position on the indicator arm, the bevel gear ratio, and the indicator reading. A convenient chart may be developed for a particular instrument which shows the range of consistency covered by each combination of angular velocity, bevel gear ratio, weight, and its position on the indicator arm. For each combination a constant, C, may be determined which, when multiplied by the indicator reading, gives the consistency in poises.

The rotary viscometer was checked against the falling coaxial cylinder (*7*) and the inclined tube falling ball (Hoeppler) (*4*) viscometers, using a number of asphalts possessing essentially simple flow and ranging in consistency from 0.0011 to 2 megapoises at 25° C. (77° F.) with the results shown in Table I.

In order to evaluate the low viscosities of certain of the asphaltic residua in the rotary viscometer it was necessary to revolve the outer cylinder at about 100 revolutions per hour. This was much faster than the speeds used with the harder asphalts, which were usually evaluated with the outer cylinder turning 0.35 to 7.0 revolutions per hour.

The data in Table II on asphalts of various consistencies and origins indicate the degree of reproducibility obtained with the rotary viscometer at a given temperature and rate of shear. Based on a large number of determinations the standard deviation is about 3 per cent.

The above checking values were obtained at the same sample age (one hour). An asphalt, if held at a fixed temperature, will show increasing consistency with elapsed time, as is indicated by the data in Table III. Such variations in measured consistency, caused by the colloidal nature of the material tested, should not be attributed to lack of precision of the apparatus.

Table I. Comparison of Results Obtained with Different Viscometers

Source of Asphalt	Ring and Ball (*1*)	Efflux Viscosity at 98.9° C. (210° F.) (*2*)	Viscosity at 25° C. (77° F.)		
			Rotary viscometer	Falling coaxial cylinder viscometer (*7*)	Inclined tube falling ball viscometer (*4*)
	° C. (° F.)	*Seconds*	*Megapoises*		
Vac reduced California	49.4 (121)	...	2.00	1.91	.....
Vac reduced Venezuela	47.2 (117)	...	1.37	1.30	.....
Mexican residuum	38.9 (102)	...	0.220	0.225	.....
Gulf Coast residuum	..	100	0.0108	0.0108	0.0108
Gulf Coast residuum	..	142	0.0070	0.0078	0.0075
Mixed residuum	..	146	0.0057	0.0057	0.0060
Gulf Coast residuum	..	115	0.00260	....	0.00266
Gulf Coast residuum	..	75	0.00110	....	0.00110

TABLE II. REPRODUCIBILITY OBTAINED BY ROTARY VISCOMETER

Source	Process	Viscometer No.	Ring and Ball	Mean Rate of Shear	Equilibrium Consistency at 25° C. (77° F.)
			° *C.* (° *F.*)	*Sec.*$^{-1}$	*Megapoises*
Mexican	Vacuum	2	38.9 (102)	0.032	0.224
		3			0.220
Venezuela	Vacuum	1	47.2 (117)	0.032	1.17
					1.17
Northeast Texas	Air-blown	1	58.9 (138)	0.032	4.7
		2			4.9
		3			4.7
Northeast Texas	Air-blown	2	100 (212)	0.0032	210
		2			200

If the rate of shear is changed for duplicate runs on a material having flow properties essentially the same as those of a simple liquid, the consistency values check closely. This is illustrated by the data in Table IV, obtained on asphalt samples one hour after being poured.

However, when similar data are obtained for asphalts exhibiting complex flow characteristics the apparent consistency in poises, at a particular temperature and sample age, increases as the rate of shear decreases. This condition, which is illustrated by the data in Table V for certain asphalts aged one hour, makes necessary the use of an arbitrarily selected rate of shear.

Data obtained under the above conditions are a means of evaluating deviations from simple flow. It is evident that the steam-reduced Mexican asphalt possesses complex flow characteristics to a less extent than the air-blown Gulf Coast asphalt.

TABLE III. INCREASE OF VISCOSITY WITH AGE OF SAMPLE

Source	Process	Ring and Ball	Age of Sample	Mean Rate of Shear	Equilibrium Consistency at 25° C. (77° F.)
		° *C.* (° *F.*	*Hours*	*Sec.*$^{-1}$	*Megapoises*
Gulf Coast	Air-blown	59.4 (139)	0.5	0.0032	15.9
			1.0	0.0032	17.6
			17.0	0.0032	19.6
			115	0.0032	22.0

TABLE IV. EFFECT OF RATE OF SHEAR FOR SIMPLE LIQUIDS

Source	Process	Ring and Ball	Mean Rate of Shear	Equilibrium Consistency at 25° C. (77° F.)
		° *C.* (° *F.*)	*Sec.*$^{-1}$	*Megapoises*
California	Vacuum	49.4 (121)	0.032	2.00
			0.0032	2.09
			0.0016	2.17
Pressure still residuum	Steam	46.1 (115)	0.032	2.70
			0.0032	2.70
			0.0016	2.72

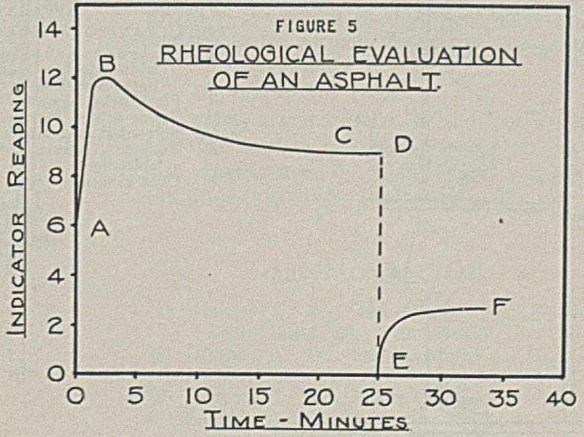
In evaluating the consistency of a complex liquid, there is usually a rate of shear above which "slippage" takes place. The phenomenon of slippage is probably caused by a greater breakdown in structure in the few layers of liquid around the stator than in the other parts of the sample. Theoretically, as the outer cylinder rotates, the annulus of material being tested rotates in layers concentric with the rotor and stator. With the size of viscometer illustrated in Figure 1, the shearing stress at the stator surface is b/a—i. e., 1.5—times that at the rotor wall. Thus, for a material showing considerable complex flow characteristics, the initial rate of shear at the stator is more than 1.5 times that at the rotor. Therefore, a sample with a large amount of structure will be broken down fastest at the stator where the rate of shear is highest. This effect is cumulative, and, in time, almost all of the shearing may be occurring in a few boundary layers near the stator with very little shearing in the outer layers of the annulus. If this type of slippage is taking place it is evident that no constant reading or equilibrium consistency will be observed. The effect on the measured consistency of this localized breakdown of structure can be minimized by making the ratio of stator radius to rotor radius as large as practical considering ease of filling the viscometer and by using low rates of shear. With the size of viscometer shown in Figure 1 no appreciable slippage was encountered in any of the asphalts tested at the two lowest rates of shear used (0.0016 and 0.0032 second^{-1}). However, at a rate of shear of 0.032 second^{-1} slippage started to occur in certain asphalts at consistencies between 10 and 50 megapoises.

TABLE V. EFFECT OF RATE OF SHEAR FOR COMPLEX LIQUIDS

Asphalt	Process	Ring and Ball	Mean Rate of Shear	Equilibrium Consistency at 25° C. (77° F.)
		° *C.* (° *F.*)	*Sec.*$^{-1}$	*Megapoises*
Mexican	Steam-reduced	54.4 (130)	0.032	3.8
			0.0032	5.6
			0.0016	6.3
Gulf Coast	Air-blown	59.4 (139)	0.032	7.4
			0.0032	22
			0.0016	29

Figure 5 illustrates some of the deviations from simple flow exhibited by complex liquids when evaluated in the rotary viscometer at a constant mean rate of shear (0.032 reciprocal second). This figure is a plot of the indicator readings against time for an air-blown Northeast Texas asphalt of 58.9° C. (138° F.) ring- and- ball softening point.

The initial period, *AB*, of increasing consistency represents the extension of the elastic elements within the asphalt and is called the elastic fore effect. The period, *BC*, of decreasing consistency is caused by a breakdown of structure with shearing. The curvature in this period will be accentuated by an increase in rate of shear. At the essentially constant value *CD* the consistency is called the equilibrium consistency and represents a balance between the thixotropic breaking down and building up of structure within the asphalt. This equilibrium value is reproducible (if slippage does not occur), and, according to available data on asphalt, it is independent of any previous shear. At point *D* in Figure 5 the weight was removed, the indicator set at zero reading, and the motor stopped. The movement, *EF*, of the indicator measures the elastic recovery or elastic aftereffect of the asphalt in attaining



equilibrium after all imposed shearing stress has been removed.

The type of data shown in Figure 5 illustrates the application of the rotary viscometer to rheological problems: The equilibrium consistency in absolute units at a given constant rate of shear may be determined; the degree of complex flow exhibited by a material may be evaluated from the equilibrium consistencies at two or more rates of shear (*9*); and the elastic properties may be studied. Many of the above flow properties may be measured in other types of viscometers. However, in applied rheology no other single apparatus combines the simplicity, general adaptability, and theoretical advantages of a constant mean rate of shear rotary viscometer.

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Automatic Method for Cleaning Tar Distillation Flasks

WILLIAM PECHENICK, 417 West Broad St., Bethlehem, Penna.

THE apparatus described can save appreciable time in cleaning flasks containing residue from tar distillations. It consists essentially of a container in which the solvent is converted from the liquid to the vapor phase. The vapor, conducted by a tube to the inverted tar flask, condenses on the walls and dissolves the residue, and the liquid is returned to the original container by a second tube. The residue in the flask is thus acted upon at all times by pure solvent.

A solvent that is effective with coal tar is *m*-xylene. Some free carbon is left on the walls of the flask being cleaned, but this can be removed by rinsing with nitric acid.

The cleaning operation should be carried on in a hood with a good draft, in order to prevent any vapors from coming in contact with the flame.

The arrangement shown in Figure 1 can be used when cleaning only one flask at a time.

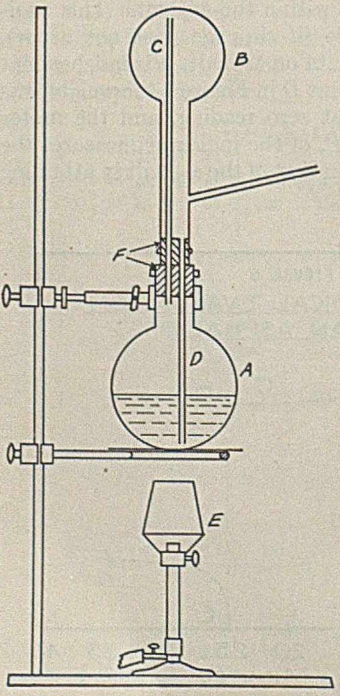


Figure 1. Apparatus for Cleaning One Flask

- *A.* Solvent container, wide-mouthed round-bottomed flask
- *B.* Flask being cleaned
- *C.* Vapor tube
- *D.* Solvent-return tube
- *E.* Bunsen burner with chimney
- *F.* Cork stoppers

If it is necessary to clean many flasks simultaneously, a more convenient apparatus can be constructed (Figure 2). For cleaning long-necked and short-necked flasks, space can be saved by alternating long and short vapor tubes, as shown.

By standing sheets of asbestos from leg to leg of the supporting frame, contact between vapor and flame can be minimized.

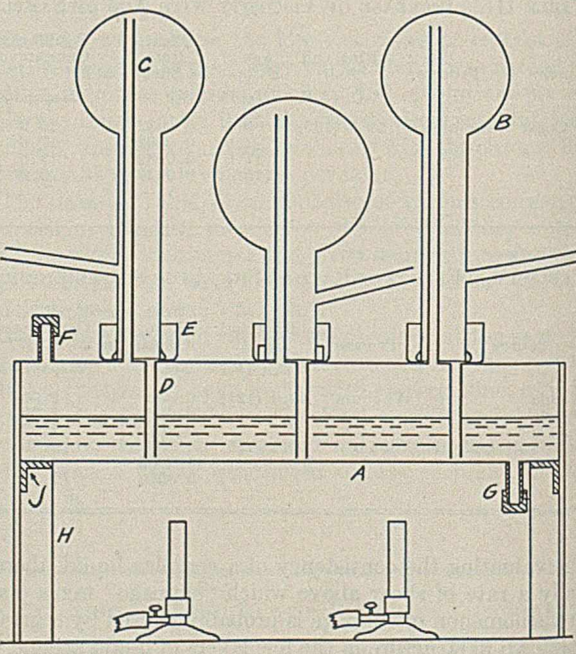


Figure 2. Cross Section of Apparatus for Cleaning Flasks Simultaneously

- *A.* Rectangular box of sheet iron, welded construction, containing solvent
- *B.* Flasks being cleaned
- *C, D.* Vapor- and solvent-return tubes of brass, brazed into corresponding holes of box
- *E.* Body of 4-ounce can with 1.5-inch hole in bottom, secured to *A* with hard solder, so as to enclose *C* and *D* and keep return solvent from straying
- *F.* 0.25-inch iron pipe, closed by cap, for admitting fresh solvent
- *G.* 0.25-inch iron pipe, closed by cap, for removing spent solvent
- *H.* Vertical members, and *J*, horizontal members of 1 × 1 × 0.125 inch angle iron, welded for support of apparatus

Apparatus for Distillation of Corrosive Liquids

As Used for Purification of Chlorosulfonic Acid

ARTHUR W. HIXSON AND ALVAN H. TENNEY, Columbia University, New York, N. Y.

IN CONNECTION with some of the authors' work (*1*) small known quantities of chlorosulfonic acid of high purity were desired. Since a detailed procedure for the preparation of pure chlorosulfonic acid is not readily available in the literature, this method may be of interest.

Sanger and Riegel (*4*) state that chlorosulfonic acid is best prepared by bubbling dry hydrogen chloride gas through strong oleum until the gas is no longer absorbed. To purify the chlorosulfonic acid, they say it should be distilled in a current of hydrogen chloride gas and the fraction between 145° and 160° C. redistilled. They mention that chlorosulfonic acid dissociates, when boiled, into hydrogen chloride gas and sulfuric acid, and into sulfuryl chloride and sulfuric acid.

As commercial chlorosulfonic acid is readily available, the preparation step may be omitted. In the apparatus shown in Figure 1, twenty-six ampoules containing known weights of chlorosulfonic acid were prepared. The purity obtained is indicated by the analyses shown for total acidity, gravimetric sulfur, and chloride by the method of Roberts (*2*, *3*).

	Acidity *Milliequivalents/g.*	Cl Content %	S Content %
Calculated	25.75	30.43	27.50
Found	25.92	29.61	27.87

The apparatus used consisted of two all-glass, helix-packed rectifying columns sealed together in tandem. The first of these, R_1, was made from a 25-cm. length of 12.5-mm. glass tubing packed with glass helices (2.5-mm. single turn) and was mounted on a 500-cc. flask, K_1. The column carried a simple stillhead, H_1, comprising a reflux finger and a thermometer well, T_1. The second still, R_2, was similar but had a 46-cm. packed length surrounded with a silvered vacuum jacket, J. Stillhead H_2 on the second column provided reflux control without contamination of or by the ground-joint lubricant. The parts of this stillhead shown in Figure 1 (right) were thermometer well T_2, reflux and total condenser C_2, reflux drop counter Q, and control valve B, keyed to "wrench" G. Condenser C_2 was designed so that only a small annular space remained between the inner cooled finger and the outer jacket. This effectively prevented any vapors from reaching the only greased joint, G.

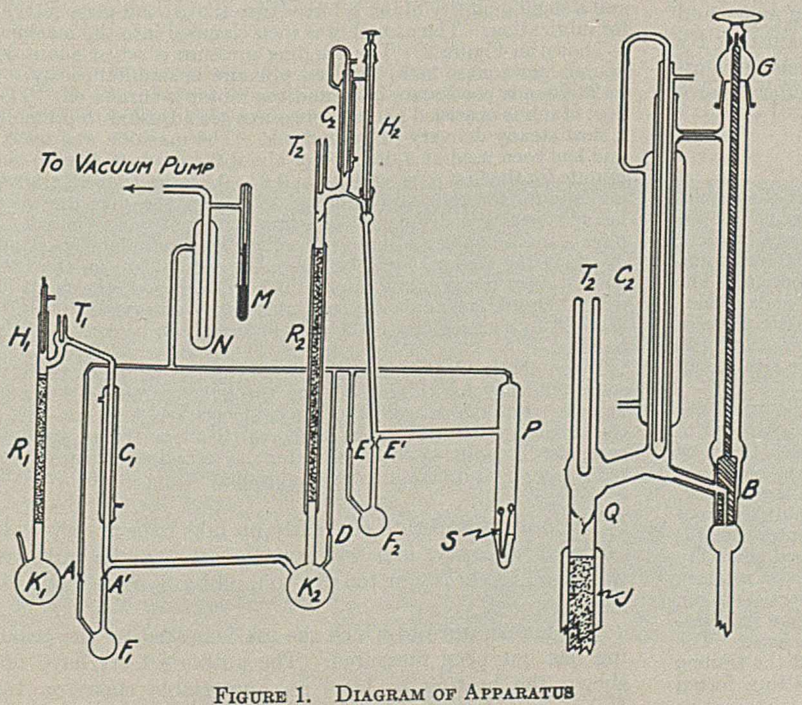
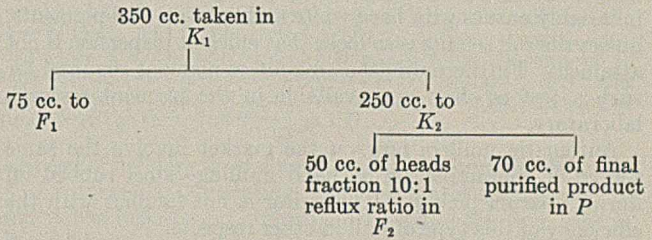


FIGURE 1. DIAGRAM OF APPARATUS

The condenser length was about 18 cm. Other parts of the detailed sketch are drawn to the same scale. Control valve B was essentially a Fresenius stopcock with a long stem, keyed at the end to fit a socket in G. The cock was so designed that a 180° turn from normal position would drain the tube above it. This valve was lubricated by the distillate only, while the joint at G was greased in the usual fashion.



Three hundred and fifty cubic centimeters of commercial chlorosulfonic acid (du Pont) were placed in K_1 after drying the apparatus. With the system sealed, an absolute pressure of about 30 mm. was maintained, as measured on manometer M, by exhaustion through a large-capacity liquid nitrogen trap, N. Approximately 75 cc. of the acid were distilled into receiver F_1. Without discontinuing the distillation, F_1 was sealed off at constrictions A and A' and 250 cc. of the acid were collected in the bottom of K_2. (The connections from A' to K_2 and E' to P had slight upward slopes and were made of tubing of sufficiently large diameter to prevent formation of a siphon.) After sealing the tube from A' to K_2 and sealing the vacuum lead at D, a heads fraction of about 50 cc. was distilled from K_2 into F_2 at about a 10 to 1 reflux ratio. The final purified product, about 70 cc., was then collected in P after sealing off F_2 at E and E'.

In the bottom of P were inverted small weighed ampoules, S, with capillary tips. On readmission of dry air into the system, these ampoules filled automatically, leaving a layer of product in the bottom of the receiver in which the capillary tips of the ampoules remained immersed. Breaking open the receiver and removing the ampoules one by one to a flame for sealing completed the operation. The layer of chlorosulfonic acid in the receiver protected the contents of the ampoules until ready for sealing, so that the exposure of the final product to the atmosphere was a matter of a few seconds through at least 30 mm. of very fine capillary.

Twenty-six ampoules containing chlorosulfonic acid in accurately weighed quantities ranging from 0.5 to 2.2 grams were thus obtained in a single preparation.

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A New All-Glass Mill

DAVID B. PALL

Research Laboratories, Interchemical Corporation, New York, N. Y.

THREE methods are currently in use for preparing test inks in studies of pigment, ink, and paint properties. The oldest and perhaps most widely used method is hand mulling, but it has the deficiencies of, first, the poor dispersion obtained, particularly with hard pigments; and secondly, contamination which invariably occurs, especially due to steel rubbed off in the spatula pickup. The first factor is important when working with hard pigments, the second when working with whites or light colors. Finally, it is difficult to disperse by this method inks which, though finally workable to a flowing ink, are extremely dry on first mixing.

For tests involving larger quantities of ink, three-roller mills of laboratory size are available. Use of one of these mills usually gives excellent dispersion, but contamination invariably ensues with hard white and light-colored pigments, unless the roll setting is so loose that efficient dispersion is not attained. Furthermore, the amount of pigment required for such a test is often not available in the pigment research laboratory.

Automatic mullers now on the market involve the same source of contamination as hand mulling—steel rubbed off during spatula pickup. The writer is not familiar with the efficiency of this type of mill in other respects.

Principle of Mill

All these deficiencies were kept in mind when the new mill was designed. The grinding surfaces are entirely glass, and are so disposed that pickup off these surfaces is not necessary. Good dispersion is achieved by using grinding pressures of the order of 50 to 300 pounds per square inch, as compared with 1 to 5 pounds per square inch in hand mulling.

The new apparatus which achieves these conditions consists essentially of two truncated cones, one of which is fitted inside the other, together with a plunger feed mechanism which forces crudely mixed ink into the annular space between the two sections, one of which is rotated with respect to the other. The ink flows out through the annular space and is collected at the end opposite the feed mechanism. By using conical grinding sections, high grinding pressure is attained while the outside force impressed is of moderate proportions.

Construction

An ordinary ground joint supplies the essential part of the mill For the model constructed in this laboratory, a special set was designed. The females differed from the regular stock models, in that they were constructed of heavier glass and in the elimination of the usual bead at the base of the ground section. The males were standard solid stoppers, with the small end beveled off to a depth of about 0.125 inch. The dimensions are those of the standard 15/35 ground-glass joint. The cost was only 40 cents more for each pair than for a pair of the same size out of stock.

The female part was used as supplied. The male part was grooved at the laboratory, in order to provide a smooth feed of unground ink through the mill (Figure 1). Various types of grooves were tried; the type finally adopted involves cutting a spiral which begins at the center of the small end of the stopper, the sense of the spiral being such with respect to the direction of rotation, that crudely mixed ink is forced from the center towards the wall of the joint. This spiral groove is continued smoothly along the wall of the stopper, again in the sense which on rotation forces material through the joint. This "feed-in" section is run along for about 0.5 inch, at an angle of about 45°, then its direction is changed to make a 15° angle in the opposite sense. The leading edge of this "feed-back" groove is sharp, but the trailing edge is tapered and smoothly rounded. The ink is thus forced forward along the groove by the feed-in section, and backward by the feed-back section, with the result that it passes into the grinding section between the two ground-glass parts. This passage is assisted by the tapered edge of the feed-back groove. The grooves were cut with a small brass wheel, using a Carborundum-water mixture.

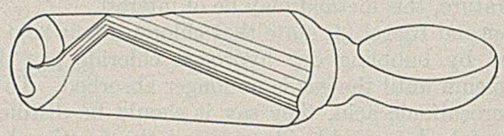

FIGURE 1. SLOTTED GROUND STOPPER

In operation, the crudely mixed ink is placed in the tubular section of the female joint, and the plunger is inserted (inset, Figure 2). The plunger consists of a mushroom-shaped rubber head, the stem of which fits into a steel cylinder and is held there by a flush setscrew. The female section is held in a rubber-lined clamp, while the male section is rotated by means of 0.05-horsepower motor, the drive shaft of which is geared down to a speed of 600 r. p. m. Speed of rotation is held at about 150 r. p. m. by operating off a variable transformer at about 60 to 75 volts. In the model constructed, the force on the plunger and on the ground stopper was supplied by oil-filled pneumatic cylinders, operated through reducing valves from the laboratory air line. The drive motor is fastened directly to one of the pistons, and made to move on castors. Thus the grinding force is transmitted through the motor. The pressure in each pneumatic cylinder is measured by means of a pressure gage covering the range 0 to 60 pounds per square inch; the pistons are 1 inch in diameter. The air lines are so arranged that the pressure in the feed cylinder can never be greater than the pressure in the cylinder supplying the grinding force. Thus the plunger can never accidentally be made to push out the stopper completely. A photograph of the mill appears in Figure 2.

Operation

With the stopper in place, the crudely mixed ink is placed in the tubular section of the female part. The plunger is inserted, and a small quantity of ink is forced into the ground-glass section for lubrication. The assembly is then clamped into the machine as shown in Figure 2. The grinding pressure is set at about 30 pounds per square inch, the feed pressure is simultaneously set to 20 pounds per square inch, and the motor is turned on. The flow of ink is observed and the pressures are adjusted to promote a slow steady delivery of ground ink. The machine was tested and has been used at a delivery of about 0.4 gram (6 grains) per minute for the first pass, and about 0.6 to 0.8 gram (8 to 12 grains) per minute for the succeeding pass. When the inks are very heavy, forming a dry cake when first mixed, it is convenient to have a small handle on the piston of the feed cylinder, by means of which the feed rate can be manually speeded up on the first pass. Since the grinding apparatus is transparent, the point at which the ink is completely fed out is easily observed. Quantities of 1 to 8 grams (15 to 120 grains) of ink can be conveniently handled.

When the crude mix contains large, hard aggregates there is some tendency for the ink coming through first to be richer in vehicle. For this reason, the ink is always repassed once after the original grind. Tests have shown that even in an extreme case, the composition of the ink after the second pass is not more than 1 per cent different from the original composition.

The mill will operate efficiently on inks over a very wide range of viscosity, and will conveniently handle mixtures which are too heavy or too dry to mull by hand without excessive work.

The temperature to which the ink is heated by the grinding has not been measured. The author's tests have not shown the heating to have an appreciable effect on the finished ink. Where this might arise, a water-jacketed female section can be employed.

Characteristics of the Mill

Freedom from contamination was tested by grinding portions of a base crudely mixed ink, using various methods, and comparing the brightness of the resulting ink. For an average laboratory-produced pigment in linseed oil, results are listed in Table I. Results for a very hard white laboratory-produced pigment are shown in Table II. In connection with the "hardness" of these pigments, it has been observed that a commercial "soft" titanium dioxide pigment, when mulled in a linseed oil 3 × 65 on a smooth glass slab, was generally contaminated to the extent that its reflectance was 0.5 to 4 per cent too low. Contamination encountered with "hard" laboratory pigments may be expected to be greater under the same conditions.

Table I. Reflectance Tests

(Typical laboratory-produced titanium dioxide pigment, 70% pigment-vehicle ratio in refined linseed oil vehicle)

Conditions of Dispersion	% Reflectance of White Ink
3 × 65 mulls, ground porcelain slab	83.3
3 × 65 mulls, smooth glass slab	90.15
All-glass mill	94.45

Table II. Tests on Very Hard White Pigment

(70% pigment-vehicle ratio in refined linseed oil vehicle)

Method of Dispersion	Brightness	Texture	Apparent Tinting Strength
4 passes on 4 × 8 inch roller mill	Very gray	Smooth	100
3 × 65 mulls unweighted muller, smooth glass slab	Intermediate between other two	Very coarse	95
2 passes on all-glass mill	Very bright	Smooth, slight evidence of some aggregates	100

Efficiency of grinding was estimated by means of texture tests and by determining the strength developed in a hard grinding colored pigment. Results indicative of the texture obtainable are listed in Table II, as are strength determinations on the same white.

The most exacting test, in so far as strength development is concerned, was carried out with a hard grinding iron blue, a commercial product dating back to 1936. A preliminary mix at a pigment-vehicle ratio of 45 per cent was prepared, and mixed further by two very loose passes over a laboratory 4 × 8 inch three-roller mill. Samples of this ink were then developed by each of three methods—namely, by the 4 × 8 inch three-roller mill, by mulling with a 15-pound weighted muller, and finally on the new mill. The results are listed in Table III. A sample of the same brand of pigment, produced five years later, was apparently of improved quality with respect to hardness, for it was developed to equal strength by both the three-roller mill and the new all-glass mill. "Strength" refers to tinting strength, and was a measure of the amount of a standard white ink required to tone the color down to match an arbitrary standard. Strengths are referred in Table III to that of the ink made by passing five times over the three-roller mill as 100.

Table III. Tinting Strength Tests

(Very hard grinding iron blue at 45% pigment-vehicle ratio in refined linseed oil)

Method of Dispersion	Apparent Tinting Strength
8-inch three-roller mill, 1 pass	80
2 passes	96
5 passes	100
15-pound weight muller, 2 × 100 strokes	80
4 × 100 strokes	90
New glass mill, 2 passes	90
4 passes	94
6 passes	95

Speed of delivery is, of course, variable to suit the demands of the operator. Operating with 1.5 grams (23 grains) of ink, it has been found convenient to make the first pass in about 3 or 4 minutes, and the second in about 2 minutes. Including time consumed in loading and cleaning, an ink can be prepared in 10 minutes or less. This compares favorably with hand mulling under any conditions, and to advantage when a very heavy ink is encountered, which is difficult to work in. On the other hand, a roller-mill grind of a small quantity of ink takes about 10 minutes, when the time required to clean the mill is considered. When a very thin ink is encountered on the three-roller mill, the new all-glass mill shows up to advantage as far as the time factor is concerned.

Discussion

Tables II and III show that the mill lies between the muller and the roller mill, with respect to grinding efficiency, and is clearly much closer to the roller mill than to hand mulling. Nearly all the commercial pigments will be developed to essentially the same strength by the new glass mill as by the three-roller mill.

Examination of Tables I and II shows that the new all-glass mill is superior to other methods of dispersion, when freedom from contamination is considered. This makes it very useful for white and light pigments.

With respect to time consumed, the mill is as fast as or faster than either of the other methods considered.

The mill is superior to hand mulling in every respect. It is superior to the three-roller mill with respect to freedom from contamination, but yields slightly poorer dispersions when very hard grinding colors are encountered. The ability to produce excellent dispersions on samples which are too small to be handled by the laboratory roller mill further expands its field of usefulness.

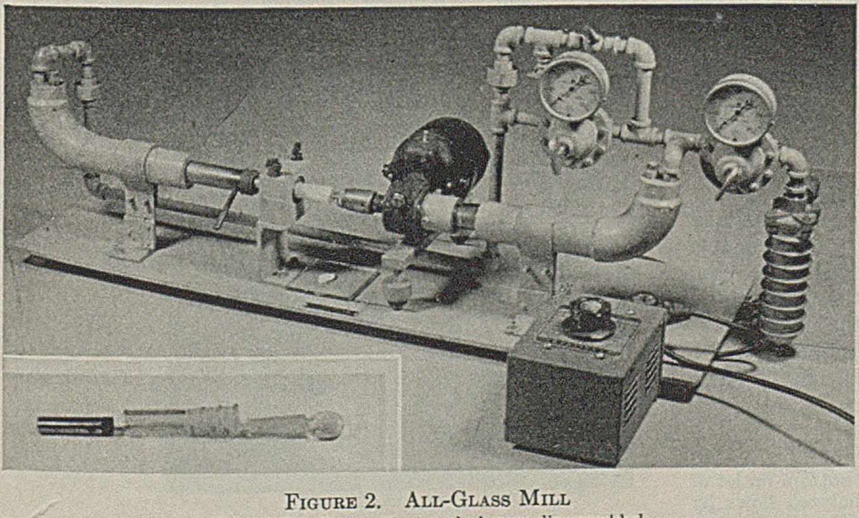

Figure 2. All-Glass Mill

Inset. Grinding sections and plunger disassembled

Summary

A new mill has been developed, by means of which inks and paints over a wide consistency range can be thoroughly ground without contamination. This new apparatus consists essentially of two truncated glass cones, one of which is fitted inside the other, together with a plunger feed mechanism which forces crudely mixed ink into the annular space between the conical sections, one of which is rotated with respect to the other. For example, the outer section of a ground-glass joint is fitted with a plunger at the small end, and ink forced by a rotating appropriately slotted stopper. The efficiency of this mill has been tested relative to that of a laboratory 4 × 8 inch three-roller mill as well as hand milling. Advantages are excellent dispersion and freedom from metallic contamination, with whites and light colors.

A Dialyzing Concentrator

CARL C. SMITH AND CHARLES D. STEVENS
Cardiac Laboratory, College of Medicine,
University of Cincinnati, Cincinnati, Ohio

A simple apparatus for simultaneous dialysis and concentration has been devised. The rates of evaporation of water from 5 per cent sucrose solutions and from distilled water through Visking casings were observed under various conditions. By use of two fans and a steam unit heater to blow air past eight Visking casings, a maximum rate of evaporation of 1.5 liters of water per hour was obtained.

A NUMBER of methods for dialyzing have been reported (*1*, *2*, *7*, *8*, *10*, *12*), and procedures have been devised for concentration by removal of solvent through membranes (*3*, *13*, *15*). Only a few techniques have been employed which permit simultaneous concentration and dialysis and in general these have been expensive or complicated. The need for a simple procedure which would permit dialysis and concentration of 20 to 30 liters of kidney extract a day led the authors to investigate the adaptability of some methods previously reported.

Simms' method (*11*) was rapid but required strong collodion bags and could be adapted only with difficulty to the authors' larger volumes of material. Wet Visking casings of 1.4 or 1.875 cm. ($^{18}/_{32}$- or $^{24}/_{32}$-inch) diameter filled with water burst when from 200 to 300 mm. of mercury pressure were applied and so could not be substituted directly in a modified Simms' apparatus. The authors have employed a maximum pressure equal to that of 140 mm. of mercury in their apparatus Thalhimer's method (*14*), employing corn sirup in dialysis, introduced considerable amounts of carbohydrate into the extracts, which was undesirable. Similar methods employing ammonium sulfate or other salts were objectionable for like reasons. Ultrafiltration through membranes on Seitz filters has been useful in industry (*9*), but was not feasible in the authors' laboratory.

They found that Kober's pervaporation technique (*4*, *5*, *6*) could be readily adapted to their laboratory equipment, and the apparatus pictured in Figures 1 and 2 has proved capable of handling materials without requiring much attention. Since few observations on rates of concentration and dialysis by any of these methods have been reported, the authors have measured rates and temperatures with their equipment under varying conditions which may afford indications of the value of this type of apparatus.

Apparatus

The apparatus consists of a reservoir, from a bottom outlet of which the material to be concentrated and dialyzed flows by gravity through glass and rubber tubing into eight Visking casings arranged in parallel, each 165 cm. (5.5 feet) long. These hang before a steam unit heater (with its fan) and one or more fans. The lower ends of the casings, which are expanded by pressure of the contained fluid, dip into a jar of water. Tap water is led through coils in the reservoir to keep the material cool, and thence through a rotameter (Fischer & Porter Co., Philadelphia, Penna.) to measure its rate of flow. From there it runs into the dialyzing jar, overflows onto a tray, and runs into the trough of the laboratory bench. To gather the data in Table I, wet- and dry-bulb thermometers were placed beside the casings directly in front of the unit heater, and a thermometer was placed inside one

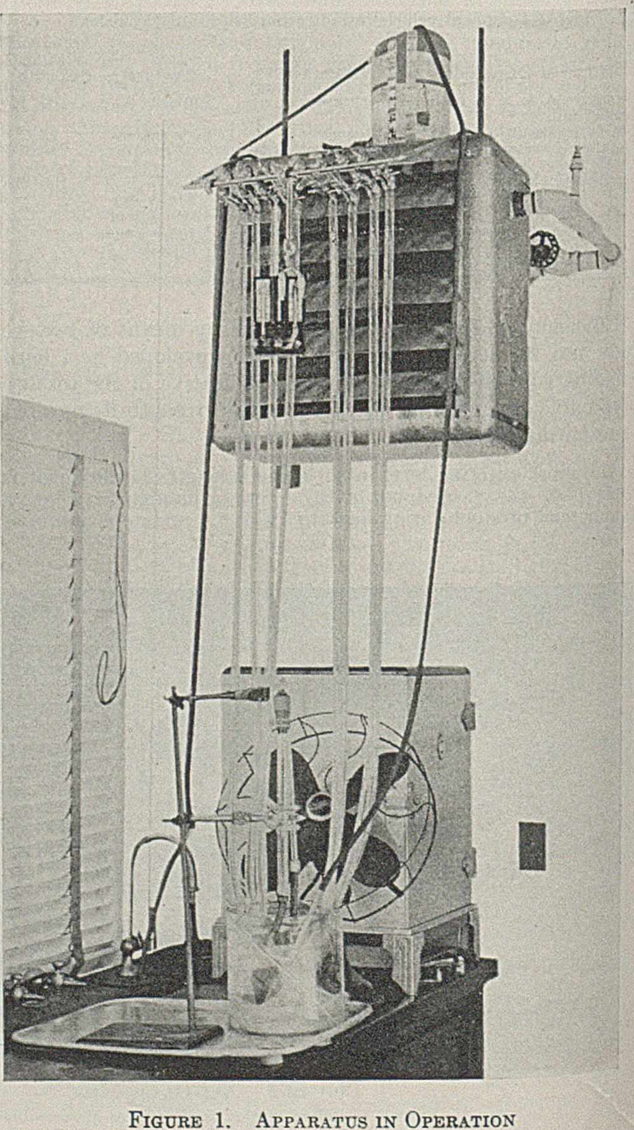

Figure 1. Apparatus in Operation

Table I. Data on Dialysis

Starting Material	Diameter of Casings	Temperature in Reservoir	Temperature in Casing	Temperature in Front of Unit Heater	Wet-Bulb Temperature	Temperature above Jar	Temperature in Jar	Tap Water Flow Rate	Fans	Heater	Duration of Experiment		Evaporation Rate	Final Sucrose Concentration		Sucrose Dialyzed Out
														Casings	Reservoir	
	Inch	°C.	°C.	°C.	°C.	°C.	°C.	L/min.			Hours	Min.	L./hr.	G./100 ml.		G./hr.
Distilled H_2O	18/32	24.5	18.5	29.5	17.8	28	21	0.99	..	..	1	20	0.23	..	..	..
	18/32	24.5	17.5	29.5	16	28.5	21	0.99	2 on	..	2	50	0.74	..	..	..
	18/32	27.5	28	64	28	35	22	0.99	2 on	On	1	10	1.29	..	..	..
	18/32	29	30	64	30.6	40	25	0.57	2 on	On	4	..	1.14	..	..	..
	18/32	25.5	19.5	29.5	18	29	22	0.54	2 on	..	1	..	0.57	..	..	..
	18/32	24.5	20	29.5	18	29	22	0.54	3 on	..	1	40	0.57	..	..	..
	18/32	29	22	29	20.6	29	22.5	0	..	..	16	..	0.12	..	..	..
	18/32	32	26	32	24	31	26	0	..	..	12	40	0.17	..	..	..
5% sucrose	18/32	24.5	18.5	30	17	28	21.5	0.99	..	..	2	10	0.17	4.68	4.85	11.5
	18/32	24.5	17.5	26.5	17	28	21.5	0.99	2 on	..	2	40	0.54	6.49	4.97	13.5
	18/32	27.5	27.5	64	28.5	32	22	0.99	2 on	On	3	..	0.95	9.21	4.97	13.3
5% sucrose	24/32	23.5	22	27	20.6	25	22	0.99	..	..	2	10	0.12	4.38	5.0^a	18.9
	24/32	24.5	17.5	27.5	16	25	22.5	0.99	2 on	..	1	20	0.65	5.28	5.0^a	23.3
	24/32	28	28	64	29	34	24.5	0.99	2 on	On	2	40	1.34	7.53	5.0^a	25.9
Distilled H_2O	24/32	23	20	29	19	28.5	22	0.99	..	..	2	40	0.29	..	..	..
	24/32	23.5	18	28	16	27.5	21	0.99	2 on	..	3	30	0.76	..	..	..
	24/32	27	28	64	28	34	22	0.99	2 on	On	2	50	1.47	..	..	..

[a] Estimated figure.

of the casings at the same level. Thermometers were also placed in the dialyzing jar, 30 cm. (1 foot) above it, in the reservoir, and on the wall 180 cm. (6 feet) to one side of the apparatus.

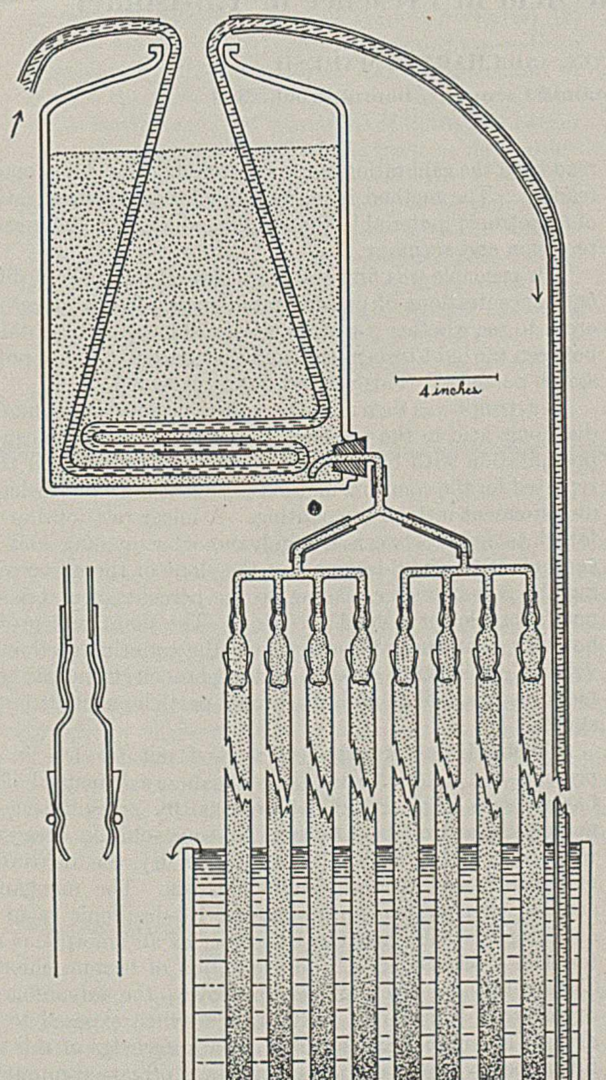

Figure 2. Reservoir, Cooling Coils, Tube Connections (with Detail), and Tubes with Lower Ends Dialyzing

Table I shows that evaporation from the casings proceeded slowly without the use of fans. The rate of evaporation was tripled if two fans were allowed to blow air past the casings, provided humidity and room temperature remained about the same. The use of steam in the unit heater practically doubled the rate of evaporation over that when only two fans were used, but produced increased temperature within the casings. The presence of sucrose in the casings always decreased the rate of evaporation. The rate of dialysis depended to a considerable extent on the surface of casings immersed in the dialysis jar, and could be increased by using longer casings.

Among the advantages of this type of apparatus in the authors' laboratory are its low cost, its automatic operation, its high rate of concentration, the readiness with which it may be adapted to handle more or less material, the removal of dialyzable materials simultaneously with concentration, the gradual passage of nondialyzable material from the upper heated zone of concentration to the lower cooler zones of the casings (provided the nondialyzable material has a higher specific gravity than water), the continual supply of the most dilute material to the zone where the evaporation rate is highest, the ease of removing the material from the casings when operations are completed, and the small amount of equipment which needs cleaning. No trouble with foam, spray entrainment, or overheating such as may occur in vacuum distillations has been encountered with this apparatus. Disadvantages encountered may be: decreased evaporation rates when high humidity prevails, breakage of casings, collection of dust on the outside of the casings facing the fans, collection of some solids on the inside of the casings if the material is overconcentrated, and the slight heating of the material within the casings when steam is run into the unit heater.

Acknowledgment

The authors are indebted to Fred Blanchard for technical assistance in gathering these data.

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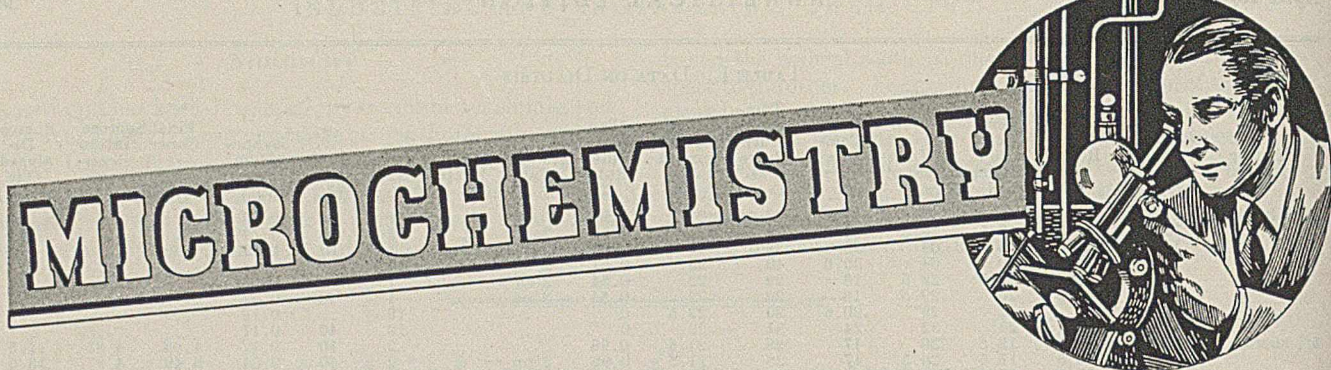

Photoelectrometric Particle-Concentration Analysis

Estimation of Anthraquinone-Beta-Sodium Sulfonate in Presence of Alpha-Isomer and of Anthraquinone-1,8-Disulfonic Acid in Presence of 1,5-Isomer

WILLIAM SEAMAN, A. R. NORTON, AND CHARLES MARESH
Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

THE microscopical quantitative analysis of heterogeneous mixtures (*1*) by methods such as simple estimation, comparison with known standards, or counting, while generally not affording the precision of most chemical analyses, is sometimes preferable to chemical methods because it is economical of time and materials. Sometimes the lack of pronounced chemical differences between the constituents of a mixture makes chemical methods of analysis impossible. Resort must then be had to physical methods, including microscopical methods. Microscopical observations are often fruitful in working with isomers which can be differentiated only by staining behavior, crystal form, refractive index, or other optical properties.

Of the various microscopical methods, counting methods are the most precise. A counting method has been reported from this laboratory for the analysis of anthraquinone-1,8-disulfonic acid in the presence of the 1,5-isomer (*2*). This was an extension of the classical methods of particle counting to the counting of crystals which have been precipitated as salts of the original substances. The precise salt which was to be precipitated was chosen in order to take advantage of differences in the optical properties, so as to be able to count one substance without interference by the others. In this paper a method is reported whereby the tedious and sometimes impossible task of counting is eliminated and instead the light due to the birefringence of the constituent to be estimated is measured, after suitable means have been taken to minimize light from the other constituents.

Photoelectrometric Principle

In specimens consisting of a mixture of anisotropic particles and amorphous or isotropic particles, the light which is transmitted by the specimen when placed between crossed Nicol prisms, and which is measured by a photosensitive element connected with a galvanometer, is proportional to the quantity of anisotropic material present, within definite limits of concentration. As in counting methods, a standard curve is first prepared for the analysis in question by analyzing a number of mixtures of known composition. Slides of samples being analyzed are prepared under standardized conditions, and the concentration of the constituent being estimated is read from the calibration curve by applying the galvanometer reading. The method is most useful for low concentrations of anisotropic material in the sample, which give the greatest precision and accuracy.

This principle was first tested on several mixtures of different concentrations of potato starch suspended in glycerol in order to see whether a regular relationship could be obtained between the light transmitted and the concentration of potato starch particles. This worked out as expected.

An attempt was then made to determine anthraquinone-1,8-disulfonic acid in the presence of the 1,5-isomer by means of precipitation with barium under conditions similar to those reported for the counting method (*2*) but using a photoelectric measurement instead of counting. A linear relationship was found to hold between the galvanometer reading and the concentration of 1,8-isomer, but the slope of the curve relating the galvanometer reading to the percentage of 1,8- was not favorable for a good precision. The point was proved, however, that one could carry over the counting method involving precipitated crystals to the photoelectrometric technique just as well as with preformed particles such as potato starch.

A method was nevertheless worked out for 1,8- in the presence of 1,5- by utilizing the manganese salt instead of the barium salt. This could not be done by precipitating the manganese salt of the 1,8- from aqueous solution because it was too soluble. It was necessary to dry the mixture of manganous acetate and disulfonic acids. The manganous acetate precipitates anthraquinone-1,8-disulfonic acid as anisotropic needles and the 1,5-isomer as an amorphous material in a manner similar to the action of barium chloride. The manganous acetate has, moreover, the advantage of drying to a transparent isotropic film when exposed to the air. (The authors are indebted for a knowledge of this useful property of manganous acetate to a private communication to this company from E. M. Chamot.) Thus, the excess manganous acetate present, which is added to a drop of the anthraquinonedisulfonic acid, will not interfere. The light transmitted by the 1,8- crystals gives galvanometer readings which are related by a linear function to the percentage of the 1,8- within certain limits of concentration.

A method of photoelectrometric particle-concentration analysis is described for the estimation of one constituent of a mixture which involves measuring, by means of a photosensitive cell and a sensitive galvanometer, the intensity of the light transmitted by that constituent. The value of the concentration is read from a standard curve. In general, the method should be capable of adaptation to any mixture of which one constituent can be made luminous and the other constituents invisible or of low luminosity by any means, such as by crossed Nicol prisms, selective staining with the use of color filters, or fluorescence. The technique may be used to replace counting particles and is less tedious, less subject to personal errors, and adaptable to mixtures where counting would be difficult and to routine analysis.

Specifically, the method has been applied to three problems: (1) to counting starch particles, as an illustration of its use with a classical example of a counting method for already formed particles; (2) to the estimation of anthraquinone-beta-sodium sulfonate in the presence of the alpha-isomer, in which case the beta-sodium salt does not itself serve as the source of transmitted light, but rather the precipitated crystals of the barium salt, which are luminous between crossed Nicol prisms, whereas the barium salt of the alpha-isomer forms an amorphous background; and (3) to the estimation of anthraquinone-1,8-disulfonic acid in the 1,5-isomer by means of a precipitation with barium, previously reported for use with a counting method, as well as by means of a precipitation with manganese. The effect of impurities upon the results has been studied.

The principle was next applied to the estimation of anthraquinone-beta-sodium sulfonate in the presence of the alpha-isomer. (Since both sodium salts occur as anisotropic plates, they could not be used directly for this method of analysis.) The barium salts were found to possess characteristics suitable for differentiation of the isomers. The barium salt of the beta-isomer appears as bright anisotropic plates, occurring singly and in clusters, whereas the alpha-barium salt is so much more insoluble that it appears as an amorphous precipitate under controlled conditions discussed below. It becomes a simple matter to measure the light transmitted by the beta-salt by means of a photosensitive element and a sensitive galvanometer.

Nomenclature, Theory, and Possible Developments of Method

The authors propose to apply the term "particle-concentration analysis" to that class of methods of analysis which is based upon an actual estimation of the density of distribution of the particles of one substance in the presence of others. These methods are to be differentiated from other methods (whether physical or chemical) which, on the one hand, involve an actual separation of one constituent from another, followed by weighing or some other means of estimation; or, on the other hand, do not require such a separation but depend upon measuring the concentration of one constituent by means of properties which are independent of any consideration of the presence of discrete particles of this constituent. In other words, the criterion for application of the term "particle-concentration analysis" lies in the fact that it is the concentration of discrete particles which is being determined.

Counting methods, either of preformed particles or of precipitated crystals, illustrate one type of method of particle-concentration analysis. By another method, described in this paper, the particle-concentration is determined by photoelectrometric means. In developing this method, no attempt was made to find conditions which would give the highest possible precision and accuracy, but rather to get a precision and accuracy which would be satisfactory for the purposes for which the methods were devised. It may, however, be desirable to consider in a general way what sources of error are inherent in the photoelectrometric method and to what extent the method could be improved.

Certain errors of technique or apparatus may arise, the correction or elimination of which should increase the accuracy.

For example, any lack of planeness in the slide or cover glass would cause local variations in the thickness of the layer examined which would lead to variations in the light transmitted. To attain the highest accuracy the glass surfaces would have to be tested or more fields examined. With needle crystals there is a possibility that the shear in the suspending medium as it spreads beneath the cover glass might cause a tendency toward parallel orientation, at least in some regions, which would give nonuniform readings. An examination of some of the authors' photomicrographs does not indicate that this has occurred in this work, but with long needle crystals this tendency might manifest itself. Possibly the easiest way to compensate for such a tendency would be to take the average of two readings in 45° positions of the stage. Another error would arise if there were a marked difference in refractive index between the particles and the medium. Even isotropic material might then appear bright between crossed Nicol prisms because of the scattering and depolarization of light at its surfaces. This would be a more important factor the finer the material. This effect could be completely eliminated if the refractive indices could be matched precisely. (The authors are indebted to C. W. Mason for the discussion of the points in this paragraph.)

Elimination of errors of apparatus or technique would lead to only a limited improvement in the attainable accuracy. The limit of improvement would be set by the uncertainty attached to the mean values upon which the standard curve is based as well as by the uncertainty of the unknown. This uncertainty is caused by the randomness of such factors as orientation of crystals, particle size, and particle distribution. Theoretically, this uncertainty can be reduced to any desired extent by averaging more and more values. Actually, one soon reaches a practical limit which is set by the fact that the uncertainty of the mean varies inversely as the square root of the number of values used in calculating it, so that the number of determinations necessary for a desired precision soon becomes prohibitive for an analyst to perform. There would seem to be a possible opportunity for the use of instrumentation in this respect, for if an automatic system could be devised (mechanical, electronic, or otherwise) it might be possible within a brief period of time to get a mean value from an enormous number of individual values and so attain a markedly enhanced precision.

Some other possible applications of the photoelectrometric methods suggest themselves. If one type of particle can be selectively stained, it should be possible by means of suitable color filters to measure that type to the exclusion of others. There may be differences in the fluorescent properties of the various particles which could be utilized. There may also be a possibility of measuring these by means other than photoelectrometric—possibly photographically or photochemically. Considerably farther in the realms of speculation would be the possibility of utilizing properties other than optical ones

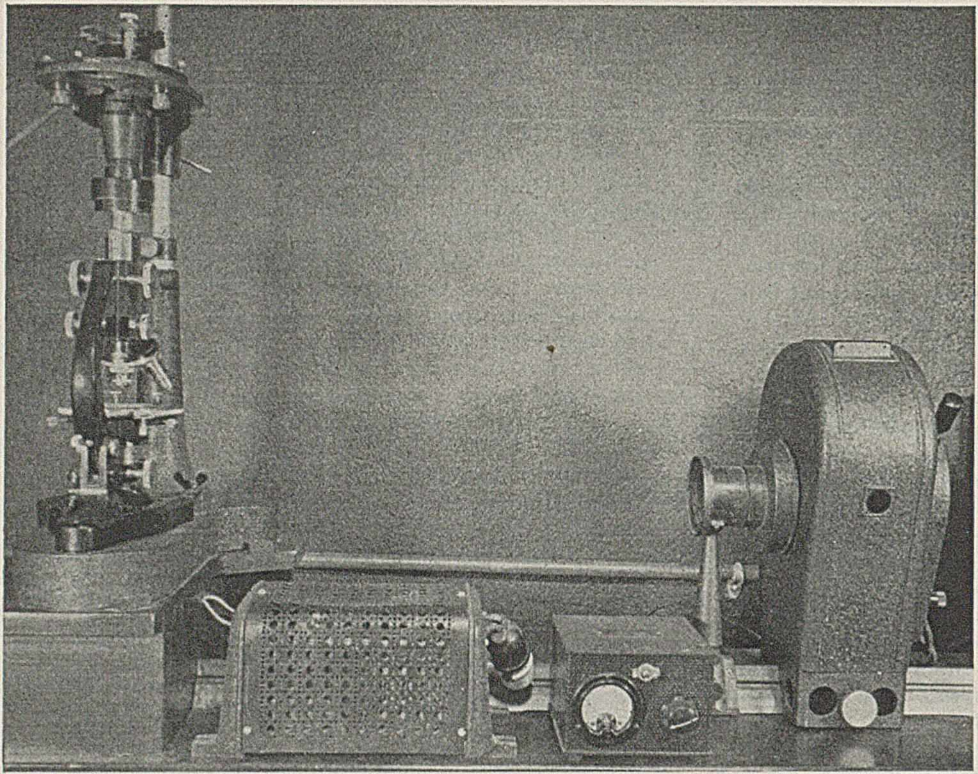

FIGURE 1. PHOTOELECTROMETRIC APPARATUS

for this purpose, as, for example, differences in magnetic permeability.

Apparatus

A Leitz petrographic microscope (Figure 1) (6 × P2 objective, 10 × p ⊕ ocular, no condenser, concave mirror) is set up on a Zeiss optical bench with a Leica rotating copying attachment to hold the self-generating, dry-disk photosensitive element. The cell is connected to a Leeds & Northrup Type R galvanometer (0.00013 microampere per mm.). The light source is a 30-watt, 6-volt lamp with a spiral filament, the amperage of which is regulated by means of a 6-ampere, 6-volt Leitz rheostat to about 4.3 amperes. A Raytheon voltage regulator (input 95/130 volts, output 115 volts, 60 watts) was used to cut down voltage fluctuations to a minimum. The light source center is set 79 cm. from the mirror center. A condenser lens is placed directly in front of the light source at such a point as to focus the filament on the microscope mirror.

In order to make it possible to reproduce standard lighting conditions, a standard starch slide, made up in Hyrax (Paul Ruedrich, manufacturing chemists), was prepared and a particular field was marked off by means of a scratch on the underside of the slide which is set on the cross hairs of the ocular. This apparatus was used merely because it was available; it could undoubtedly be simplified by using less expensive equipment and making it more adaptable to routine analysis. A fixed light source below the microscope stage as well as a microscope with fixed tube length, fixed magnification, and polaroid plates instead of Nicol prisms would be more practical where extensive use would be made of such a method as described here for the examination of one type of material.

Estimation of Potato Starch

The applicability of the photoelectrometric principle was first tested by means of potato starch suspensions in glycerol. Three concentrations were prepared and measured in a Howard mold-counting cell. Readings were made on different preparations of the same samples on three different days. Each time, the apparatus was dismantled and then reassembled. The measurements (Figure 2) thus indicate the variations which can be expected from all sources in using the apparatus.

Estimation of Anthraquinone-Beta-Sulfonate

CHEMICALS. The ordinary reagent grade of barium chloride dihydrate was used.

Anthraquinone-alpha-sodium sulfonate had been purified through the monomethylaniline salt which had been recrystallized to a constant melting point of 211.5° – 212.3° C. (corrected) and could be hydrolyzed to the acid melting at 213.8° – 214.9° C. (corrected).

Anthraquinone-1,5-disodium disulfonate was purified through the monomethylaniline salt which had a constant melting point of 248.5° – 250.0° C. (corrected).

Anthraquinone-2,7-disodium disulfonate was prepared from the crude compound by recrystallization from water.

Anthraquinone-beta-sodium sulfonate, anthraquinone-1,8-disulfonic acid, and anthraquinone-2,6-disodium disulfonate were prepared as described in (*2*). (Anthraquinone-alpha-sodium sulfonate, anthraquinone-1,5-disodium disulfonate, anthraquinone-beta-sodium sulfonate, anthraquinone-1,8-disulfonic acid, and anthraquinone-2,6-disodium disulfonate were prepared by W. J. Mader.)

PREPARATION OF SAMPLE SOLUTION. A 0.5-gram sample is weighed out into a 15 × 2.5 cm. (6 × 1 inch) test tube and the beta constituent is extracted with 10 ml. of boiling water, solution of the beta being aided by means of a stirring rod. After cooling the mixture to room temperature, the excess alpha is filtered off; the filtrate containing the more soluble beta is used in subsequent tests. It may be necessary to refilter one or more times in order to obtain a clear filtrate.

METHOD OF PRECIPITATION. *Concentrations of Beta 0.5 Per Cent and Higher.* Although two types of cells were tried, a brass

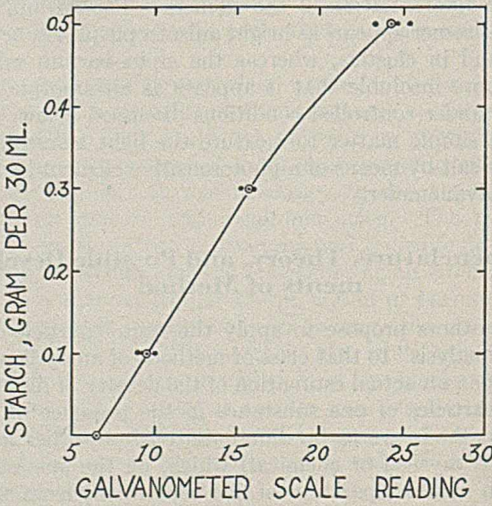

FIGURE 2. POTATO STARCH READINGS

⊙ Mean values

● Individual values

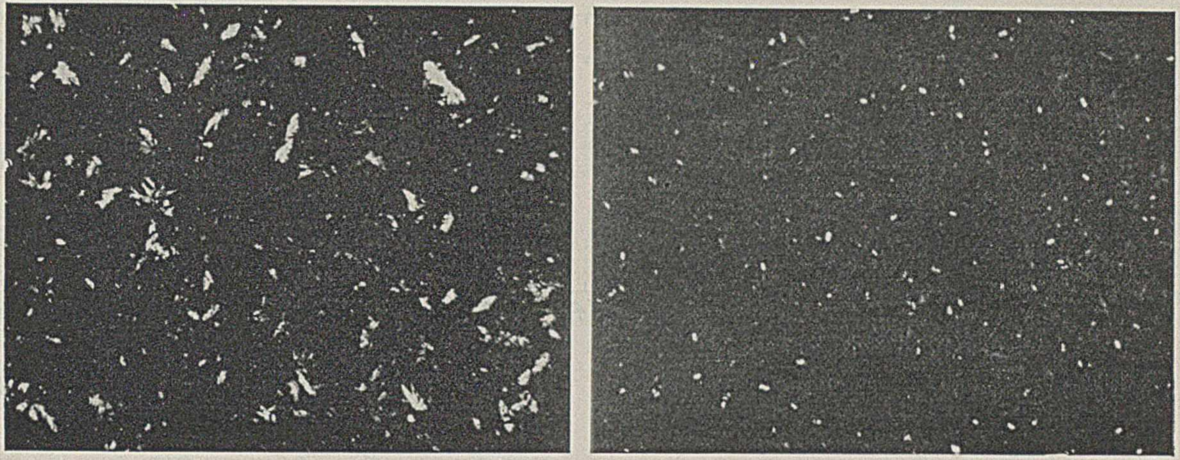

FIGURE 3. ANTHRAQUINONE-BETA-SULFONATE

Left. 2.5 per cent
Right. 1 per cent

ring and a Howard mold-counting cell, it was found unnecessary to use any of these for this work. The estimation may be carried out on an ordinary microscope slide. A drop of the filtrate is added to the slide by means of a 0.1-ml. pipet. One drop of 10 per cent barium chloride solution is then added directly to the first drop from a 10-ml. buret without stirring. After standing for 5 minutes, the drop is stirred with a small rod, scratching the slide and taking care not to spread the drop to a size greater than that of the 1.88-cm. (0.75-inch) cover glass. After an additional 5 minutes, the stirring is repeated and the drop is covered with a 1.88-cm. (0.75-inch) cover glass. Anthraquinone-alpha-barium sulfonate precipitates immediately, whereas the beta-isomer comes out only on standing. Readings are taken 30 minutes after addition of the barium chloride solution.

Under the conditions prevailing in this precipitation, a sample containing more than 2 per cent beta gave erratic and very often low results. A high beta content often tends to give many fine crystals and clusters of the barium salt instead of the usual fewer large crystals. Figure 3 (left) shows the type of field obtained with a high concentration of beta (2.5 per cent); Figure 3 (right) shows a field within the proper concentration range of beta (1.0 per cent). The greater variation in crystal size is also the explanation for the lower precision in the case of samples with a higher beta content. Thus, any sample containing more than 2 per cent beta must be run by using only a fractional part of the full sample. A sample showing a field filled with beta-barium salt and still giving a low light value, as well as any sample which is doubtful, should be repeated using a fractional sample. After observing a few slides representing decreasing sample weights with the difference in weight being made up with pure alpha, it becomes simple to pick out samples which are giving low results because of the physical condition of the barium beta salt. This reduction in the size of the sample is continued until a maximum percentage of beta is obtained; further dilution gives a constant percentage of beta within the lessened precision caused by multiplication of the error.

Concentration of Beta below 0.75 Per Cent. In order to obtain crystals for concentrations below 0.75 per cent beta, the slide must be allowed to come almost to dryness without a cover glass. The slide is stirred every 5 minutes as long as the rod leaves an even field. The drop is spread to a diameter of about 1.88 cm. (0.75 inch) and the readings must be made just before the preparation dries, which usually requires about 20 minutes. If the reading is made too late, this is obvious because the barium chloride crystallizes and the galvanometer needle goes off the scale.

ADJUSTING APPARATUS PRIOR TO MAKING READINGS. The lamp amperage is set at about 4.3 amperes and the filament is focused on the center of the mirror by means of the condenser lens and the lamp adjustment. The standard potato starch field is then set at the cross hairs. With the tube length set at 170 mm. and the Nicol prisms crossed, the maximum value is obtained for the field by manipulation of the mirror. The final adjustment is made by altering the lamp amperage to give a deflection of 28.5 cm. on the galvanometer scale from the zero position, which in all of this work was set at 5.5 cm. The 5.5-cm. position must be checked from time to time, for there is a gradual drift upward due to the heating action of the beam of light. Because of the difficulty, at times, in making the 28.5-cm. adjustment precisely, no attempt was made to adjust it any closer than between 28.5 and 29.0 cm.

METHOD OF TAKING READINGS. Three slides for each sample and standard were prepared and nine readings were taken on each, three fields across the top, three fields across the center, and three fields across the bottom. The optical system should be checked against the standard starch field before taking readings on each slide and the lamp should be on at least for 30 minutes before the readings are made in order to allow the filament to come to equilibrium. It is not necessary to return the galvanometer to zero after each slide is read. Occasionally the galvanometer suddenly jumps to give an unusually high reading, or it jumps off the scale because some fibrous material is included in the field. Such fields must be examined and discarded if the high reading is caused by the presence of foreign matter. Before readings were made for each slide, the particular field was refocused in order to take care of possible thickness differences, although it was found that the effect of neglecting this precaution was negligible.

STANDARDIZATION CURVES. Table I gives the mean galvanometer readings for a number of determinations with various percentages of pure beta mixed with pure alpha. Each mean reading is accompanied by the number of values from which it was obtained. Each individual value is itself the mean of nine readings on one microscope slide preparation.

In the case of values obtained with the high concentration method, a straight line was constructed by the method of least squares. Figure 4 gives the straight line, including the individual values from which the mean values were calculated.

TABLE I. STANDARD MIXTURES OF ALPHA AND BETA SALTS

% Beta	Mean Galvanometer Reading	No. of Readings	Standard Deviation of Single Reading (± % Beta)[a]
Method Used for 0.5% and Higher			
0.50	23.1	17	0.12
0.63	23.4	6	0.22
0.75	25.8	8	0.17
0.88	26.7	12	0.15
1.00	29.4	16	0.24
1.25	30.6	10	0.26
1.50	35.0	8	0.27
1.75	37.1	10	0.33
2.00	38.1	17	0.37
2.25	37.3	9	0.50
2.50	45.3	8	.38
Method Used for Less Than 0.75%			
0.25	20.0	12	0.05
0.50	25.8	9	0.08
0.75	30.4	10	0.05

[a] Standard deviation for mean would be that for a single reading divided by square root of number of readings.

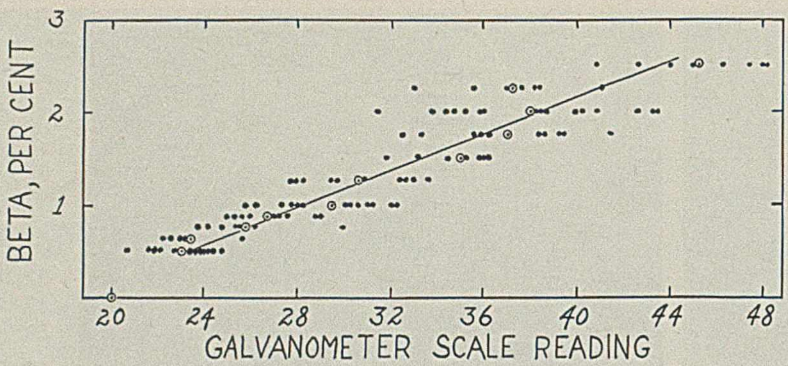

FIGURE 4. CALIBRATION CURVE

Per cent beta between 0.5 and 2.0
⊙ Mean values
● Individual values

Between beta concentrations of 0.5 to 2.0 per cent, the beta content can be calculated by the following equation which is derived from the curve:

$$\%\ \text{beta} = \frac{\text{galvanometer scale divisions} - 18.2}{10}$$

In the case of the low concentration method, a straight line was drawn through the mean values as shown in Figure 5. The beta content for this range of concentration can be calculated by the following equation which is derived from the curve:

$$\%\ \text{beta} = \frac{\text{galvanometer scale divisions} - 15.2}{20.6}$$

ACCURACY. From the deviations of the individual values from the curves, the standard deviation of a single value has been calculated. This refers to the accuracy, since the deviations are from known values. The precision would frequently be better than the accuracy, but it is not reported because it is of minor importance in this connection. The standard deviation was calculated separately for each concentration and is given in Table I. There is an upward trend of the standard deviation with higher beta concentrations, as would be expected.

In Table II are given results for some commercial samples analyzed. The percentage of beta found for commercial samples is often lower than the percentage of beta added, undoubtedly because of traces of impurities. The precision for commercial samples is of the same order of magnitude as that of pure mixtures.

CORRECTION FOR BACKGROUND. The 100 per cent pure alpha samples gave galvanometer readings of 20.1 ± 0.8 divisions (standard deviation). Some commercial batches, when precipitated and the readings taken immediately, gave blank values which were less than 19.3 (20.1 − 0.8). For this reason, a correction must be applied whenever the blank value differs from 20.1 by more than the standard deviation of 0.8 division. This correction takes care of differences in background due to impurities. The blank values are obtained by taking readings before the beta-barium salt starts to come out. It is, in reality, the light value of the field containing everything but the beta. Samples 1 and 3 of Table II were corrected for background. Samples 2 and 4 did not require corrections.

FACTORS AFFECTING READINGS. Stirring of the preparations was found essential in order to obtain uniform slides, while seeding by scratching gave larger crystals of the beta and eliminated erratic slides.

After standing for 30 minutes, the high concentration slides were always found to have reached equilibrium. Shorter times were likely to cause lower values. In the case of the low concentration method where the preparation was left uncovered, time is an important factor, as shown by the following readings for a 0.75 per cent beta sample: At 10, 15, 20, and 25 minutes after the precipitation the readings obtained were 22.4, 23.4, 24.3, and 25.0 cm., respectively. The slide started to go to dryness at the beginning of the 25-minute reading and all subsequent readings were much too high, giving deflections of the galvanometer which were off the scale. For this reason, the readings must be made just before going to dryness.

Impurities have a marked effect on readings, especially some of the disulfonic acid derivatives of anthraquinone. Sodium chloride has no serious effect. Table III shows the effects of sodium chloride and of some of the anthraquinonedisulfonic acids which were added to known mixtures of pure alpha and beta in the dry state.

Estimation of Anthraquinone-1,8-Disulfonic Acid as Barium Salt

The primary purpose of this work was to see whether the counting method (*2*) previously described (involving the

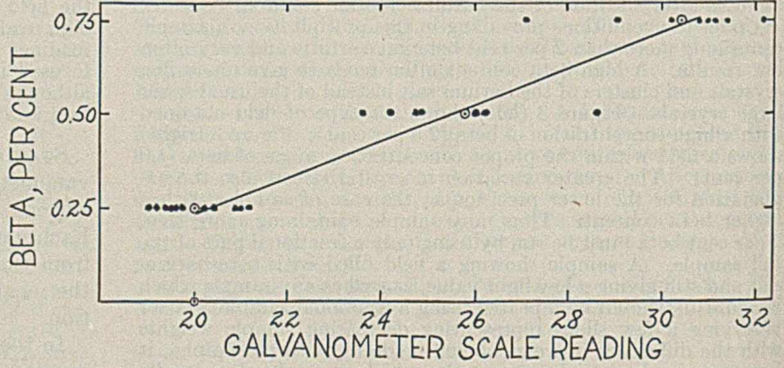

FIGURE 5. CALIBRATION CURVE

Per cent beta below 0.75
⊙ Mean values
● Individual values

TABLE II. ANALYSES OF COMMERCIAL SAMPLES OF ANTHRAQUINONE-ALPHA-SODIUM SULFONATE

Sample No.	Beta Added to Sample %	Beta Found %
1	0	0.0 (corrected for background)
	0.5	0.5 (corrected for background)
	0.7	0.5 (corrected for background)
	1.0	0.8 (corrected for background)
	1.5	0.9 (corrected for background)
2	0	0.0
	0.5	0.3
	0.7	0.7
	1.0	0.8
	1.5	1.2
3	0	0.8 (corrected for background)
	1.0	1.6 (corrected for background)
4	0	0.0
	1.0	0.7

Table III. Effects of Impurities on Values for Beta Content

Beta Present	Impurities Added NaCl	1,5-	1,8-	2,6-	2,7-	Beta Found
%	%	%	%	%	%	%
1.5	2.0	...	...	...	...	1.4
1.0	2.0	...	...	...	...	0.9
0.5	2.0	...	...	...	...	0.7
2.0	...	1.0	...	...	...	1.1
2.0	...	0.5	...	...	...	0.9
1.0	...	1.0	...	...	...	0.5
1.0	...	0.5	...	...	...	0.5
0.5	...	1.0	...	...	...	0.0
0.5	...	0.5	...	...	...	0.0
2.0	...	...	1.0	...	...	0.1
2.0	...	...	0.5	...	...	0.2
2.0	...	...	0.2	...	...	0.7
1.0	...	...	1.0	...	...	0.0
1.0	...	...	0.5	...	...	0.0
1.0	...	...	0.2	...	...	0.3
0.5	...	...	1.0	...	...	0.0
0.5	...	...	0.5	...	...	0.0
0.5	...	...	0.2	...	...	0.0
1.0	...	...	...	1.0	...	0.3
1.0	...	...	...	0.5	...	0.2
1.0	...	...	...	0.3	...	0.4
1.0	...	...	...	0.1	...	0.3
0.5	...	...	...	0.5	...	0.0
1.0	...	...	...	...	0.5	0.2
1.0	...	...	...	...	0.3	0.3
1.0	...	...	...	...	0.1	0.2

preliminary precipitation of the barium salt of the 1,8- acid in the form of small needles against an amorphous background of barium sulfate) could be replaced by a photoelectrometric estimation of the precipitated needles. The method of precipitation of the crystals in preparation for the photoelectrometric estimation, the method of sampling of the precipitated crystals, and the microscopic cell which was used were the same as outlined in the previous paper. Instead of a calibration curve based on counting crystals, one was prepared which was based on photoelectrometric measurements in accordance with the technique described in the section on estimation of anthraquinone-beta-sodium sulfonate in the presence of the alpha-isomer. Figure 6 gives the curve obtained for known mixtures containing 0, 2, 5, and 10 per cent, respectively, of 1,8- acid.

The 1,8-anthraquinone-disulfonic acid content can be calculated by the following equation which is derived from the curve:

$$\% \ 1{,}8\text{-} = \frac{\text{galvanometer scale divisions} - 17.6}{0.26}$$

Attempts were made to increase the sensitivity of the method by increasing the number of needles per field for a given concentration by a decrease in the dilution of the sample, but without success because of the formation of clusters of crystals (most likely 1,5-barium salt). Higher concentrations of barium chloride caused the same effect. The barium chloride was then replaced as a precipitant by manganous acetate. The accuracy and precision of this method, together with the accuracy of the manganese method, are discussed in the next section.

Effect of Impurities. It was assumed that the study of the effect of impurities which was made previously (*2*) for the counting method would apply here. The possibility that the calibration curve which was made up on the basis of the free acids might not apply for the sodium salts was investigated and it was found that substitution of sodium salts for the free acids did not influence the crystal count.

Estimation of Anthraquinone-1,8-Disulfonic Acid as Manganese Salt

Chemicals. The manganous acetate, sodium chloride, and sodium sulfate were c. p. grade. The remaining chemicals have been described under the estimation of anthraquinone-beta-sulfonate.

Reagent Solutions. The anthraquinone-1,8-disulfonic acid, anthraquinone-1,5-disulfonic acid, anthraquinone-2,6-disodium sulfonate, anthraquinone-2,7-disodium sulfonate, sodium chloride, and sodium sulfate were dissolved to make solutions containing 1 gram in 100 ml. of solution. Anthraquinone-alpha-sodium sulfate and anthraquinone-beta-sodium sulfonate were made up to contain 0.5 gram per 100 ml. of solution. The sulfuric acid was 0.1 *N;* 0.4 ml. equals 2 mg. of sulfuric acid.

Standard Solutions. Mixtures of the reagent solutions were made up so that each solution contained 10 mg., distributed between the sulfuric acid and the various sulfonic acids. All solutions had 0.4 ml. of 0.1 *N* sulfuric acid plus 8 mg. of total sulfonic acids. The various solutions of known sulfonic acid content were prepared by mixing appropriate volumes of the solutions named.

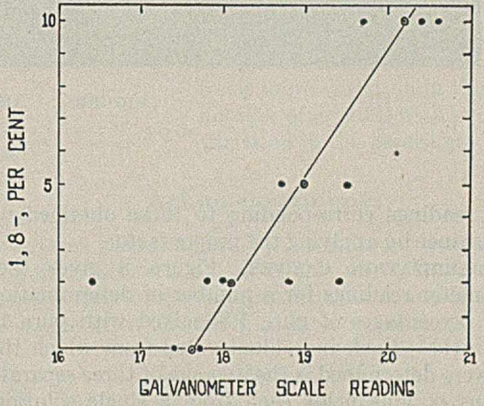

Figure 6. Estimation of Anthraquinone-1,8-Disulfonic Acid by Barium Chloride

⊙ Mean values
● Individual values

Preparation of Sample Solution. Solutions of actual samples were made up by dissolving sufficient sample in water to make a solution containing the equivalent of 10 mg. of sulfonic acids and sulfuric acid in from 1.36 to 1.37 ml.

Method of Precipitation. The estimation was carried out on a microscope slide. Three precipitations were made on each slide. A drop of the sample solution was placed on the slide by means of a 0.1-ml. pipet in a 19-mm. ring of vaseline formed with a piece of 19-mm. tubing. One drop of manganous acetate solution (10 grams per 100 ml. of solution) was then added by means of a10-ml. buret without stirring. Each preparation was stirred after standing for 5 minutes under the warmth of an electric bulb, and every 5 minutes thereafter as long as the rod left an even field. Readings can be made immediately after drying and up to 24 hours later.

Samples containing less than 4 per cent of 1,8- do not form crystals and it is necessary to add 1,8- to the sample to bring the 1,8- content above 4 per cent. The values obtained with samples containing more than 10 per cent of 1,8- are erratic, so that it is necessary with such samples to mix them with known amounts of 1,5-.

Figure 7 shows samples containing 5 and 10 per cent 1,8-, respectively.

Adjusting Apparatus Prior to Making Readings. The adjustment of the apparatus was the same as for the determination of anthraquinone-beta-sodium sulfonate, except that the zero point was adjusted to the actual zero on the scale for convenience and the standard starch field was made to give a deflection of 23.0 cm.

Method of Taking Readings. In this analysis, much higher readings were obtained than for the anthraquinone-beta-sodium sulfonate method, and in samples containing 9 per cent and more of 1,8-anthraquinonedisulfonic acid, it was necessary to alter the shunt resistance of the galvanometer. The resistance was increased approximately 10 times, thereby decreasing the deflection approximately 10 times. The reading was then recalculated to the basis of the original resistance. The reading obtained with the high resistance was corrected

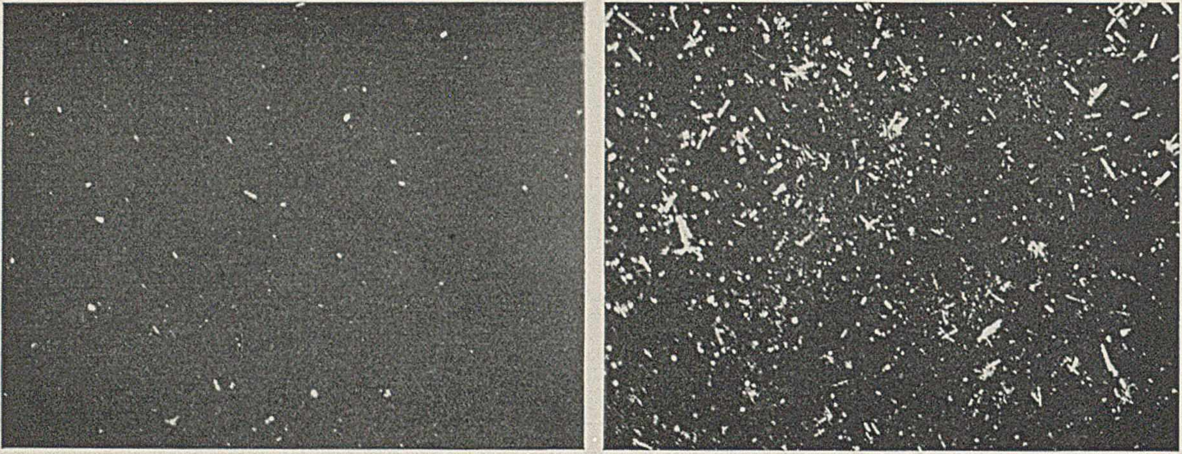

FIGURE 7. ANTHRAQUINONE-1,8-DISULFONIC ACID

Left. 5 per cent
Right. 10 per cent

to give readings corresponding to those obtained with the low resistance by applying the proper factor.

STANDARDIZATION CURVES. Figure 8 gives the mean galvanometer readings for a number of determinations with various percentages of pure 1,8- mixed with pure 1,5- and sulfuric acid. Each individual value from which the mean values were determined is the average of three separate determinations of nine fields each from a single solution. The percentage of 1,8- may be calculated by the formula:

$$\%\ 1,8\text{-} = \frac{\text{galvanometer scale reading} + 9.0}{6.8}$$

EFFECT OF IMPURITIES. With samples having concentrations of 1,8- of about 5 per cent in addition to 1,5- and sulfuric acid, the effect of 1 per cent of impurities such as the sodium salts of 2,6-, 2,7-, alpha-, and beta-anthraquinonesulfonic acids, sodium chloride, and sodium sulfate is very serious. In one series of experiments, the 2,6- and beta produced black fields containing no 1,8- crystals; the 2,7- and the sodium sulfate showed a few 1,8- crystals in addition to other anisotropic crystals; and alpha and sodium chloride showed many fine particles which were definitely not 1,8- crystals. Samples containing 0 per cent 1,8- with 1,5- and sulfuric acid and 1 per cent of impurities showed dendrites and crystallized clusters which would not be confused with 1,8-, but nevertheless interfered with the analysis. In mixtures containing 10 per cent of 1,8- acid, no interference was noted except in the case of sodium sulfate. Table IV shows the effects on the values of the impurities studied.

The effect of impurities upon this method in some cases is due to the crystallization of chemicals other than the 1,8-manganous salt when these impurities are present in too high a ratio to the 1,8-. In other cases, impurities have a tendency to prevent the crystallization in the anisotropic form of the 1,8-manganous salt. In order to be certain that impurities are not lowering the values obtained for 1,8- content, successive known quantities of 1,8- should be added, and the 1,8- found by the analysis should check the amount added plus the amount found originally. A doubtful sample may be checked by increasing the ratio of 1,8- to impurity (by adding pure 1,8-) for, as shown in Table IV, no serious interference takes place when the ratio of impurity to 1,8- is no more than 1 to 10 except in the case of sodium sulfate. A sample showing dendrites or other crystalline forms not characteristic of 1,8- must likewise be rerun with a known quantity of 1,8- added to overcome the influence of impurities present.

TABLE IV. EFFECTS OF IMPURITIES

(Manganous acetate method for anthraquinone-1,8-disulfonic acid)

1,8- Present	Impurities Added 2,6-	2,7-	β-	α-	NaCl	Na_2SO_4	1,8- Found
%	%	%	%	%	%	%	%
10	1.0	...	...	...	...	...	10.2
10	...	1.0	...	...	...	...	10.7
10	...	...	1.0	...	...	...	9.9
10	...	...	...	1.0	...	...	9.2
10	...	...	...	...	1.0	...	10.2
10	...	...	...	...	...	1.0	11.8

TABLE V. ACCURACY OF METHODS FOR ANTHRAQUINONE-1,8-DISULFONIC ACID

1,8- Present	Standard Deviation of Single Reading, 1,8- Barium method	Manganese method
%	± %	± %
0	0.7	...
2	4.8	...
4	...	0.3
5	2.1	0.6
7	...	0.5
9	...	1.9
10	2.8	1.5

Comparison of Barium and Manganese Methods

Table V gives a comparison of the accuracy of the values read from the curves by the barium and the manganese methods. The manganese method is more accurate than the barium method. Because of the good agreement of the mean values with the straight line drawn through them, the precision of this method is of about the same order as the accuracy. The effect of the errors involved in the adjustment of the apparatus on the values by the barium method is much greater than for the manganese method.

The barium method has an advantage that concentrations of 1,8- below 4 per cent can be analyzed. Although the concentration range for analysis is limited, the manganese method is much more rapid because it requires only a short time for the preparation of the sample. Because of this factor, it would be possible to run a number of determinations rapidly and thus obtain an accuracy for the mean value which would be equal to the standard deviation divided by the square root of the number of values.

Effect upon Precision of Variations in Adjusting the Apparatus

A standard potato starch field was marked off and readings were taken by removing the slide after each reading in order

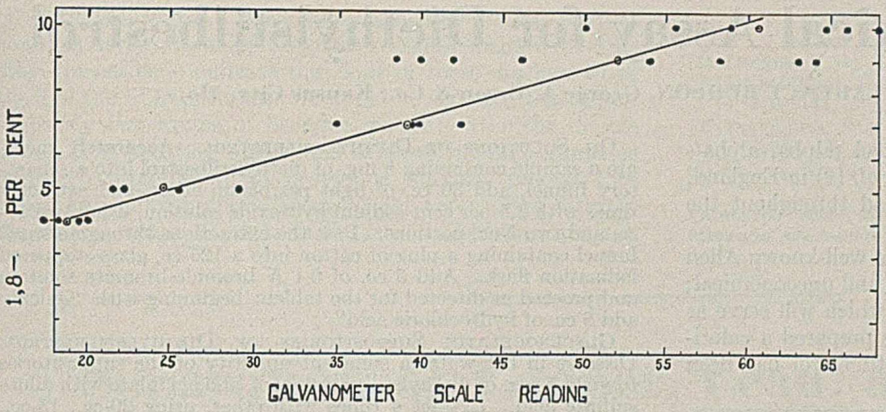

Figure 8. Estimation of Anthraquinone-1,8-Disulfonic Acid by Manganous Acetate

⊙ Mean values. ● Individual values

to check the exactness with which the field could be found. The mean of nine readings was 27.7, and the standard deviation 0.80.

When the mirror was reset but the slide was not moved after each observation, in order to test this operation, the average of nine readings was 27.7 and the standard deviation 0.35.

Next, a series was run by shutting off the lamp but not disturbing anything else. Out of nine readings, it was found necessary to readjust the amperage to 4.6 four times. The average of nine readings was 26.5, and the standard deviation 0.35.

These errors, which represent those encountered in the analysis of preformed particles, give a net standard deviation for a single reading of $\sqrt{0.80^2 + 0.35^2 + 0.35^2}$, or 0.94 divisions. In terms of anthraquinone-beta-sodium sulfonate this corresponds to 0.1 and 0.05 per cent, respectively, for the high and low concentration methods of analysis. In terms of anthraquinone-1,8-disulfonic acid by the barium method this corresponds to 3.5 per cent and by the manganese method to 0.1 per cent. The standard deviation for precipitated particles by the photoelectrometric method varies with the particular method in question, and for a definite method it also varies with the concentration of the substance to be determined. As the concentration increases, there is likely to be more variation in the size and number of crystals with a consequent variation in the precision.

Acknowledgments

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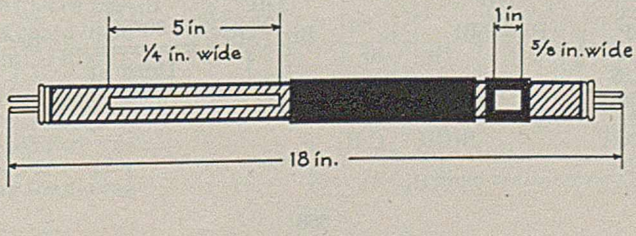
A Fuzz Detector for Viewing Glass Weighing Vessels in Organic Quantitative Microanalysis

DOUGLASS F. HAYMAN and WILHELM REISS
Merck & Co., Inc., Rahway, N. J.

THE fuzz detector is a viewing light devised for detecting foreign material on the surface of glass vessels. It has been found very useful in the inspection of micro absorption tubes and other micro glassware for cleanliness prior to weighing. As shown in the accompanying figure, the detector consists of a standard 18-inch, 15-watt fluorescent lamp (white or daylight type) covered with several coats of black enamel, except for two openings. The opening used for the viewing of carbon and hydrogen absorption tubes is 5 inches long and 0.25 inch wide and the other opening, used for shorter objects, is 1 inch long and 0.625 inch wide. A rotating tube made of heavy black paper placed around the lamp permits either opening to be covered while the other one is in use.

For the detection of fuzz on absorption tubes, filter tubes, etc., the tube are held up in front of the lamp about 0.5 inch from the narrow opening, so that the operator cannot see the light source but only the light coming over the surface of the tube. When the tubes are rotated slowly, any lint or foreign material on the glass surface appears sharply outlined against the black background of the painted portion of the lamp. The surface of the glass is lightly stroked with chamois while still under observation and the successful removal of lint and foreign material can be readily observed. Foreign material in the tip ends of absorption tubes is easily removed by using a steel wire with a knurled end.

The smaller opening is very useful for viewing glass vessels such as weighing bottles, Rast molecular weight tubes, chemical samples, etc. In the Rast molecular weight determination the tube can be carefully checked for any foreign material before the first weighing and again after each addition of sample and of camphor to ensure that none of the material remains in the upper part of the tube.



Semimicrochemical Assay for Diethylstilbestrol

C. W. SONDERN AND CLARENCE BURSON, George A. Breon & Co., Kansas City, Mo.

SINCE the discovery of diethylstilbestrol (alpha, alpha'-diethyl-4,4'-stilbenediol) by Dodds *et al.* (*2*) in England, the use of this potent estrogen has spread throughout the world.

The bioassay of diethylstilbestrol by the well-known Allen and Doisy method is both time-consuming and uneconomical; therefore a chemical procedure is needed which will serve as an analytical tool. [Since this paper was prepared a colorimetric method for the assay of diethylstilbestrol has been described by Dechne, (*1*).] Sprung (*4*) and Francis and Hill (*3*) describe a bromometric titration method for phenols, using standard bromide-bromate solution which may be applied to this drug. Bromination of known quantities of diethylstilbestrol (Table I) has established that the method is suitable for determining diethylstilbestrol in the amounts normally found in pharmaceutical preparations (1 to 40 mg.)

TABLE I. BROMINATION OF KNOWN AMOUNTS OF DIETHYLSTILBESTROL

(Dried at 100° C.)

Weight of Sample *Mg.*	Diethylstilbestrol Found *Mg.*	Recovery %
1	0.960	96.0
1	0.982	98.2
2	2.05	102.5
2	1.94	97.0
5	4.98	99.6
5	4.91	98.2
5	5.00	100.0
10	9.92	99.2
10	9.81	98.1
10	10.18	101.2
40	39.81	99.55
40	40.06	100.15
40	40.06	100.15
40	40.37	100.93

Method

ANALYSIS OF TABLETS. Weigh not less than 20 tablets; reduce them to a fine powder, and place an accurately weighed aliquot equivalent to about 10 mg. of diethylstilbestrol in a micro-Soxhlet extractor. Extract with ether for 1 hour, transfer the extract to a 125-cc. glass-stoppered iodination flask, and evaporate to dryness on a water bath. Dissolve the residue in 5 cc. of warm aqueous 2.5 per cent sodium hydroxide solution, cool, and add 10 cc. of standard U. S. P. XI bromide-bromate solution (0.1 *N* bromine solution) by means of a pipet.

Quickly add 5 cc. of hydrochloric acid, insert the stopper, and place 5 cc. of 10 per cent potassium iodide solution around the stopper. Set aside in a dark place for 30 minutes at 25° to 30° C. Remove the stopper just sufficiently to introduce the potassium iodide solution and shake the flask thoroughly, taking care that no bromine vapor escapes. Carefully rinse the stopper and the neck of the flask with a little distilled water and then titrate the liberated iodine with 0.05 *N* sodium thiosulfate solution, using starch indicator at the end of the titration.

Each cubic centimeter of bromide-bromate solution is equivalent to 2.233 mg. of diethylstilbestrol.

The presence of material capable of bromination will seriously affect the accuracy of the assay—for example, 60 mg. of stearic acid U. S. P. may contain sufficient oleic acid as impurity to introduce an error of 8 per cent in a determination of 10 mg. of diethylstilbestrol. Consequently, a blank determination on the filler and lubricant material in tablets should be made.

OIL SOLUTIONS OF DIETHYLSTILBESTROL. Accurately measure a sample containing 5 mg. of diethylstilbestrol into a separatory funnel, add 30 cc. of light petroleum ether, and extract 4 times with 2.5 per cent sodium hydroxide solution, using two 10-cc. and two 5-cc. portions. Pass the extractions through a small funnel containing a plug of cotton into a 125-cc. glass-stoppered iodination flask. Add 5 cc. of 0.1 *N* bromide-bromate solution and proceed as directed for the tablets, beginning with "Quickly add 5 cc. of hydrochloric acid".

GLYCEROGELATIN SUPPOSITORIES OF DIETHYLSTILBESTROL. Dissolve in hot water a sufficient quantity of the suppositories to yield 5 mg. of diethylstilbestrol, cool, and acidulate with dilute sulfuric acid. Extract 4 times with ether, using 20-cc., 15-cc., 15-cc., and 10-cc. portions, and pass through a funnel containing a plug of cotton into a suitable vessel. Evaporate the extract nearly to dryness and pass steam over the residue for 1 hour to volatilize and remove any phenolic preservative present in the gelatin. Evaporate most of the water and dissolve the residue in 2.5 per cent sodium hydroxide. Transfer to an iodination flask, add 5 cc. of 0.1 *N* bromide-bromate solution, and proceed as directed for the tablets, beginning with "Quickly add 5 cc. of hydrochloric acid".

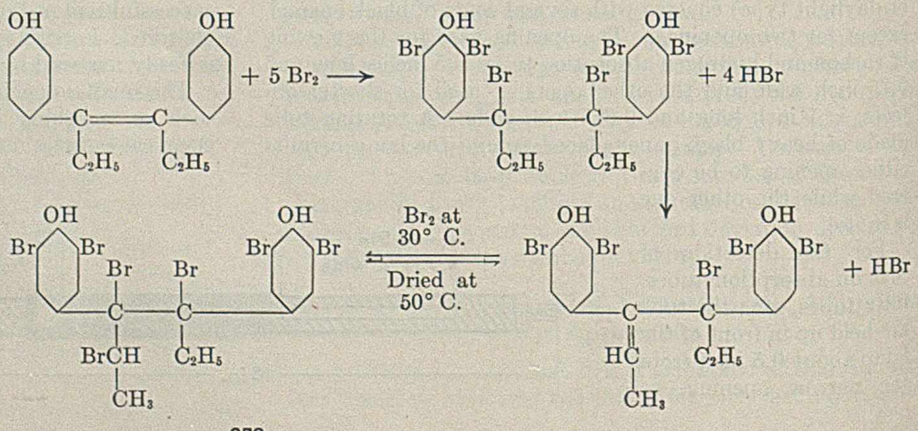
TABLE II. TEMPERATURE-TIME FACTOR IN BROMINATION OF DIETHYLSTILBESTROL

Temperature ° *C.*	Time *Min.*	Bromine Used *Atoms*
5–10	60	9.9
5–10	180	10.0
5–10	380	10.2
5–10	960	11.6
15	15	9.5
15	30	11.0
20	15	10.0
20	30	11.2
25	15	11.0
25	30	12.0
30	15	12.0
30	30	12.0
30	360	12.0
60	60	12.0

From the brominations shown in Table II it is evident that diethylstilbestrol in a cold solution first removes ten atoms of bromine from solution. The removal of two atoms more takes place slowly in the cold, rapidly at higher temperatures. The removal of ten atoms can be made consistent by controlling the time and temperature, but since twelve atoms will eventually be removed if the reaction goes to completion it seems more logical to brominate for 30 minutes at above 25° C.

Discussion

Under the conditions described in the analytical procedure, twelve atoms of bromine enter into the reaction, accompanied by the release of 5 moles of hydrogen bromide for each mole



of diethylstilbestrol. Presumably the bromination product contains seven atoms of bromine. Studies made with 4,4′-dihydroxystilbene indicate that four of these are located in the 3,5- and 3′,5′-positions. It would be expected that simultaneously two atoms of bromine would add at the double bond. The splitting out of one of these bromine atoms as hydrogen bromide would provide a vinylene linkage into which two more bromine atoms could enter. The diagram appears to explain the data in the most satisfactory manner.

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Separation of Copper, Lead, and Zinc with Salicylaldoxime

L. P. BIEFELD AND W. B. LIGETT
Purdue University, Lafayette, Ind.

THE separation of copper from other metals which form complexes with salicylaldoxime is possible because copper salicylaldoximate may be precipitated in weakly acidic solutions, whereas the salicylaldoximates of most other metals are precipitated only from neutral or slightly basic solutions (*1–6, 10*). Lead has been separated from silver, zinc, and cadmium by precipitation in strongly ammoniacal solution (*7*). The effect of hydrogen-ion concentration upon the precipitation of zinc with salicylaldoxime has been reported briefly (*5*).

The purpose of the present investigation was to make a more detailed study of the effect of pH on the precipitation of zinc salicylaldoximate, and to determine the best conditions for a separation of copper, lead, and zinc based upon pH control and ammonia-complex formation.

Precipitation of Zinc Salicylaldoximate

The fact that zinc forms an insoluble complex with salicylaldoxime was first reported by Ephraim (*4*). Pearson (*9*) studied the properties of the precipitate and concluded that it was not suitable for the quantitative determination of zinc because the pH range for complete precipitation was too narrow, the precipitate was appreciably soluble in various neutral salt solutions, and the compound slowly decomposed above 80° C. The compound precipitated by Pearson contained 19.45 per cent zinc by analysis and evidently was $Zn(C_7H_6O_2N)_2$, which contains 19.36 per cent zinc. Flagg and Furman (*5*) found that if zinc salicylaldoximate, together with the solution from which it has been freshly precipitated, is warmed to 90° C. for 10 minutes, a compound corresponding to $Zn(C_7H_5O_2N)$ results. This compound, containing 32.61 per cent zinc, can be dried at 110° C. without decomposition. Since the compound obtained by Flagg and Furman is obviously more suitable for quantitative purposes, the work described below is based upon precipitation of the compound $Zn(C_7H_5O_2N)$.

Reagents and Apparatus. The salicylaldoxime used was obtained from the Eastman Kodak Company. A 1 per cent solution was prepared by dissolving 1 gram of the reagent in 5 ml. of alcohol and slowly pouring the alcohol solution into 95 ml. of water warmed to 80° C. The reagent solution was cooled and filtered before use.

The zinc solution was prepared from reagent grade zinc nitrate. It was standardized by precipitation and weighing as $ZnNH_4PO_4$, and by precipitation as $ZnNH_4PO_4$ and ignition to ZnP_2O_7.

A glass electrode pH meter as described by Mellon (*8*) was used. It was calibrated with Clark and Lubs buffer solutions.

The reagents used in standardization of the zinc solution, those used in preparation of the buffers, and the ammonia used for adjustment of pH were all of reagent grade.

Calibrated weights and volumetric ware were used. Redistilled water was employed for the preparation of all solutions, for dilutions, and for washing the precipitates.

Precipitation and pH Measurement. In each case, 25 ml. of a 1 per cent salicylaldoxime solution were added dropwise to 25 ml. of zinc solution containing 0.0999 gram of zinc and ammonia in an amount estimated to give the desired pH. Water was added to make 100 ml. The mixture was mechanically stirred during addition of the reagent. After all the reagent had been added, solution and precipitate were heated to about 90° C. for 10 minutes, cooled to room temperature, filtered with suction on No. 4 Jena glass crucibles, washed with water, and dried at 110° C. for 1 hour. Ferric chloride solution was used to test for complete washing of the precipitate, thorough washing

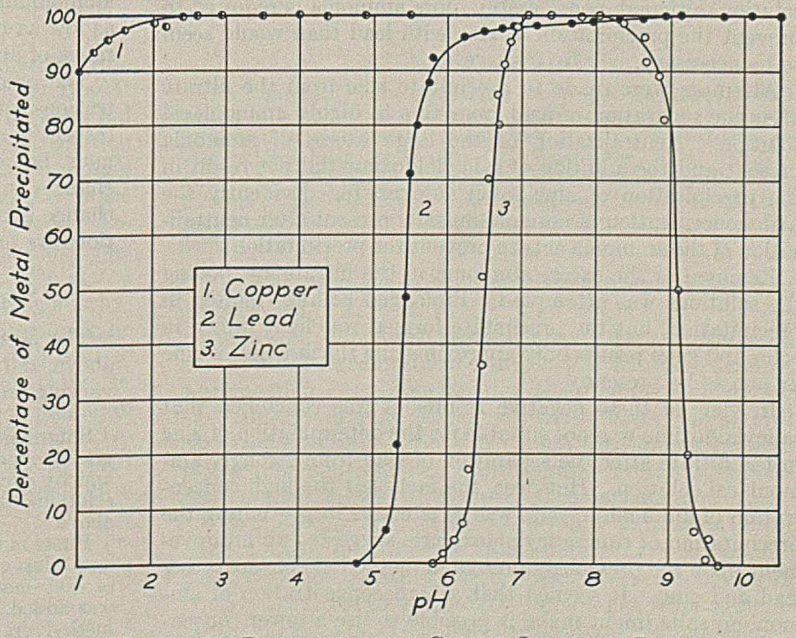

Figure 1. Precipitation of Copper, Lead, and Zinc

being indicated by the absence of coloration in a final portion of filtrate. The pH measurement was made upon the filtrate before the addition of any wash water.

pH Range for Precipitation. The theoretical factor 0.3261 for zinc in $Zn(C_7H_5O_2N)$ was used in calculating the results which are presented in Figure 1, curve 3. As shown by the curve, the precipitation of zinc salicylaldoximate is complete only in the pH range 7.1 to 8.1. It is completely soluble below pH 5.8 and above pH 9.7 if the pH is regulated with ammonia.

Separation of Copper and Lead

Curves 1 and 2, Figure 1, reproduced from papers by Biefeld and Howe (*2*) and Ligett and Biefeld (*7*), respectively, show that the separation of copper from lead by precipitation with salicylaldoxime may be effected easily by control of the pH. The adjustment of the pH is usually made with acetic acid. Hydrogen ion is formed by the reaction between the metal ion and the reagent, and if a considerable amount of copper is present the hydrogen-ion concentration may be so increased that precipitation of copper will be incomplete (*2*). The simplest procedure is to buffer the solution with acetate ion. However, this is not satisfactory if it is desired to determine lead in the filtrate by precipitation with salicylaldoxime because the lead complex is appreciably soluble in acetate solutions (*5*).

It was found that the correct pH could be readily attained by the use of modified methyl orange as indicator. After the addition of reagent to the solution of copper and lead, one or two drops of indicator were added. Then the solution was neutralized with ammonia, finishing with 0.5 *M* ammonia added dropwise with stirring. After standing for a few minutes, the supernatant liquid again shows the acid color of the indicator. This is due to the fact that the precipitation reaction does not immediately reach equilibrium after neutralization and a small additional amount of hydrogen ion is formed as the reaction goes to completion. It was unnecessary to bring the solution back to the neutral point again.

Separation of Lead and Zinc

Curve 2, Figure 1, is reproduced from a previous paper of the authors (*7*). Together with curve 3, it indicates why a separation of lead from zinc is possible in highly ammoniacal solution, although considerably more ammonia is required to prevent the precipitation of zinc with lead than would seem to be necessary.

Attempts were made to precipitate zinc from the filtrate after the separation of lead from zinc in highly ammoniacal solution. Neutralization of the large excess of ammonia present and the addition of salicylaldoxime did not result in the precipitation of zinc salicylaldoximate. Evidently the high concentration of ammonium salts present after neutralization of the ammonia acts to prevent the precipitation.

Removal of the excess ammonia in the filtrate by boiling the solutions was attempted. Prolonged boiling resulted in precipitation, but the precipitate formed was light brown in color and gave results only approximating the amount of zinc known to be present.

In view of these negative results, it was concluded that salicylaldoxime was not suitable for the determination of zinc in the filtrate after the separation of lead from strongly ammoniacal solution. However, the fact that the high concentration of ammonium salts was so effective in preventing the precipitation of zinc salicylaldoximate suggested an improvement upon the previously presented method (*7*) of separating lead and zinc. It seemed that a high concentration of ammonium salts might make it possible to use a lower concentration of ammonia when attempting to separate lead and zinc with salicylaldoxime. This would be desirable, because if too much ammonia is present in this determination, an appreciable amount of the lead is not precipitated, and if too little ammonia is present, zinc salicylaldoximate coprecipitates with the lead complex.

The purpose of the experiments outlined below was to determine whether the permissible range of ammonia concentration in the separation of lead from zinc might be widened by the use of a high concentration of salts.

Reagents and Apparatus. Lead and zinc solutions were prepared from the corresponding reagent grade nitrates. The lead solution was standardized by precipitation as the sulfate. The same care with reagents, volumetric ware, and weights was taken as in the precipitation of zinc salicylaldoximate, with the added precaution that the ammonium nitrate used was tested for insoluble matter.

Procedure for Separation. A 12-ml. portion of 1 per cent salicylaldoxime was added to a solution containing 0.0398 gram of lead and 0.0400 gram of zinc. This is an excess of reagent over that required for the precipitation of both metals. Then 5 grams of ammonium nitrate were added, followed by varying amounts of concentrated ammonia solution and water to make 65 ml. The precipitate was allowed to stand in contact with the solution, with occasional stirring, for 1 hour. It was filtered, washed with 20 per cent alcohol, and dried at 110° C. for 1 hour. The amount of lead was calculated from the weight of precipitate, using the factor 0.6053 for lead in $Pb(C_7H_5O_2N)$. The results are given in Table I.

Table I. Separation of Lead and Zinc

(0.0398 gram of lead present)

Concd. NH_3 Added *Ml.*	Precipitate Found *Gram*	Lead Found *Gram*	Error *Mg.*
3.0	0.0659	0.0399	+0.1
3.5	0.0661	0.0400	+0.2
4.0	0.0656	0.0397	−0.1
5.0	0.0656	0.0397	−0.1
5.0	0.0655	0.0397	−0.1
7.0	0.0658	0.0398	0.0
9.0	0.0655	0.0397	−0.1
10.0	0.0657	0.0398	0.0

Discussion of Results. The data of Table I demonstrate that a wide range of ammonia concentrations will suffice to keep the zinc from precipitating and still permit complete precipitation of lead salicylaldoximate, provided a large amount of ammonium nitrate is present. In the absence of ammonium nitrate, however, concentrations of ammonia as low as those given are not adequate, and the permissible range of ammonia concentration is much less.

The precipitate obtained in the presence of high concentrations of ammonium nitrate is very satisfactory with respect to ease of handling. Freshly precipitated, it is gelatinous, but during a period of about 30 minutes it gradually changes to a form which is easily filtered. The progressive change is readily apparent when three or four separate solutions are precipitated at intervals of a few minutes.

Separation of Copper, Lead, and Zinc

The procedure described is based upon the facts outlined above, and is intended to be applicable to solutions containing varying proportions of the three metals.

Solutions. The copper solution was prepared from reagent grade copper nitrate, and was standardized by electrodeposition and by precipitation with salicylaldoxime. The lead and zinc solutions and the reagent solution were prepared as described above.

Procedure for Analysis. Portions of the copper, lead, and zinc solutions were taken to give solutions with varying quantities of each metal. A 30-ml. portion of 1 per cent salicylaldoxime was added. The solutions were then made neutral to modified methyl orange by the dropwise addition of 0.5 *M* ammonia solution. The resulting precipitate and solution were allowed

Table II. Determination of Copper, Lead, and Zinc

Copper				Lead				Zinc			
Metal present	Precipitate found	Metal found	Error	Metal present	Precipitate found	Metal found	Error	Metal present	Precipitate found	Metal found	Error
Gram	*Gram*	*Gram*	*Mg.*	*Gram*	*Gram*	*Gram*	*Mg.*	*Gram*	*Gram*	*Gram*	*Mg.*
0.0089	0.0471	0.0089	0.0	0.0597	0.0987	0.0597	0.0	0.0694	0.1896	0.0695	+0.1
0.0089	0.0469	0.0089	0.0	0.0597	0.0986	0.0597	0.0	0.0694	0.1893	0.0694	0.0
0.0312	0.1649	0.0312	0.0	0.0199	0.0329	0.0199	0.0	0.0926	0.2526	0.0926	0.0
0.0312	0.1645	0.0311	−0.1	0.0199	0.0330	0.0200	+0.1	0.0926	0.2527	0.0926	0.0
0.0223	0.1177	0.0223	0.0	0.0796	0.1311	0.0794	−0.2	0.0231	0.0633	0.0232	+0.1
0.0223	0.1178	0.0223	0.0	0.0796	0.1313	0.0795	−0.1	0.0231	0.0631	0.0231	0.0
0.0446	0.2354	0.0446	0.0	0.0398	0.0656	0.0397	−0.1	0.0463	0.1259	0.0461	−0.2
0.0446	0.2356	0.0446	0.0	0.0398	0.0656	0.0397	−0.1	0.0463	0.1258	0.0461	−0.2

to stand 0.5 hour, filtered on a Gooch crucible, washed with 20 per cent alcohol, dried at 110° C., and weighed as $Cu(C_7H_6O_2N)_2$. The factor for copper is 0.1893.

The filtrate was transferred to a beaker and 0.7 gram of ammonium nitrate and 1.0 ml. of concentrated ammonia were added for each 10 ml. of solution. This resulted in precipitation of lead salicylaldoximate. After standing 1 hour, the precipitate was filtered on a Gooch crucible, washed with 20 per cent alcohol, dried at 110° C., and weighed as $Pb(C_7H_5O_2N)$. The factor for lead is 0.6053.

Zinc was determined in the filtrate by precipitation and weighing as $ZnNH_4PO_4$. The results are given in Table II.

Summary

Zinc salicylaldoximate begins to precipitate at pH 5.8, is completely precipitated in the range 7.1 to 8.1, and is again soluble above pH 9.7 if the pH is regulated with ammonia.

Copper, lead, and zinc in the same solution may be separated with salicylaldoxime by precipitating the copper in weakly acidic solution, filtering it off, and then making the filtrate strongly ammoniacal to cause precipitation of the lead complex. The correct pH for precipitation of the copper complex is easily obtained by the use of modified methyl orange. The separation of lead from zinc in highly ammoniacal solution is improved by the addition of a large amount of ammonium nitrate. In the presence of a high concentration of ammonium nitrate, a wide range of ammonia concentration may be used to prevent coprecipitation of zinc salicylaldoximate while still permitting complete precipitation of the lead. Zinc cannot be quantitatively precipitated as the salicylaldoximate in the strongly ammoniacal filtrate from the lead separation.

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Color Reactions of Organic Nitrogen Compounds with Selenious Acid-Sulfuric Acid Solution

BARTLETT T. DEWEY[1] AND ALBERT H. GELMAN, North Pacific College of Oregon, Portland, Ore.

SELENIOUS and selenic acids were proposed as reagents for the identification of the opium alkaloids by Brandt (*1*), Lafon (*3*), and Ferreira da Silva (*2*). Mecke (*5*) observed the colors produced on the addition of a 0.5 per cent solution of selenious acid in concentrated sulfuric acid to the opium alkaloids, and recommended this solution as a reagent for the identification of minute quantities of these compounds. Levine (*4*) observed the color reactions of phenols and phenolic ethers with selenious acid–sulfuric acid reagent. He stated that the color production is a specific test for phenolic hydroxyl groups. The production of colored compounds he attributed to the oxidizing action of selenious acid, and he stated that a red or red-brown precipitate accompanying or following the primary color reaction is due to the reduction of selenious acid with the liberation of elemental selenium. Levine concluded that a positive reaction cannot be accepted as indicative of the presence of the opium alkaloids unless other phenolic compounds are absent.

The present work reports the color reactions of some organic nitrogen compounds with selenious acid–sulfuric acid solution.

Experimental

One milligram of the compound was placed on a spot plate and a drop of a 0.5 per cent solution of selenious acid in concentrated sulfuric acid was added. Chemicals used were Eastman grade supplied by Eastman Kodak Co., Rochester, N. Y., and c. p. quality of the Pfanstiehl Chemical Co., Waukegan, Ill. To determine if the reaction is characteristic of the selenious acid reagent, a similar test was carried out simultaneously with sulfuric acid.

The color changes which took place during a 3-hour period are recorded in Table I.

Some compounds produced the same color in the sulfuric acid as in the selenious acid–sulfuric acid solution: benzidine, *o*-bromoaniline, *m*-bromoaniline, *p,p'*-diaminodiphenylmethane, dibenzylamine, diphenylnitrosoamine, diphenylthiocarbazone, methyl-*o*-toluidine, methyl-*m*-toluidine, methyl-*p*-toluidine, *p*-nitroaniline, *p*-nitrosodiphenylamine, *m*-phenylenediamine hydrochloride, and *p*-phenylenediamine.

The following compounds gave either a faint pink or no color at all: allylthiourea, *o*-aminobenzoic acid, *m*-aminobenzoic acid, *p*-aminobenzoic acid, *dl*-α-amino-α-methylbutyric acid, *d*-arginine monohydrochloride, asparagine, barbituric acid, *o*-chloroaniline, *p*-chloroaniline, creatinine, *l*-

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[1] Present address, 1704 Cascade Ave., Boulder, Colo.

Table I. Color Changes

Compound	H_2SO_4	H_2SeO_3–H_2SO_4
o-Aminodiphenyl	Pink	Pale green
p-Aminodiphenyl	Colorless	Pink to dirty gray
4-Aminodiphenylamine HCl	Purple to pale green	Brown to red-brown to purple
Aniline	Yellow	Yellow to pale blue
Benzeneazodiphenylamine	Green to pink-purple to purple	Green to blue-black to purple
p-Bromoaniline	Colorless	Pink
Carbanilide	Colorless	Yellow
m-Chloroaniline	Pink	Pink to brown
Cholesterol	Pink	Pink to brown
Cysteine HCl	Colorless	Yellow to pink
2,4-Diaminodiphenylamine	Rose-red to dark red to brown to gray-green	Rose-purple
Dibenzylaniline	Colorless	Rose-pink to pale purple
s-Dimethylcarbanilide	Colorless	Pale pink to light brown
Di-2-naphthylamine	Yellow	Brown
Di-*p*-phenetylurea	Colorless	Green to olive-green to yellow to tan
Diphenylamine	Colorless	Intense blue to dirty green to brown
Diphenylbenzidine	Colorless	Blue
Diphenylcarbamine Cl	Colorless	Green to blue-green to intense blue
s-Diphenylcarbazide	Colorless	Purple to blue to brown to greenish brown
s-Diphenylcarbazone	Rose-pink to red-orange	Dark blue to purple to brown
s-Diphenylethylenediamine	Colorless	Faint pink to pale yellow to brown
4,5-Diphenylglyoxalone	Salmon-pink to colorless	Pink to orange-brown to brown
Diphenylpiperazine	Colorless	Yellow to yellowish green to brown
1,4-Diphenylsemicarbazide	Pale pink	Intense bluish purple to dirty gray-green to brown
4,4-Diphenylsemicarbazide	Greenish brown to brown	Intense blue to blue-green
Diphenylthiocarbazide	Pink to blue-green to red-orange	Purple to brown
s-Di-*o*-tolylthiourea	Colorless	Greenish yellow to yellow
s-Di-*p*-tolylthiourea	Colorless	Greenish yellow to green to red-orange
s-Di-*o*-tolylurea	Colorless	Colorless to pale yellow
s-Di-*m*-tolylurea	Colorless	Pale blue to faint yellowish green
s-Di-*p*-tolylurea	Colorless	Faint blue to pale yellow
Formyl diphenylamine	Colorless	Blue to gray
l-Leucine	Colorless	Purple to pink
Methyldiphenylamine	Colorless	Pinkish blue to purple to rose-brown
Methylthiocarbanilide	Colorless	Yellow-green to orange to purple
1-Naphthylamine	Colorless	Greenish brown to reddish brown
2-Naphthylamine	Colorless	Greenish yellow to yellowish brown
4-Nitrodiphenylamine	Purple to blue to blue-gray	Purple
p-Nitrophenylhydrazine	Yellow to yellow-green	Yellow to brown
Phenylthiourea	Colorless	Pale yellow
Thiocarbanilide	Faint pink	Greenish yellow to yellow-orange
Tolidine	Faint pink	Yellow
o-Toluidine HCl	Colorless	Yellow to brown to blue-green to blue to reddish brown
p-Toluidine HCl	Colorless	Greenish blue to brown
Triphenylguanidine	Colorless	Pale blue to pale yellow
Tryptophan	Faint yellow	Yellowish brown

cystine, diethylaniline, *s*-diethylcarbanilide, diiodotyrosine, *p*-dimethylaminobenzaldehyde, dimethylaniline, diphenylguanidine, di-*o*-tolylguanidine, ethylamine hydrobromide, ethylenediamine, glycine, guanidine hydrochloride, hexamethyleneamine, hydroxylamine hydrochloride, *dl*-isoleucine, methylaniline, morpholine, *o*-nitroaniline, *m*-nitroaniline, *l*-oxyproline, phenobarbital, β-phenylalanine, phenylhydrazine, phenylurea, α-picoline, *l*-proline, isopropanolamine, pyridine, quinoline, *dl*-serine, sulfanilic acid, thiourea, tribenzylamine, triethanolamine, triisopropanolamine, urea, and *dl*-valine.

In general, compounds containing two or three aromatic nuclei gave the most intense reactions. Colors could be easily distinguished from those produced by the sulfuric acid alone. Compounds containing one aromatic nucleus produced pale colors or none at all. Freshly distilled aniline produced a pale blue color after 30 minutes' contact with the reagent. Aniline which remained for 3 hours in air after distillation gave an intense blue color immediately upon the addition of the reagent. Few aliphatic amines showed any coloration except a pink or brown, which was probably due to the precipitation of selenium.

The minimum amounts necessary to produce the characteristic colors were determined for those compounds which gave intense colors.

Solutions in ethanol, benzene, toluene, or chloroform were prepared. Amounts of the solutions containing from 100 micrograms to 0.01 microgram of the compound were placed in porcelain evaporating dishes and the solvent was removed on a steam bath. A few drops of selenious acid–sulfuric acid reagent were added to each one and the dishes were rotated so that the reagent flowed over the bottoms of the dishes.

The smallest quantities of the compounds which gave recognizable colors are recorded in Table II. Five compounds were sensitive in amounts as small as 0.1 microgram. The sensitivity of the test was only one one-hundredth as great when the selenious acid–sulfuric acid solution was added to the ethanol or chloroform solutions of the compounds on a spot plate. It was possible to detect as small amounts of the compounds when the reagent was added to the benzene or toluene solutions as when the solvent had been removed.

Table II. Minimum Production of Color

Compound	Limit in Micrograms
4-Aminodiphenylamine HCl	0.5
Benzeneazodiphenylamine	0.1
2,4-Diaminodiphenylamine	1.0
Di-2-Naphthylamine	0.1
Diphenylamine	10.0
Diphenylbenzidine	1.0
Diphenylcarbamine chloride	7.0
s-Diphenylcarbazide	1.0
4,5-Diphenylglyoxalone	0.5
Diphenylpiperazine	10.0
1,4-Diphenylsemicarbazide	0.1
4,4-Diphenylsemicarbazide	50.0
Diphenylthiocarbazide	0.1
Formyl diphenylamine	10.0
Methyldiphenylamine	10.0
Methylthiocarbanilide	30.0
4-Nitrodiphenylamine	0.1
Thiocarbanilide	1.0
Tolidine	2.0

Conclusions

Color production with selenious acid–sulfuric acid solution is not a specific reaction of phenolic compounds. Many nitrogenous compounds—especially those containing two or three aromatic nuclei—give intense color reactions with this reagent.

The colors produced with selenious acid–sulfuric acid reagent provide a sensitive method for detecting and distinguishing between certain nitrogen compounds. The colors produced by 1-naphthylamine, 2-naphthylamine, and di-2-naphthylamine can be readily distinguished. Diphenylguanidine shows no color. Triphenylguanidine yields a pale but definite blue which changes to yellow. Neither becomes colored when treated with sulfuric acid alone.

The test with selenious acid–sulfuric acid reagent for the presence of the opium alkaloids cannot be considered conclusive unless interfering phenols and nitrogen compounds are known to be absent.

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A Modified Micropipet

For Density Determinations in Heavy Water Analysis

FRED ROSEBURY AND W. E. VAN HEYNINGEN[1]
College of Physicians and Surgeons, Columbia University, New York, N. Y.

THE instrument here described is a modification of the miropipet of Keston, Rittenberg, and Schoenheimer (*3*) from which drops of water of highly uniform size are expelled and measured for density by the falling-drop method of Barbour and Hamilton (*1*), as adapted by Vogt and Hamilton (*4*) and Fenber-Eriksen, Krogh, and Ussing (*2*).

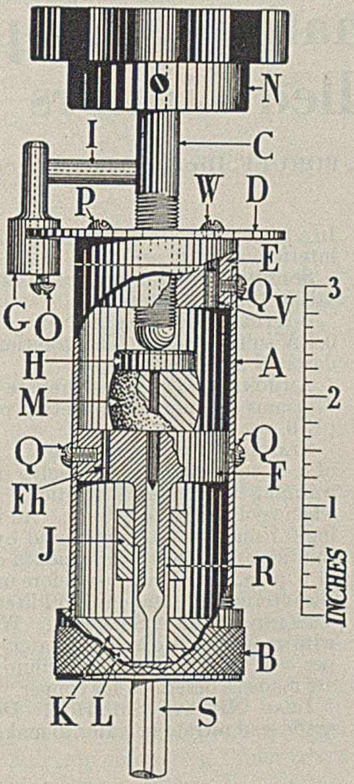

FIGURE 1. MICROPIPET CONSTRUCTION

Figure 1 shows the construction of the instrument. All parts are of stainless steel or cold-rolled steel unless otherwise stated.

The screw, *C*, having a pitch of 9.3 mm. (0.037 inch), to which is attached the Bakelite knob, *N*, and the stop-arm, *I*, is threaded into the upper cap, *E*, and presses upon the head of the piston, *H*, the shank of which is seated in the hole in the platform, *F*. The shank of *H* has a diameter of 2.90 mm. (0.114 inch) and the hole is 2.95 mm. (0.116 inch) in diameter (No. 32 drill). The pressure of *C* is opposed by a thick compression gasket, *M*, of pure live gum rubber which fits snugly on *H* and thereby also serves as a seal to the clearance space between *H* and *F*. The extension at the bottom of *F* is turned as shown to correspond to the inside and outside diameters of a short length of glass tubing, *R*. These diameters in the authors' instrument are, respectively, 6.0 mm. (0.237 inch) and 8.3 mm. (0.327 inch). *R* is sealed to the capillary glass tubing, *S*, which has the same outside diameter, and an inside diameter of not more than 2 mm. In order to preclude air pockets, the glass and glass-metal joints must be smooth, and the bottom of the hole in *F* must be smoothly countersunk as indicated. The end of *H* is turned conical for the same reason. *J* is a piece of rubber pressure tubing or a rubber stopper with a snug-fitting hole, and *K* and *L* are rubber gaskets having the diameters, respectively, of the inside of the housing cylinder, *A*, and of the thread undercut at the bottom of the screw cap, *B*. These gaskets are cemented together with rubber cement and are provided with tight-fitting holes accurately centered for *S*. *B* is threaded to *A* and is knurled on the outside. The hole in *B* through which *S* passes is 9.52 mm. (0.375 inch) in diameter.

The top plate, *D*, carries one or two movable stops, *G*, which in use are held rigidly in place with the setscrews, *O*. *D* and *E* may be integral or firmly attached together with the screws, *P*. *F* and *E* are held securely in their respective places within *A* by means of the screws, *Q*. The upper cap is provided with a filler hole, *V*, which is protected from dust with the screw, *W*, from which the threads have been turned off.

The remainder of the pipet (Figure 2) consists of the stopcock, *T*, the reservoir, *U*, and the connecting rubber tubing. The end of the capillary tubing, *S*, is drawn out to a smaller diameter. *U* when not in use is hung on a hook which is carried on the bracket, *X*. This bracket also carries an adjustable clamp, *Y*, to which *S* is attached and is in turn carried on any smoothly operating rack-and-pinion device, *Z*, with a vertical travel of about 10 cm. (4 inches), and which is rigid enough to carry the weight of the pipet when it is filled with mercury. (The authors use the modified head and spindle of a No. 620 Delta drill press, in which the two ball-bearing assemblies are replaced by solid bearings each carrying a setscrew which engages the keyway in the upper end of the spindle, thus preventing rotation of the spindle but permitting the normal vertical motion.)

In assembling and setting up the instrument for use, the following procedure is suggested:

All parts should be carefully cleaned before assembly. *F* (Figure 1) is first screwed in place in *A*. The glass system is passed through *B* and rubber gaskets *L* and *K*, inserted in *J*, and then cemented to the platform extension with de Khotinsky or other suitable cement. *J* is slid over the joint and *B* is brought up and screwed tight. Mercury is then poured into *U* (Figure 2), stopcock *T* is opened, and the mercury is allowed to flow into both branches of the capillary. When the mercury has risen so as slightly to overflow the hole in *F*, the stopcock is closed, *H* carrying the gum rubber compression gasket is inserted, *E* carrying plate *D* is fastened in place with screws *Q*, and the main screw with knob *N* is screwed in and brought down, so as to press firmly but not too heavily upon the head of the piston. A little experimenting will determine the proper pressure.

Petroleum jelly should be applied sparingly to the thread and to the rounded end of *C* before assembling. Additional mercury is introduced through *V* until it can just be seen at the bottom of the hole, and *W* is then inserted. Since *H* and *M* are in place, this mercury runs down through holes *Fh* to fill the lower compartment, but has no connection with that in the capillary; its function is to prevent leaks at the two joints. Stops *G* are put in place on *D*, only one stop being used when maximum drop size is required.

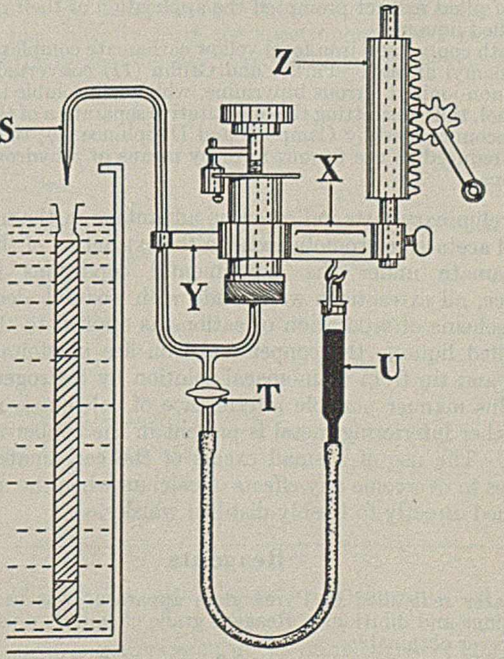

FIGURE 2. DIAGRAM OF PIPET

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[1] Present address, Cambridge University, England.

In operation, C is first backed off around to the stop, U is held at a high level, and with the drawn-out end of S dipping into the vessel containing the sample to be measured, T is opened, allowing a drop or two of mercury to run out. The reservoir is then brought to a lower level, thus drawing some of the sample into the end of the pipet, the stopcock is closed, and the sample vessel is removed. The end of the pipet is cleaned with hard filter paper and then lowered with the rack and pinion, so that the end of the capillary dips into the cylinder containing immiscible fluid having a density slightly less than that of water (*3*) and maintained at constant temperature in a water bath (Figure 2). N is then turned down against the stop, thus expelling a drop of the sample, the volume of which is determined by the formula:

$$V = \pi r^2 P \frac{A}{360}$$

in which V is the volume, r the radius of piston shank H, P the pitch of screw C, and A the angle in degrees through which C has been turned. The pipet is then raised and as the end of S passes through the surface of the fluid in the cylinder the drop is detached and its rate of fall between two marks is determined with a stop watch

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Photometric Determination of Copper and Iron in Distilled Liquors

LOUIS GERBER, RALPH I. CLAASSEN, AND C. S. BORUFF, Hiram Walker and Sons, Inc., Peoria, Ill.

COPPER and iron are so frequently estimated in biological experimentation that a number of methods and reagents for their determination have been described. In view of the low concentrations of copper and iron found in alcoholic liquors, the colorimetric procedures only were considered.

The merits of sodium diethyldithiocarbamate as a color reagent for copper have been established by Conn and co-workers (*3*), Coulson (*4*), and Parker and Griffin (*11*). Drabkin (*5*), using a spectrophotometer in his critical study of the color produced by the diethyldithiocarbamates of copper, nickel, cobalt, and bismuth, reported fair agreement with Beer's law for copper concentrations in the range 0.02 to 0.1 mg. in 10 ml. of isoamyl acetate as extraction solvent. Iron in biological materials has been determined colorimetrically with 2,2′-bipyridine as the color reagent by Hill (*9*), Jackson (*10*), and others. Not recommended in the report of Harrison (*8*) is the application of the reagent to the estimation of iron in beer described by Gray and Stone (*6*). However, the success of Parker and Griffin (*11*) with the above reagents in the determination of iron and copper in the same sample of plant extract prompted the application of their method to distilled liquors.

Both copper and iron form yellow carbamate complexes soluble in isoamyl alcohol. Parker and Griffin (*11*) converted the iron into non-ionized ferrous bipyridine, which is insoluble in isoamyl alcohol, thus permitting the quantitative separation of the copper. As recommended by Campbell and Dauphinee (*2*), the iron was first reduced to the ferrous form by means of *p*-hydroxyphenylglycine.

Preliminary tests indicated no advantage in the use of isoamyl acetate or bromobenzene in the extraction of the copper carbamate under the experimental conditions involved. Hence, all extractions were made with isoamyl alcohol. In the scheme of separation of cations as applied to the ash of distilled liquors, the copper and iron are precipitated with lead and tin from ammoniacal solution by hydrogen sulfide. In this manner possible interference of calcium is removed; no other interfering metal is present in the copper-iron fraction. The use of a small excess of the carbamate reagent serves to overcome any effects of calcium when the method is applied directly to freshly distilled whisky.

Reagents

Water redistilled in Pyrex glass apparatus was used for all solutions and dilutions. Reagent grade chemicals must be used wherever obtainable.

2,2′-BIPYRIDINE. Dissolve 0.2 gram of 2,2′-bipyridine (also marketed as α,α'-dipyridyl) in 100 ml. of 10 per cent acetic acid. In a few hours the solution turns pink, but this coloration does not interfere with its use.

SODIUM DIETHYLDITHIOCARBAMATE. Dissolve 1 gram of the salt in 100 ml. of water.

p-HYDROXYPHENYLGLYCINE. 0.1 gram dissolved in 100 ml. of 0.4 *N* sulfuric acid. This solution must be freshly prepared the day it is used.

AMMONIUM ACETATE. Prepare a normal solution by dissolving 77 grams of ammonium acetate per liter of solution. Adjust to pH 6.

STANDARD COPPER SOLUTION. Weigh accurately 0.2000 gram of C. P. copper wire and dissolve in 15 ml. of nitric acid (1 + 4), warming to complete solution. Expel fumes by boiling and, when cool, dilute to 200 ml. An intermediate standard containing 0.1 mg. per ml. is prepared by a tenfold dilution of the first solution. The working standard containing 1 microgram per ml. (1 p. p. m.), prepared just before use, is made by diluting 10 ml. of the intermediate standard to 1 liter.

STANDARD IRON SOLUTION. Weigh 0.2000 gram of pure iron wire or electrolytic iron accurately, dissolve in about 10 ml. of 10 per cent sulfuric acid, and dilute to 200 ml. Further dilutions are made as described for copper.

LEAD NITRATE SOLUTION. Dissolve 1.6 grams of reagent grade lead nitrate in water to make 1 liter of solution.

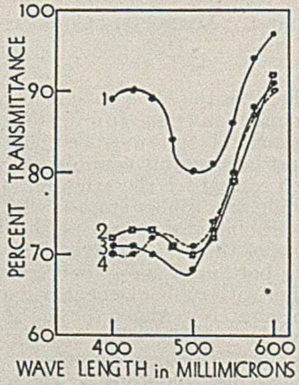

FIGURE 1. INFLUENCE OF REAGENTS ON TRANSMITTANCE CURVE OF IRON BIPYRIDINE

1. 1 p. p. m. of iron
2. Iron extracted with isoamyl alcohol
3. Iron plus carbamate plus isoamyl alcohol extraction
4. Iron plus 1 p. p. m. of copper plus all reagents

Effect of pH on Intensity and Stability of Color

Color development, characteristics, and stability were investigated using a Coleman Universal spectrophotometer, single monochromator type, with band width of 35 mμ.

To establish the influence of pH on the color 1 ml. of the intermediate standard (containing 0.1 mg.) of iron was diluted to about 50 ml. with water, and 1 ml. of the *p*-hydroxyphenylglycine solution and 2 ml. of 2,2′-bipyridine reagent were added. The solution was adjusted to the desired pH, as measured with a glass electrode, by the addition of ammonium hydroxide and transferred to a 100-ml. volumetric flask. The solution was diluted to the mark and mixed thoroughly. A blank was prepared from all reagents used with exclusion of the standard iron solution. The pink colored solution was read in the spectrophotometer against the blank.

Table I shows that the color is not so stable in the solutions at higher pH. Transmittances greater than 90 per cent do not accurately represent color intensity; hence, these values are approximations. The effect of reaction on the copper carbamate color was followed by adjusting to the desired pH 1 ml. of the intermediate standard solution (100 p. p. m.) previously diluted and treated with 1 ml. of the carbamate reagent, diluting to 100 ml., and extracting a 25-ml. portion with 10 ml. of isoamyl alcohol. The data of Table II reveal no significant differences in stability within the range pH 5 to 12.

TABLE I. TRANSMITTANCE OF AQUEOUS SOLUTIONS OF FERROUS BIPYRIDINE AT WAVE LENGTH 500 mμ

Time after Mixing	pH 5	pH 6	pH 7	pH 8	pH 9
	Transmittance				
Min.	%	%	%	%	%
10	81	80	84	83	82
60	81	79	88	90	96[a]
120	81	79	90	94[a]	98[a]

[a] Faint pink coloration visible.

TABLE II. TRANSMITTANCE OF ISOAMYL ALCOHOL SOLUTIONS OF COPPER DIETHYLDITHIOCARBAMATE AT WAVE LENGTH 450 mμ

Time after Mixing	pH 5	pH 6	pH 7	pH 8	pH 9	pH 12
	Transmittance					
Min.	%	%	%	%	%	%
20	33	35	39	35	33	31
120	33	35	39	35	32[a]	31[a]
240	34	34	39	35	33	32

[a] Slight turbidity, removed by centrifuging.

Effect of Reagents on Color Development

Inasmuch as the complexes for iron and copper were developed simultaneously in the same solution, it was necessary to know what influence the reagents exerted on the color development of these complexes. From the data previously obtained it was decided to buffer the solution at pH 6. Two reference spectral transmittance curves were prepared from standard solutions of copper and iron containing 1 microgram per ml. (curve 1, Figure 1, and curve 1, Figure 2). Extraction with isoamyl alcohol of the aqueous solution containing the colored iron complex decreased the transmittance at 500 mμ 10 per cent (curve 2, Figure 1). Addition of the carbamate reagent, with or without the presence of copper, had very little influence on the transmittance of the extracted aqueous solution at 500 mμ (curves 3 and 4, Figure 1). Curve 2 in Figure 2 reveals that the 2,2′-bipyridine does not influence the transmittance of the isoamyl alcohol solution of the copper complex; but from curve 4, same figure, it is evident that the presence of iron in an amount equal to or more than that of the copper interferes with full color development. The addition of a fivefold excess of carbamate reagent relieves the competition of the copper and iron, curve 5, without in any way influencing the transmittance of the reference solution as shown in curve 3. It is apparent that it is essential to have all reagents used in the actual determination present in the preparation of the standard curves of reference.

Preparation of Standard Reference Curves

The standard reference curves for copper and iron were prepared, utilizing the information obtained in the preliminary tests.

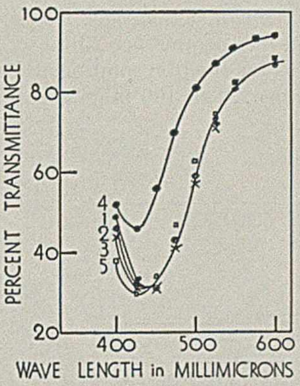

FIGURE 2. INFLUENCE OF REAGENTS ON TRANSMITTANCE CURVE OF COPPER CARBAMATE IN ISOAMYL ALCOHOL

1. ● 1 p. p. m. of copper plus carbamate
2. ○ 1 p. p. m. of copper plus all reagents
3. × 1 p. p. m. of copper plus excess carbamate
4. ● 1 p. p. m. of copper plus 1 p. p. m. of iron plus all reagents
5. □ 1 p. p. m. of copper plus 1 p. p. m. of iron plus excess carbamate

Copper standards varying in content from 2 to 100 micrograms in 20 ml. of solution (corresponding to 0.1 to 5 p. p. m.) were treated in the order given with 1 ml. of *p*-hydroxyphenylglycine solution, 2 ml. of 2,2′-bipyridine solution, 4 drops of concentrated ammonium hydroxide, 5 ml. of *N* ammonium acetate solution, and 1 ml. of carbamate reagent. Each standard was then extracted in a separatory funnel with 15 ml. of isoamyl alcohol. This volume of isoamyl alcohol was found sufficient to remove in one extraction all the carbamate complex formed by 100 micrograms of copper. The yellow alcohol layer was cleared by a short centrifugation at about 2000 r. p. m. and read in the spectrophotometer against a blank solution incorporating all reagents and steps except for the copper solution. The standards for iron varied from 2 to 100 micrograms in 20 ml. of solution and were treated in the same manner as the copper standards. Readings were made on the aqueous layer following a short centrifuging. Above concentrations of 60 micrograms in 20 ml. the bipyridine solution became the limiting factor for color development and it was necessary to increase the strength of the color reagent to accommodate all of the iron present.

The transmittance-concentration curves are given in Figure 3 for wave length 500 mμ for iron and wave length 450 mμ for copper. From the relationship between optical density, D, and transmittance, T, expressed and defined by Ashley (*1*) the equation $D_\lambda = \log \frac{1}{T} = K_\lambda cl$ may be derived. When c is expressed in moles per liter and l in centimeters, K_λ becomes the molecular extinction coefficient and may be calculated from the expression $K_\lambda = \frac{D_\lambda}{cl}$. Preference is given to this form of the Bouguer-Beer equation, as the value for D may be read directly from the spectrophotometer used. In Figure 3 the optical density is plotted against the concentra-

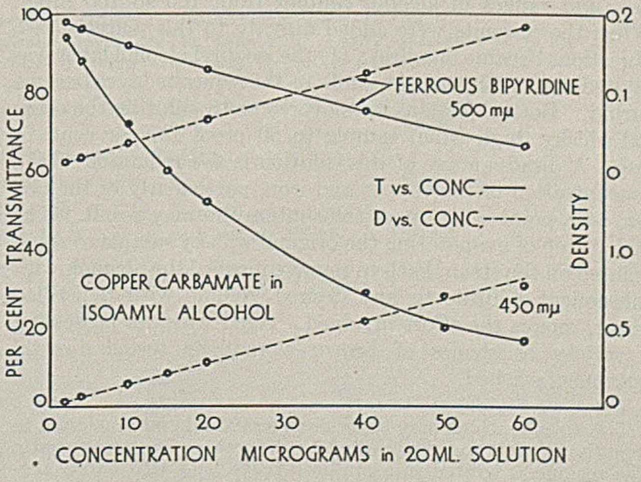

FIGURE 3. TRANSMITTANCE CONCENTRATION CURVE FOR FERROUS BIPYRIDINE AND COPPER DIETHYLDITHIOCARBAMATE IN ISOAMYL ALCOHOL

tion for each of the metals. For the copper solutions Beer's law is obeyed in the range 2 to 60 micrograms per 20 ml. of solution (0.1 to 3 p. p. m.), whereas for the iron solutions the law holds less exactly over the range 20 to 100 micrograms per 20 ml. of solution (1 to 4 p. p. m.).

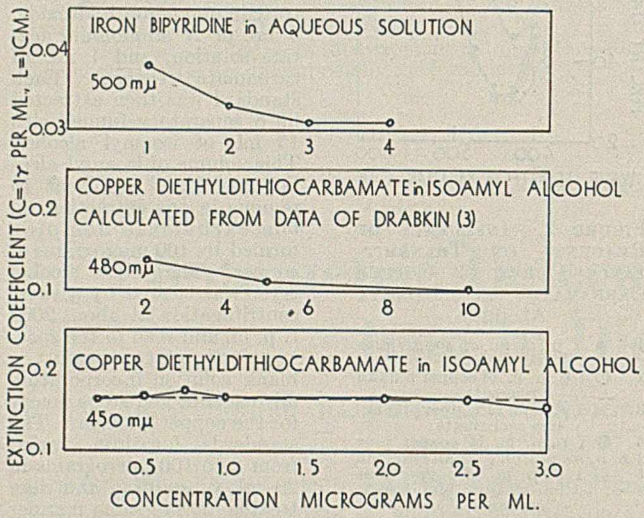

Figure 4. Extinction Coefficients for Copper and Iron Complexes

Under the conditions imposed and the concentrations used the procedure is much more satisfactory for copper than for iron. This is apparent from the values for the extinction coefficients shown in Figure 4 as calculated for a concentration of 1 microgram per ml. and cell depth of 1 cm. For comparison, the data of Drabkin (*5*) for wave length 480 mμ obtained by precise visual spectrophotometry have been converted to the same basis. For copper diethyldithiocarbamate in isoamyl alcohol there is apparently closer concordance with Beer's law at concentrations of 3 micrograms per ml. and less. Best agreement with Beer's law—that is, the optimum range for iron—is at concentrations of 40 to 80 micrograms per 20 ml.

Application to Distilled Liquors

Freshly distilled whisky, called "high wine", is clear, colorless, and ranges in alcohol content from 100 to 160 proof. When the reagents were added directly to this material two objections became manifest: (1) the isoamyl alcohol layer was diluted about 50 per cent, and (2) the aqueous layer became turbid. Both objections were overcome by diluting the original whisky (high wine) sample to 50 proof (25 per cent) or less. A disadvantage of this dilution is the reduction of the concentration of the copper and iron, particularly of the latter, to a point where poor color intensities may result. The added step of evaporating the original whisky sample to small volume on the steam bath to remove most of the alcohol, with subsequent dilution to any desired volume with redistilled water, repays the effort involved. Aged whiskies possessing a variety of shades of brown cannot be tested directly but must be ashed.

The sample, which may be as small as 100 ml., is transferred to a platinum dish and evaporated to dryness on the steam bath. The residue is ignited in a muffle furnace held at a barely perceptible redness. In about 30 minutes the residue assumes the form of a gray gossamer, which is taken up with 1 ml. of concentrated hydrochloric acid, warmed a few minutes on the steam bath, and transferred with redistilled water to a 25-ml. volumetric flask. Of the solution 20 ml. are transferred to a separatory funnel and treated with the reagents as described above for the reference standards. The yellow isoamyl alcohol solution obtained is read against the alcohol layer from a blank carried through at the same time, and the pink aqueous layer is read against the corresponding layer of the blank. Concentrations may be calculated from the equation $K_\lambda = \frac{D_\lambda}{cl}$ or read directly from the standard curve of reference.

As there are no interfering ions present in the ash of the freshly distilled or aged whisky, copper and iron may be determined directly on the solution thus obtained. When other metals such as calcium and magnesium are also to be determined, a preliminary separation is effected by precipitation of the copper and iron from ammoniacal solution with hydrogen sulfide. When this separation is to be carried out 5 mg. of lead are added as a gatherer before precipitation, as recommended by Greenleaf (*7*).

Copper and iron may be determined simultaneously in degassed but otherwise untreated beer by the direct method described above. Gray and Stone (*6*) utilized 2,2′-bipyridine in a direct procedure for beer, making visual comparison with permanent iron standards in a block comparator. The usual advantages are found in the use of the spectrophotometer.

Twenty milliliters of the degassed beer in a 50-ml. Erlenmeyer flask were treated with the reagents as above and placed in a water bath at 70° C. for 30 minutes. The solution was allowed to cool and transferred to a separatory funnel with 5 ml. of water. Copper carbamate was extracted with 15 ml. of isoamyl alcohol and clarified by centrifuging. The colors were read in the spectrophotometer against the alcohol and aqueous layers of beer not subjected to the reagents but diluted with water to the proper volume.

The analytical data for a few representative samples are given in Table III.

Table III. Copper and Iron Content of Distilled Liquors and Beer

Sample		Iron Added *P. p. m.*	Iron Found *P. p. m.*	Copper Added *P. p. m.*	Copper Found *P. p. m.*
High wine	D[a]	None	0.2	None	0.62
	D[a]	1	1.08	1	1.67
	D[a]	2	2.10	2	2.70
	D[b]	None	0.2	None	0.60
	D[b]	1	1.05	1	1.57
Whisky	R[c]	None	0.5	None	1.76
	B[c]	None	0.2	None	0.82
Beer	L[d]	None	0.38	None	4.2
	L[d]	1	1.42	1	5.1

[a] Alcohol removed by evaporation.
[b] Alcohol concentration reduced by dilution.
[c] Ashed sample.
[d] Sample degassed only.

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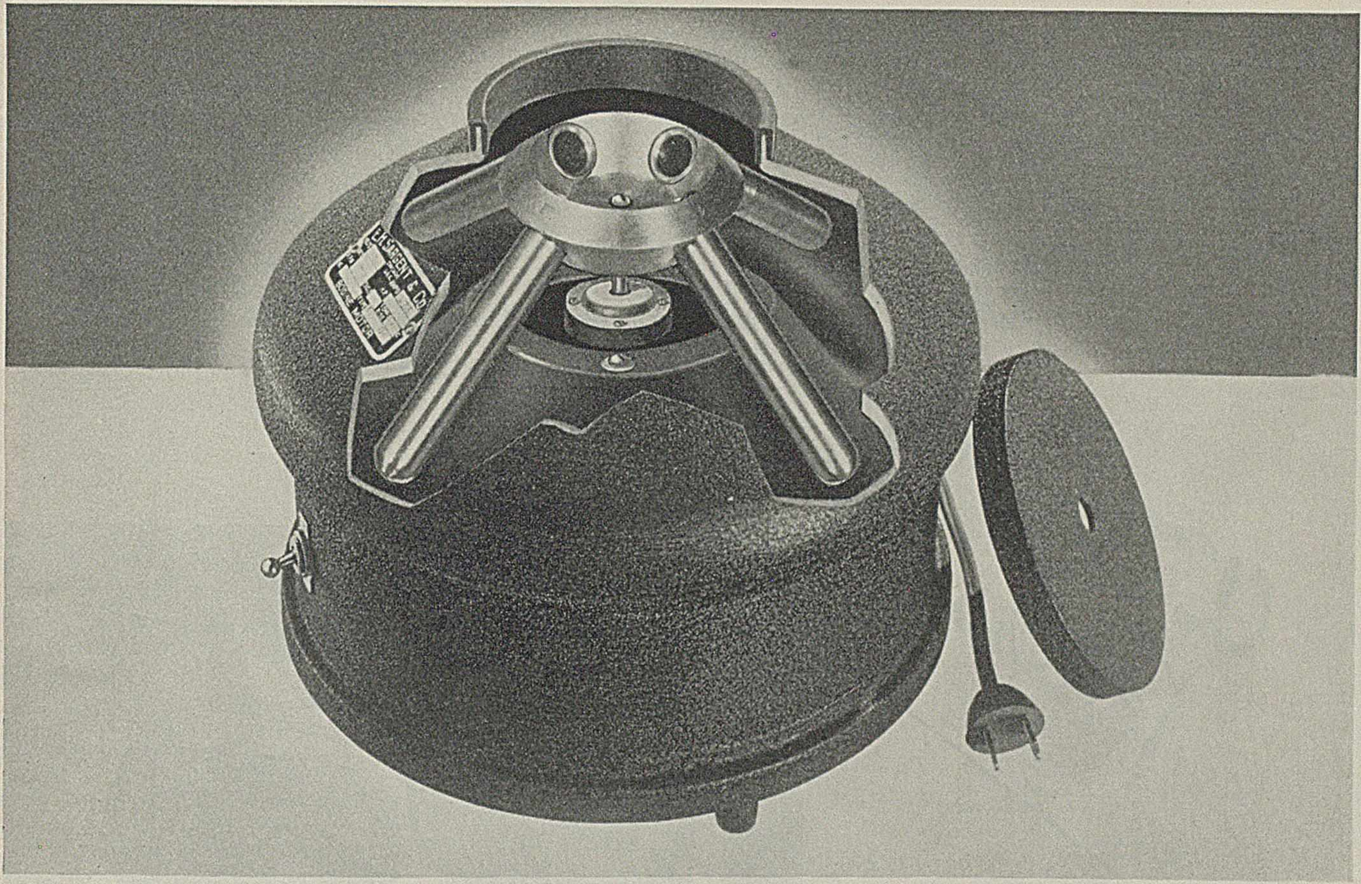
Presented before the Division of Analytical and Micro Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.



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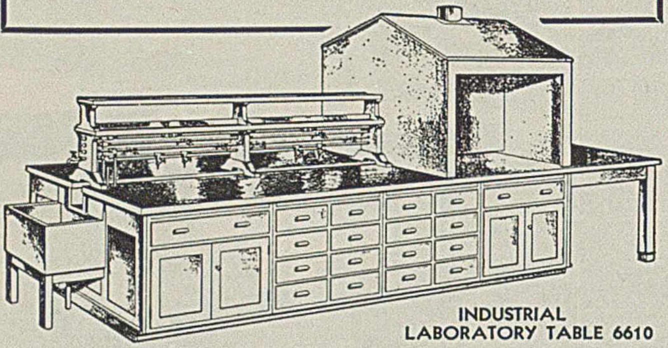

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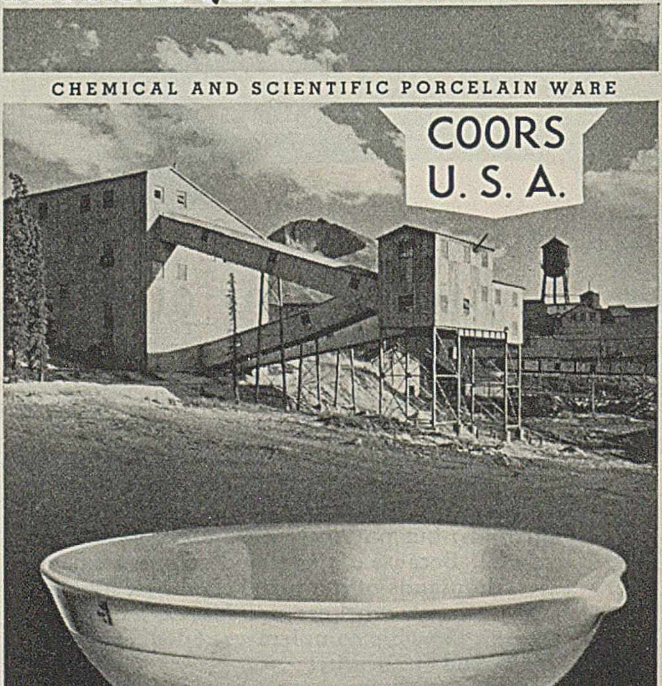

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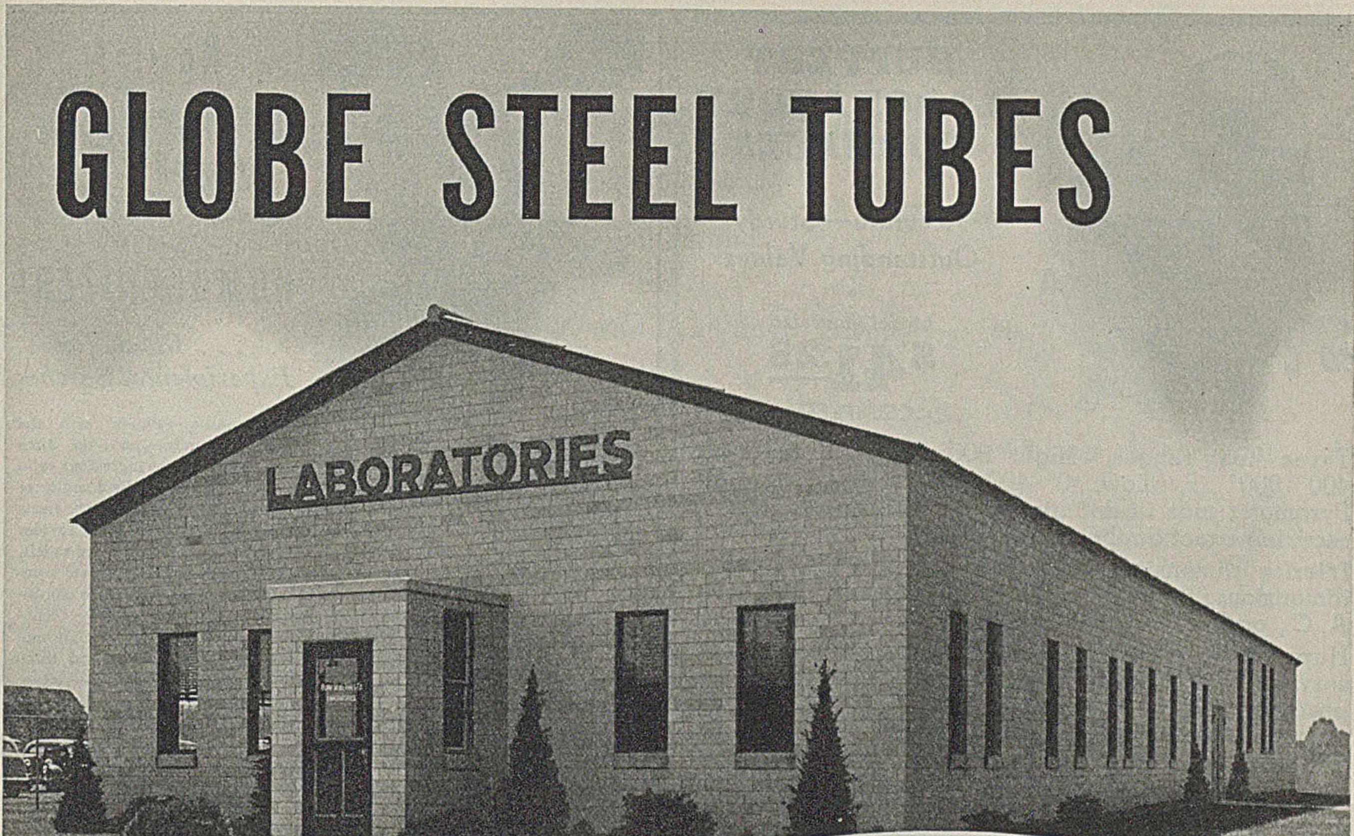
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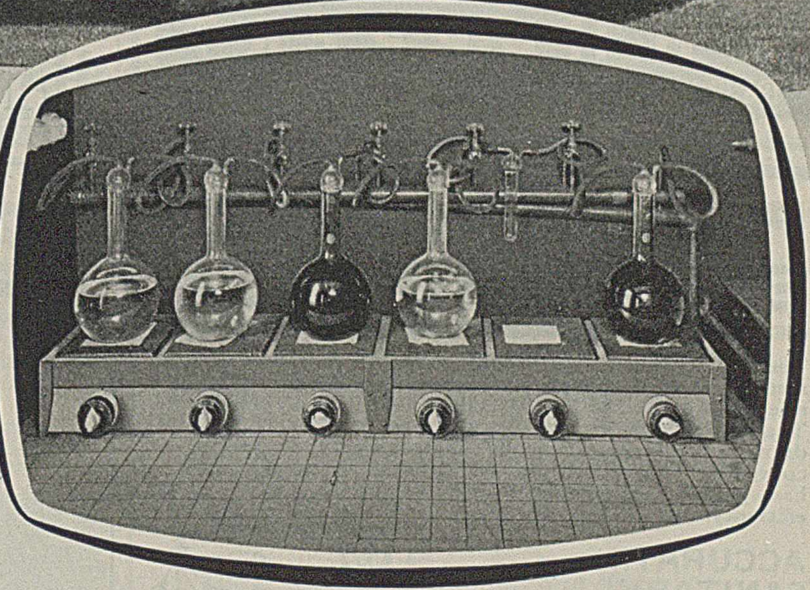

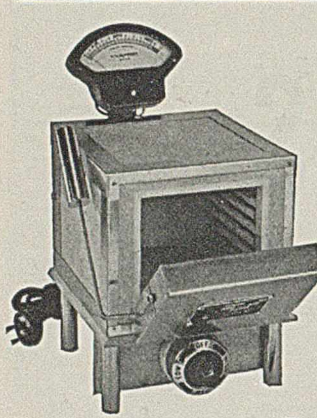

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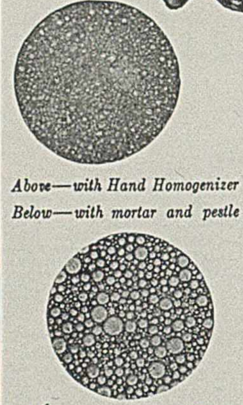

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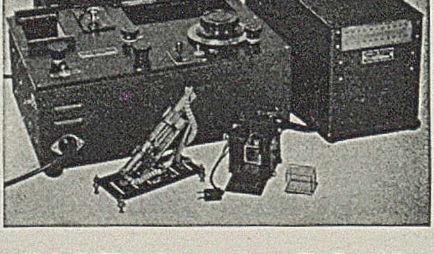

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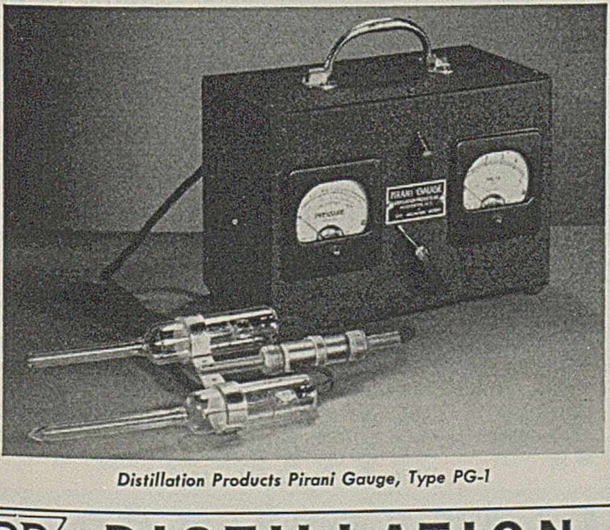

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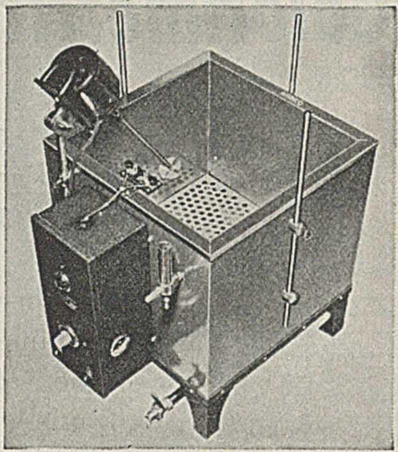

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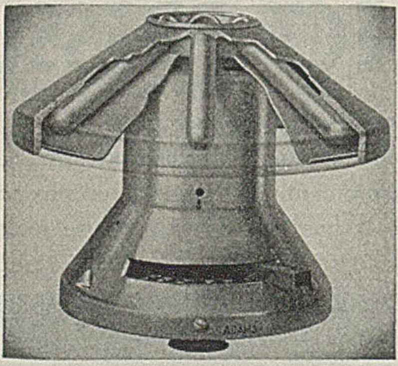

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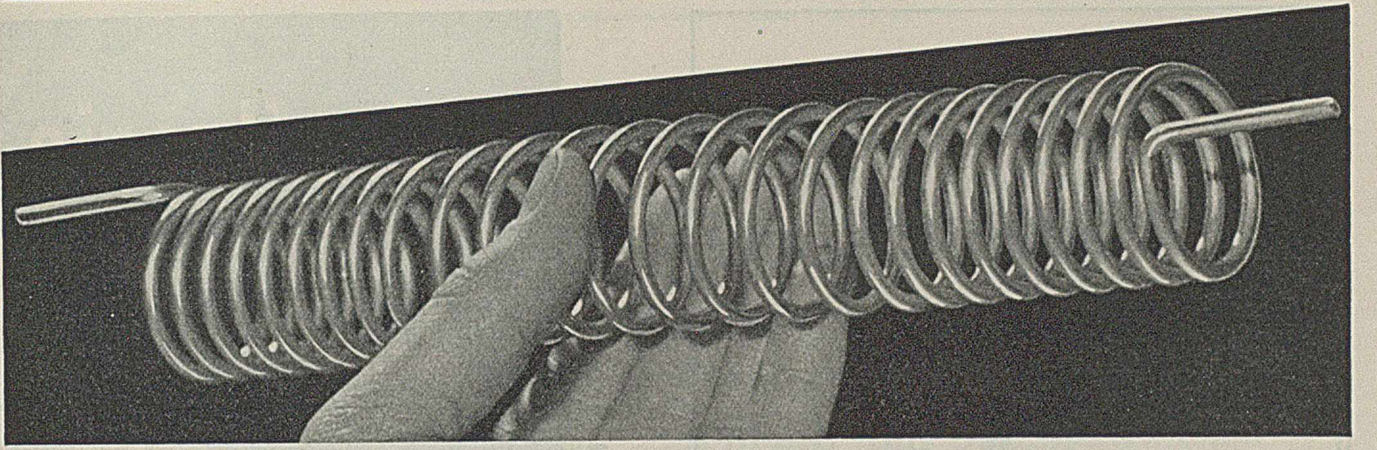

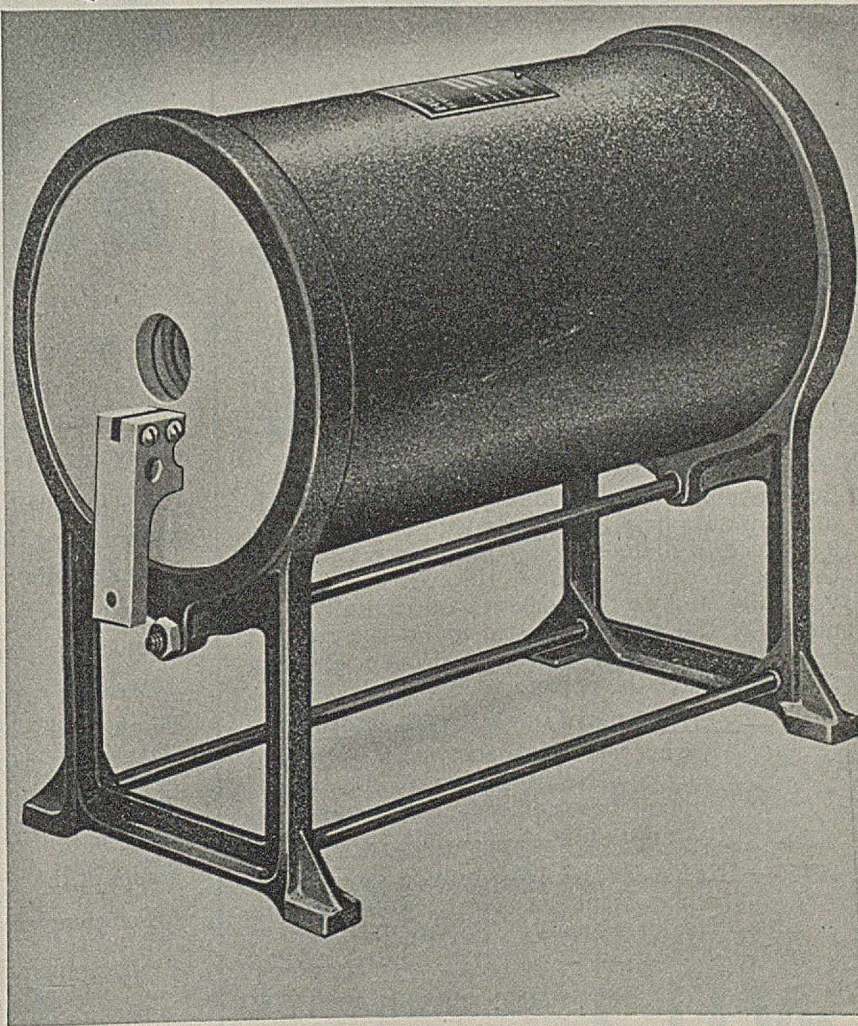

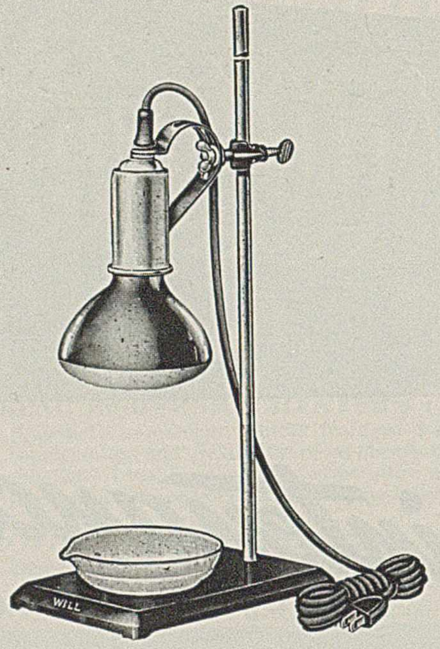

Faster Drying

with the

INFRA-RED

RADIANT HEATER

For many purposes this new heater offers faster, cheaper, easier drying and dehydrating. It employs the new G-E 250 watt infra-red lamp with integral reflector which has an average service life of 5000 hours.

The heater assembly as illustrated is designed for convenience, adjustability, and economy. It fits any standard laboratory support rod up to 9/16 inch in diameter. By means of a wing nut, the socket can be rotated through 360 degrees vertically and to 180 degrees horizontally. By means of the clamp adjustment on the rod the heat intensity can be varied by raising or lowering the lamp above the object.

19750—RADIANT HEATER—Infra-Red. Comprising clamp, socket with cord and plug, and No. 19755 Lamp, but without support base and rod. For operation on 105–120 volts. $4.50

19755—INFRA-RED LAMP only. 250 watts for replacement in No. 19750 Radiant Heater assembly. For 105–120 volts. $1.75

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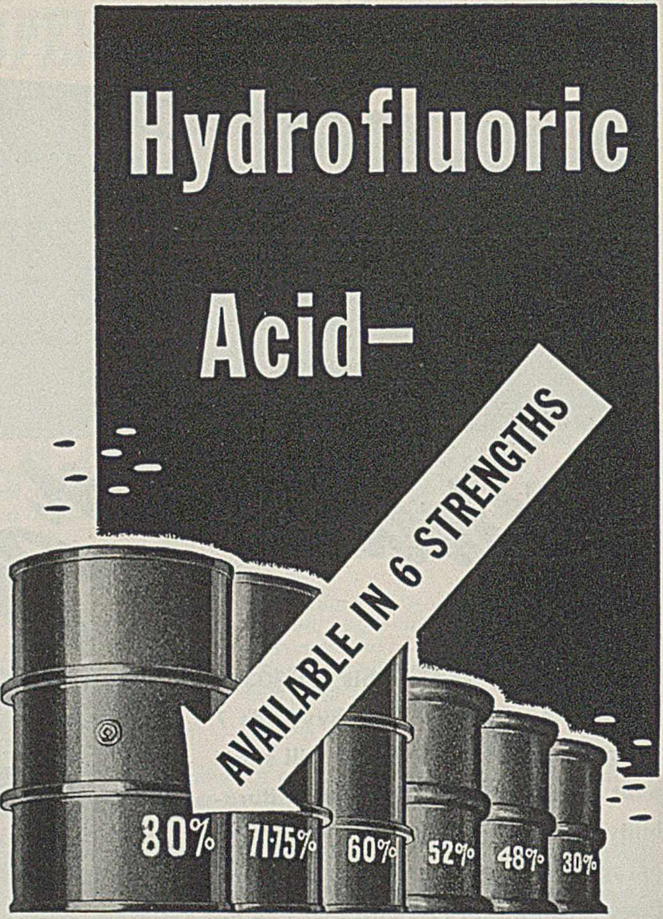

FOR etching and frosting electric light bulbs and other glass products, for cleaning stainless steels, as an aid in straw bleaching processes, and for many other industrial purposes, hydrofluoric acid possesses many advantages.

Particularly valuable to the industrial user is the high grade, iron-free hydrofluoric acid produced by Pennsylvania Salt Manufacturing Company, who purchased the facilities of Sterling Products Company, Easton, Pa., some time ago.

Meeting the most exacting requirements, this hydrofluoric acid is available in five strengths for domestic users—30%, 48%, 52%, 60% and 80%. Also, for export, there is supplied 71-75% acid. Shipment of hydrofluoric acid is in rubber drums for strengths under 60%. Stronger grades of the acid are packed in steel containers.

For complete information applicable to your specific problems, write to Pennsylvania Salt Manufacturing Co., Widener Building, Philadelphia, Pa.

FOR DEFENSE BUY UNITED STATES SAVINGS BONDS AND STAMPS

PENNSYLVANIA SALT MANUFACTURING COMPANY
Chemicals
1000 WIDENER BUILDING, PHILADELPHIA
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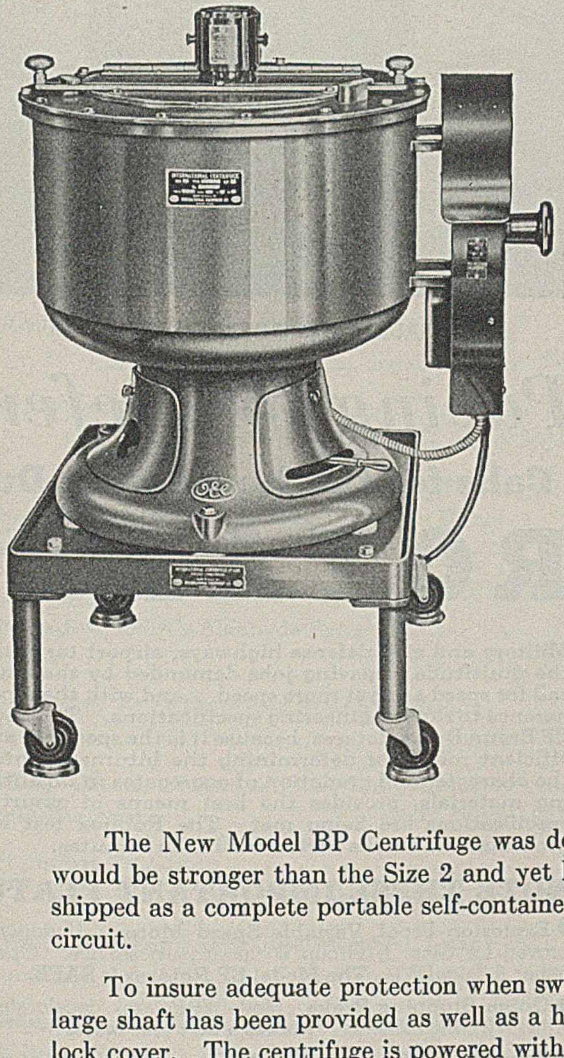
NEW BLOOD PLASMA CENTRIFUGE

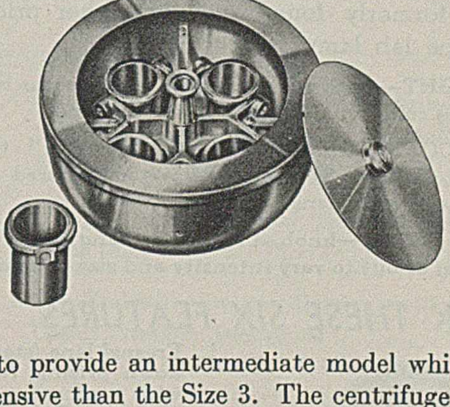
INTERNATIONAL MODEL BP

Designed Especially For The 600 ml. and 650 ml. Bottles

SPEED 2500 R.P.M.

Windshielded Head To Minimize Heating of Blood





The New Model BP Centrifuge was designed to provide an intermediate model which would be stronger than the Size 2 and yet less expensive than the Size 3. The centrifuge is shipped as a complete portable self-contained unit, wired and ready to plug into any lighting circuit.

To insure adequate protection when swinging the large 600 and 650 ml. bottles an extra large shaft has been provided as well as a heavy all welded steel boiler plate guard with bar lock cover. The centrifuge is powered with a specially designed motor and is equipped with an indicating tachometer and 50 step speed control rheostat.

The four place head shown above will accommodate the Cutter 650 ml. Saftifuge bottles, the Baxter 600 ml. Centrivac bottles and the T. C. Wheaton 550 ml. blood bottles, as well as the Fenwal and Kimble 650 ml. refillable blood plasma bottles. The head and cups are entirely windshielded by enclosure in a bowl and cover of spun aluminum which provide a dead air space in which the bottles swing, thus reducing air friction and minimizing heating of the blood.

Send for Descriptive Literature

INTERNATIONAL EQUIPMENT CO.

352 WESTERN AVENUE BOSTON, MASS.

Makers of Fine Centrifuges for More than Forty Years

A Quality Lamp at a New Low Price

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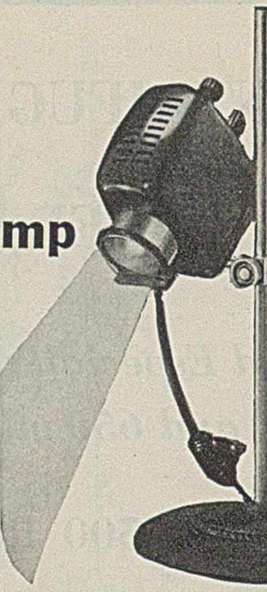


Support Model Lamp—No. 17482—8" metal base, 15" support rod, 5" extension rod. Complete with switch and 100 watt bulb . . . $14.95

foot candles at one foot distance

Ideal for bright or dark field microscopy or wherever else apparatus requires concentrated light, this versatile, quality lamp has all the important construction features formerly found only in higher priced "research" type lab lamps.

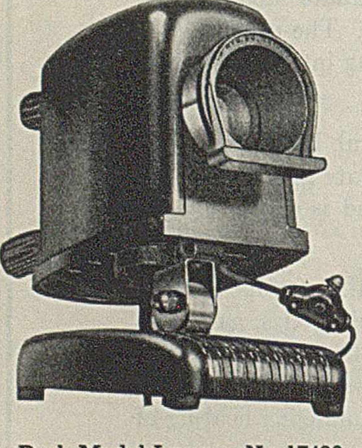
COLD LIGHT—glass of the Fresnel lens absorbs heat to give cold light 12" away from the lens.

COLOR CORRECTED—to give a "daylight" type beam, excessive reds and yellows are filtered out by the Fresnel lens.

SPOT OR FLOOD—knob at rear of housing moves the lens in or out to vary intensity and size of beam.

CHECK THESE SIX FEATURES

1. Fresnel lens (step-down prisms) has wide acceptance angle. Refracts light to lens center at high intensity.
2. Bakelite lamp-house is well ventilated.
3. Takes standard Type G-16½, 100 watt bulb with rated life of 200 hours.
4. No transformers or rheostats required. Plugs into any 115 volt line.
5. On-off switch wired into 8 ft. cord.
6. Spring clip on lamp-house front takes filters for additional light diffusion or color correction.



Desk Model Lamp—No. 17486—overall height about 7". Complete with 100 watt bulb and switch $11.95

Order today for immediate delivery. Both Support and Desk Model Lamps carried in stock.

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Laboratory Supplies and Reagents
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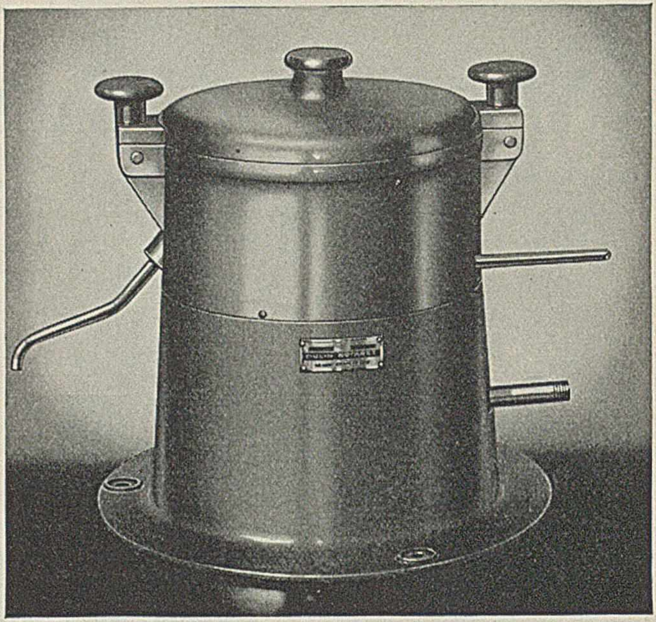

BRAUN DULIN ROTAREX, MODEL EP

Paving for Defense

Calls for the New Braun Dulin

ROTAREX

Military and civil defense highways, airport tarmacs, all of the multitude of paving jobs demanded by the emergency call for speed and yet more speed. . .and with that speed, adherence to rigid engineering specifications. The new Model EP Braun Dulin Rotarex, because it is the speediest and most efficient means of determining the bitumen content and the character and gradation of aggregates in bitulithic paving materials, provides the best means of assuring that specifications are being met. The Rotarex test is clean, accurate, and can be performed in ten minutes.

NOTE THESE IMPORTANT FEATURES

- **Explosion-Proof, Variable Speed Motor.** Underwriters approved for Class 1, Group D (hazardous) service. Operates on either A.C. or D.C. **The Model EP Rotarex is SAFE.**
- **Quick Stopping Brake.** Model EP Rotarex decelerates rapidly without jarring contents. **Makes a fast test faster.**
- **Solvent Can Be Added While Running.** No need to stop the Rotarex during the test. Another time-saving feature.
- **Modern Design.** The new Rotarex has been reengineered throughout. Efficient, accurate, up to the minute in every detail.
- **1000 Gram Capacity.** Suitable for making tests on any job.

Check every paving job with a Model EP Rotarex to insure fidelity to specifications. Address Dept. I-4 for descriptive bulletin C-136.

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