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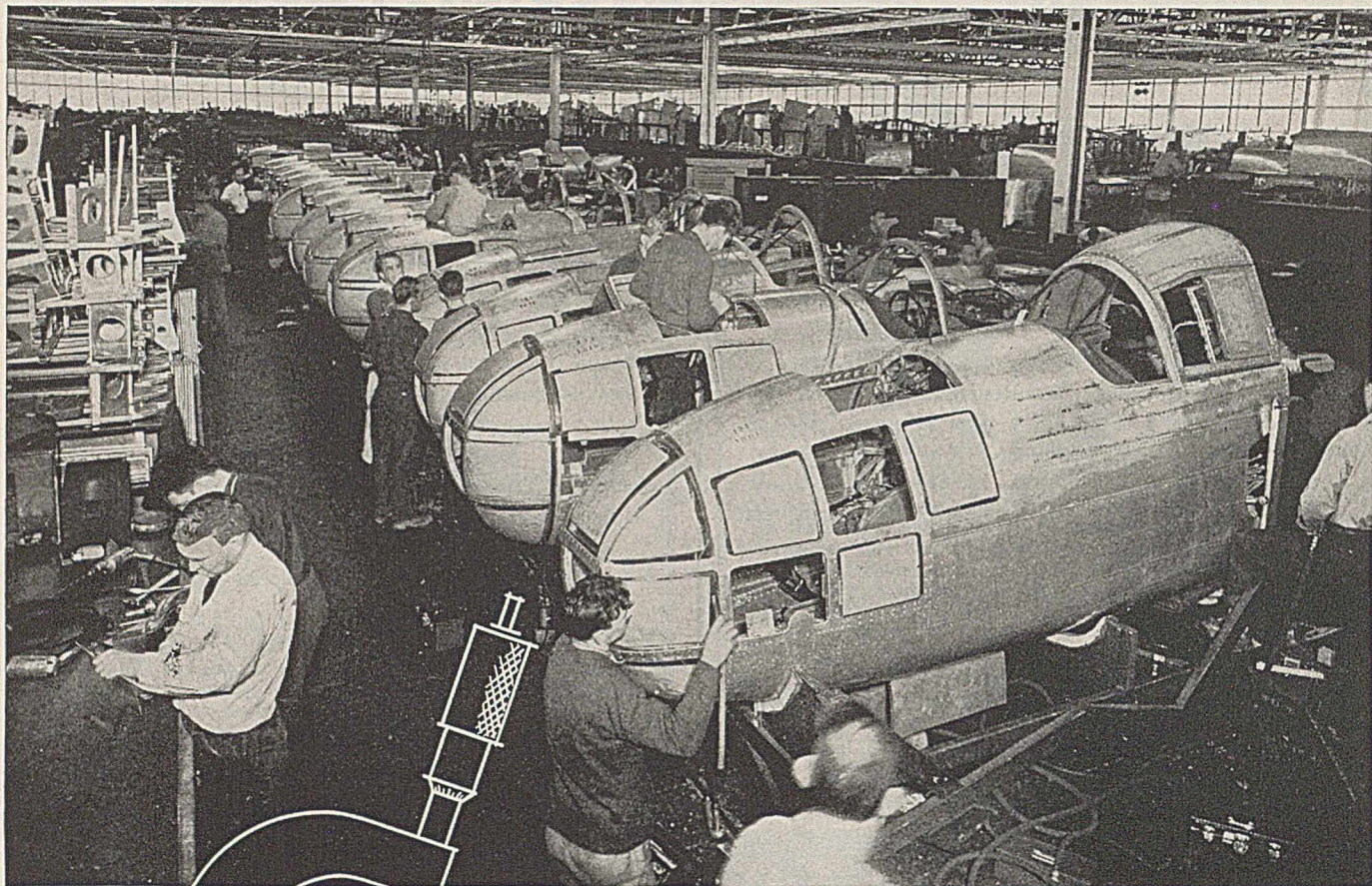
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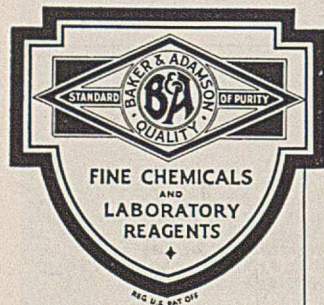
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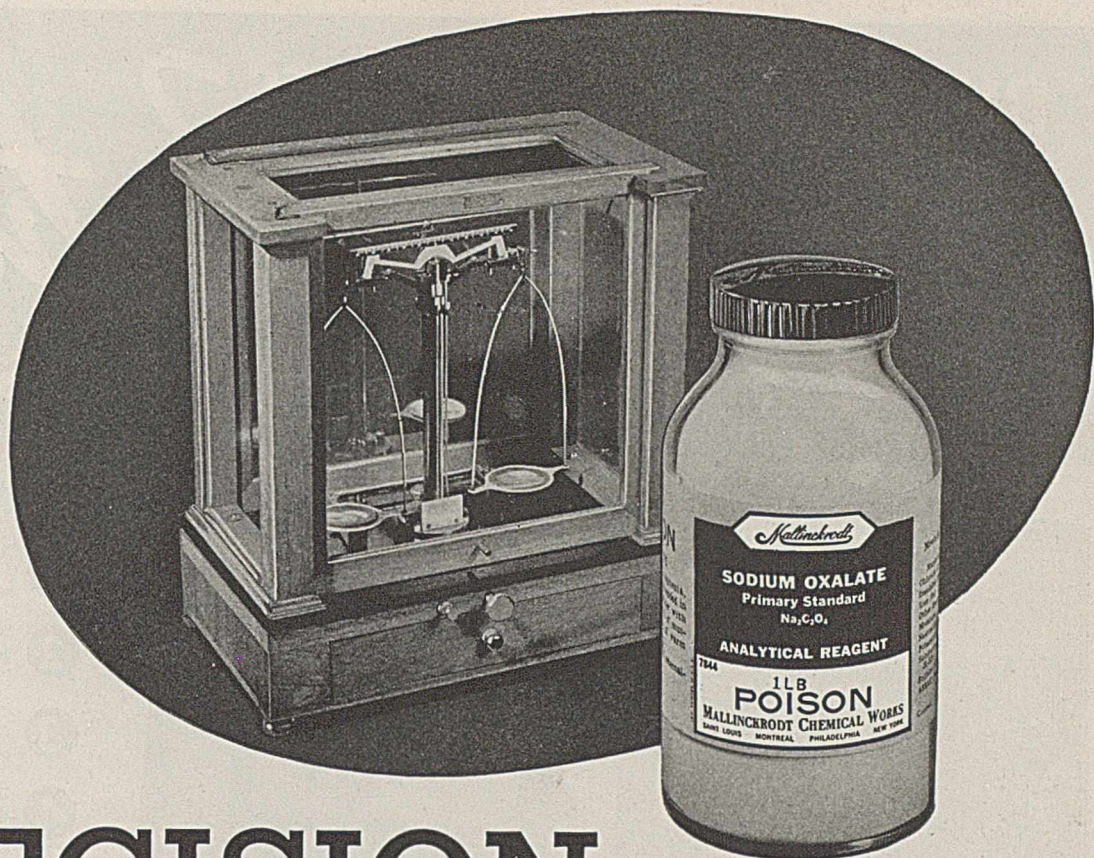
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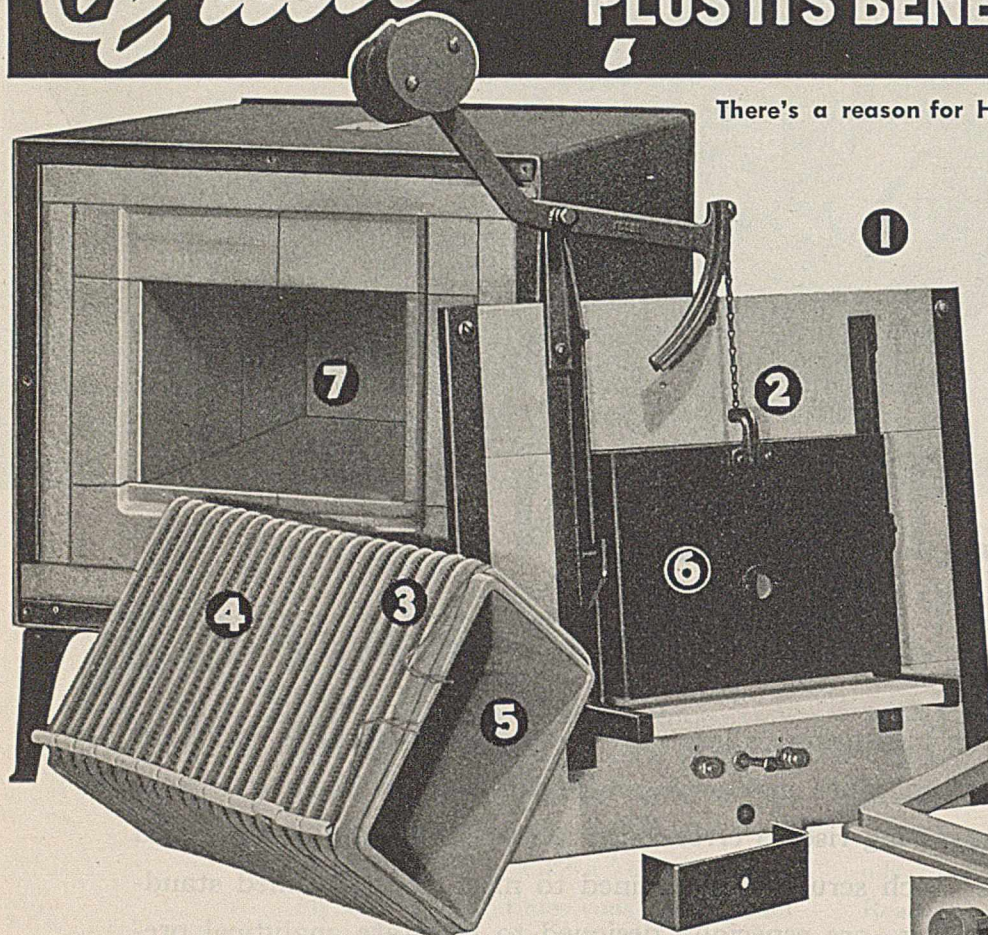
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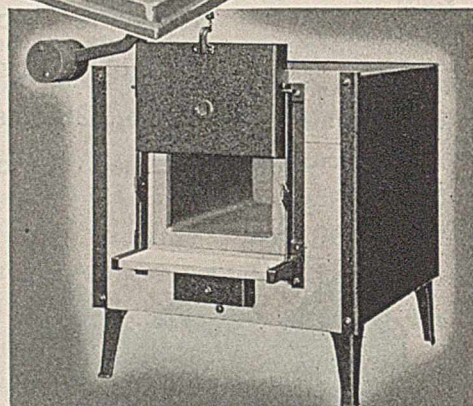


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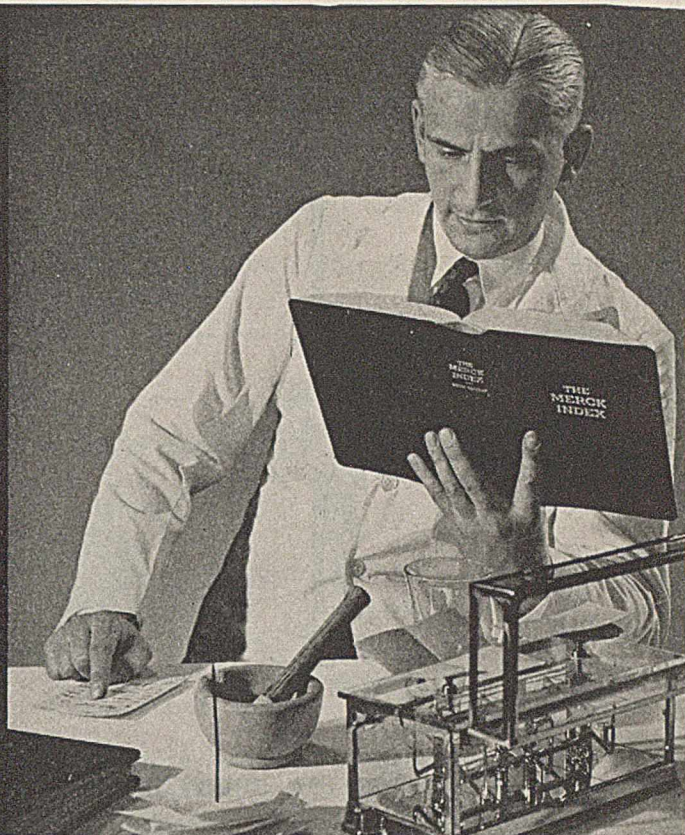
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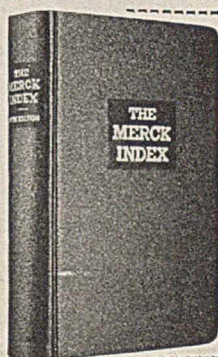
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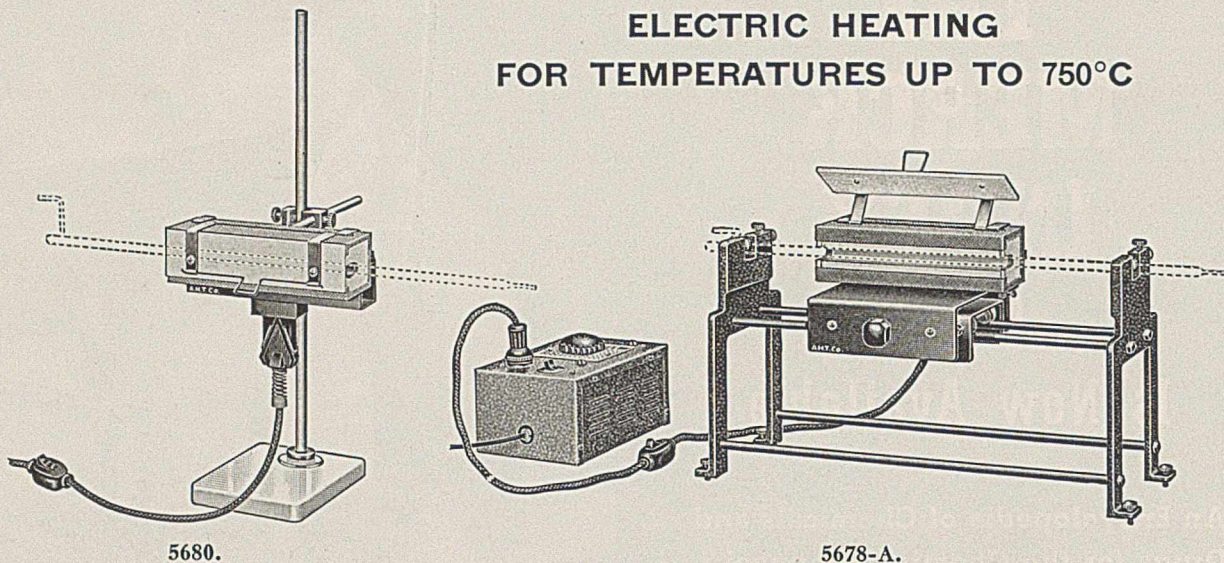
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Testing Mold-Resistant Properties of Oil Paints

A Laboratory Method

ALEX M. PARTANSKY AND ROBERT R. MCPHERSON

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ONE of the first to draw the attention of the American public to the prevalence of mold growth on oil paints was Gardner (2), who as early as 1913 pointed out that "in damp localities, especially along the sea coast, mildewing of painted exterior surfaces is common". Since that time and especially during recent years the importance of controlling mold growth on painted surfaces has attracted the attention of technical men.

pigment content (particularly zinc oxide), made up with high-grade rapid-drying spar varnish, which dry to a hard smooth film.

After 2 years of extensive experimental work on mold-growth prevention, during which upward of 200 commercial paints of various types were tested, the writers have yet to see a paint that would not mold under the conditions of the procedure described below, unless a good preservative had been added.

In the study of paint preservatives and the mold-resistant properties of paints in general the method most widely used in this country is that of field exposure in the southeast coastal states, usually Florida.

The chief disadvantage of the field test for the preliminary evaluation and comparison of paint preservatives, besides its slowness, is the lack of uniformity in the natural weather conditions, not only throughout the year (tests can be started, therefore, only once a year during the rainy season) but between the same seasons of different years. It is also difficult to compare data obtained in different localities, for there is no such thing as "standard weather" (13).

To minimize weather variability and to remove the possibility of misleading results, field tests to be conclusive require repetition for several seasons.



FIGURE 1. MOLD GROWTH ON WALL NEAR REFRIGERATION PIPES

The paint mildewing problem is particularly serious in industrial plants where, owing to the nature of the processes involved, high humidity and fairly warm temperatures are maintained. Here the mold growth not only gives an unsightly appearance to the rooms and injures the paint, but presents a serious danger in contaminating the product. Figures 1 and 2 are unretouched photographs taken in two such plants in the middle west area. In both cases the walls were repainted 3 to 4 months previous to photographing.

It is generally agreed that under favorable conditions, a luxuriant mold growth readily develops on slow-drying long-oil (low in pigment) paints made up with impure oils containing mucilaginous and nitrogenous matter, which on drying give a soft and hygroscopic film (3, 8, 9, 12). On the other hand, mildew troubles have been considerably lessened though not entirely eliminated (6, 7, 8, 10, 12) in paints of high

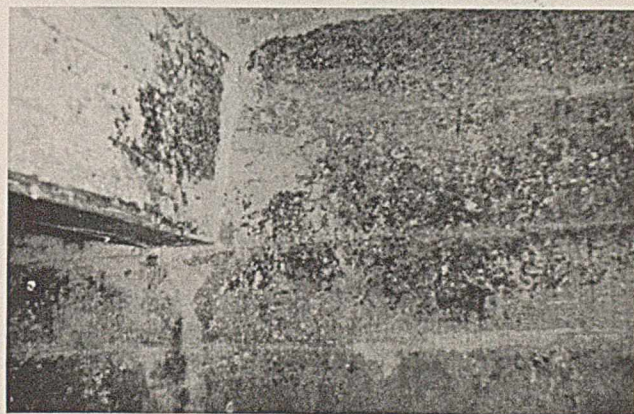


FIGURE 2. EXTENSIVE MOLD GROWTH ON WALL
Near concrete ceiling, through which there is a slow seepage of moisture from floor above

A good laboratory method carried out under standardized conditions has a great advantage over the field exposure method for all preliminary or routine testing. It is not only independent of the season and can be started whenever desired, but since all conditions can be reproduced exactly for every test, results obtained at different times are comparable to each other.

Besides the advantage of standardization of the procedure, a laboratory method for testing mold-resistant properties of paints can be made to include and to intensify the principal factors favoring molding of paints under the conditions of actual service—namely, heavy seeding with selected molds found to grow well on paints, high humidity, warmth, and darkness. As a result, the time required for testing is shortened from several months to a few weeks.

A search of the literature revealed only two laboratory methods, both of which were described in the early work of Gardner (5).

In the first method drops of treated paint were placed on top of Czapek's agar seeded with mold in Petri dishes and the inhibition zone was observed around the paint spots after 10 days of incubation. The inhibition zone test, however, does not tell whether the mold would or would not grow on a particular paint but only indicates the presence or absence of water-soluble fungicide capable of inhibiting mold growth on agar.

The second method consisted of hanging paint panels seeded with a water suspension of molds in a chamber maintained at 30° C. and 85 per cent relative humidity; however (5), these panels developed no mold growth in 4 months.

In trying to devise a rapid laboratory method for testing mold-resistant properties of paint the authors endeavored to elaborate on the technique of seeding with spores, a method tried by Gardner on paints, and also commonly employed in testing other materials, such as canvas (11). However, consistent results could not be obtained and the method was finally abandoned in favor of the present "grafting" procedure. Some of the experience gained, however, is very instructive.

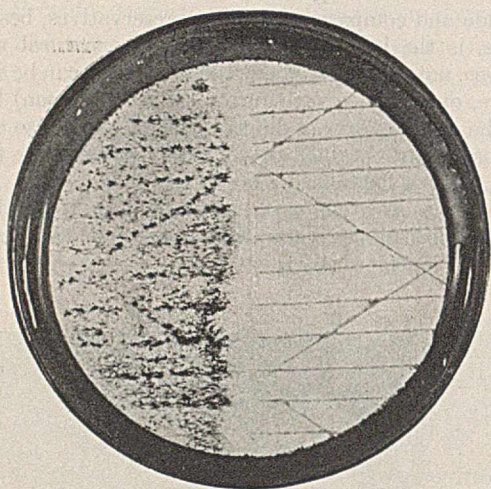


FIGURE 3. TEST PANEL

Showing mold growth primarily following lines of scratching. Paint on right contains preservative.

For instance, (1) scratching or otherwise breaking the surface of the dry paint film helps to start the mold growth along the scratch (Figure 3); (2) mold growth started locally, as on a drop of agar placed on the paint surface, does not spread far from the point of infection; (3) addition of "nutrients", such as malt extract, to the paint itself prior to painting is of little assistance in subsequent molding, while soaking the paint panels in malt extract solution helps to start the mold growth,

but also frequently results in bacterial contamination which actually interferes with the mold growth; (4) excessive moistening of the paint surface is detrimental to mold growth.

In the authors' new laboratory method for testing mold resistance of oil paints the seeding is done by placing the painted surface in contact with an actively growing mold mycelium. When this "grafting" procedure is carried out with due care and exactly as outlined below, the seeding is successful in at least 99 per cent of the cases.

The mold now used in paint testing work by the present method, No. 29, is a rapid-growing *Aspergillus* forming dark brown spores. It was originally isolated 2 years ago from a molded paint and selected for the paint-testing work from a group of 35 molds because of its exceptionally abundant and vigorous growth on oil paints and its high resistance to toxicants. This choice is also supported by the fact that most of the molds reported as growing on oil paints in nature belong primarily to either *Aspergillus* or *Penicillium* genera (1, 4).

Standard Procedure

PANELS (Figure 4). Wooden disks 7.5 cm. (3 inches) in diameter and 0.625 cm. (0.25 inch) thick, cut from clear western white pine sapwood with grain running parallel to the plane surface, are used in the test. These disks are convenient to handle and fit the standard size glassware. It was necessary to standardize the material, since the substratum over which the paint is applied somewhat affects the readiness with which the paint molds.

The disks are sanded on all sides and the edges are slightly rounded off to prevent paint from pulling away from the edges. Since the pitch content of the wood varies considerably, for the sake of uniformity, to eliminate the additional variables, and to prevent discoloration of white paints, the panels prior to painting are extracted with a high-solvency naphtha (the authors use Skelly Solvent of B. R. 100° to 140° C.).

PAINT APPLICATION. The paint manufacturer's directions as to the priming, thinning, number of coats, drying time between coats, etc., are followed when given. In the absence of instructions two coats are applied according to good painting practice. For painting the panels the authors use 0.78 cm. (0.31 inch) wide, 1.875-cm. (0.75-inch) bristle brushes made by the George E. Watson Company. During painting care is taken to prevent mixing of paints by using a clean dry brush for each paint (the used brushes are washed in several changes of turpentine and then in acetone).

To afford a direct comparison between the original and the fungicide-treated paints, one surface of each disk is divided by a shallow groove made with some blunt instrument along the diameter running parallel to the wood grain. One half (as well as the adjacent edge) is painted with the test paint, while the other is painted with the original untreated paint. When the latter is not available some comparable paint known not to contain preservatives is used.

After the paints are thoroughly dry and at least 5 days have elapsed after application of the second coat, the panels are soaked overnight in distilled water (this softens the paint film in a manner similar to rain action), and are then ready for seeding. Sometimes it is advantageous, before soaking the panels in water, to dip the unpainted backs of the disks into molten paraffin to prevent warping and paint peeling.

SEEDING. After soaking, the test panels are wiped dry with a towel and are laid painted side down on a 36- to 42-hour old culture of mold 29, grown on malt agar in 10-cm. Petri dishes. For growing seeding mold cultures the authors use agar containing 25 grams of Difco malt extract, 2 grams of Difco yeast extract, and 15 grams of agar per liter of water. After hardening, the agar is seeded by swabbing with a water suspension of the mold. Aseptic microbiological technique is carefully observed during preparation of the seeding cultures. The disks are pressed down gently but firmly to ensure a good contact between the paint and the mold mycelium.

The age of the seeding mold culture, or rather the stage of its development, is critical; for best results it should be used exactly at the time when the sporangia are developing but before they begin turning dark. About 42 hours at 25° C. are required for the mold to reach this stage.

The test panels remain on the seeding culture for 20 to 24 hours at 25° C., in which time the mold not covered by the disks becomes dark.

MOLDING. After seeding, the paint surface is gently sprayed with water from an atomizer to wash off any agar particles or other extraneous matter that might be present, and the disks are embedded (painted side up) in Petri dishes by means of paraffin. Just enough paraffin is added to cover the bottom of the disk and to fix it in place, leaving a groove between the edge of the disk and the side of the dish. The necessary moisture for mold growth is provided initially by spraying the paint surface from an atomizer and by placing 5 cc. of water in the groove; the water in the groove is periodically replaced as it evaporates. The disks embedded in Petri dishes are incubated in a chamber kept at 25° to 30° C. and 60 to 70 per cent relative humidity. Better mold growth is obtained when the test disks are periodically watered and incubated in an ordinary incubator, as described, than when they are incubated in a saturated atmosphere of 95 to 100 per cent humidity.

(both natural and artificial) can be tested at any particular stage of the breakdown.

The grafting method of seeding has also been found applicable for testing the mold resistance of canvas, awnings, etc., and for seeding with molds other than the one recommended for paint testing.

Conclusions

A rapid, dependable, and convenient laboratory method for testing mold-resistant properties of oil paints which gives consistent, reproducible results has been developed.

By the use of "half and half" panels, the treated and the original paints receive an identical treatment in all respects

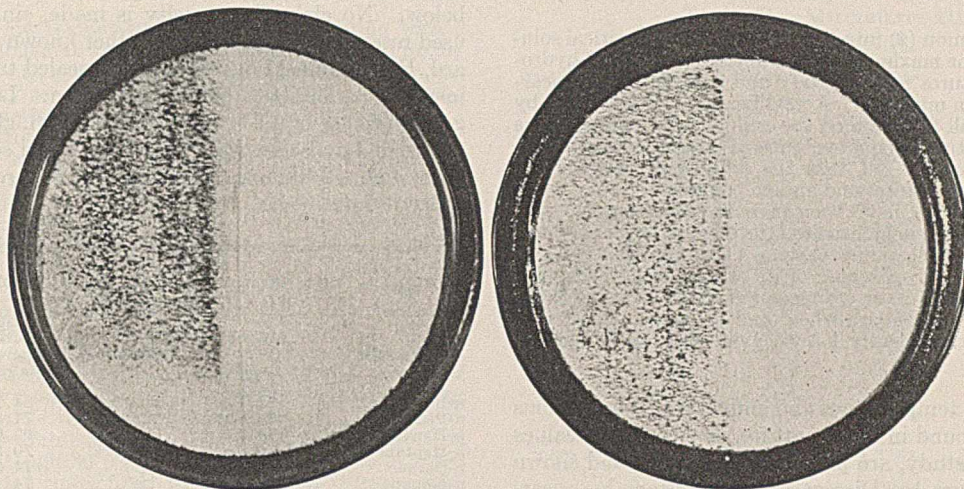


FIGURE 4. TEST PANELS SEEDED WITH MOLD 29 BY GRAFTING METHOD

Note reeding of mold growth due to diffusion of preservative from treated paint on right into control paint on left side of panel at left.

READING AND RECORDING RESULTS. By this procedure it usually takes not more than 3 weeks to obtain the maximum growth, although with exceptionally hard paints a longer time may be required. However, it was found convenient, for the sake of comparison, and since both the rate and the maximum extent of growth are important, always to make readings 7 and 21 days after seeding.

For recording mold growth a binomial system with ten as the maximum value for each reading is used. In this system the first number of the pair indicates the "extent of growth" and the second the "intensity of growth". By the extent is meant the fraction of the surface that is covered with mold. To illustrate the interpretation of these readings: "4-10" means "an abundant growth over about 40 per cent of the surface", while "10-1" means "a scanty growth over the entire surface".

Discussion

The method described above has been used with excellent results in the authors' laboratory for over 18 months. As a general rule a very good agreement is obtained between the duplicate plates. Any discrepancies in the results are usually due to the fact that the preservative is present in the so-called borderline concentration, at which minor differences in conditions determine whether or not the growth takes place.

Another very important feature of this laboratory method is that it allows separation of the two factors involved in the molding of the paint panels during field testing—(1) the original effectiveness of the preservative treatment and (2) the effect of weathering and breakdown of the paint film (including the loss of the toxicant). In other words, by this method the mold-resistant properties of the original paint as well as of the paint films subjected to weathering

throughout the entire procedure, thus permitting a direct comparison between them.

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CORRECTION. In the article entitled "Analysis of Cationic Surface-Active Agents of Trivalent Nitrogen Type" [*IND. ENG. CHEM., Anal. Ed.*, **12**, 402 (1940)] there are two minor errors. In the paragraph beginning "Hopper, MacGregor, and Wilson," the fifth sentence should read "Sulfuric acid because of its low volatility" In Table III the average of sample A should be given as 79.9 per cent.

RALPH HART

Critical Solution Temperatures and Aniline Points of Some Butane Hydrocarbons

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A NUMBER of correlations of physical properties of hydrocarbons or hydrocarbon mixtures are based upon aniline points. In order to extend the usefulness of these correlations, aniline point data for various butane hydrocarbons are needed. Since necessary data were lacking in the literature, the current study was undertaken to determine the aniline points of some of the butane hydrocarbons.

Chavanne and Simon (2) introduced the use of the critical solution temperature, the maximum miscibility temperature of hydrocarbon-aniline mixtures for the study and analysis of hydrocarbons or hydrocarbon mixtures. A modification was advanced by Tizard and Marshall (13) termed the aniline point, which is the miscibility temperature of equal volumes of hydrocarbon and aniline. Evans (5) pointed out that the differences between the critical solution temperatures and aniline points are usually small and that the two terms have been used indiscriminately. Ormandy and Craven (10) demonstrated the adverse effect of water, 1 per cent of water in the aniline causing a 5.9° C. rise in the aniline point of *n*-heptane. Because of its ease of purification and wide use, Brame and Hunter (1) recommended *n*-heptane (from *Pinus sabiniana*) as a standard when used with an aniline whose water content was sufficiently low to yield an aniline point of 70.0° C.

Critical solution temperatures and aniline points for various hydrocarbons as found in the literature, as well as the values derived from this study, are presented in Table I and shown graphically in Figure 1. Disregarding the butane hydrocarbon values shown, the data indicate minimum values in the several series which require experimental values for lower hydrocarbons for an accurate extension of the various curves. The values derived in this study clearly demonstrate these minima.

Because of the low boiling points of the butanes, none of the existent methods as described was applicable for this work. An apparatus adaptable to work with butanes has several im-

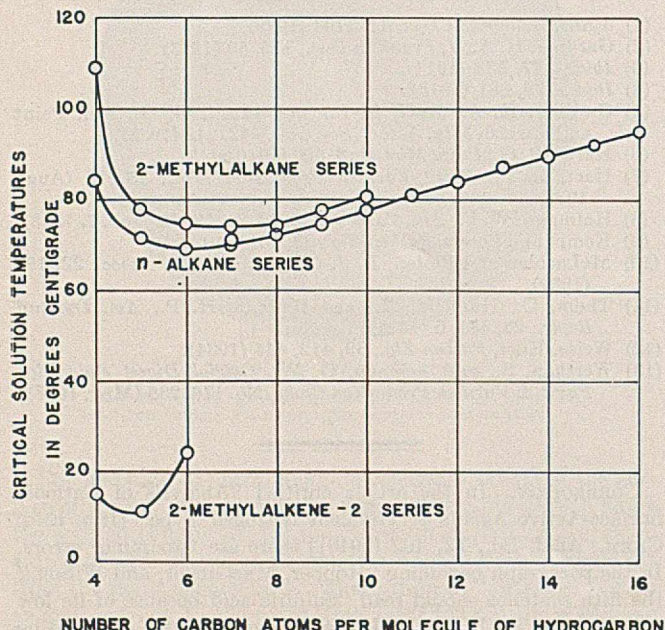


FIGURE 1. CRITICAL SOLUTION TEMPERATURES vs. MOLECULAR SIZE OF HYDROCARBONS

portant limitations—it must withstand high pressures, since, for example, isobutane has a vapor pressure on the order of 250,000 kg. per sq. meter (350 pounds per square inch) at 110° C., it must be light enough to permit weighing on an analytical balance, and, finally, it must be of a form permitting manipulation in a bath of liquid nitrogen used in the filling of the apparatus. The apparatus developed is described below. No claim for novelty is made, since the procedure used resembles in some details other known methods. Shepard, Henne, and Midgley (11) used sealed tubes but reported insufficient details to allow duplication. Levin (7) has suggested the use of a 10-cm. length of 7-mm. glass tubing sealed at one end and closed by a small cork and sealing wax at the other end. Wilkinson (14) used a semimicroapparatus which was not described.

TABLE I. ANILINE POINTS AND CRITICAL SOLUTION TEMPERATURES

Hydrocarbon	Aniline Point °C.	Reference	Critical Solution Temperature °C.	Reference
<i>n</i> -Butane	83.1	This work	84.1	This work
<i>n</i> -Pentane	70.7	(6)	71.4	(11)
<i>n</i> -Hexane	68.6	(6)	69.0	(11)
<i>n</i> -Heptane	70.6	This work	70.8	This work
<i>n</i> -Octane	71.7	(6)	71.8	(11)
<i>n</i> -Nonane	74.5	(6)	74.4	(11)
<i>n</i> -Decane	77.5	(6)	77.5	(11)
<i>n</i> -Undecane	80.6	(6)	80.6	(11)
<i>n</i> -Dodecane	83.7	(6)	83.7	(11)
<i>n</i> -Tridecane	87.0	(12)
<i>n</i> -Tetradecane	89.5	(12)
<i>n</i> -Pentadecane	92.0	(12)
<i>n</i> -Hexadecane	88.0	(6)	95.0	(12)
Isobutane	107.6	This work	109.0	This work
Isopentane	77.8	(3)
2-Methylpentane	74.7	(3)
2-Methylhexane	72.8	(6)	74.1	(4)
2-Methylheptane	74.0	(3)
2-Methyloctane	77.5	(3)
2-Methylnonane	80.3	(3)
Isobutene	14.9	This work	15.8	This work
2-Methylbutene-2	11.0	(1)
2-Methylpentene-2	24.0 ^a	(6)

^a Isohexene mixture.

Apparatus

The containers used for the determinations of the miscibility temperatures are best described by reference to Figure 2. The tubes were blown from Pyrex tubing 3 mm. in inside diameter and 5 mm. in outside diameter, and had a chamber 4 cm. in length with a capillary at one end and a handle at the opposite end attached to the sealed-off portion. The end with the capillary ended in a length of tubing sufficient to permit handling during the sealing-off operation and to permit temporary closure with a small cork. A slip of paper in the closed handle contained an identification number.

Materials

ANILINE. Five hundred cubic centimeters of aniline (J. T. Baker's c. p. analyzed grade) were slowly distilled in a dry apparatus and the central 100-cc. portion boiling at 184.4° C. (corrected) was collected. This fraction was immediately sealed in ampoules in 10-cc. portions and stored until used.

***n*-HEPTANE.** One liter of *n*-heptane (California Chemical Company's c. p. grade) was slowly distilled with the use of a high-temperature fractionation column of the Podbielniak type and the middle 100-cc. portion boiling at 98.4° C. (corrected) was collected.

***n*-BUTANE.** The c. p. grade of *n*-butane as supplied by the Phillips Petroleum Corporation was found to be above 99.9 per

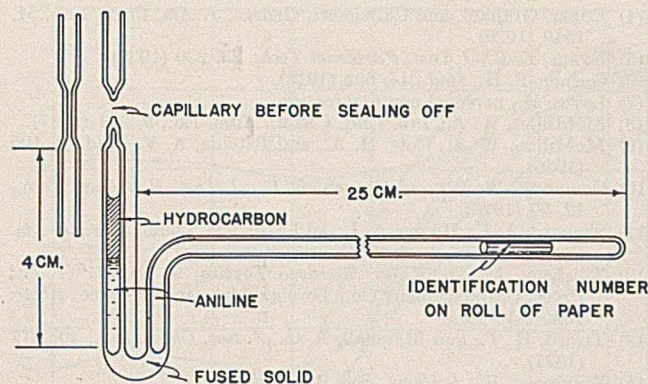


FIGURE 2. DIAGRAM OF APPARATUS

cent purity by a low-temperature fractional distillation with a column of the Podbielniak type. The material contained no unsaturated components, as shown by zero absorption in 87 per cent sulfuric acid and by zero contraction on catalytic hydrogenation according to the method of McMillan, Cole, and Ritchie (9).

ISOBUTANE. Isobutane (Matheson's "pure commercial" grade) was passed through four wash bottles filled with 95 per cent sulfuric acid, through an Ascarite-filled tower, through 40 per cent potassium hydroxide, and finally through a tower filled with anhydrous calcium chloride, after which it was condensed in a steel bomb cooled with a dry-ice and kerosene bath. Analysis of the product by low-temperature fractional distillation showed over 99.9 per cent purity, with zero absorption in 87 per cent sulfuric acid and zero contraction on hydrogenation demonstrating the absence of unsaturated components.

ISOBUTENE. *tert*-Butyl alcohol (Eastman Kodak Company's purest grade) was dehydrated with oxalic acid to yield isobutene which was dried by passage through a tower filled with anhydrous calcium chloride, after which it was condensed in a steel bomb cooled by a dry-ice-kerosene bath. The isobutene was redistilled from the bomb through 30 per cent potassium hydroxide, dried by passage through a tower filled with anhydrous calcium chloride, and recondensed in a steel bomb cooled in a dry-ice-kerosene bath. The yield of purified product was 88 per cent of the theoretical based on the *tert*-butyl alcohol. The isobutene was over 99.9 per cent pure by a low-temperature fractional distillation, 100.0 per cent unsaturated according to hydrogenation, and 100.0 per cent isobutene by reaction with anhydrous hydrogen chloride according to the method of McMillan (8).

Procedure

Precautions were taken to have and to maintain dry materials, equipment, and conditions at all times. The miscibility tubes were always tightly stoppered except while pipetting or weighing and until sealed off. All weighings were made to 0.1 mg. on an analytical balance equipped with a special stirrup of chromel wire used to hold the tubes. All pipetting was performed as rapidly as possible.

By means of a capillary-tipped pipet, aniline was introduced into a weighed miscibility tube, then the capillary and upper part of the tube were heated in a narrow flame to volatilize adhering droplets of aniline, the resultant vapor was sucked out quickly by vacuum, and the tube was cooled and reweighed. The miscibility tube containing the weighed aniline was immersed in liquid nitrogen to the bottom of the capillary constriction. The liquefied hydrocarbon was then cooled to partial crystallization (except *n*-heptane) to ensure freedom from dissolved water, and the hydrocarbon was introduced into the miscibility tube on top of the aniline by means of a capillary-tipped pipet. The capillary of the miscibility tube was sealed off by means of a hand gas-oxygen blast torch, care being taken to obtain smooth seals and to avoid the loss of glass. The sealed tube was removed from the liquid nitrogen bath, warmed to room temperature, and again reweighed together with the glass tip which had been removed during the sealing operation. The volume ratio of hydrocarbon to aniline was determined by the following equation:

$$\text{Ratio} = \frac{\text{weight of hydrocarbon} \times 1.0252}{\text{weight of aniline} \times \text{density of hydrocarbon at } 60^\circ \text{ F.}}$$

where 1.0252 is the density of aniline at 60° F. based on water at 4° C., this Fahrenheit temperature being used since it is the general standard in the petroleum industry.

The prepared miscibility tube was introduced and shaken in a bath consisting of a 2-liter jar filled with water or glycerol, heated

on a small adjustable electric hot plate and equipped with an efficient stirrer and a totally immersed thermometer. The thermometers used were of the Anschutz type graduated to 0.2° C. but could be read to 0.1° and had been tested by the National Bureau of Standards. Heating and cooling (by means of chipped ice with isobutene whose miscibility temperature was below that of the room) were effected at about 0.2° C. per minute within the range of 1° of the value as ascertained by an initial trial. Readings were taken with both ascending and descending temperatures which agree within 0.1° C. Only values obtained with descending temperatures were recorded, check values being obtained. The sudden appearance of a milky cloud in the clear mixture was taken as the criterion for reading the miscibility temperature with descending bath temperatures. The temperatures observed are thought to be accurate, owing to efficient stirring, slow rates of temperature change, and approximately similar rates of lag of the thermometer and of the miscibility tube, since both were of the same order of size.

TABLE II. MISCIBILITY DATA

Hydrocarbon	Sample Number	Weight of Hydrocarbon Gram	Weight of Aniline ^a Gram	Volume Ratio	Miscibility Temperature ° C.
<i>n</i> -Heptane d 60° F./4° C. 0.6878	1	0.0415	0.1121	0.552	67.5
	2	0.0495	0.1238	0.597	67.8
	3	0.0542	0.0915	0.883	70.0
	4	0.0615	0.0917	1.00	70.7
	5	0.0652	0.0891	1.09	70.7
	6	0.0780	0.0930	1.22	70.7
	7	0.0769	0.0888	1.29	70.3
	8	0.0796	0.0772	1.54	69.7
<i>n</i> -Butane d 60° F./4° C. 0.5843	9	0.0499	0.1492	0.587	75.5
	10	0.0473	0.1277	0.650	77.7
	11	0.0485	0.1076	0.791	80.4
	12	0.0593	0.1128	0.923	82.4
	13	0.0538	0.1008	0.937	82.8
	14	0.0674	0.1059	1.12	83.8
	15	0.0923	0.1437	1.13	83.8
	16	0.0917	0.1345	1.20	83.8
Isobutane d 60° F./4° C. 0.5646	17	0.0729	0.0976	1.31	84.1
	18	0.0954	0.0933	1.79	83.6
	19	0.0398	0.1157	0.624	92.7
	20	0.0452	0.1162	0.707	98.3
	21	0.0528	0.1137	0.843	103.6
	22	0.0554	0.0999	1.01	107.8
	23	0.0563	0.0946	1.08	108.6
	24	0.0644	0.1061	1.10	108.8
	25	0.0795	0.1225	1.18	109.0
	26	0.0740	0.1034	1.30	108.8
	27	0.0669	0.0925	1.31	108.9
	28	0.1147	0.1017	2.04	102.9
Isobutene d 60° F./4° C. 0.6030	29	0.0529	0.1203	0.748	11.8
	30	0.0489	0.1011	0.822	13.2
	31	0.0531	0.0986	0.915	14.2
	32	0.0725	0.1171	1.05	14.9
	33	0.0728	0.1109	1.12	15.7
	34	0.0740	0.1071	1.17	15.5
	35	0.0692	0.0978	1.20	15.4
	36	0.0693	0.0933	1.26	15.6
	37	0.0836	0.0968	1.47	15.8
	38	0.1009	0.0892	1.92	15.5

^a Aniline, d 60° F./4° C., 1.0252.

Discussion

The miscibility data developed are tabulated in Table II. The derived critical solution temperatures and aniline points recorded in Table I were obtained by graphing miscibility temperatures vs. the volume ratios of hydrocarbon to aniline. *n*-Heptane was used with this procedure for comparison with other results, an aniline point of 70.6° C. and a critical solution temperature of 70.8° C. being obtained. The literature records values for the aniline point and critical solution temperatures of *n*-heptane varying from 68° C. (10) to 71° C. (6). The effect of water in raising the miscibility temperature has already been mentioned, but it is not believed that this explanation is applicable to these results in view of the precautions taken in this study. The values for the three butane hydrocarbons appear to be generally consistent with the other data as shown by Figure 1.

Summary

A method for the determination of the miscibility temperatures for mixtures of volatile hydrocarbons and aniline is presented. The aniline points of *n*-butane, isobutane, and iso-

butene were found to be 83.1°, 107.6°, and 14.9° C., respectively, and the critical solution temperatures for the same hydrocarbons were found to be 84.1°, 109.0°, and 15.8° C., respectively. The derived values confirm the indicated minima for the various hydrocarbon series.

Acknowledgment

The author wishes to express his appreciation to L. L. Claxton who assisted in the determination of the miscibility temperatures and to A. A. Moreau, Jr., who assisted in the preparation of the miscibility tubes.

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Colorimetric Determination of Iron with Salicylaldoxime

A Spectrophotometric Study

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SALICYLALDOXIME has been used for determining copper (3), nickel (1), lead (6), and palladium (5) by gravimetric precipitation methods, since it forms with these metals chelate rings of the "inner complex" type. By careful regulation of the hydrogen-ion concentration of the solutions, separations of certain of these metals may be made. Ferric iron forms a soluble complex and interferes with the determination of the other four metals, since this complex is entrained by the insoluble complexes and cannot be washed out. The entrainment is a function of the pH of the solution (2).

Ephraim observed the reaction of ferric ion with salicylaldoxime, and called the color formed brown-violet (4). By means of this color reaction, he determined when washing was complete in the gravimetric precipitation method for copper and nickel. Ferric chloride was added to successive portions of the washings from the precipitate until no color, and consequently no salicylaldoxime, was present. Here, then, ferric ion was used as a qualitative test for salicylaldoxime.

It seemed likely that a reversal of Ephraim's process, using salicylaldoxime as a color-forming reagent for ferric iron, would be practicable. For this reason a critical study of the complex was made, the basic purposes being to discover the optimum conditions under which it could be used for colorimetric determinations, and to define precisely the limits of usefulness of the method.

Apparatus and Solutions

Since this investigation was to be quantitative, ordinary visual methods of colorimetric comparison were not suitable. Neither could filter photometers be used, since they give only reproducible approximations of the color situation under given

conditions. A spectrophotometer was the logical choice; it enables transmittancy values to be obtained over the entire visible spectrum. A recording General Electric instrument was used for the work at hand.

Transmittance cells 1.961 cm. in thickness and a spectral band 10 m μ in width were used. In every case, the cell placed in the "blank" beam contained the same amount of pH buffer and reagent as the corresponding volume of the unknown solution.

The salicylaldoxime (Eastman No. 2956) consisted of white crystals and melted at 57.5° C. A 0.1 per cent solution of the reagent was made by dissolving the weighed solid in 5 ml. of ethanol and diluting to the proper volume with redistilled water. Only enough reagent for one day's work was prepared at one time, since, upon standing for more than one week, the solution decomposes somewhat and turns slightly brown.

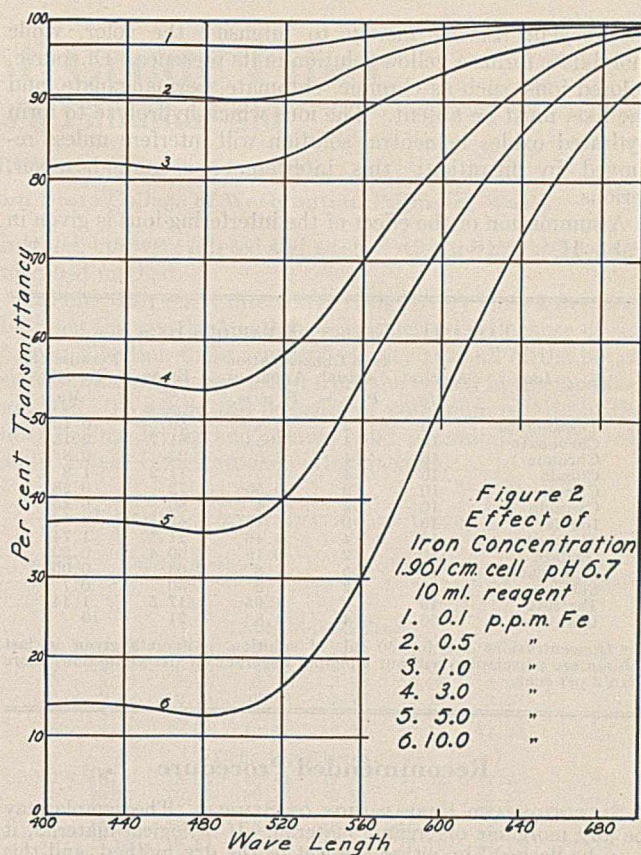
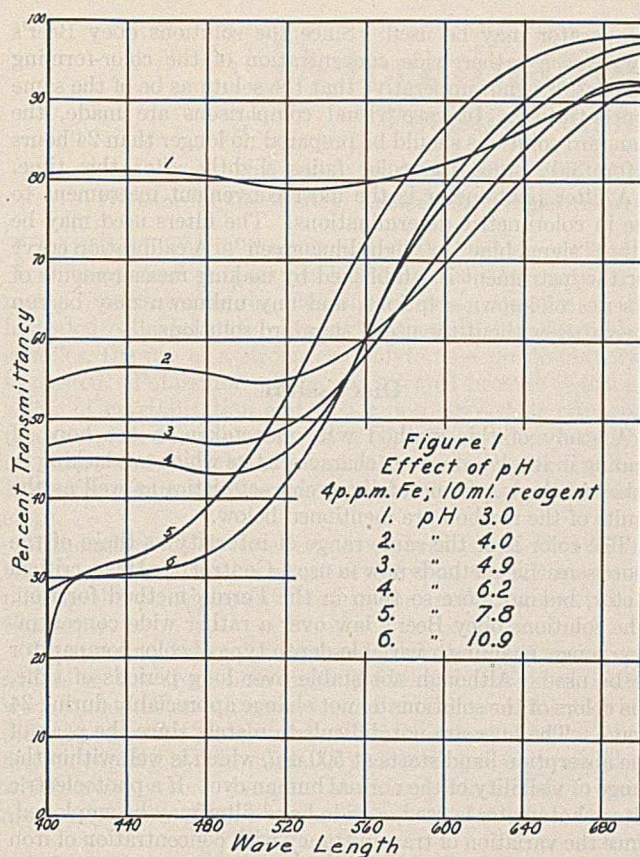
Standard iron solutions were made by dissolving weighed amounts of iron wire of known purity in redistilled nitric or hydrochloric acid. Hydrogen peroxide was added to oxidize all the iron, and the excess peroxide was destroyed by boiling. These solutions were diluted with redistilled water to a concentration of 0.05 mg. of iron per ml. This solution is such that 1 ml. when diluted to 50 ml. is equivalent to one part per million of iron.

A solution of ammonium acetate, approximately 1 molar, was used for a pH buffer. This was made from the purest solid obtainable dissolved in iron-free water. When pH values other than that obtained from the use of the buffer solution were desired, hydrochloric acid and ammonium or sodium hydroxide were used. The alkaline solutions were filtered before use to remove silica. Measurements of pH were made with a universal glass electrode potentiometer outfit (7), which was calibrated with Clark and Lubs buffer solutions.

The solutions used for the tests for interference were, for the cations, the nitrates, chlorides, or sulfates, and for the anions, the sodium, potassium, or ammonium salts.

In the preparation of the colored solutions, the following order was used: Into a 50-ml. volumetric flask was introduced from a 5-ml. buret the desired amount of iron. Any diverse ions were then added to this solution, followed by an excess of reagent. The pH was adjusted with the ammonium acetate solution, or with acid or alkali, and the solution was diluted to the proper volume. Transmittancy curves were obtained within 5 minutes after the solution was prepared, part of the material being reserved for pH determinations.

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TABLE I. TRANSMITTANCY VALUES AT 480 μ

Concentration of Iron P. p. m.	Transmittancy	
	Observed %	Calculated %
1.0 ^a	81.0	81.0
0.5	90.0	90.0
0.1	97.0	97.9
3.0	53.5	53.2
5.0	35.2	35.0
10.0	12.5	12.2

^a Basis for calculations.

Color Reaction

The color developed by salicyldoxime in the presence of ferric iron is purple at a pH of 3 and yellow at 10. Between these two values the solutions appear as various combinations of these hues, that in neutral solution being red-orange. The variation of the transmittancy with pH is shown in Figure 1. It is evident that a careful control of pH is necessary in order to obtain reproducible hue and intensity of color. For this study, a solution with a pH of approximately 7 was used because of the ease with which this value may be maintained and the lack of variation of transmittancy in the immediate vicinity of neutrality. Ammonium acetate solution, having a pH of almost 7, was used as a buffering agent.

Figure 2 shows the transmittancy at pH 6.7 for different iron concentrations. In Table I are given the calculated and observed values for the transmittancy at 480 μ . Since the variation is slight, there is no great deviation from Beer's law, and a variable-depth type color comparator may be used for determinations.

At the pH chosen for the work the colored solutions are stable for more than 24 hours. Reagent concentration has no effect on the color so long as an excess is present. The maximum color is developed within 30 seconds of the time of preparation of the solutions. In an acidic medium, the color is

developed immediately, but fades rapidly. In basic solution, the maximum color is developed only after 15 minutes.

The smallest amount of iron detectable with the reagent in a 30-cm. Nessler tube is 1 part in 20,000,000 parts of solution. The upper limit for Nessler tube work is 4 p. p. m. This may, however, be extended considerably by dilution.

The colored complex is not extracted from the aqueous solution by ethyl alcohol, carbon disulfide, benzene, or ethyl acetate, and only slightly by chloroform.

Influence of Ions

Of the anions studied, chloride, bromide, thiocyanate, chlorate, perchlorate, sulfate, and acetate did not interfere with either the intensity or the hue, even when present in concentrations exceeding that of the iron by 500 times. Fluoride ion may be present in quantities up to 10 mg., with 0.2 mg. of iron, without causing serious interference. More than this quantity must be avoided.

Tartrate, citrate, oxalate, cyanide, carbonate, borate, and phosphate interfere seriously, probably because of forming complexes with ferric iron. For reproducible results, these must be entirely absent. Iodide and sulfite interfere, because of their reducing action; sulfite may be removed by preliminary oxidation.

Few of the colorless cations have any effect on the color. Sodium, lithium, potassium, ammonium, calcium, barium, strontium, magnesium, manganese (ous), and cadmium have no effect, even when present in concentrations 250 times that of the iron. Lead, zinc, mercury, beryllium, and aluminum do not interfere if sufficient reagent for them also is present. Presumably they form colorless complexes with salicyldoxime.

The only ions tested which form colored soluble complexes with salicyldoxime are ferric iron, molybdate, cobalt, and uranyl. Cobalt and the uranyl ion have colors of their own,

the reagent serving merely to intensify the color, while molybdate forms a yellow solution in its presence. Of course, colored ions, such as chromic, chromate, permanganate, and the like, must be absent. The ions which hydrolyze to form hydrated oxides in neutral solution will interfere unless removed by filtration; this interference is not, however, serious.

A summation of the effect of the interfering ions is given in Table II.

TABLE II. EFFECT OF VARIOUS IONS

Ion	Amount Mg.	Iron Concentration ^a		Error %	Permissible Quantity Mg.
		Actual P. p. m.	Apparent P. p. m.		
Tetraborate	5	2	0.4	80	0.12
Carbonate	10	4	1.53	61.7	0.13
Chromic	10	4	3.0	25	0.8
Cobalt	10	4	4.5	11.2	1.8
Citrate	10	2	0.56	72	0.28
Cyanide	10	2	0.4	80	0.25
Iodide	10	2	1.13	43.5	0.46
Molybdate	10	4	4.46	11.5	1.74
Oxalate	10	2	0.19	90.4	0.22
Phosphate	10	5	1.8	63	0.05
Sulfite	10	2	1.3	30	0.7
Tartrate	10	2	1.65	17.5	1.14
Uranyl	50	4	4.8	21	10

^a Concentrations are for 50 ml. of solution. Amounts given in last column are permissible without affecting accuracy of determinations more than 2 per cent.

Recommended Procedure

SELECTION AND PREPARATION OF SAMPLE. The sample may be any inorganic or organic material. If biological material, it may be "ashed" by either the wet or the dry method, and this ashed material treated as the original sample in the remainder of the procedure.

MEASUREMENT OF SAMPLE. Take enough of the sample to contain 0.01 to 1 mg. of iron, and transfer to a 250-ml. conical flask.

TREATMENT OF SAMPLE. Dissolve the sample, if a solid, by digesting with 10 ml. of nitric acid (1 to 3) and boil to remove oxides of nitrogen. Remove from the flame, cool, and add 10 ml. of 3 per cent hydrogen peroxide to oxidize all the iron. No adverse effect was caused by excess hydrogen peroxide. Copper and nickel may be prevented from interfering by precipitating them as the insoluble salicylaldoxime complexes from a basic solution. Sodium carbonate is added to the acidic solution until a dark red colloid of iron forms. Salicylaldoxime is added in excess, and the precipitate filtered from the solution. The carbonate complex may be destroyed by acid, and the determination carried on in the routine manner. Cobalt, molybdenum, uranium, and chromium should be absent or removed from the solution at this point. Phosphate may be precipitated by the zirconyl ion, and the excess zirconium eliminated by a subsequent procedure. Fluoride and borate may be destroyed by boiling with perchloric acid, which volatilizes them as hydrofluoric acid and boron hydride, respectively.

Add ammonia until the solution is just basic to litmus, then hydrochloric acid until it is just acidic to the same indicator. Filter any insoluble material from the solution, wash the precipitate well, and unite the washings with the original solution. This procedure tends to eliminate the interference caused by the ions which would precipitate when the pH is adjusted to its final value. However, the precipitate should be well washed, as most of the hydrated oxides are voluminous and tend to entrain other ions.

Add 10 ml. of a 0.1 per cent solution of salicylaldoxime, and, after stirring well, dissolve in the solution about 1 gram of ammonium acetate. For the first unknown sample, an excess of salicylaldoxime should be added, in order to prevent interference from those elements which form colorless complexes. If these are not present, as may be determined by a simple test, the amount of material originally recommended is sufficient.

Dilute the solution to 100 ml. in a volumetric flask and mix well. If the colors of the solutions are too intense for visual comparison, these solutions may be diluted to greater volume.

MEASUREMENT OF DESIRED CONSTITUENT. The unknown may be compared in Nessler tubes with a series of standards made in the same manner. If desired, a Duboscq type color

comparator may be used. Since the solutions obey Beer's law over a rather wide concentration of the color-forming element, it is not imperative that the solutions be of the same concentration. In case visual comparisons are made, the standard solutions should be prepared no longer than 24 hours before use, since the color fades slightly after this time.

A filter photometer is the most convenient instrument to use in colorimetric determinations. The filters used may be either "signal blue" or "light blue-green". A calibration curve for the instrument is established by making measurements of a series of known solutions, and any unknown may be run thereafter without the use of standard solutions.

Discussion

A study of this method was undertaken in the hope of finding in it advantageous characteristics which are lacking in other methods. Some of these characteristics as well as the faults of the method are mentioned below.

The color is of the same range of intensity as those of the more sensitive methods now in use. Control of pH is a critical factor, but no more so than in the Ferron method for iron. The solutions obey Beer's law over a rather wide concentration range, enabling a variable-depth type of color comparator to be used. Although not stable over long periods of time, the colors of the solutions do not change appreciably during 24 hours. The hues are not difficult to match, since the peak of the absorption band starts at 500 μ , which is well within the range of visibility of the normal human eye. If a photoelectric filter photometer is used, a wide-band filter may be employed, since the variation of transmittancy with concentration of iron complex is the same from 400 to 500 μ , one third of the visible spectrum. This increases the amount of light falling on the photoelectric cells of the instrument, and increases its sensitivity. Corning glass filters, No. 556, "signal blue", or No. 428, "light blue-green", are satisfactory.

The reagent is inexpensive, and very little of it is required. Since it may also be used for the routine determinations of copper and nickel, it is unnecessary to obtain a special reagent for the colorimetric determination of any iron which might be present in alloys containing these metals.

No special techniques are necessary in carrying out a determination of iron by the proposed method; hence routine analyses may be made by "determinators".

Summary

A spectrophotometric study of the complex formed by the action of ferric iron on salicylaldoxime has indicated that this complex might be used for the colorimetric determination of ferric iron. The complex is most suitably used for this purpose in a neutral solution, pH being a critical factor in the determination. The range of concentrations is from 0.05 to 10 parts per million of iron, with the limits being extended each way by proper dilution or concentration. Interfering substances are easily removed, the reagent is highly specific, and no special techniques are necessary.

Salicylaldoxime is recommended as a reagent for the colorimetric identification and determination of small amounts of ferric iron.

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Determination of Crude Fiber

Potassium Sulfate as a Filtration Aid

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DIFFICULTY in filtering the crude fiber of occasional mixed-feed samples has led the authors to search for a method for hastening the filtration process. Because of the hydrated colloidal state of many of these hard-to-filter fiber samples, the use of a strong electrolyte as a precipitant was suggested. Potassium sulfate was selected because it has no water of crystallization and is not decomposed at temperatures employed in ashing the fiber (2). Thus, there would be no difference in weight of samples because of water loss due to the temperature differential between the drying and ashing steps.

Although many devices have been used to aid fiber filtration, a search of the literature revealed no modification employing the principles involved in the method presented in this paper.

Experiments designed to show whether the use of potassium sulfate in the crude-fiber method alters the value obtained were conducted on mixed-feed samples that were filtered with difficulty by the usual method. Mixed-feed samples that filtered rapidly by the official (1) method and feces samples, which often present the greatest difficulty in filtration, were also analyzed by the two methods.

Methods Employed

The official method of the Association of Official Agricultural Chemists (1) for crude fiber in feeds was employed, with the exception that powdered potassium sulfate was added to the fiber sample, suspended in hot water, before filtering through a Gooch crucible.

The sample was transferred from the digestion flask to the filtering cloth after the sodium hydroxide digestion, the alkali was permitted to drain off, and the fiber was washed with hot water. If difficulty was encountered at this point in the filtration, powdered potassium sulfate was sprinkled on the sample. The sample was then washed with about 100 cc. of hot water into a 250-cc. beaker and powdered potassium sulfate (10 to 20 grams) was added with stirring to the hot suspension. The presence of undissolved potassium sulfate at this point does not interfere. When the sample was permitted to stand for a few seconds, the suspended hydrated fiber precipitated. The supernatant liquid could be readily decanted from the fiber and the fiber washed into the Gooch crucible with hot 5 per cent potassium sulfate solution. Filtration was very rapid in all samples, and it was not necessary to decant the sample to attain rapid filtration. The difficultly filtered colloidal state of the fiber had been transformed into an easily filtered condition. To wash the sample in the Gooch with hot water successfully, only small amounts of water could be used. When the potassium sulfate in the fiber had been reduced below a certain concentration by washing, the fiber resumed its hydrated form and stopped the filtration process. Permitting the suspended fiber to cool before treatment with potassium sulfate decreased the efficiency of the method.

The fiber was washed with 10 to 25 cc. of hot 5 per cent potassium sulfate solution and then with 10 cc. of 95 per cent ethyl alcohol. The crucible was rinsed on the outside with water and wiped dry to remove any potassium sulfate adhering to the outer and bottom surfaces of the Gooch crucible before drying to constant weight at 110° C. After weighing, the sample was ashed at from 600° to 800° C., cooled, and reweighed.

Discussion of Results

Results are presented in Table I. Samples 1 to 6 represent six mixed-feed samples which could be filtered and washed within 5 minutes by either the official or the modified method. Samples 7 to 12 represent six feed samples which required from 20 minutes to 24 hours to filter by the official method, but were filtered and washed within 5 minutes by the modified method. The six sheep feces samples required from 1 to 24 hours to filter through the Gooch crucible by the official

method, but were filtered and washed within 5 minutes by the modified method.

Results with easily filtered feeds show very close agreement between the standard and modified method. Because of the ease of filtration there was a possibility that all of the potassium sulfate might be washed from the Gooch in the modified method. To assure the presence of potassium sulfate in the fiber during drying and ashing, solid potassium sulfate was added to the Gooch crucible after washing.

TABLE I. DETERMINATION OF CRUDE FIBER

Sample No.	Official Method			Modified Method			Comparison of Methods %
	1 %	2 %	Av. %	1 %	2 %	Av. %	
Easily Filtered Feeds							
1	7.35	7.53	7.44	7.38	7.37	7.38	-0.06
2	5.54	5.55	5.55	5.58	5.56	5.57	+0.02
3	3.99	3.95	3.97	3.98	3.93	3.96	-0.01
4	2.12	2.23	2.18	2.18	2.19	2.19	+0.01
5	5.61	5.47	5.54	5.81	5.68	5.75	+0.21
6	12.16	12.06	12.11	12.27	12.18	12.23	+0.12
Difficultly Filtered Feeds							
7	18.19	18.09	18.14	17.56	17.83	17.70	-0.40
8	20.87	20.59	20.73	20.81	20.93	20.87	+0.14
9	17.49	17.63	17.56	17.90	17.81	17.86	+0.30
10	16.56	16.78	16.67	16.66	16.68	16.67	0.00
11	17.07	16.82	16.95	17.10	17.16	17.13	+0.18
12	15.08	15.26	15.17	15.35	15.28	15.32	+0.15
Difficultly Filtered Feces							
13	23.64	23.61	23.63	23.05	22.79	22.92	-0.71
14	21.00	21.58	21.29	19.86	20.00	19.93	-1.36
15	43.45	44.29	43.87	43.51	43.74	43.63	-0.24
16	44.42	42.91	43.67	42.64	42.84	42.74	-0.93
17	44.18	43.80	43.99	42.70	42.92	42.81	-1.18
18	34.73	34.34	34.54	33.70	33.95	33.83	-0.71

There was close agreement between the two methods for feeds which were difficult to filter, except for sample 7. This sample contained considerable quantities of hempseed meal and was very difficult to filter by the official method, requiring filtration by suction overnight. It was readily filtered by the modified method, but gave results somewhat lower than by the official method.

Table I shows consistently lower values but much closer agreement between duplicates for the modified method than the official method as applied to feces. The authors believe that the values obtained by the official method on samples which are difficult to filter are subject to question because of the long delay in the filtering process. It may, therefore, be assumed that the modified method is more nearly correct for these samples.

Conclusions

The use of potassium sulfate in the filtration of the crude fiber after alkali digestion reduced the filtration and washing time to the normal on all difficultly filtered samples studied.

The modified method gave the same per cent of fiber except in the case of feces and in the sample containing hempseed meal. Results by the modified method in these cases were lower but are believed to be more nearly correct.

Duplicates filtered rapidly by the modified method show closer agreement than those filtered slowly by the official method.

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Test for Residual Chlorine

Use of Adsorption Reaction between Iodine and Alpha-Naphthoflavone

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THE influence of pH and iodide-ion concentration on the accuracy of iodometric tests for residual chlorine in water has been noted by Gilreas and Hallinan, who devised a direct colorimetric technique in which α -naphthoflavone (7, 8-benzoflavone) is used as an indicator (3). This method is particularly valuable in routine control of the chlorination process, in that the essential reactions are practically unaffected by amounts of nitrites, ferric iron, and colloidal manganese dioxide likely to be encountered; but it is influenced by chlorine adsorption compounds and by colored or turbid matter somewhat as is the well-known *o*-tolidine test, although in each case a comparator system is used to compensate color and turbidity. Where either is excessive, however, as in sewage and trade wastes, and where attempts are to be made to differentiate the more active chlorine compounds from organic chloramines or adsorption compounds, a supplementary technique is needed. Such a technique should be applicable at least to a rough approximation at the low concentrations of hydrogen and iodide ions that may aid the differentiation. It is the purpose of this presentation to describe an iodometric test for chlorine that may be used under these circumstances.

Colored matter in water is usually in solution and thus is separable by filtration from the water-insoluble iodine-adsorption compound formed in the α -naphthoflavone test, while sources of turbidity are usually insoluble in alcohol, which may be used subsequently to dissolve the adsorption compound. The iodine would appear separable also from interfering oxidizing agents, which are unlikely to be both insoluble in water and soluble in alcohol. The influence of α -naphthoflavone upon the color of the alcoholic solution is negligible unless the reagent has deteriorated, as when left in sunlight for a considerable time. Care should be taken to guard against photochemical decomposition of either the indicator or the potassium iodide. Furthermore, it would seem that conditional hydrogen and iodide-ion concentrations could be dropped close to the threshold for the α -naphthoflavone adsorption reaction:



and possibly provide a differentiation of chlorine from organic chloramines or chlorine adsorption compounds for some particular reaction time. A distinct advantage of the proposed system is freedom of the final iodine determination from the influence of such conditional hydrogen and iodide-ion concentrations used initially.

Standard Technique

Fifty milliliters of chlorine solutions of known concentrations were treated with a dry mixture of potassium iodide and buffer. [Unless otherwise noted, pH 6.7 and 20 grams of potassium iodide per liter of sample were used. Buffers were chosen to avoid calcium precipitation and unnecessary increase in chlorine demand. Per liter of sample the following amounts of buffers were used: pH 6.7, 20 grams of potassium sodium tartrate; pH 8.9, 16 grams of sodium diethyl barbiturate, 3 grams of potassium sodium tartrate, and 1 gram of potassium hydrogen tartrate; pH 10.0, 20 grams of sodium diethyl barbiturate (barbital-sodium). In a few instances ammonia-acetic acid buffer was used to give pH 8.9: 20 ml. of mixture of 5 molar ammonium hydroxide with 5 molar acetic acid.]

This was dissolved as rapidly as possible and, after 2 minutes, 0.5 ml. of a 0.2 per-cent solution of α -naphthoflavone in 95 per

cent ethyl alcohol was admixed. After 3 minutes' contact, the adsorption compound was coagulated by violent agitation for a few seconds and collected immediately on hard paper in a Gooch crucible with the aid of vacuum. The first available portion of clear filtrate was tested for unadsorbed iodine with a fresh portion of indicator. If any was found, the products were discarded and the procedure was repeated with an appropriate smaller portion of sample diluted to 50 ml. with chlorine-zero water so that the indicator would be in excess. The precipitate was washed with about 2 ml. of chlorine-zero water, the filtrate and washings were discarded, the residue was then dissolved, and the filter was washed with about 5 ml. of 0.1 per cent alcoholic solution of potassium iodide.

The yellow solution was compared with permanent color standards prepared from inorganic solutions as described in Table I, by viewing longitudinally in flat-bottomed shell vials, 13 mm. in outside diameter, using north light reflected from a

TABLE I. PREPARATION OF PERMANENT COLOR STANDARDS

Chlorine in 50-Ml. Sample P. p. m.	Color Solution ^a Ml.
0.00	0.08
0.05	0.38
0.10	0.70
0.20	1.30
0.30	1.91
0.40	2.52
0.50	3.15
0.60	3.78
0.80	5.00

^a Potassium chloroplatinate (K_2PtCl_6) 2.0 grams; copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 3.75 grams; concentrated sulfuric acid 2.5 ml.; concentrated hydrochloric acid 100 ml.; dissolved in distilled water and diluted to 1 liter.

Amounts of color solution given are diluted to 5.0 ml. with distilled water.

white matte surface. [The values given in Table I are approximate for conditions of maximal recovery (pH 6.7). They should be compared with chlorine standards and modified or simply recalibrated as necessary for the particular technique and reagents. Apparently, little error is introduced by substitution of different lots of the potassium sodium tartrate or of indicator or even indicator properly stored 3 years.] As little as 0.05 p. p. m. of chlorine in the sample yielded a perceptible yellow color in the final alcoholic filtrate; but greater coloration was obtained by adding *p*-aminodimethylaniline hydrochloride to the alcoholic iodine solutions, the resulting colors being similar to those obtained when the reagent is used with chlorine as described by Byers and Mellon (2). The interfering substances discussed in their report (3), ferric and nitrite ions, and also oxidized manganese are eliminated by this technique. In the author's experience the stability of the *p*-aminodimethylaniline hydrochloride reagent, either dry or in solution, did not compare favorably with that of either *o*-tolidine or α -naphthoflavone. Accordingly, as the resulting increased sensitivity seemed of little value, no attempt was made to develop a definite procedure for its use.

Since pH and iodide-ion concentration might influence either the rate of oxidation of iodide by chlorine or the subsequent adsorption of iodine by the indicator, these factors were varied in a few comparative chlorine tests by this technique using the standard *o*-tolidine test (1) to give a basic estimate of chlorine content. The results given in Table II may be taken as a rough indication of what may be expected. In any case, chlorine controls should be made with the actual

TABLE II. COMPARATIVE CHLORINE VALUES WITH α -NAPHTHOFLAVONE FILTRATION TECHNIQUE

pH	KI G./ liter	Actual ^a Chlorine Range		Apparent Chlorine		Chlorine \div Actual Chlorine Concentration, <i>R</i>		Mean <i>R</i>
		Min.	Max.					
6.7	20	0.24	0.32	0.96	0.85	1.08	0.96	1.19
	20	0.75	0.80	0.81	1.07	0.94
	1	0.22	0.24	0.93	1.00	0.92	..	0.95
	1	0.50	0.70	0.96	0.96	0.96
8.9	20	0.28	0.28	0.89	(0.67) ^b	0.89
	20	0.80	0.90	0.83	0.75	(0.70) ^b	..	0.79
	1	0.28	0.28	0.79	(0.72) ^b	(0.58) ^c	..	0.79
	1	0.70	0.70	0.81	0.81
10.0	20	0.26	0.26	0.85	..	(0.75) ^c	..	0.85
	20	0.80	0.90	0.63	0.73	0.68
	1	0.27	0.28	0.54	0.56	..	(0.17) ^c	(0.38) ^c
	1	0.72	0.80	0.69	0.78	..	(0.71) ^c	0.74

^a Actual chlorine value estimated by *o*-tolidine test under standard conditions.

^b Ammonia-acetic acid buffer used. None of parenthesis values enters mean.

^c With second lot of barbital. None of parenthesis values enters mean.

TABLE III. CHLORINE EQUIVALENT OF IODINE LIBERATED BY COLLOIDAL MANGANESE DIOXIDE

(With 20 grams of potassium iodide per liter of sample. Single observations)

pH	Manganese Dioxide as P. p. m. Manganese					
	0.0	0.625	1.25	2.5	5.0	10.0
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
6.7	0.02	0.02	0.03	0.07	0.15	0.50
8.9	0.00	0.00	0.00	0.00	0.00	0.00

reagents in use at the time and should include tests with known chlorine concentrations at pH and iodide-ion concentrations covering the ranges to be employed.

The method has been found useful in determining the chlorine demand of tannery wastes too highly colored for direct colorimetric or titrimetric tests. The oxidizing action of highly colored manganese dioxide sols (prepared in the manner previously used, 4) on potassium iodide was also studied, with results shown in Table III; pH 6.7 represents the threshold for interference in about 2 minutes' reaction time with

0.5 p. p. m. of manganese (4) at the iodide concentration found optimum for colorimetry (3) and employed here. There appears to be a concomitant variation in the concentration of manganese used and consequent liberated iodine. The observations at pH 8.9 agree with those made by the direct colorimetric test (3) in showing no interference.

Summary

When potassium iodide and α -naphthoflavone are added to chlorinated water, the iodine liberated is rapidly adsorbed from solution by the colloidal indicator and may be separated from water-soluble colored matter by filtration. The precipitate may be dissolved in a volume much smaller than that of the original sample by passing alcoholic potassium iodide solution through the filter, which retains any insoluble material. The yellow iodine solution may be compared with permanent color standards calibrated against known concentrations of chlorine. This procedure is useful in the examination of highly colored sewages and trade wastes, and in investigations of the effect of variations in pH and iodide concentration on the reactions of interfering substances. The addition of *p*-aminodimethylaniline hydrochloride for increased coloration is permissible, since interfering substances such as nitrite, oxidized iron, or manganese have been eliminated but this reagent is relatively unstable.

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Analysis of Black Enamels

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THE analysis of black enamels and paints containing small proportions of pigment which consists entirely of carbon presents considerable difficulty.

Enamels of this type are used for painting passenger cars of the Independent Subway System operated by the City of New York—for example, Underframe Black enamel is applied on equipment under the body of the car, and Hand Rail Black enamel is used for painting the grab handle and step at the end of the car and exposed galvanized iron parts. A Sign Box Black enamel is used inside the destination sign box, and a Striping Black enamel for painting a stripe between two different colors on a painted surface.

These enamels usually contain from 2 to 4 per cent of pigment and 96 to 98 per cent of vehicle. The pigment consists entirely of carbon, either carbon black or lampblack, and the vehicle is a varnish containing synthetic or fossil gums.

Considerable difficulty has been experienced in this laboratory in obtaining a clean-cut separation of the pigment from the vehicle and in determining the correct amount of pigment in the sample. Because of the small proportion of pigment present, a slight variation in the weight of the extracted pigment produces a considerable error in the final result.

Existing Methods

All attempts to separate the pigment from the vehicle by the method of the American Society for Testing Materials (1)—treating the sample with a standard mixture of solvents and centrifuging—proved unsuccessful, as the carbon remains in suspension and no amount of centrifuging will cause it to settle to the bottom. Attempts to filter off the carbon were also unsuccessful, as it is so finely divided that it goes through the filter paper. In addition it was found that the solvents employed in the above mixture precipitate the gums present in the vehicle. Subsequent treatments with additional solvents failed to redissolve the precipitated gums, as a result of which the pigment values obtained were as much as 100 per cent too high.

Similar results were obtained by using the extraction mixture consisting of benzene, methyl alcohol, and acetone, recommended by Gardner (2) for blue and green paints. Unsatisfactory results were also obtained by following the method recommended by Gardner (2, p. 951) for determining the pigment in black baking enamels—i. e., diluting the sample liberally with benzene, settling, and filtering or centrifuging.

In addition to the above extraction mixtures, other solvents were used to obtain a complete separation of the pigment from the vehicle, such as methyl isobutyl ketone, Cellosolve (ethylene glycol monoethyl ether), and methyl Cellosolve, but in each case the separation of the pigment from the vehicle was incomplete and the carbon invariably remained in suspension.

The method developed by the writer gives a complete separation of the vehicle oils and resins from the pigment and eliminates the troublesome suspensions of the carbon in the extraction mixture. It has now been in use in the laboratory of the Board of Transportation of the City of New York for about 2.5 years and has given entirely satisfactory results.

Procedure

Weigh from 6 to 7 grams of the paint into a weighed centrifuge tube of 60-cc. capacity. Add about 25 cc. of an extraction mixture, consisting of 4 parts of mineral spirits and 6 parts of petroleum ether, mix thoroughly with a glass rod, add more extraction mixture to make a total of 50 cc., and centrifuge for 15 to 20 minutes at a speed of about 2000 r. p. m., or until the pigment has well settled. Decant the clear supernatant liquid and repeat the extraction twice with the same extraction mixture. This treatment will dissolve the oils and part of the gums and resins present in the vehicle of the paint. The balance of the gums will be precipitated and will thereby carry down the suspended carbon particles, leaving a clear supernatant liquid.

After decanting the supernatant liquid, treat the gummy residue in the centrifuge tube with about 20 cc. of a 50-50 mixture of acetone and ethyl ether and stir thoroughly with the glass rod to break up all the lumps. To this add sufficient of the mineral spirits-petroleum ether mixture used above to bring the volume to 50 cc. and centrifuge again for 15 to 20 minutes. Repeat the extraction two or three times with the acetone-ethyl ether solvent mixture followed by the mineral spirits-petroleum ether mixture, or until the extraction liquid appears free from color. These extractions will remove the greater part of the gums from the residue, but some will still remain occluded in the carbon.

Transfer the entire residue of carbon and gums from the centrifuge tube into an Erlenmeyer flask and saponify with 75 cc. of

N alcoholic potassium hydroxide under a reflux condenser for about 3 hours. Let stand for 1 hour to allow the carbon to settle as much as possible, then decant the alkaline liquid through a weighed and previously ignited Gooch crucible, and wash the residue in the crucible with a 50-50 mixture of alcohol and acetone to remove the last traces of gums and resins. Continue washing until all alkaline salts are washed out, dry the Gooch crucible in the air oven, and weigh. The difference between this weight and that of the crucible will give the weight of the carbon plus any mineral matter present. Ash the carbonaceous residue in the crucible, cool, and weigh again. The loss in weight obtained will represent the weight of the carbon removed by ignition, which is calculated to percentage on the basis of the sample taken for analysis.

In following this method it is important to use the solvents in the extraction mixtures in the proportions indicated, as slight deviations from these proportions will make it impossible to break up the carbon suspensions.

The ease with which the separation of the carbon from the vehicle in this type of enamels can be accomplished depends to a great extent on the nature of the gums and resins employed in the vehicle. With some enamels, such as those with a glyceryl phthalate base, it may be preferable to saponify the sample directly, omitting the preliminary treatment with solvents in the centrifuge.

Results of analyses by the above method were found to check within 0.2 to 0.3 per cent.

Acknowledgment

The author wishes to acknowledge with appreciation the valuable assistance of J. Boorstein and N. Utkovitz, who carried out the experimented work in connection with this paper.

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Iron Content of Bread and Bread Ingredients

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INCREASING attention is being paid to the mineral constituents of foodstuffs, and among these iron is one of the most important. Considerable work has been done on the determination of iron in various types of food, feeds, and biological materials. Discrepancies in the reported results may be due to the analytical method rather than to actual differences in total iron content, especially in the case of prepared foods such as bread.

During a study of the iron content of a special cereal product it was found that the sum of the iron contents of the ingredients was much greater than the iron content of the finished cereal. Since the colorimetric determination used was identical in all cases, the most reasonable explanation for the discrepancy was a loss of iron during ashing. In view of the fact that some iron salts volatilize even at the lowest ashing temperatures, a loss of iron in products of varied composition is not unexpected.

Farrar (2) used calcium carbonate to prevent the volatilization of ferric chloride during the ashing process. Jackson (6), in a critical study of ashing methods, found that the use of calcium carbonate was not satisfactory, and recommended a wet-ashing method using nitric, sulfuric, and perchloric acids. In an attempt to find a simple and accurate method for ashing, various procedures were studied in this laboratory, and

it was found that sodium hydroxide solution added to the sample before ashing prevented the loss of iron. A series of determinations in which the quantity of caustic solution was varied indicated the value of this modification of the ashing procedure. This method of ash treatment assures that all portions of the sample are in contact with the alkali. Samples covered with calcium carbonate before ashing may not be uniformly alkalinized. The use of nitric, sulfuric, and perchloric acids in a wet-ashing procedure will no doubt retain all the iron originally present in the sample, but the sodium hydroxide ashing method offers simplicity and ease of manipulation as well as apparent accuracy.

After ashing, the thiocyanate colorimetric determination described by Winter (10) was followed. The method has been used in this laboratory for a period of years. The results have been consistent and have agreed excellently with bioassays for iron on wheat products where the availability of the iron is usually considered to be 100 per cent. Saywell and Cunningham (7) found close agreement between the thiocyanate and *o*-phenanthroline colorimetric procedures. Gray and Stone (4) compared thiocyanate and dipyriddy, and found that the two colorimetric methods gave close checks. Comparisons of the various colorimetric methods have not been made in connection with this study, as it was felt that

the selection of the most generally satisfactory colorimetric reagent can be made most conclusively by a collaborative project. The essential point of this report as regards analysis is the simplified ashing procedure, not the actual colorimetric determination.

Method

Take 1 gram of sample and place in a high-quality silica ashing dish. Add 5 ml. of 1N sodium hydroxide solution per gram of sample, mix thoroughly with the material, dry in a 100° C. oven, and ash in an electric muffle at low redness. In some cases where the iron content is low it is convenient to use more than a 1-gram sample.

The iron standards were prepared from iron wire of highest purity. Blanks on all reagents indicated no measurable quantity of iron present as impurities. The sodium hydroxide solution was prepared from electrolytic caustic and tests indicated that it did not contain iron, at least in quantities that affect this determination.

Figure 1 shows the variation in iron content when determinations were made on the same material with increasing quantities of caustic solution, the indicated number of milliliters of 1N sodium hydroxide being added to 1 gram of sample before ashing. After the maximum iron content was reached, no further increase with additional caustic solution was shown. This was added proof that the use of caustic had not introduced an error.

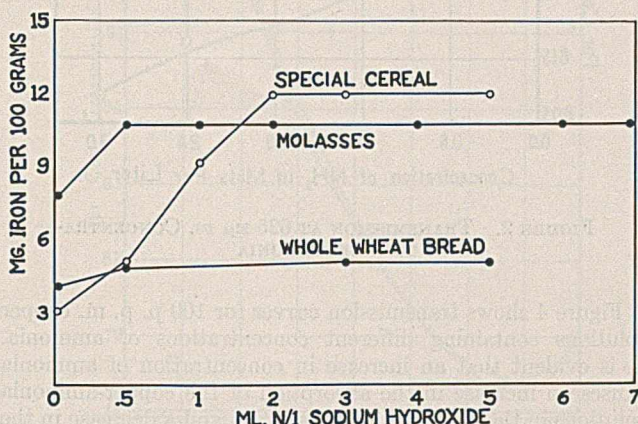


FIGURE 1. VARIATION OF IRON CONTENT WITH ADDITION OF SODIUM HYDROXIDE

White bread with a pH of 5.5 and containing chlorides and other minerals serves excellently to illustrate the loss of iron on dry-ashing when the alkaline ashing procedure is not used, as shown in Tables I and II. The same sample was used for

TABLE I. EFFECT OF ALKALINE ASHING PROCEDURE ON IRON FOUND IN WHITE BREAD

Air-Dried White Bread Gram	1 N NaOH Added Ml.	Iron Found Mg.
1	0	0.0153
1	5.0	0.0181

TABLE II. RECOVERY OF IRON ADDED TO WHITE BREAD BEFORE ASHING

(1 gram of air-dried bread, with and without alkaline ashing procedure)

Iron Naturally Present Mg.	Iron Added Mg.	1 N NaOH Added Ml.	Iron		Loss %
			Calcd. Mg.	Found Mg.	
0.0181	0.0227	0	0.0408	0.0317	23
0.0181	0.0227	5.0	0.0408	0.0408	0
0.0181	0.0453	0	0.0634	0.0295	53
0.0181	0.0453	5.0	0.0634	0.0634	0

TABLE III. IRON CONTENT OF BREAD AND BREAD INGREDIENTS (Mg. of iron per 100 grams of material)

	Sodium Hydroxide Ashing Method Mg.	Literature Data Mg.
Breads		
White		
Dry basis	1.8	
38% moisture basis	1.1	1.27 (9), 1.07 (8), 1.00 (1) ^a
Whole-wheat		
Dry basis	5.4	
38% moisture basis	3.3	1.93 (9), 3.43 (8), 1.75 (1)
Rye		
Dry basis	3.7	
38% moisture basis	2.3	1.60 (1)
Flours		
White, 0.44% ash, 13.25% moisture	1.3	1.73 (9), 1.00 (8), 0.9 (1)
Clear, 0.72% ash, 13.00% moisture	2.0
Whole-wheat, 1.90% ash, 10.00% moisture	5.0	2.50 (1)
Rye (medium), 1.15% ash, 10.00% moisture	2.6	2.83 (1)
Wheat products		
Wheat germ, 4.35% ash, 11.00% moisture	10.0
Red Dog flour, 2.80% ash, 11.00% moisture	10.7
Bran, 7.40% ash, 10.00% moisture	12.7	28.3 (8), 8.52 (1)
Cereals		
Oatmeal	8.0	5.1 (9), 6.5 (8), 3.8 (1)
Yellow cornmeal	7.4	6.8 (8), 1.3 (1)
Special cereal (U. S. Patent 2,041,129)	11.9 ^b
Miscellaneous bakery ingredients		
Baker's yeast, 30% solids	3.1
Nonfat milk solids	2.1
Molasses (highest grade), 1.25% ash, 25% solids	10.7	3.2 (8)
Commercial egg yolk		
Dry basis	11.7
54% moisture basis	5.4	6.52 (9), 7.6 (1)
Raisins	2.8	3.80 (8)
Honey (medium dark)	3.2	1.15 (1)

^a Bridges reference is compiled data.
^b Bioassay conducted by Walter H. Eddy of Teachers College, Columbia University, showed 11.8 mg. of iron per 100 grams of material.

the determinations in both tables, and the iron found by the alkaline ashing procedure in Table I was used in calculating the total iron present in the recovery experiments. The use of the alkaline ashing procedure ensures complete recovery of added iron, whereas dry-ashing without added caustic gives erratic results.

Comparisons of the iron content of various types of bread and bread ingredients with results reported in the literature are presented in Table III. In wheat products the quantity of iron bears a close relationship to the ash content. When reporting iron in flour it is important, therefore, to indicate the grade of flour. Iron in molasses varies markedly with the grade, as shown by Harris *et al.* (5). The iron content of commercial egg yolk tends to be lower than the quantity found in egg yolks separated in the laboratory. This is explained by the impossibility of completely separating egg white and egg yolk on a commercial scale

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Colorimetric Determination of Copper with Triethanolamine

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THE strong odor and the loss of reagent resulting from the high volatility of aqueous ammonia suggested the possibility of using substituted ammonias for the colorimetric determination of copper. Several of the ethanolamines were tried, and a spectrophotometric study of the colorimetric determination of copper with triethanolamine was then made. A comparative study of the colorimetric determination of copper with ammonia was also made. Only a few representative results are reported here.

Apparatus and Reagents

The transmission measurements were made with a photoelectric spectrophotometer developed by the authors (1). The wave lengths given are the average wave lengths of wave bands approximately 10 $m\mu$ wide. The transmission measurements are on the basis that the transmission of the absorption cell containing water or the reagents (except copper) is 100.0 per cent. The absorption cells have a thickness of 1.000 ± 0.005 cm. and a capacity of 10 ml.

A stock solution of copper sulfate, containing 10,000 p. p. m. of Cu^{++} , was made by dissolving 39.282 grams of c. p. copper sulfate pentahydrate in enough water to give 1 liter of solution. A 500 p. p. m. solution, prepared by diluting the stock solution, was used to make up most of the solutions of lower concentration.

A solution of triethanolamine, Eastman P1599, was made by diluting 127 grams of the compound to 500 ml. in a volumetric flask. This gave a solution 25 per cent by weight.

Analytical grade or c. p. salts were used.

Effect of Reagents

Because of the time required to make a number of transmission measurements at different wave lengths, most of the measurements were made at 625 $m\mu$, which is near the wave length of maximum absorption for copper triethanolamine solutions (650 $m\mu$) and copper-ammonia solutions (600 $m\mu$).

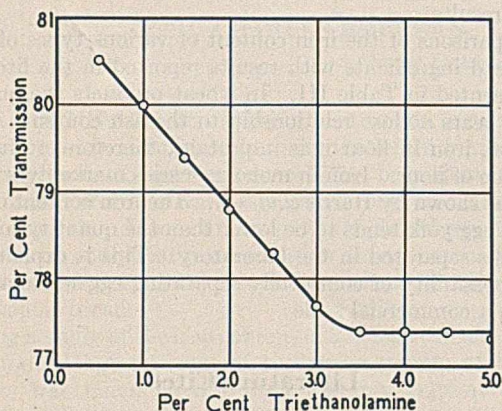


FIGURE 1. TRANSMISSION AT 625 $m\mu$ vs. CONCENTRATION OF TRIETHANOLAMINE

The effect of increasing the concentration of triethanolamine on the transmission at 625 $m\mu$ of a 100 p. p. m. Cu^{++} solution is shown in Figure 1. The transmission becomes practically constant after reaching the minimum at 3.5 per cent. This represents a distinct advantage over copper-ammonia solutions. The transmission at 625 $m\mu$ of the copper-ammonia

solutions was still diminishing at the highest ammonia concentration measured (approximately 3 molar), as shown in Figure 2.

Figure 3 (center) shows the effect of a variation in the concentration of triethanolamine on the transmission, at different wave lengths, of 100 p. p. m. Cu^{++} solutions. The change in transmission is slight, except in the violet end of the spectrum. The difference could not be detected visually in 50-ml. Nessler tubes (tall-form).

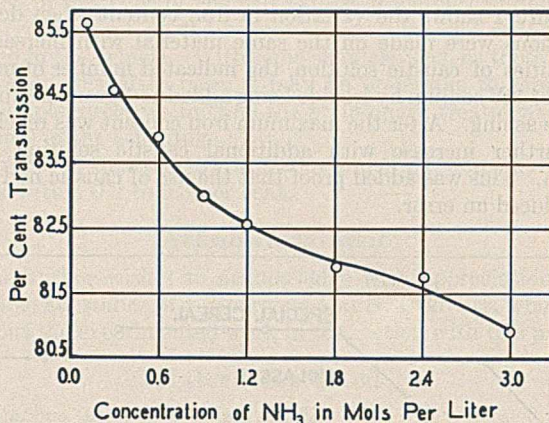


FIGURE 2. TRANSMISSION AT 625 $m\mu$ vs. CONCENTRATION OF AMMONIA

Figure 4 shows transmission curves for 100 p. p. m. copper solutions containing different concentrations of ammonia. It is evident that an increase in concentration of ammonia causes an increase in the absorption of the copper-ammonia solutions in the red end of the spectrum and a decrease in the blue.

Effect of Salts

Since in practice an acid is generally used to dissolve the sample, salts are usually present when the colorimetric determination is carried out. Hence, the effect of salts on the transmission of the copper solutions should be determined.

TRIETHANOLAMINE SALTS. Figure 3 (lower) shows the change in the transmission of a solution containing 100 p. p. m. of Cu^{++} and 5 per cent triethanolamine caused by triethanolamine nitrate. The triethanolamine nitrate solution was prepared by mixing 0.5 ml. of concentrated nitric acid with the copper solution, adding 25 per cent triethanolamine solution until the blue color of the copper-triethanolamine complex appeared, and then adding 5.0 ml. in excess. This solution was diluted to 25.0 ml. in a volumetric flask. An increase is observed in the transmission of the copper-triethanolamine solution except in the violet end of the spectrum. Triethanolamine chloride and triethanolamine sulfate produced a similar increase in the transmission at 625 $m\mu$.

AMMONIUM SALTS. The effect of ammonium chloride, ammonium sulfate, and ammonium nitrate on the transmission, at 625 $m\mu$, of the solutions containing 100 p. p. m. of Cu^{++} and 5 per cent triethanolamine was determined for a wide range of salt concentration. All these salts, in the concentration range 1 to 20 mg. per ml., reduced the transmission at

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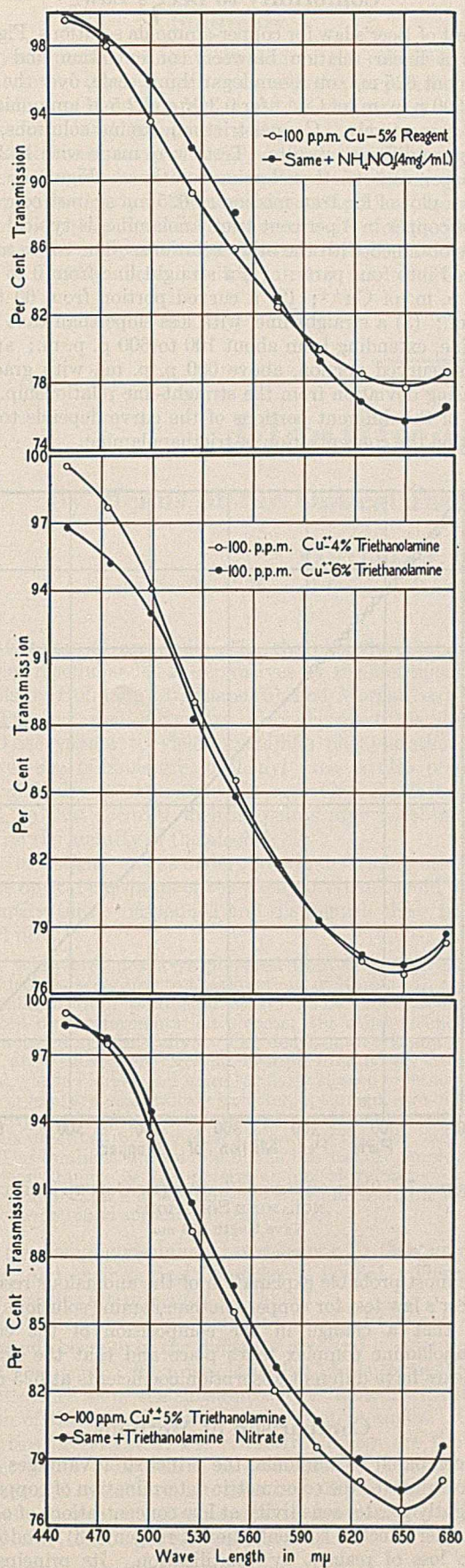


FIGURE 3. TRANSMISSION-WAVE LENGTH CURVES FOR COPPER-TRIEETHANOLAMINE SOLUTIONS

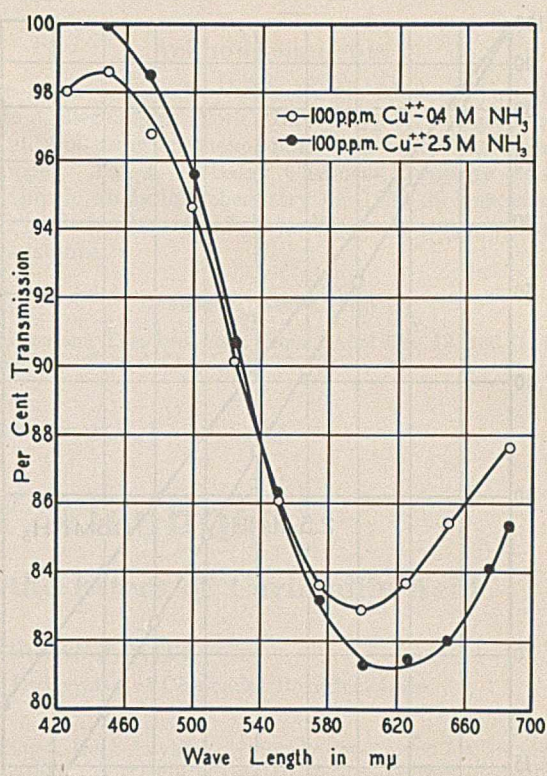


FIGURE 4. TRANSMISSION-WAVE LENGTH CURVES FOR COPPER-AMMONIA SOLUTIONS. EFFECT OF AMMONIA CONCENTRATION

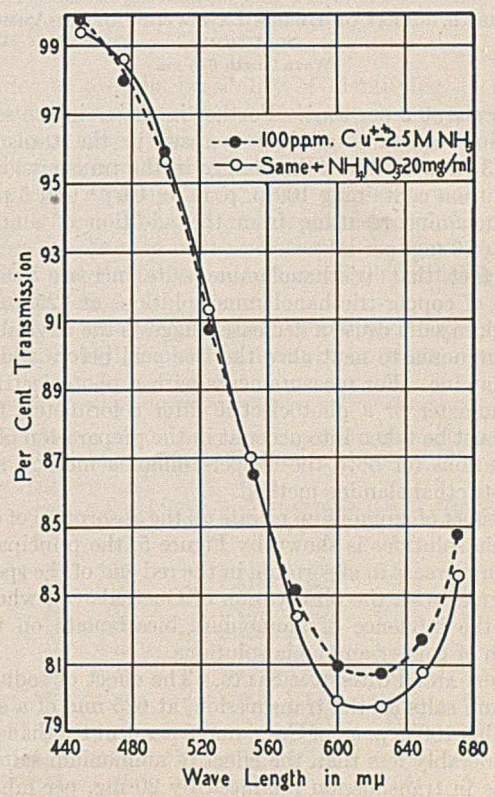


FIGURE 5. TRANSMISSION-WAVE LENGTH CURVES FOR COPPER-AMMONIA SOLUTIONS. EFFECT OF AMMONIUM NITRATE

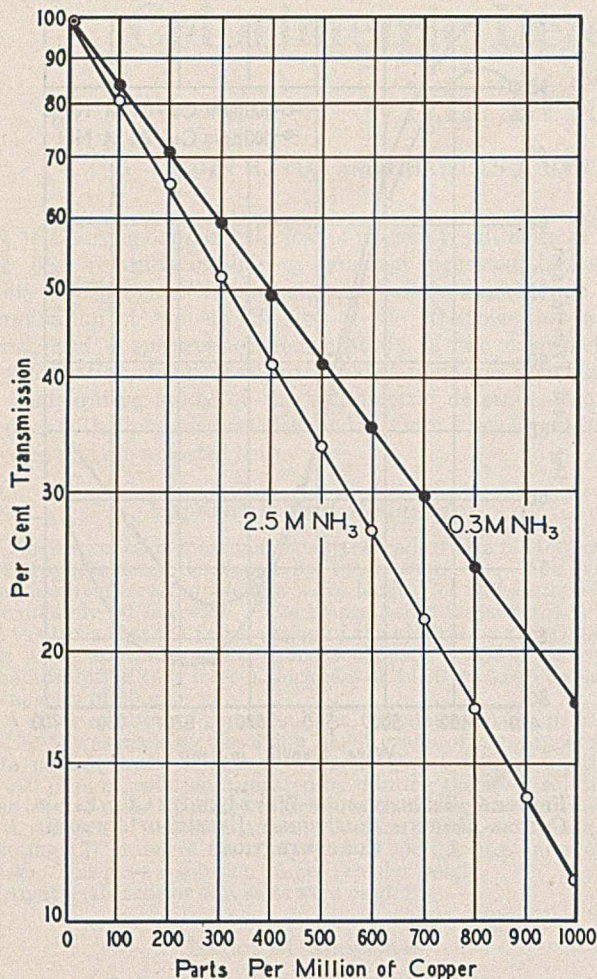


FIGURE 6. TEST OF BEER'S LAW WITH COPPER-AMMONIA SOLUTIONS
Wave length 625 $m\mu$

625 $m\mu$ about 2 per cent. Further increases in the salt concentration caused a gradual increase in the transmission. Figure 3 (upper) shows the change in the transmission curve of a solution containing 100 p. p. m. of Cu^{++} and 5 per cent triethanolamine resulting from the addition of ammonium nitrate (4.0 mg. per ml.).

The fact that triethanolamine salts increase the transmission of copper-triethanolamine solutions at 625 $m\mu$, while ammonium salts cause a decrease, suggests the advisability of using ammonia to neutralize the free acid before adding triethanolamine. For measurements with a photoelectric spectrophotometer or a photoelectric filter colorimeter, the salt effect must be taken into account in the preparation of standard solutions for both the copper-ammonia method and the copper-triethanolamine method.

The effect of ammonium nitrate on the absorption of copper-ammonia solutions is shown by Figure 5, the principal effect being an increase in absorption in the red end of the spectrum. This agrees with the observation of Goethals (2), who determined the influence of ammonium bicarbonate on the absorption of copper-ammonia solutions.

SODIUM AND POTASSIUM SALTS. The effect of sodium and potassium salts on the transmission, at 625 $m\mu$, of a solution containing 100 p. p. m. of Cu^{++} and 5 per cent triethanolamine is considerably less than the effect of ammonium salts. The decrease in transmission produced by 20 mg. per ml. of salt is as follows: potassium chloride, 0.6 per cent; sodium nitrate, 0.5 per cent; sodium acetate, 1.4 per cent; sodium citrate, 0.0 per cent.

Conformity to Beer's Law

A test of Beer's law for copper-ammonia solutions, Figure 6, shows a linear relation between concentration and transmission at 625 $m\mu$, on a semilogarithmic scale, over the range 0 to 1000 p. p. m. of Cu^{++} for 0.3 M and 2.5 M ammonia solutions, respectively. Copper-triethanolamine solutions, however, gave different results. Tests were made with 1, 2, 3, 4, and 5 per cent triethanolamine solutions. Figure 7, which shows a plot of log transmission at 625 $m\mu$ against concentration of copper in 3 per cent triethanolamine, is typical of the results obtained with the other solutions. The curve may be resolved into four parts: (1) a straight line from 0 to about 60 p. p. m. of Cu^{++} ; (2) a curved portion from 60 to 100 p. p. m.; (3) a straight line, with less slope than that of the first line, extending from about 100 to 600 p. p. m.; and (4) another curved portion, above 600 p. p. m., with gradually increasing deviation from the straight-line relationship. The range of the different portions of the curve depends to some extent on the concentration of triethanolamine.

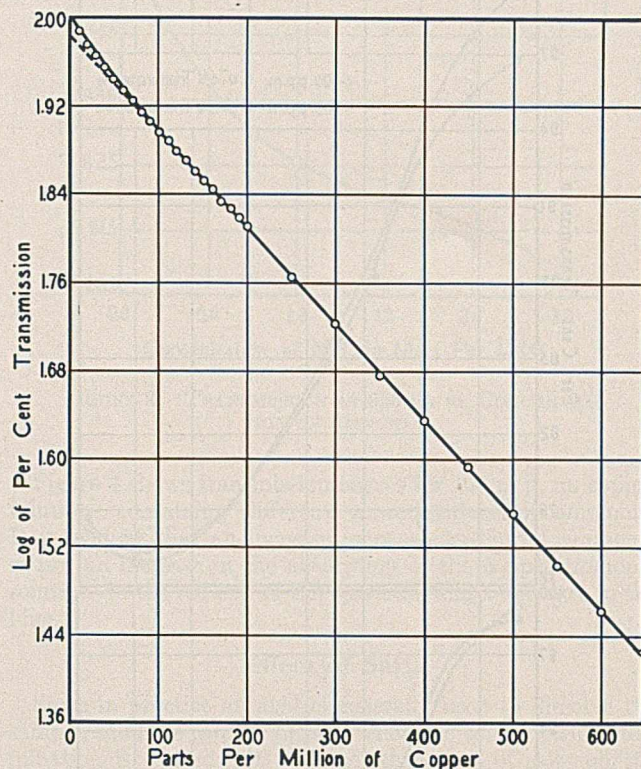


FIGURE 7. TEST OF BEER'S LAW WITH COPPER-TRIEETHANOLAMINE SOLUTIONS
Wave length 625 $m\mu$

The most probable explanation of the anomalous results of the Beer's law test for copper-triethanolamine solutions seems to be that a change in the composition of the copper-triethanolamine complex takes place and that the different complexes have different absorption coefficients at 625 $m\mu$.

Comparison of Methods

As compared to ammonia, the principal advantages of triethanolamine for the colorimetric determination of copper are: (1) slightly greater sensitivity at low concentrations of copper, (2) smaller effect of concentration of reagent, (3) no odor, and (4) no loss of reagent by volatilization. Its principal disadvantage is the failure of the colored solutions to conform to Beer's law over the entire useful range of copper concentrations.

Summary

A spectrophotometric investigation of the colorimetric determination of copper with triethanolamine included a study of the effect of concentration of the reagent, and of ammonium, sodium, and potassium salts on the transmission of copper-triethanolamine solutions; and a test of the conformity to Beer's law at several concentrations of triethanolamine. A comparative study of the ammonia method was also made.

There is little difference in the sensitivities of the copper-ammonia and copper-triethanolamine methods, though the latter is slightly more sensitive at low concentrations of copper.

Acknowledgments

The authors wish to thank R. H. Müller, Washington Square College, New York University, for suggesting the possibility of using triethanolamine as a colorimetric reagent for copper. The J. T. Baker Chemical Company research fellowship in analytical chemistry for 1938-39 was awarded to one of the authors (C. J. B.). They are very grateful for this assistance.

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Identification of Alcohols

By Means of the Optical Properties of the Esters of Carbanilic Acid

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THE esters of carbanilic acid, the phenylurethans, have been recommended as derivatives for the identification of alcohols by Hofmann (2), Snape (6), and Morgan and Pettet (4). Primary and secondary alcohols react readily with phenyl isocyanate to yield crystalline phenylurethans. In the presence of moisture, diphenyl urea is also produced. Some difficulty is experienced in removing the latter compound, so that accurate melting points may be obtained to establish the identity of the alcohol.

This investigation was undertaken to determine whether or not the optical constants of the phenylurethans could be used to identify these compounds and distinguish them from diphenyl urea.

The phenylurethans were prepared from fifteen normal primary alcohols according to the directions of Kamm (3), and were recrystallized from petroleum ether. (The ethyl alcohol was produced by the fermentation process; the other alcohols were manufactured synthetically.) The decyl, undecyl, and dodecyl esters, after subsequent recrystallization from 50 per cent ethyl alcohol, yielded larger and more regularly shaped crystals.

The crystal system, optical character, optic sign, sign of elongation, dispersion, and extinction angle were determined by the methods described by Winchell (7) and by Chamot and Mason (1). The urethans are soluble in the oils usually employed for immersion liquids in the determination of refractive indices. Glycerol and water and solutions of potassium mercuric iodide in glycerol were found suitable for this purpose.

All the compounds investigated belong to the monoclinic system, and their optical character is biaxial. Their other characteristics are presented in Table I.

Not all the optical data could be obtained for each of the compounds because of the difficulty involved in orienting the crystals properly. The determination of the optical sign is difficult, since all of the substances investigated, with the exception of the benzyl ester, have large optic angles. Of the properties investigated, the refractive indices are the most characteristic. They serve to establish the identity of the urethans and to differentiate them from diphenyl urea. The undecyl ester sometimes shows slightly lower indices when recrystallized from 50 per cent ethyl alcohol.

The procedure followed in identifying an unknown alcohol is similar to the method applied by Poe and Sellers (5) for the identification of strychnine. The ester is prepared and recrystallized from petroleum ether and allowed to dry in air. A few of the crystals are suspended in a medium of a refractive index corre-

sponding to the beta value previously determined for the urethan in question. A crystal is rotated to the position of extinction with the long axis of the crystal more nearly parallel to the 6 o'clock-12 o'clock direction in the polarizing microscope. In this position, most of the crystals will not be visible if the alcohol is the one anticipated. The crystal forms of the ethyl, amyl, hexyl, and benzyl esters are such that their orientation should be established by means of an interference figure before applying the test for the refractive index.

As a confirmatory test the value of gamma, or (for the nonyl ester) alpha, may be checked in a similar manner. In the determination of alpha or gamma, the long axis of the crystal should be more nearly parallel with the 3 o'clock-9 o'clock direction in the polarizing microscope.

In order to test the possibility of identifying an alcohol when water is present, methyl, ethyl, propyl, butyl, and amyl alcohols were mixed with equal parts of water and treated with phenyl isocyanate. The resulting mixtures of the urethans and diphenyl urea were extracted with boiling petroleum ether. The optical characteristics of the crystals of the urethans formed in the presence of diphenyl urea were not altered and the urethans were readily identified by their refractive indices.

Mixtures of methyl and ethyl, propyl and isopropyl, and butyl and isobutyl alcohols in equal proportions were made.

TABLE I. OPTICAL PROPERTIES OF SOME ESTERS OF CARBANILIC ACID AND OF DIPHENYL UREA

Ester	Melting Point ° C.	Extinction Angle	Optic Sign	Refractive Indices			Elongation	Dispersion
				Alpha	Beta	Gamma		
Methyl	47	16	+	1.542	1.590	1.667	±	$\rho > \nu$
Ethyl	52	20	-	1.516	1.580	1.618	±	$\nu > \rho$
n-Propyl	50	33	-	1.525	1.596	1.641	±	$\nu > \rho$
n-Butyl	57	31	-	1.507	1.592	1.655	±	$\nu > \rho$
n-Amyl	45	45	-	1.464	1.598	1.693	±	$\rho > \nu$
n-Hexyl	40	40	-	1.465	1.589	1.670	±	$\rho > \nu$
n-Heptyl	65	44	+	1.502	1.553	1.615	±	$\rho > \nu$
n-Octyl	74	16	-	..	1.559	1.627	±	None
n-Nonyl	60	36	-	1.472	1.570	1.613	±	$\rho > \nu$
n-Decyl	61	6	-	..	1.536	1.605	±	None
n-Undecyl	52	12	-	..	1.546	1.605	±	None
n-Dodecyl	74	27	-	..	1.548	1.618	±	None
Benzyl	77	11	+	1.570	1.587	1.679	±	$\nu > \rho$
Phenyl-ethyl	78	28	+	1.596	1.629	1.681	±	$\rho > \nu$
Phenyl-propyl	45	29	+	1.549	1.604	1.703	±	$\nu > \rho$
Diphenyl urea	235	40	+	1.583	1.621	> 1.703	±	$\rho > \nu$

Urethans were prepared from these mixtures and recrystallized from petroleum ether. The mixture of ethyl and methyl did not produce crystals characteristic of the individual urethans. The other mixtures yielded crystals which could be identified. Care must be exercised to prevent one of the components from being separated out by the solvent.

Summary

The optical crystallographic data for fifteen esters of carbanilic acid have been determined and compared with similar data for diphenyl urea. The optical properties provide a means of identifying the urethans even when they are mixed

with diphenyl urea. A method for confirming the identity of an alcohol is outlined.

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Method for Analysis of Boiler Scales and Sludges

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Detailed procedures are given which employ colorimetric and turbidimetric methods in conjunction with a Phototester for the analysis of boiler deposits. Tabulations show the results obtainable with these procedures as compared with time-consuming gravimetric methods involving reprecipitation of the constituents sought.

Owing to the difficulty normally encountered in obtaining a representative sample from the large surface of a boiler, a high degree of analytical accuracy is usually not so important as rapidly and conveniently obtained knowledge of the type of deposit involved.

IN CONSIDERING analytical methods for the chemical analysis of a boiler scale, it is important to select procedures that will accurately depict the type of chemical deposition that has been formed—that is, whether the deposit contains unusual amounts of calcium, magnesium, aluminum, iron, silicate, sulfate, carbonate, or phosphate. Owing to the large amount of surface area available in a boiler on which a deposit may form, two different samples will not check perfectly as to chemical analysis. If, therefore, a particular sample of boiler scale has a calcium oxide content of 30.0 per cent, any method of analysis that finds a calcium oxide content in this sample of from 29.0 to 31.0 per cent is satisfactory. The same generality applies to the other constituents that are likely to be found in a boiler deposit.

Inasmuch as time is always at a premium in an analytical laboratory, the method that allows the required degree of accuracy in the shortest time is the most desirable, especially for plant control purposes.

Gravimetric procedures, as applied to scale analysis, are usually time-consuming. This is particularly true with some types of deposits. For example, scales that contain considerable phosphate along with calcium, iron, and aluminum require the addition of a standard iron solution, as well as the reprecipitation of the iron and aluminum oxide group found. This sort of analytical procedure when used solely for plant control purposes is time-consuming. If the reprecipitation

step is omitted, the procedure required is still long, and the results obtained are not satisfactory.

In analyzing this type of scale gravimetrically the usual procedure is as follows:

The phosphorus pentoxide is determined on an aliquot of the filtrate from the silica determination. In precipitating the iron and aluminum hydroxides from another aliquot of this same filtrate, sufficient standard iron solution to react with the phosphorus pentoxide present is added, followed by ammonia. In the precipitation that occurs, the phosphorus pentoxide is thrown down as ferric phosphate, and the iron and aluminum originally present in the deposit are precipitated as hydroxides.

The sum of the phosphorus pentoxide present and the ferric oxide added, subtracted from the ignited precipitate, gives the amount of iron and aluminum oxide present in the scale. The ferric oxide is determined on a separate aliquot either by precipitation with cupferron or colorimetrically. Subtracting this result from the iron and aluminum oxides found gives the aluminum oxide present.

In spite of the fact that the standard iron solution is purposely added to precipitate the phosphate present and to prevent the phosphate from reacting with and removing calcium at this stage in the procedure, unless the precipitate referred to above is dissolved and reprecipitation made, considerable calcium may be present in the iron and aluminum oxide, thereby giving a final result that is too high in aluminum oxide and correspondingly low in the amount of calcium oxide found.

In Table I results are given on a phosphate scale as well as on a known mixture containing iron, aluminum, calcium, magnesium, and phosphorus. Analysis was made with and without the reprecipitation of the iron and aluminum oxide group. The results of the calcium and aluminum determinations only are given. These data illustrate the necessity of employing reprecipitation.

TABLE I. DETERMINATION OF CALCIUM AND ALUMINUM

	Scale Sample ^a		Synthetic Mixture ^b	
	Al ₂ O ₃	CaO	Al ₂ O ₃	CaO
Added, %			20.0	30.0
Found by gravimetric procedure ^c , %	11.7	29.1	25.3	25.1
Found by gravimetric procedure ^d , %	5.4	35.5	20.8	29.3
Found by simplified procedure, %	5.2	36.8	19.6	29.8

^a Scale contained 12.0% loss on ignition, 6.2% SiO₂, 5.4% Al₂O₃, 5.9% Fe₂O₃, 35.5% CaO, 2.2% MgO, 24.7% P₂O₅, 2.5% SO₃, 1.0% CO₂, 3.9% Na₂O.

^b Synthetic mixture contained 5.0% Fe₂O₃, 25.0% P₂O₅, 2.0% MgO, 20.0% Al₂O₃, 30.0% CaO, 10.0% SiO₂, 8.0% SO₃.

^c Procedure involved addition of standard iron solution to precipitate phosphate present. No reprecipitation employed.

^d Procedure involved addition of standard iron solution as in ^c. Employed reprecipitation of R₂O₃ found.

TABLE II. COMPARATIVE ANALYSES OF TYPICAL SCALES

(G, gravimetric method, employing reprecipitation of R₂O₃ group; S, simplified procedure; X, both methods employing same procedure)

Sample No.	Organic Loss		SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		CaO		MgO		SO ₃		CO ₂		P ₂ O ₅	
	G %	S %	G %	S %	G %	S %	G %	S %	G %	S %	G %	S %	G %	S %	G %	X %	G %	S %
1	12.6	14.2	14.5	14.5	9.6	10.4	7.5	7.5	23.5	24.5	5.4	5.0	3.4	2.7	2.0	17.5	16.5	
2	14.6	16.0	13.6	13.5	8.4	9.0	8.0	8.0	23.8	25.2	5.6	4.3	4.1	2.5	0.0	18.5	18.0	
3	7.4	7.2	10.7	12.1	3.3	4.5	4.5	3.6	34.6	34.0	12.6	12.0	4.6	5.0	23.6	0.0	0.0	
4	6.2	7.6	13.4	12.1	1.1	0.0	1.6	1.6	34.2	34.0	7.3	9.1	0.0	0.0	1.6	27.9	27.0	
5	27.2	26.2	11.6	11.6	8.2	9.0	9.5	8.0	19.3	19.9	6.7	5.7	2.9	2.7	0.0	12.5	12.7	
6	6.2	5.7	4.9	5.1	0.3	0.0	1.0	0.1	42.1	41.3	7.6	7.2	0.0	0.1	0.0	37.0	35.4	
7	16.8	19.7	3.7	2.2	0.0	0.0	44.3	41.1	7.6	10.0	1.4	0.1	0.0	0.0	1.0	23.8	22.6	
8	43.4	44.1	1.1	2.0	3.4	0.0	0.1	0.7	28.1	29.0	7.8	6.6	0.8	1.9	3.3	14.1	14.6	
9	10.1	9.6	2.0	3.2	1.8	0.7	1.0	2.0	42.7	42.2	6.4	5.0	4.0	4.7	26.8	5.5	5.2	
10	13.8	13.9	7.8	6.0	5.7	3.1	4.5	4.0	29.2	28.6	9.2	9.3	2.7	3.3	6.6	20.6	20.5	

Recent work in the authors' laboratory on the application of colorimetric and turbidimetric methods to the analysis of water indicated that if such methods could be applied to the analysis of boiler scale, the time required for analytical results might be materially reduced. Considerable time was spent, therefore, in a search of the literature. Inasmuch as the authors desired to determine each constituent without first separating it from the other constituents likely to be present, every method studied had to be investigated for possible interference from constituents other than the one being sought. The procedures which are given in detail below are, therefore, not original. Known methods have been modified and assembled to give a complete procedure (Figure 1) for the analysis of boiler scales, which requires approximately only one third to one half the time required for the prolonged satisfactory type of gravimetric analysis referred to above.

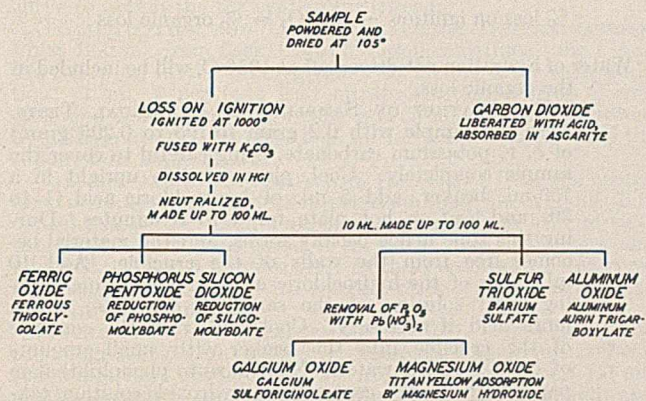


FIGURE 1. PROCEDURE OUTLINE FOR SIMPLIFIED METHOD

This procedure also permits the use of a much smaller sample. When it is desired to analyze a deposit from a definite spot, particularly of a high-pressure boiler where the amount of deposit formed is almost negligible, smallness of sample required becomes important. It also makes the method of value to research studies on boiler operation, where because of the type and size of experimental boiler commonly used, the amount of scale formed may be small.

In the simplified method the dried sample is ignited, fused with potassium carbonate, dissolved in dilute hydrochloric acid, neutralized with sodium hydroxide, and made up to definite volume. An aliquot is taken for each constituent to be determined, and the proper reagents are added to develop either a color or a turbidity which is proportional to the amount of the desired constituent present. This amount of color or turbidity is measured by means of the Phototester. A calibration curve is used to obtain per cent composition.

In Table I the results obtained by means of the simplified method are compared with those obtained by gravimetric procedures.

Table II compares the analyses of a group of typical scales by means of the simplified method with the gravimetric method employing double precipitation. While the percentage error is high in some individual determinations, the results are sufficiently accurate to show the characteristics of the deposit that has been formed. The examples given cover a wide range of scale types.

Figure 2 shows a picture of the Phototester which was developed in this laboratory to be used in conjunction with the simplified method. The Phototester operates on the principle that the current which flows in the circuit containing a photoelectric cell is proportional to the illumination which the cell receives. In the methods given below either chemical precipitation or the development of a depth of color proportional to the amount of the constituent present is obtained. As either is increased, light transmission and subsequent current generation are decreased. By the use of standard solutions, curves have been made by plotting the microammeter reading against the per cent composition. In all cases the color or turbidity is developed directly in 17-ml. (0.5-ounce) test bottles which are carefully selected for uniform transmission of light.

The Phototester was designed to be portable; hence, ruggedness was necessary even to the point of sacrificing a small amount of accuracy. The power source consists of self-contained flashlight batteries. Provision is made, however, for attaching a storage battery or a bell-ringing transformer. The storage battery yields the most constant voltage and is to be preferred when portability is not required. Connected in series with the source of current are a 6- to 8-volt tungsten-filament lamp, a toggle-type switch, and a rheostat. The rheostat is necessary to compensate for any fluctuations of voltage and consequent deviations of the microammeter needle from the zero setting.

The illumination from the lamp is directed through a slot toward the photoelectric cell. The test bottle is placed between this slot and the photoelectric cell, which is of the blocking-layer type and is connected directly in series with the microammeter. A blue filter is mounted in front of the photoelectric cell.

The whole is contained in a wooden carrying case, which has additional space for extra test bottles, calibration curves, and a limited number of reagents.

At present the Phototester is being used widely for making water analyses both in the field and in the laboratory.

Reagents

c. p. anhydrous potassium carbonate, hydrochloric acid (1 to 39 and 1 to 19), and 0.5 per cent sodium hydroxide.

Fe-1 Reagent. Add 500 ml. of c. p. concentrated hydrochloric acid to 500 ml. of distilled water.

Fe-2 Reagent. Thioglycolic acid as obtained from the Eastman Kodak Company, Eastman Catalog No. P-2249.

Fe-3 Reagent. Concentrated ammonium hydroxide, c. p.

P-1 Reagent. Dissolve 37.5 grams of c. p. ammonium molybdate in 600 ml. of distilled water, add 300 ml. of concentrated c. p. sulfuric acid, cool, and make up to 1000 ml.

P-2 Reagent. (1) Dissolve 90 grams of sodium bisulfite in 800 ml. of distilled water. (2) Dissolve 7 grams of sodium sulfite, anhydrous, in approximately 100 ml. of distilled water. To solution 2 add 1.5 grams of 1-amino-2-naphthol-4-sulfonic acid, mix until dissolved, and add to solution 1. Make up total volume to 1000 ml. with distilled water.

Si-1 Reagent. Dissolve 75 grams of c. p. ammonium molybdate in 800 ml. of water, add 60 ml. of concentrated c. p. sulfuric acid, cool, and make total volume up to 1000 ml.

Si-2 Reagent. Dissolve 430 grams of sodium citrate, U. S. P., in distilled water, and add sufficient water to make total volume 1000 ml.

Si-3 Reagent. Same as P-2 reagent.

SO₄-1 Reagent. Add 500 ml. of c. p. concentrated hydrochloric acid to 500 ml. of distilled water.

SO₄-2 Reagent. c. p. barium chloride dihydrate, 20 to 30-mesh. Lead nitrate solution, 2 per cent in distilled water.

Ca-1 Reagent. Dissolve 80 grams of sodium sulforicoleate (Glyco Products Company quality) in 896 ml. of 0.1 N sodium hydroxide. Make up to 1 liter with distilled water.

Ca-2 Reagent. Dissolve 10 grams of oleic acid in 1000 ml. of denatured alcohol, Formula 30.

Mg-1 Reagent. Dissolve 8.55 grams of calcium carbonate in hydrochloric acid, evaporate to dryness, and make up to 1000 ml. with distilled water.

Mg-2 Reagent. Dissolve 0.360 gram of Eastman's titan yellow in 1000 ml. of 50 per cent alcohol (Formula 30).

Mg-3 Reagent. Dissolve 20 grams of sodium hydroxide in distilled water and make up to 1 liter.

Standard phosphorus pentoxide solution for aluminum oxide determination. Dissolve 1.915 grams of potassium dihydrogen phosphate in distilled water and make up to 1 liter. Forty milliliters of this solution made up to 1 liter will give a solution containing 0.04 mg. of phosphorus pentoxide per ml. (1 ml. is equivalent to 10 per cent phosphorus pentoxide).

Standard ferric oxide solution for aluminum oxide determination. Dissolve 0.1965 gram of crystallized ferrous ammonium sulfate [$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] in 50 ml. of distilled water and 20 ml. of concentrated sulfuric acid. Warm the solution and add potassium permanganate solution until the iron is completely oxidized. Dilute to 1 liter; 1 ml. contains 0.04 mg. of ferric oxide (1 ml. is equivalent to 10 per cent ferric oxide).

A-1 Reagent. Dissolve 115 grams of ammonium acetate crystals in approximately 800 ml. of distilled water. Add approximately 60 ml. of concentrated c. p. hydrochloric acid, suf-

ficient to adjust the pH of the reagent to 3.85. Adjust the final volume to 1000 ml.

A-2 Reagent. Dissolve 1.333 grams of aurin tricarboxylic acid in approximately 10 ml. of ammonium hydroxide. Evaporate to dryness over a steam bath, dissolve the evaporated salt in distilled water, and make up to 1000 ml.

A-3 Reagent. Add 27 ml. of concentrated ammonium hydroxide to 1000 ml. of saturated ammonium carbonate solution. Two milliliters of A-1 and 1 ml. of A-3 made up to 15 ml. with distilled water should give a pH of 7.1.

Procedure

OPERATION OF PHOTOTESTER. Adjust the rheostat of the Phototester so that when the light is turned on and a bottle of distilled water is dropped into place, the meter will read zero. Remove the distilled water sample, replace it by the bottle containing the sample in which color or turbidity has been developed, and make the reading.

When an aliquot sample is required, dilute the sample with distilled water up to full sample size before adding the chemical reagents.

PREPARATION OF SAMPLE. Grind a representative sample to a very fine powder. The small size of the quantity used for analysis necessitates a thoroughly uniform sample, which can be obtained only through pulverizing the sample completely.

MOISTURE. Dry the pulverized scale at 105° C. before weighing out samples for an analysis, so that all calculations may be made on the dry basis. Moisture may be determined if desired by weighing before and after drying, but such a figure is usually meaningless.

ORGANIC AND VOLATILE MATTER. Weigh out accurately into a previously weighed platinum crucible 40 mg. of dried material, and place in an electric muffle or over a burner, taking care not to raise the temperature of the crucible and contents too rapidly. Heat for 45 minutes or to constant weight at 950° to 1000° C. Cool in a desiccator and weigh.

$$\frac{\text{Mg. of total loss} \times 100}{40} = \% \text{ loss on ignition}$$

$$\% \text{ loss on ignition} - \% \text{ CO}_2 = \% \text{ organic loss}$$

Water of hydration not driven off at 105° C. will be included in the organic loss.

PREPARATION OF SAMPLE FOR INDIVIDUAL TESTS. Fuse the sample with 0.2 gram (0.195 to 0.205 gram) of c. p. potassium carbonate, being careful to cover the sample completely. Cool, place crucible upright in a 150-ml. beaker, add 5 ml. of hydrochloric acid (1 to 39), and heat on hot plate for 4 to 6 minutes. During this time a floc usually forms, and the material becomes free from the walls of the crucible. Add 10 ml. more of the hydrochloric acid, and continue heating until solution of the sample is complete, adding more acid if necessary. Cool, and wash the contents of the crucible into the beaker with small amounts of cold, distilled water. Neutralize to phenolphthalein paper with 0.5 per cent sodium hydroxide solution, taking care not to contaminate the sample with phenolphthalein. Usually the formation of a floc is an indication that the neutral point is being approached. Now add sufficient 1 to 19 hydrochloric acid solution to dissolve any floc that is formed, avoiding an excess of acid. Transfer to a 100-ml. volumetric flask (flask 1), and make up to volume. Mix well, and pipet a 10-ml. uniform sample into a second 100-ml. volumetric flask (flask 2). Make this up to volume.

IRON OXIDE DETERMINATION (2). Pipet 15 ml. from flask 2 into a 17-ml. (0.5-ounce) test bottle. Add 1 drop of Fe-1 reagent and 1 drop of Fe-2 reagent. Mix well, and add 1 ml. of Fe-3 reagent. Mix again and after 2 minutes read in the Phototester. Interpret the reading by means of the iron oxide curve to obtain the per cent of ferric oxide.

PHOSPHATE DETERMINATION (3). Pipet 15 ml. from flask 2 into a 17-ml. (0.5-ounce) test bottle. Add 0.5 ml. of P-1 reagent, then 0.5 ml. of P-2 reagent. Mix well by shaking and allow to stand for 5 minutes. Read in the Phototester. Interpret the reading by means of the phosphate curve to obtain the per cent of phosphorus pentoxide.

SILICA DETERMINATION (2, 6). Pipet 10 ml. from flask 2 into a 17-ml. (0.5-ounce) test bottle. Add 1 ml. of Si-1 reagent, mix, and wait 5 minutes. Add 2 ml. of

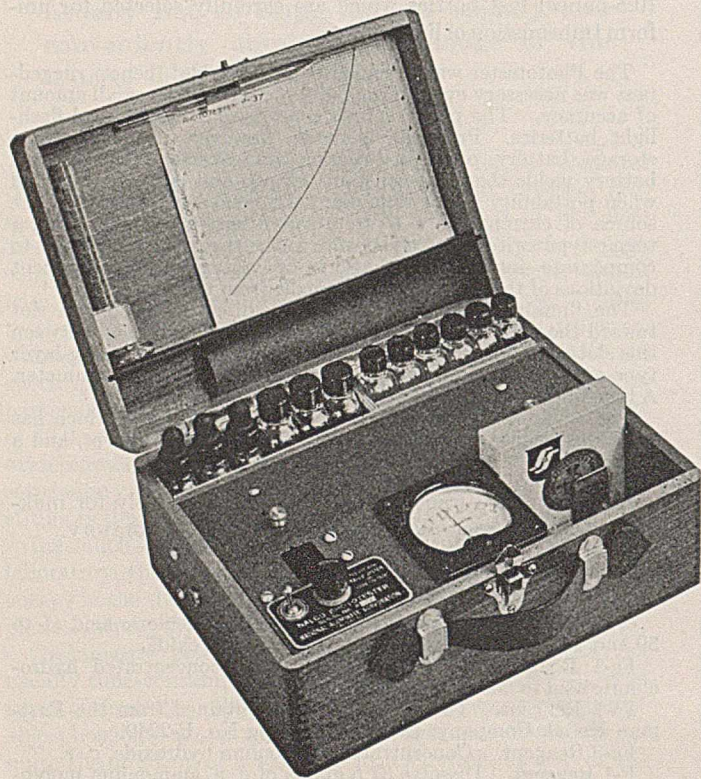


FIGURE 2. PHOTOTESTER

Si-2 reagent, and mix. Add 0.5 ml. of Si-3 reagent, followed by sufficient distilled water to fill up to the base of the neck of the bottle. Mix, and after 1 minute read in the Phototester. Interpret the reading by means of the silica curve to obtain the per cent silica.

CARBON DIOXIDE. The equipment for this method was constructed in the authors' laboratory and is a modification of the Underwood method (8). This assembly is made up as follows (Figure 3).

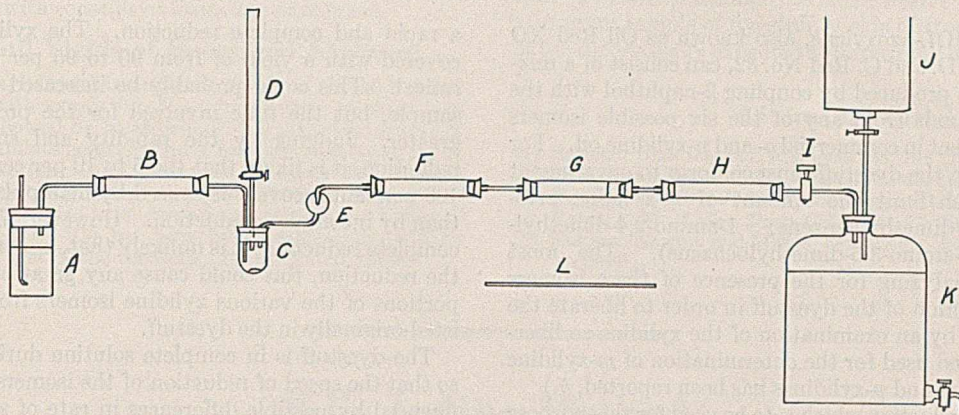


FIGURE 3. APPARATUS FOR DETERMINATION OF CARBON DIOXIDE

A blank must be run on the distilled water, and a correction made if appreciable silica is found. If the final color obtained is green instead of blue, it is well to renew the Si-3 reagent.

SULFATE DETERMINATION (1). Pipet 15 ml. from flask 1 into a 17-ml. (0.5-ounce) test bottle. Add 1.0 ml. of SO₄-1 reagent and 0.15 to 0.30 gram of SO₄-2 reagent. Shake well, and allow to stand for 5 minutes. Mix again, and read immediately in the Phototester. Interpret the reading by means of the sulfate curve to obtain the per cent sulfur trioxide.

CALCIUM OXIDE AND MAGNESIUM OXIDE DETERMINATIONS. Pipet 12.0 ml. from flask 1 into a 15-ml. centrifuge tube. Add the following in the order given with mixing after each addition: 1 ml. 2 per cent lead nitrate solution, 1 drop of concentrated ammonium hydroxide, and 2 ml. of distilled water. Centrifuge at 2500 to 3000 r. p. m. for 5 minutes, or until the supernatant liquid is clear.

CALCIUM OXIDE DETERMINATION (7). Pipet from the centrifuge tube 6.25 ml. of the clear supernatant liquid into a 17-ml. (0.5-ounce) test bottle. Add 2 ml. of Ca-1 reagent and 1 ml. of Ca-2 reagent. Add distilled water to fill to the base of the neck and mix well. After 5 minutes read in the Phototester. Interpret the reading by means of the calcium oxide curve to obtain the per cent calcium oxide.

MAGNESIUM OXIDE DETERMINATION (5). Pipet from the centrifuge tube 5.0 ml. of the clear supernatant liquid into a 17-ml. (0.5-ounce) test bottle. Add 5.0 ml. of distilled water, 1.0 ml. of Mg-1 reagent, and 1.0 ml. of Mg-2 reagent. Mix well, and add 1.0 ml. of Mg-3 reagent. Add distilled water to fill to base of neck, and mix again. After 1 minute read in Phototester. Interpret the reading by means of the magnesium oxide curve to obtain the per cent magnesium oxide.

ALUMINA DETERMINATION (4). Pipet 1 ml. from flask 1 into a 17-ml. (0.5-ounce) test bottle. Add sufficient standard phosphorus pentoxide solution (1 ml. equivalent to 10 per cent of phosphorus pentoxide) to make the total phosphorus pentoxide present in the sample equivalent to 30 per cent. Also add sufficient standard ferric oxide solution (1 ml. equivalent to 10 per cent ferric oxide) to make the total ferric oxide present in the sample equal to 15 per cent. If either the per cent of phosphorus pentoxide or the per cent of ferric oxide in the original sample exceeds the values given (30 per cent phosphorus pentoxide or 15 per cent ferric oxide) use half sample—i. e., 0.5 ml. from flask 1 or 5 ml. from flask 2.

To the sample with the required phosphorus pentoxide and ferric oxide present, add one drop of phenolphthalein and sufficient 0.5 per cent sodium hydroxide solution to make the solution a faint pink. Make up with distilled water to approximately 10 ml. Add 2 ml. of A-1, mix; add 1 ml. of A-2, mix, and let stand for 10 minutes. Add 1 ml. of A-3 reagent, and make up to the base of the neck with distilled water. Mix by inverting the test bottle 3 times. Read immediately in the Phototester. Interpret the reading by means of the alumina curve to obtain the per cent alumina. If an aliquot sample was required, multiply by the proper factor.

A is a bubble counter containing concentrated sulfuric acid, B is a small drying tube containing soda-lime, and C is the reaction bulb containing the sample. D is a 10-ml. buret containing hydrochloric acid (1 to 1), E is a steam trap condenser, and F is a drying tube filled with Dehydrite, the ends being plugged with glass wool.

G is an absorption tube (10 cm., 4 inches, long, 8 mm. in inside diameter) filled with Ascarite, except for a small amount of Dehydrite at the exit end. H is a small drying tube containing soda-lime, I is a stopcock, J is a water reservoir, and K is a large aspirator (2-liter capacity) containing water. L is a glass tube of the same length as G.

All connections should be tight. Small vacuum rubber tubing is recommended for the connections and "no air" rubber stoppers for the Dehydrite and Ascarite tubes. All permanent connections may be sealed with shellac if necessary.

PROCEDURE. Between F and H place glass tube L instead of absorption tube G. With a reaction bulb in place, sweep out the apparatus by passing air through for 10 minutes at the rate of approximately three bubbles per second. Fit absorption tube G with pieces of rubber tubing containing solid glass plugs, thus sealing both ends of the tube. Weigh the tube with the plugs in place. Weigh a 40-mg. sample in another reaction bulb. Stop suction on apparatus, remove plugs from absorption tube, and place in the absorption train, as indicated in Figure 3. Add 2 ml. of carbon dioxide-free distilled water to the reaction bulb and put the bulb in place. Start suction at the same rate as above, and add dropwise 1.5 ml. of acid from the buret. Heat the sample almost to boiling with a microburner, continue bubbling for about 5 minutes, and then shut off the suction. Remove the absorption tube, stopper as before with glass plugs, and weigh. The increase in weight is carbon dioxide.

$$\frac{\text{Gain in weight in milligrams} \times 100}{40} = \% \text{ CO}_2$$

The Dehydrite in the drying tube must be changed at the first indication of moisture. The Ascarite in the absorption tube requires changing when more than one third of it has turned white.

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Reduction of 2-Naphthol-Azoxyene

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2-NAPHTHOL-azoxyene, also known as Oil Red XO and F. D. and C. Red No. 32, can consist of a mixture of the isomers produced by coupling 2-naphthol with the diazonium compounds from any of the six possible isomers which may be present in commercial *o*- and *p*-xylylene oil. For use as a food color, the dyestuff must conform to government specifications which limit the amount of *m*-xylylene present (1-amino-2,6-dimethylbenzene; 1-amino-2,4-dimethylbenzene; and 1-amino-3,5-dimethylbenzene). The most obvious way of analyzing for the presence of these isomers involves the reduction of the dyestuff in order to liberate the xylylene, followed by an examination of the xylylene so liberated. (The method used for the determination of *m*-xylylene in admixture with *o*- and *p*-xylylenes has been reported, 5.)

Any method of reduction which is to be used for this purpose must yield a quantity of xylylene that will approach the theoretical amount to be expected from the dyestuff; or else the method must indicate in some other manner that the isomeric composition of the xylylene obtained is the same as that which was combined in the dyestuff.

Usually the reduction of azo dyestuffs for the purpose of isolating and identifying the diazo component is carried out in aqueous medium with the aid of such reducing agents as zinc, stannous chloride, or sodium hydrosulfite. The 2-naphthol-azoxyenes are insoluble in water. Hence, as would be expected, when a reduction is attempted in an aqueous medium, using the ordinary reducing agents mentioned, it is impossible to get adequate contact of the dyestuff with the reducing agent. Consequently, low yields of xylylene are obtained in any reasonable time of reduction.

Rowe (4) has reported the use of a dispersing agent to keep azo dyestuffs from aggregating during reduction with alkaline sodium hydrosulfite solution. This may be one method of solving the problem, but it seemed preferable to run the reduction in actual solution, if possible.

In order to use the ordinary methods of reduction advantageously, a water-miscible solvent would have to be used. To make possible the use of such solvents as the aromatic hydrocarbons, in which the 2-naphthol-azoxyenes are most soluble, one could probably use methods involving reduction with hydrogen in the presence of a nickel catalyst, as has been reported by Brochet (1); or tetralin in the presence of a palladium catalyst, as has been reported by Kotake and Mita (3). For the purpose in view, it was considered desirable to reduce the dyestuff by the more usual agents, such as zinc and hydrochloric acid, thus necessitating the use of a water-soluble solvent. The solvent should, in addition to its solubility in water, not undergo reduction itself, and it should possess vapor pressure or other properties that would facilitate its separation from the liberated xylylene.

2-Naphthol-azoxyene is fairly soluble in hot alcohol. Reduction was tried in this medium with zinc and hydrochloric acid and with stannous chloride and hydrochloric acid, but the addition of such water as was introduced with the acid resulted in precipitation of the dyestuff. The use of alcoholic solutions of stannous chloride with added hydrochloric acid was unsuccessful for the same reason.

The problem was finally solved by taking advantage of the excellent solvent properties of 1,4-dioxane, in which the dye dissolved readily. Stannous chloride and hydrochloric acid did not seem to act efficiently in the presence of dioxane. Heating with zinc and hydrochloric acid, however, resulted in

a rapid and complete reduction. The xylylene could be recovered with a yield of from 90 to 95 per cent of the theoretical. This could probably be increased by using a larger sample, but the time involved for the procedure would be greater. Judging by the rapidity and smoothness of the reduction, it is likely that the 5 to 10 per cent difference from 100 per cent recovery is caused by manipulative losses rather than by incomplete reduction. However, if it were due to incomplete reduction, it is unlikely that, under the conditions of the reduction, this could cause any great change in the proportions of the various xylylene isomers from that which existed originally in the dyestuff.

The dyestuff is in complete solution during the reduction, so that the speed of reduction of the isomers would not be influenced by possible differences in rate of solution. Once in solution, it is most likely, according to Conant and Pratt (2), that all the isomers would reduce at similar rates. These authors, working with water-soluble azo dyes, showed that the structure of the aromatic nucleus which carries the hydroxyl group is the determining factor as regards the "apparent reduction potential" (the normal potential of the reversible system that will just cause appreciable reduction, 20 to 30 per cent in 30 minutes, under the conditions specified). All the compounds which they studied, which had the hydroxyl group on a naphthalene ring, fell in one class as regards the apparent reduction potential. All the 2-naphthol-azoxyenes would, therefore, be expected to fall in one group. Consequently, if there were incomplete reduction, the ratio of the isomers to one another should not be altered, provided the dyestuff was completely dissolved during the reduction. The analysis for the isomeric composition of the recovered xylylene could accordingly be used to draw conclusions concerning the isomeric composition of the original dyestuff.

Reduction of 2-Naphthol-Azoxyene and Recovery of Xylylene

Ten grams of the 2-naphthol-azoxyene were dissolved in 100 ml. of dioxane in a 2-liter, 2-necked flask equipped with a reflux condenser and a dropping funnel. Twenty grams of zinc dust were added and the mixture was brought to a boil. While boiling, concentrated hydrochloric acid was added at a slow rate, with occasional shaking, until no further lightening of the yellow color was caused by further addition of acid, and boiling was continued for a few minutes. (About 40 ml. of hydrochloric acid were used.)

The mixture was cooled, diluted with 100 ml. of water, and made strongly alkaline to phenolphthalein paper with an excess of 40 per cent sodium hydroxide solution. It was then distilled with steam. At first a clear distillate consisting mainly of dioxane and water distilled over and then a turbid distillate containing the xylylene and an alkali-soluble substance. A small portion of the distillate was collected in a test tube from time to time, a few drops of 20 per cent sodium hydroxide solution were added, and the tube was cooled in ice. The removal of xylylene was considered complete when the test liquid was clear by transmitted light. A slight turbidity which could be observed against a dark background was disregarded. Usually a total volume of less than 1 liter of distillate was collected.

The distillate was made strongly acid with considerable excess of sulfuric acid (benzopurpurine 4B indicator paper), and again distilled with steam until the absence of striations in the upper part of the condenser indicated a sufficient removal of the dioxane. The residual liquor was made alkaline with sodium hydroxide solution and the xylylene extracted with one 100-ml. portion and three 50-ml. portions of ether. A further extraction with 50 ml. of ether should leave no more than a few milligrams of oil after evaporation of the ether; otherwise the extraction should be continued. The combined ether extracts were washed with small

portions of water until the washings were no longer alkaline to phenolphthalein paper.

A 250-ml. beaker was heated on a steam bath in direct contact with the steam, wiped with a cloth, allowed to cool in the open, then weighed. The beaker was heated directly with steam and the ether extract added in several portions, each portion being allowed to concentrate to a small volume before the next was added. By this rapid evaporation, creeping of the oil up to the edge of the beaker with consequent losses was minimized.

Analysis and Yields of Recovered Xylidine

The recovered xylidine was analyzed for total amine content by diazotization with excess 0.1 *N* sodium nitrite solution in a stoppered flask, followed by treatment with a measured excess of 0.1 *N* sodium sulfanilate solution and a back-titration with 0.1 *N* sodium nitrite solution. The recovered xylidine will have a diazotization value close to 100 per cent (about 98 to 100 per cent) xylidine if the method has been carried out properly. Yields of xylidine (calculated as 100 per cent by diazotization) will be about 90 to 95 per cent of the theoretically calculated value.

Summary

The dyestuff 2-naphthol-azoxylylene (Oil Red XO or F. D. and C. Red No. 32) may be reduced smoothly in dioxane solution by means of zinc and hydrochloric acid for the purpose of determining the proportion of combined *m*-xylidine in the dyestuff by means of the analysis of the recovered xylidine. With a 10-gram sample of dyestuff, yields of from 90 to 95 per cent of the theoretically expected xylidine may be recovered.

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Wijs Iodine Method

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ALTHOUGH it has been shown repeatedly that the Wijs iodine value can be relied upon to give consistent results and values lying very close to those of the other available methods, the iodine value in general is lower than the theoretical unsaturation, as measured by the hydrogen value (3, 5). How much this value is lower in the case of the Wijs method has never been determined, as far as the author is aware, although in experiments on linoleic and linolenic acids, extending over some years, values never greater than 98.8 per cent of theory were obtained, whether the determination was made on the acid or the derived ester. Since linolenic acid, prepared through its hexabromide, is much more difficult to debrominate than linoleic, it was considered unlikely that the constant ratio of iodine value to unsaturation could be due to a coincidence or to the presence of residual traces of bromine which could not be identified by analysis.

To investigate this problem further, it was decided to prepare an unsaturated acid by some means other than debromination. Elaidic acid was chosen, since its high melting point allows a much better separation from linoleic acid than is possible with oleic.

TABLE I. CONSTANTS OF ETHYL ELAIDATE

Pressure, mm.	Boiling Point Data					
	1	2	4	7.5	12	16
Temperature, ° C. (corr.)	159.5	171	185	200	212	221
Temperature, ° C.	Refractive Indices					
	25.0	29.2	31.5	40.0	51.3	57.6
Refractive index	1.4486	1.4470	1.4461	1.4428	1.4384	1.4359
Specific Gravity						
15.5°/4° C.				25.0°/4° C.		
Apparent True	0.8704			Apparent True		
	0.8706			0.8635		
				0.8636		

Four hundred grams of pure olive oil were saponified in the usual manner, and the resulting 361.1 grams of fatty acids separated into liquid and solid acids by the Twitchell method, with the exception that the entire solid acid fraction from the first precipitation was discarded. The resulting 191.8 grams of liquid acids were fractionally chilled in a 50 per cent acetone solution, by volume, at -15° C. The filtrates from the first four crystallizations were combined and the fatty acids precipitated by diluting with hot water. The yield was 147.8 grams, of iodine value 110.30. The acids were then elaidinized in the usual way with nitric acid and sodium nitrite, the mixture was washed thoroughly with hot water to remove traces of nitric acid, and

the elaidic was separated from the unchanged oleic acid by repeated crystallizations at -20° C. from a 20 per cent acetone solution. The elaidic acid (50.1 grams) was then converted into the lithium salt and recrystallized three times from 80 per cent alcohol, reconverted into the acid (20.0 grams of melting point 43.5° C.), esterified, and triple-distilled under a pressure of 0.5 mm. of mercury. The melting point on a small sample of the saponified ester was 43.5° C., which was not changed on crystallizing the derived lithium salt five times from 80 per cent alcohol solution. Solid acids by the method of Bertram (2) were less than 0.01 per cent.

Various constants, together with boiling point data at reduced pressures using equipment previously described (4), are given in Table I.

Wijs iodine values, by the method of the American Oil Chemists' Society (1), are given in Table II, together with data on two highly purified unsaturated esters prepared by the debromination process (4).

TABLE II. WIJS IODINE VALUES

	Found	Theoretical	% of Theory
Ethyl linoleate	162.49	164.7	98.6
	162.29		
Methyl linolenate			
(from hexabromide of m. p. 181.9°)	257.33	260.57	98.8
Ethyl elaidate	80.85	81.81	98.8
Elaidic acid	88.82	89.93	98.8

The Wijs iodine value, as prescribed in the official methods of the American Oil Chemists' Society, gives results on the unsaturated acids and esters of the oleic series that lie very close to 98.8 per cent of the theoretical unsaturation. The reliability of the method is somewhat greater than is generally supposed, although corrections should be applied when the iodine value is to be used as a measure of the purity of a compound.

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Kinematic Viscometer for Liquid Asphaltic Products

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A new type of kinematic viscometer has been developed for measuring viscosities in centistokes of the whole range of commercial asphaltic liquid road materials at a single temperature. It incorporates features in design to facilitate the operations of filling, adjustment of hydrostatic head, and cleaning. Three capillaries of decreasing bore diameters arranged in series with intervening bulbs permit measurements of viscosities over an extended range without changing capillaries or pressures, as is necessary in other types of instruments.

AT PRESENT the Saybolt Furol viscometer is used to determine the viscosities of asphaltic liquid road materials (A. S. T. M. Method D88-38). Undesirable features of this method are that the results are expressed in empirical rather than absolute units and that it is necessary to use a number of temperatures in order to cover the desired viscosity range.

The second of these becomes particularly noticeable in connection with revised specifications for cutback asphalts recently issued by the Asphalt Institute (1). In order to simplify the designation of liquid road materials, a more systematic classification has been set up in these specifications, based on viscosities at a single temperature (60° C., 140° F.). However, depending upon the viscosity of the particular sample, one of four different temperatures has to be employed for the determination and a conversion made to 140° F. The conversion will always be approximate, owing to differences in the temperature-susceptibility of various oils.

Absolute viscometers are now coming into general use to measure the viscosities of lubricating oils, but most of these instruments are not applicable to dark and opaque materials through which a meniscus cannot be seen. The Koppers (3) and Vogel Ossag (2) absolute viscometers overcome this difficulty, but have other disadvantages. Thus they are more difficult to use in routine testing than the Saybolt Furol viscometer; specific gravity has to be known in order to calculate the viscosities; and to cover the full viscosity range, a number of capillaries or pressures have to be

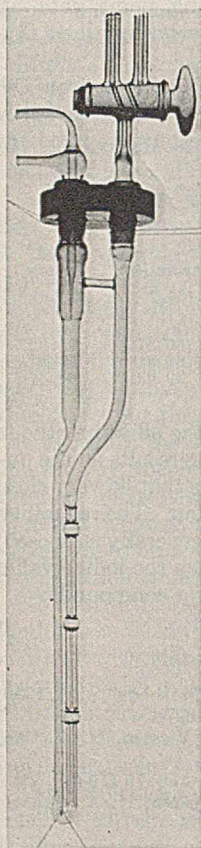


FIGURE 1

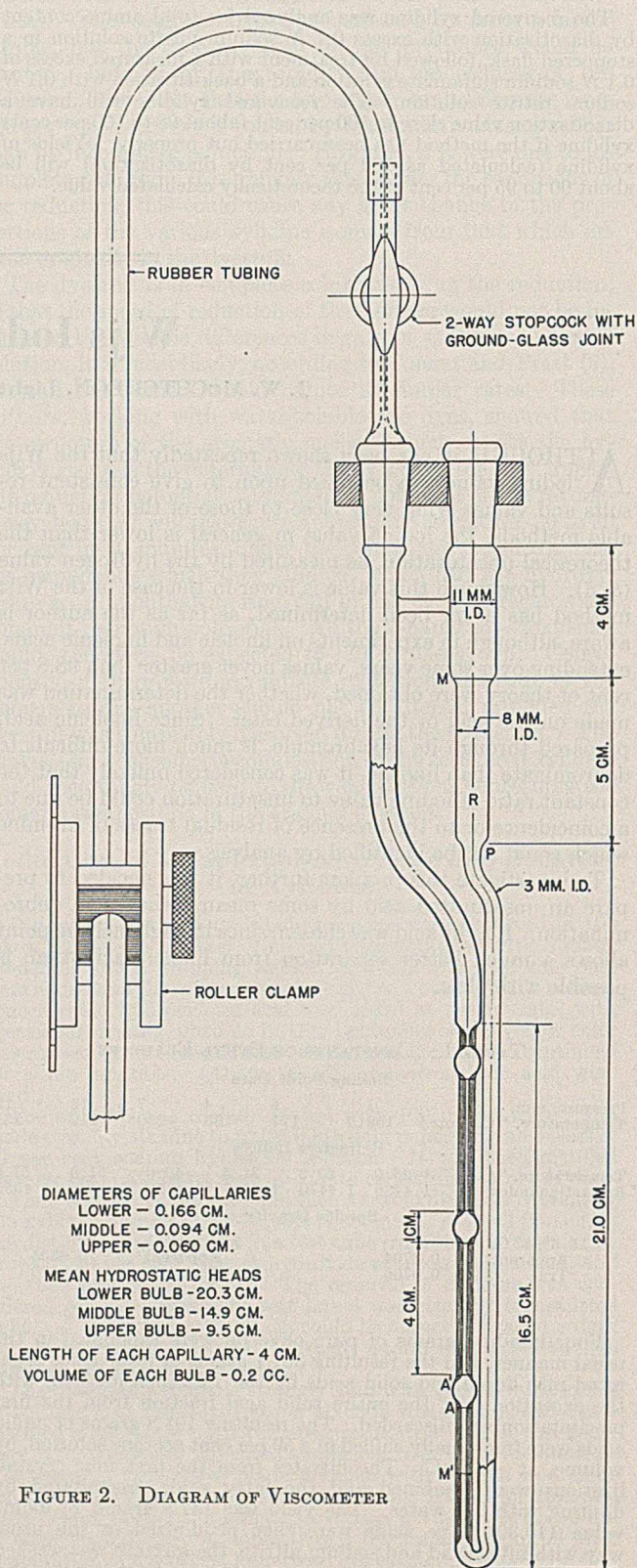


FIGURE 2. DIAGRAM OF VISCOMETER

used, the selection of which involves a certain amount of judgment on the part of the operator.

In order to overcome these difficulties a simple and rapid viscometer has been designed which permits testing, at one temperature, of the whole range of liquid road materials covered by the new Asphalt Institute specifications.

Design of Modified Ostwald Viscometer

The essential principle of the Ostwald viscometer has been retained and certain new features have been incorporated to permit use for testing asphaltic liquid materials.

It will be seen from Figures 1 and 2 that the principal novelty in the design is in the use of three capillaries of decreasing bore arranged in series with intervening bulbs. The lower largest capillary is used for measuring the most viscous liquids, the time of flow being taken for the liquid to pass from marks *A* and *A'* (Figure 2) on the lower and upper necks of the first bulb. If the time of flow is found to be less than a predetermined minimum, say 50 seconds, the liquid is allowed to continue flowing upward through the second capillary of finer bore and the time interval measured for the liquid to fill the second bulb. The smallest capillary at the top is used for measuring the viscosity of liquids that fill the second bulb in less than 50 seconds. No judgment is required on the part of the operator as to the viscosity range of the liquid being measured, since the minimum time limit of flow automatically determines what bulb is to be used.

To decide on the dimensions of the instrument it was necessary to choose minimum and maximum limits for time of flow. Fifty seconds was chosen as the minimum. With a good stop watch of the continuous movement type an error of no more than ± 0.1 second need be encountered in timing the flow which would correspond to an error of 0.2 per cent in the viscosity measurement. For routine testing a maximum limit of 500 seconds does not seem too long and was therefore adopted.

Since the viscosity is directly proportional to the time of flow, the minimum of 50 seconds and maximum of 500 seconds correspond to a tenfold range of viscosity. The dimensions of the bulbs and capillaries and the magnitudes of the hydrostatic heads were chosen so that the tenfold viscosity range of each succeeding bulb follows immediately after that of the preceding. Thus a liquid that takes 50 seconds to flow through the first bulb would take 500 seconds for the second, and a liquid that takes 50 seconds for the second would require 500 seconds for the third. Hence with this instrument it is possible to measure liquids of a thousandfold range of viscosities without exceeding the time limits of 50 to 500 seconds.

The radii of the capillaries were estimated by application of Poiseuille's law. The coarsest capillary was selected to measure liquids of viscosity range from 1500 to 15,000 centistokes; the middle, from 150 to 1500 centistokes; and the top, from 15 to 150 centistokes. Since the volume of each bulb is only 0.2 cc., the linear velocity of flow is small and it can be shown that the kinetic energy correction is negligible. The flow equation then reduces to a simple linear relation between the kinematic viscosity and the time of flow—namely, $V = Ct$. Each capillary with its bulb has a characteristic calibration constant, *C*, which differs from the next by a factor of approximately 10.

The instrument was designed to operate with only 6 ml. of sample. This is a definite advantage over the Saybolt Furol instrument, which requires 90 ml. for a determination.

The dimensions have also been chosen to minimize the effect of surface tension. The inside diameter of the receiver tube, *R*, was selected to be approximately equal to the average diameter of the bulbs. With the dimensions so chosen, the possible error that could result in the viscosity determination from variation in surface tension of the liquid asphaltic materials would never be greater than 0.1 per cent.

The capillaries and bulbs have been placed directly below the receiver arm to minimize the effect of tilting on the hydrostatic head. If the arms are not bent in the manner shown but remain straight and separated, a noticeable error can result from even a slight tilting. In Table I, where calculations are given for the instrument described, showing the error in the viscosity measurement for several angles of deviation from the vertical, it is seen that the error is negligible if the receiver arm is placed in the same line as the capillary arm.

TABLE I. TILTING EFFECT

Angle	Error in Viscosity	
	Arms separated ^a %	Arms in line %
1°	0.53	0.01
2°	1.10	0.06
5°	3.04	0.38
10°	7.11	1.54

^a Calculations for arms separated by 2.8 cm. and for upper bulb of mean hydrostatic head of 9.5 cm.

The viscometer is held in position by means of a Bakelite block holder, which in turn fits into a circular recession in a Bakelite top on the thermostat. The viscometer is cemented to the holder, so that it will always assume the same position when the block holder is clamped in place.

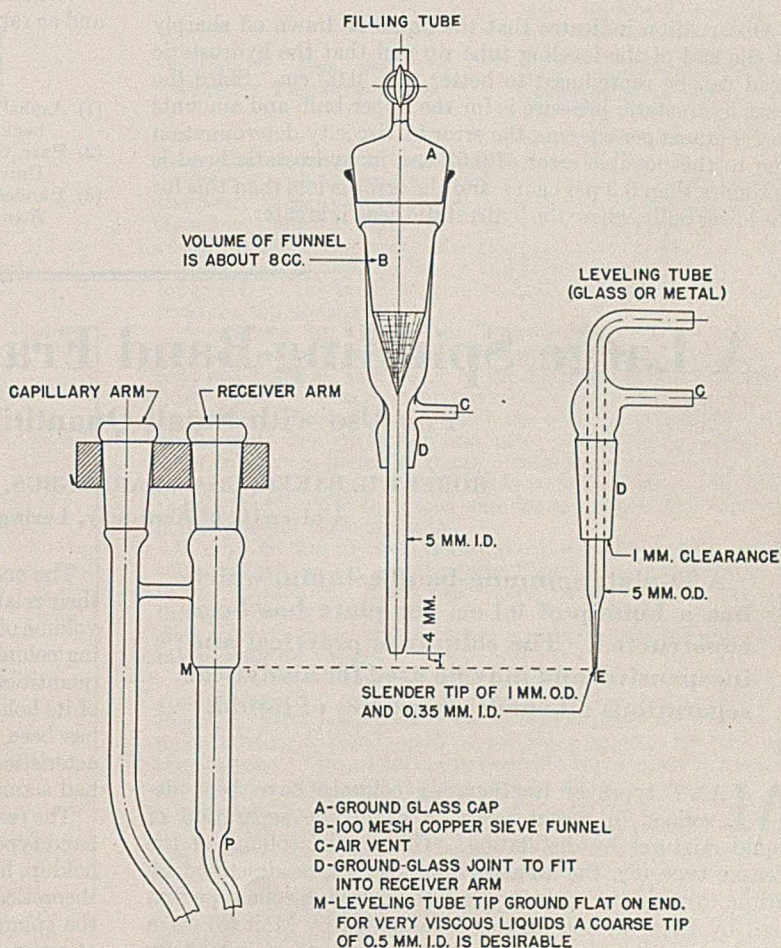


FIGURE 3. FILLING TUBE AND SUCTION LEVELING TUBE

Operation of Viscometer

The filling operation is effected by means of the filling tube illustrated in Figure 3. The asphaltic liquid is warmed to a temperature (60° to 82.22° C., 140° to 180° F.) sufficient to permit its being poured into the 100-mesh copper funnel sieve. The liquid passes through the sieve into the receiver arm of the viscometer and catches at point *P* where the narrow connecting tube joins the receiver tube reservoir. The flow down through the connecting tubing is controlled by means of pressure changes caused by a roller device (devised by V. Lantz, of these laboratories, and shown in Figure 2) which squeezes a rubber tubing connected to the left arm of the viscometer. To control the rate of flow from the filling tube into the viscometer and to adjust the flow so that the upper surface of the liquid approaches mark *M* about the same time that the lower surface approaches mark *M'* on the lower capillary, the ground-glass cap with control rubber tubing is placed on the filling tube. In this way complete control is obtained for the filling operation.

The lower level of the liquid is not immediately brought up to *M'* but left somewhat below, while the upper level is brought to 1 or 2 mm. above *M* into the expanded part of the receiving arm. When temperature equilibrium is attained, the lower level is brought exactly to the mark by means of the control roller device and tubing connected to the left arm of the viscometer. Finally, the upper level is brought down to *M* by use of the suction leveling tube shown in Figure 3.

TABLE II. COMPARATIVE VISCOSITY MEASUREMENTS

Samples	Time of Flow, Modified Ostwald Viscometer Seconds	Viscosity		Difference %
		Modified Ostwald viscometer	Koppers viscometer	
		Centistokes		
1	56.5, 56.6	21.7 (5)	21.8 (1)	0.37
2	371.3, 370.7	142.6	142.3	0.21
3	121.4, 121.5	395.4	397.9	0.63
4	233.2, 233.8	760.3	762.4	0.28
5	55.5, 55.7	2,119	2,125	0.28
6	104.8, 104.6	3,990	3,972	0.45
7	589.5, 584.7	22,371	22,252	0.53

Observation indicates that the liquid is drawn off sharply at the end of the leveling tube tip and that the hydrostatic head can be reproduced to better than 0.02 cm. Since the least hydrostatic pressure is for the upper bulb and amounts to 7.0 grams per sq. cm., the error in viscosity determination due to the possible error of 0.02 cm. in hydrostatic head is not more than 0.3 per cent; and the error is less than this for the lower bulbs where the hydrostatic head is greater.

After a viscosity measurement has been made, the liquid may be removed readily by applying a vacuum to the leveling tube. Benzene or carbon tetrachloride may be introduced into the left arm, and as it is sucked through the instrument it sweeps the viscometer clean of oil. As the vacuum is continued, the cleaning solvent is soon evaporated. The cleaning operation is thus effected simply without removal of the viscometer from the thermostat bath.

The viscometer is readily calibrated by the use of oils of known viscosity (such as the alpha and beta oils of the American Petroleum Institute) at low enough temperatures to get good flow times. Since the effect of temperature on the calibration constants is less than the experimental error for any usual range in temperature, the bulbs may be calibrated with a single oil by choosing several different temperatures to give the appropriate viscosity range.

Precision and Accuracy

To illustrate the reproducibility of measurement and accuracy of determination of viscosity, data are given in Table II for measurements made with both this modified Ostwald instrument and the Koppers instrument on cutback asphalts. The reproducibility of measurement can be estimated by examination of the column in Table II giving repeated measurements for the times of flow. It is seen that the reproducibility is generally within 0.1 to 0.2 per cent. The modified Ostwald and Koppers instruments yield viscosity determinations that agree within 0.2 to 0.6 per cent over a range of viscosities from 16 to 22,000 centistokes which will include all the liquid road materials from the 0 grade to the 6 grade (example: SC-0 to SC-6).

With a little experience the viscometer can be used as easily and as rapidly as the Saybolt Furol viscometer.

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A Large Spinning-Band Fractionating Column

For Use with Small Quantities of Liquids

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A 70-plate spinning-band column, which has a holdup of 0.1 cc. per plate has been constructed. The column is practical and inexpensive, and may be used for analytical separations on small quantities of liquid.

MANY types of fractionating columns have been described in recent years to effect the separation of liquid mixtures by distillation. The packed column of the Fenske type (6), the all-glass bubble-cap type described by Bruun (3), and the recently described spinning-cone type first used by Urey (9) and further investigated by Mair (8) seem to represent the most efficient ones proposed, if judged by their plate rating or height of equivalent theoretical plate.

The one inherent weakness in all the columns mentioned is their relatively large holdup, which necessitates a fairly large volume of liquid to be fractionated. The value of a fractionating column for analytical separations, especially where small quantities of liquids are to be distilled, is primarily a function of its holdup per theoretical plate. Since very little attention has been given this point, the authors determined the characteristics of several columns which, experience indicated, had a small holdup and a fair separating power.

The results, listed in Table I, clearly show that the spinning-band type of column described by Lesesne (?) has the smallest holdup, height of equivalent theoretical plate, and holdup per theoretical plate. It is peculiar that all the columns except the spinning-band type give approximately the same height of equivalent theoretical plate regardless of the mixture used in making the determination, while the spinning-band type

TABLE I. HOLDUP AND PLATE VALUE OF COLUMNS

Column	Length Cm.	Plate Value by <i>n</i> -CCL- Benzene	H. E. T. P. Cm.	Plate Value by <i>n</i> -Heptane-Methyl- cyclohexane	H. E. T. P.	Holdup per Theoretical Plate Cc.
Podbielniak	137	10.0	13.7	9.6	14.2	0.30
Vigreux	30	5.1	6	4.2	7.3	0.33
Widmer	36	4.4	8.2	4.4	8.2	0.49
Spinning band	44	19.7	2.2	6.2	7.1	0.12

shows a widely differing value when *n*-heptane-methylcyclohexane is used instead of carbon tetrachloride-benzene. No similar observation could be found in the literature, though Fenske states that the process of enrichment is different for carbon tetrachloride-benzene than for *n*-heptane-methylcyclohexane. In the packed columns used by Fenske, carbon tetrachloride-benzene gives a slightly lower height of equivalent theoretical plate than *n*-heptane-methylcyclohexane. The difference is small, however, compared to the large difference observed in this case.

These preliminary data indicated the desirability of constructing a large column of the spinning-band type. Though the mechanical features do not seem to warrant the easy construction of a long column of this type, nevertheless a 545-cm. (18-foot) column has been built which has proved to be practical and inexpensive.

Construction of Still

The supporting frame of the column was made from two 5-cm. (2-inch) pipes held together at intervals of 73 cm. by crosspieces of boiler plate, welded in place and designed to facilitate the plac-

ing of the outer jackets. This frame was bolted to the wall and was sufficiently stable to be used as a ladder as well as a support.

The column consisted of a glass inner tube, about 6.7-mm. in inside diameter and 545 cm. long, not including the still head. It was made from 150-cm. (5-foot) lengths of Pyrex tubing which were easily fused together after lining them up in the frame of the still. The spinning band which revolved inside this long glass tube was made from strips of Monel metal 30 cm. long, 6 mm. wide, and 1 mm. thick, held together by links made from soft Monel metal wire having a diameter of 0.20 cm. This long spinner with no bearing but the glass tube was fastened to the pulley shaft by a piece of the same kind of wire. The spinner had a clearance of approximately 0.6 mm. and at speeds of 950 r. p. m. had practically no vibration. The still has been run continuously for more than a week at a time with no apparent wear.

Though the column is rather long, it was decided to have the heater coil jacket and insulating jacket made of glass in order to observe conditions inside the tube. This was made possible by constructing the two outer jackets in sections which could be slipped over the inner tube. The heater coil for each section was wound around a Pyrex glass tube, outside diameter 3 cm., which was 72.5 cm. long. The coil, which was made from 24 B. S. gage Nichrome wire 7.2 meters (24 feet) long (40 ohms), was first wound into a tight coil 3 mm. in diameter and then stretched and wound diagonally around the glass tube. Pieces of asbestos paper were placed under the coil and bent up partly to cover the coil. The outer insulating jackets were made from

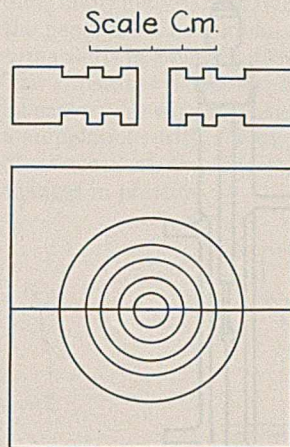


FIGURE 2. END AND TOP VIEW OF TRANSITE BLOCK

glass tubes of the same length and 5.2 cm. in diameter.

The boiler plate crosspieces placed at 73-cm. intervals between the 5-cm. (2-inch) pipes of the frame were 6 mm. thick and designed as shown in Figure 1. The hole in the center was large enough to allow the large outer glass jacket to go through, thus enabling one to slip the heater and insulating jackets over the lower end of the inner continuous tube and build the sections from the top down.

A side and top view of the Transite blocks which held the outer and inner tubes at each section end is shown in Figure 2. A hole was bored in the center of the block to fit the inner tube fairly tightly. Two circular grooves were cut on both the top and bottom of the blocks in which the outer jackets fitted. The blocks were then cut in half and, after placing them around the inner tube, were bolted to the iron crosspiece. Before the inner tube was built, the holes in the blocks were lined up and the holes to bolt the blocks to the frame were bored to make sure that the inner tube was perfectly in line.

A cross section of the Transite block with the heater and insulating tubes in place is shown in Figure 1, which is drawn to scale. Heater coil wires and thermocouple wires came out through holes in the Transite blocks. With the arrangement all-glass columns of any length can be readily constructed and easily taken apart for repairs.

The bottom end of the inner tube had an interchangeable ground-glass joint, while the still head was designed as shown in Figure 3. It was constructed with a trap at the bottom of the reflux condenser to enable all of the returning liquid to flow through the side tube. This allows one to take off a representative fraction at all times and to measure the return to the still. With a simple screw adjustment the rate of take-off can be readily regulated.

By fitting the spinner with a packing, the still can be used for vacuum distillation. It has been run at a pressure of 1 mm. for several hours without any difficulty in maintaining a vacuum. A 150-liter (40-gallon) drum was placed in the system to keep the pressure constant when fractions were taken off through the fraction cutter. The pressure above the boiler liquid, as measured by a manometer filled with butyl phthalate and calculated to mercury, was only 1.7 mm. This small pressure drop enables the still to be used for vacuum work.

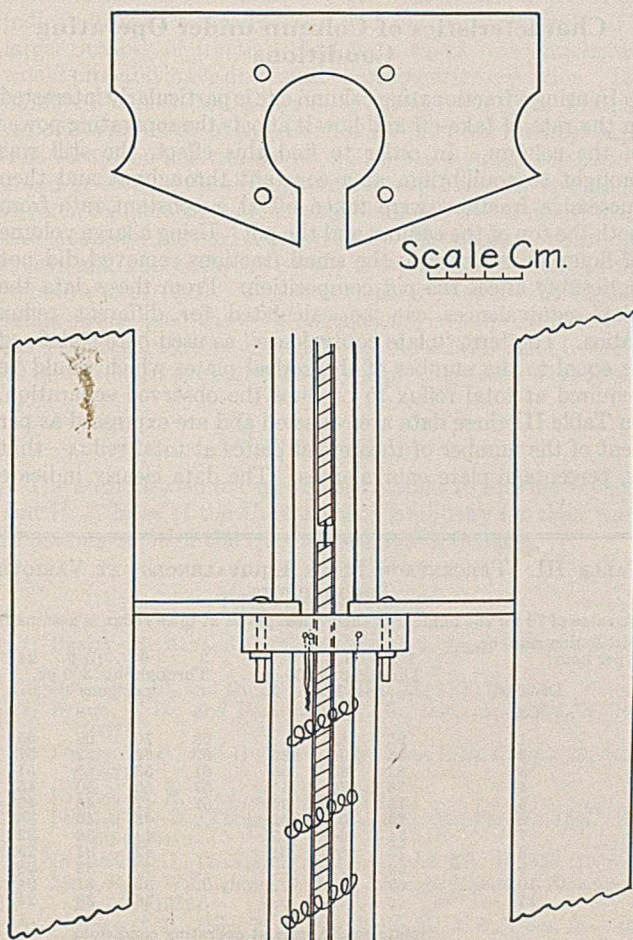


FIGURE 1. CROSS SECTION OF TRANSITE BLOCK
Heater and insulating tubes in place. Top view of iron crosspiece

TABLE II. DETERMINATION OF TIME TO REACH EQUILIBRIUM

Hours after Operating Conditions Reached	Frac-tion No.	Through-put per Min. Cc.	Refractive Index 20°		Mole Fraction <i>n</i> -Heptane		Theoretical Plates	H. E. T. P. Cm.
			Head	Pot	Head	Pot		
0.0 ^a	1	2.7	1.4010	1.4178	0.60	0.125	35.0	15.3
2.0	2	2.7	1.3933	1.4180	0.820	0.120	51.8	10.5
3.0	3	2.7	1.3906	1.4182	0.910	0.115	64.5	8.5
10.5	4	2.7	1.3904	1.4190	0.920	0.095	69.4	7.8
17.0	5	2.7	1.3898	1.4192	0.930	0.090	72.3	7.5
21.0	6	2.7	1.3908	1.4197	0.900	0.085	68.0	8.0

^a One hour required before reflux started and 0.5 hour later rate of throughput was adjusted to 2.7 cc. per minute. This was called zero time. Speed 980 r. p. m.

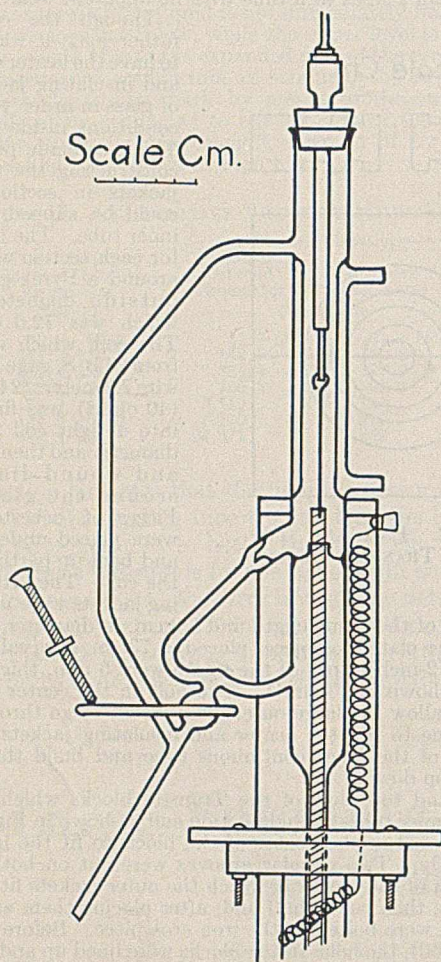


FIGURE 3. STILL HEAD

Characteristics of Column

The theoretical plate value of the still was determined by using a mixture of *n*-heptane and methylcyclohexane. Both compounds were distilled through the still and only those fractions were used which agreed with the index of refraction given in the literature. The plate value was calculated using the formula derived by Fenske (5) and a relative volatility value of 1.07 (1). The mole per cent values of the two constituents in the head and pot fractions were determined from the data of Bromiley and Quiggle (2).

Table II gives the data collected to determine the time necessary for equilibrium to be established. The still in 3 hours reached a plate value of 64.5 plates and then slowly climbed to an average of about 70 plates. These data were taken at a throughput of 2.7 cc. per minute. At a through-

put of 5 cc. per minute the value at equilibrium was 48 plates. This approaches the maximum throughput, as slight flooding was observed at the joints of the spinner. Lesesne (?) also observed that the plate value fell off with increased throughput. Increasing the speed to 1900 r. p. m. did not appreciably affect the plate value, which is also characteristic of the spinning-cone type of column.

The total holdup of the column, including the still head as measured by the method of Fenske (10), was only 7.9 cc. Subtracting the non-drainable holdup of the head—namely, 0.8 cc.—leaves only 7.1 cc. as the holdup of the column.

The nondrainable holdup of the still and head is 2.8 cc. A holdup as small as 7.1 cc. or 0.1 cc. per plate would allow one to fractionate as little as 25 cc. of liquid and at the same time have the separating power of a still rating approximately 70 theoretical plates.

All descriptions of columns in the literature stress the low height of equivalent theoretical plate and fail to mention the relationship between holdup and number of plates. This relationship controls the sharpness of separation and, when dealing with small quantities of liquids, is just as important as the height of equivalent theoretical plate. Where head room is available it is much better to have a column rating one theoretical plate for 7.0 cm. of height but holding 0.1 cc. of liquid than to have one theoretical plate for 1.0 cm. of height but holding 0.7 cc. of liquid. The data for this column indicate that it is outstanding in low holdup per theoretical plate and at the same time has a high separating power.

Characteristics of Column under Operating Conditions

In using a fractionating column one is particularly interested in the rate of take-off and how it affects the separating power of the column. In order to find this effect, the still was brought to equilibrium at a constant throughput and then successive fractions were taken off at a constant rate from both the top of the column and the pot. Using a large volume of liquid to start with, the small fractions removed did not noticeably affect the pot composition. From these data the plate equivalences can be calculated for different reflux ratios. The term "plate equivalence" as used here is defined as equal to the number of theoretical plates which would be required at total reflux to produce the observed separation. In Table III these data are collected and are expressed as per cent of the number of theoretical plates at total reflux—that is, percentage plate equivalences. The data clearly indicate

TABLE III. PERCENTAGE PLATE EQUIVALENCES^a AT VARIOUS THROUGHPUTS

(A value of 70 for the number of theoretical plates at total reflux is assumed)

Distillation rate, cc. per hour:	Throughput 160 cc. per hour			Throughput 300 cc. per hour			
	1.25	2.4	6.0	3	6	10.9	24
Distilled Cc.							
1	95	81	..	68	70	69	65
2	83	90	98	62	62	62	57
3	82	80	66	61	53	55	51
4	76	70	45	57	50	50	45
5	75	61	36	57	47	43	40
6	78	61	32	..	45	40	36
7	71	64	32	..	44	36	32
8	73	64	31	..	42	34	29
9	69	40	32	28
10	69	37	31	24
11	36	30	24

^a Arbitrarily defined as $\frac{\text{plate equivalence at operating conditions}}{\text{theoretical plates at total reflux}} \times 100$.

TABLE IV. THEORETICAL PLATES AND COLUMN EFFICIENCIES COMPARED TO TOTAL REFLUX

Reflux Ratio, L/D	Composition of Mole Fractions of Methylcyclohexane Pot Head		Theoretical Plates at Operating Conditions	Minimum Theoretical Plates at Total Reflux	Efficiency, %
Throughput 160 cc. per hour					
122.7	0.830	0.165	56	47	84.0
67.5	0.820	0.175	91	45	50.0
27	0.475	0.170
Throughput 300 cc. per hour					
100	0.740	0.160	51	40	80.0
50	0.470	0.135	41	26	63.4
27.5	0.375	0.125
12.5	0.275	0.110

that the separating power of the column rapidly decreases to a minimum and that this value is dependent on the reflux ratio. Being a batch still, this minimum value will not remain constant but the rate of change will be much slower than the change preceding this steady state.

To find the true theoretical plate value of the column under operating conditions, the method of Dodge and Huffman (4) was used. Only data at the point where the rate of change was very small were used, since it was evident that the number of theoretical plates under operating conditions decreased to this minimum value. These data are listed in Table IV in the fourth and fifth columns. The ratio of these two values expressed as per cent represents the efficiency of the column for the indicated operating conditions.

The data gave conditions that were not operative when the reflux ratio was less than 50. The enrichment is too large, indicating that a steady state had not been reached. If a larger number of fractions had been taken, the enrichment would probably have decreased to an operative condition. The number of theoretical plates at operating conditions of reflux ratio 67.5 and a throughput of 160 cc. per hour is rather high. The record of this run shows that some trouble was experienced in keeping the throughput constant, because of changes in room temperature. This would indicate that a steady state had not been reached and probably this number would decrease and approach the 84 per cent efficiency noted at the reflux ratio of 122.7. The data indicate that at the highest reflux ratios used the over-all efficiency is approximately 80 per cent regardless of throughput. At reflux ratios between 50 and 67.5 the over-all efficiency is probably near 60 per cent.

Acknowledgment

The authors wish to express their thanks to Flavius Wyman and H. J. Rose of the University of Kentucky for their work in making some of the calculations and drawings.

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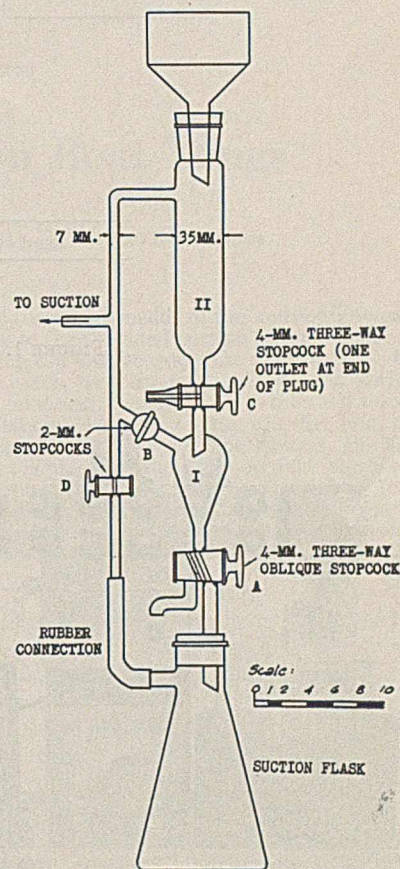
Suction Filtration Apparatus for Sampling Filtrates under Constant Pressure

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IN MANY laboratory operations requiring suction filtration, it is necessary to remove small portions of the filtrate in rapid succession for purposes of testing.

In order to obtain clear filtrates continuously while handling many materials on Büchner funnels, constant pressure on the paper must be maintained; a sudden release of the pressure results in a cloudy filtrate when the filtration is resumed. The apparatus illustrated has been satisfactorily used in this laboratory for several years. It eliminates slow and clumsy manipulations with a suction flask and allows rapid removal of aliquots of the filtrate without any disconnections or changes in pressure.



For normal operation, all stopcocks are opened, allowing the filtrate to flow into the suction flask. To sample the filtrate, close stopcock A, allow chamber I to fill with the desired quantity, close stopcock B, turn stopcock C allowing chamber I to come to atmospheric pressure, and draw off filtrate by turning stopcock A to the second position. Then close A, turn C to the off position, and slowly open B. The liquid, which has collected in chamber II, may be run into chamber I and drawn off, or it may be run into the suction flask. The suction flask may be removed at any time after A and D are closed.

Accurate Timing Equipment for Viscosity Determinations

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Standard Oil Development Co., Linden, N. J.

A method and apparatus for obtaining accurate timing for short intervals are described. The accuracy is better than ± 0.1 per cent on intervals of 100 seconds and over.

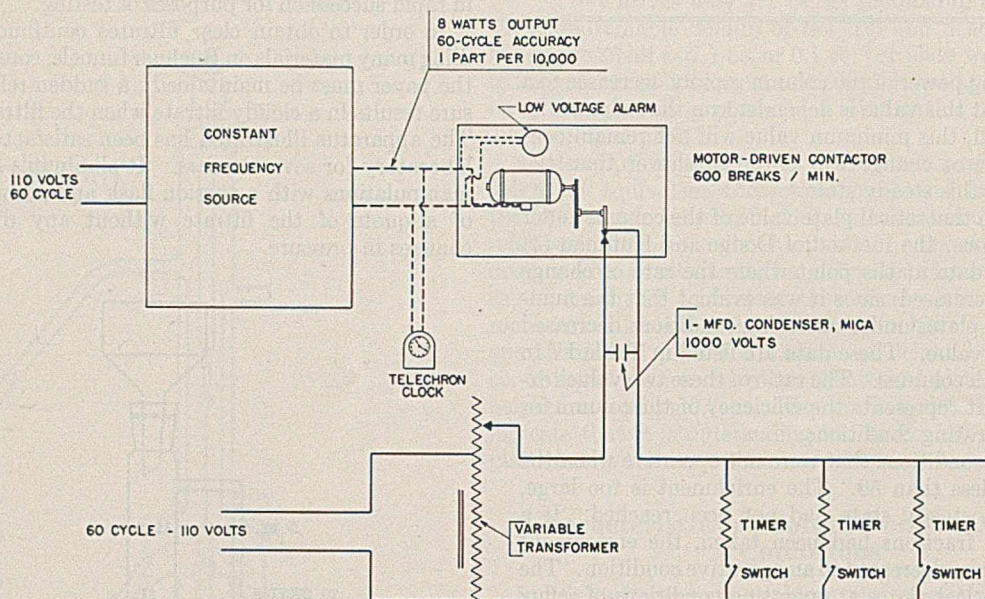


FIGURE 1. WIRING DIAGRAM OF TIMING SYSTEM

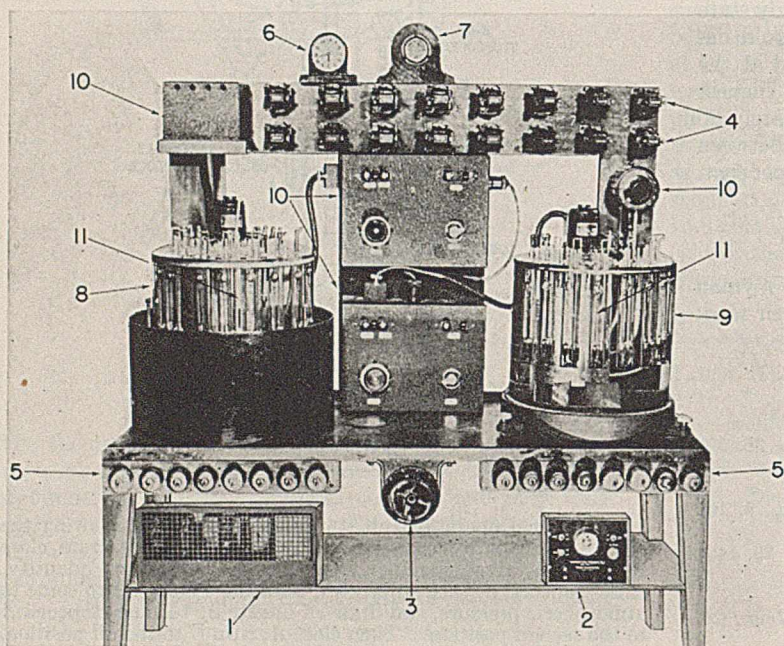


FIGURE 2. APPARATUS

- | | |
|---------------------------------|---|
| 1. Constant-frequency generator | 7. Voltmeter |
| 2. Motor-driven contactor | 8. 210° F. bath |
| 3. Variable transformer | 9. 100° F. bath |
| 4. Electric counters | 10. Temperature control equipment for baths |
| 5. Toggle switches | 11. Ubbelohde viscometers |
| 6. Telechron clock | |

THE determination of viscosities requires rigid control of both time and temperature if accurate measurements are desired. The timing problem has been particularly difficult to solve, since one is concerned not only with absolute time, but also with being able to reproduce short-time intervals with a high degree of accuracy.

This laboratory carries out daily a large number of viscosity determinations and has had considerable experience with various types of timing devices, all of which have presented some objectionable features. This statement applies particularly to stop watches. Electric clocks and timers normally are satisfactory, provided electric power of constant frequency is available. Even when the power is supplied by a large utility system, however, variations may be as high as ± 0.2 cycle, which may cause an error of ± 0.3 per cent in the timing. This accuracy has been improved upon by the installation of a constant-frequency generator and accessory apparatus which have been in use for almost 2 years and have proved satisfactory.

The electrical wiring diagram is shown in Figure 1. The constant-frequency generator consists of a tuning fork oscillator, the tuning

fork being enclosed in a partial vacuum. These units have an accuracy of better than 10 parts per million when they leave the factory. This is very much better than needed and an accuracy of 50 parts per million or 1 part in 20,000 is easily maintained with frequency variations of ± 2 cycles and fluctuations of ± 10 volts in the power supply. This unit was originally developed for manufacturers of timing equipment and uses standard radio tubes which can be obtained at any radio store. The generator need only be turned on when needed, because factory accuracy is obtained a few seconds after throwing the switch. As can be seen in Figure 2, the generator is a small and compact unit, about 18 inches long, 12 inches deep, and 10 inches high. The Telechron clock across the output of the oscillator is checked against Arlington time signals and a time-rate error of less than 0.3 second per day is obtained. The output of this generator is about 8 watts and, therefore, a special high-torque, low-power motor is required.

The motor-driven contactor, operated from the output of the generator, consists of a motor geared to an output speed of 600 r. p. m. In order to obtain good, snappy operation on the counters, the breaker points are set so that the circuit is closed for 135° and open for 225° on each revolution. The capacitance of the condenser across the breaker points shown in Figure 1 should be determined experimentally.

Various counting devices on the market operate on 110-volt 60-cycle power supply. With alternating current there is, however, an unfavorable heterodyning effect between the constant-frequency source which drives the motor-driven contactor and the power to the counters. This has the effect

of supplying varying amounts of power to the counters and, in order to eliminate any possible skipping, the voltage on the counters is controlled to 125 ± 2 volts.

This is easily done by means of a variable transformer, 3 (Figure 2). The voltmeter, 7, is connected across the output of the variable transformer and is mounted conveniently near the counters, 4, so that the operator can glance at it from time to time. However, it is felt that direct current-operated counters would eliminate this condition entirely. The use of direct current may introduce a little contact trouble, but with some experimentation the correct condenser across the breaker points will cut this to a minimum. With alternating current, no trouble whatsoever has been experienced with the breaker points and occasionally as many as twenty counters have been operated at one time.

In order to check the counters against each other, they are started and stopped in pairs. To check against the Telechron clock, the counters are started every minute until six or eight are running simultaneously. Then, after approximately 10 minutes, the counters are turned off in pairs. This procedure will compensate any error due to the operator. The switches, 5, are well constructed toggle switches, such as are used in regular electrical installations.

The ultimate accuracy in any short-period determination on this equipment is ± 0.1 second and in order to bring the timing accuracy to less than ± 0.1 per cent, total efflux times of about 100 seconds or over should be used.

A New Design of Combustion Boat Tong

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SKILLED workers are able to insert a combustion boat into a furnace with great agility, using a hooked wire. As an aid to the less skilled worker or in case the combustion boat has to be removed and replaced in the furnace at an exact position during a run, a very simple and useful type of combustion tongs has been designed in the author's laboratory. These tongs have been in use for over a year without upsetting a single combustion boat.

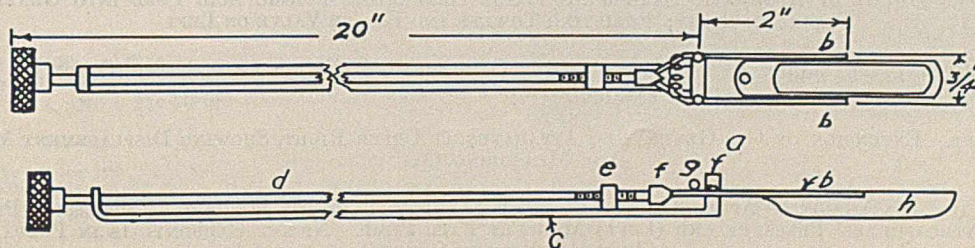
The tongs are illustrated in the drawing. The boat is firmly clamped during the time it is being placed in the combustion tube and being removed from it.

a is a brass disk of such diameter as to fit smoothly into the combustion tube. *bb* are small jaws pivoted on disk *a* in such a manner that the whole assembly slides smoothly in the tube. When parallel the jaws are spaced at the width of the combustion boat being used. *c* is a bar fastened to the bottom of *a*, and is about twice as long as the distance to be reached in the tube. The end is turned up as a guide for *d*.

d is a rod fitted with a knob for turning and with a threaded portion passing through a block, *e*, which is fastened to *c*. *f* is a cone on the end of *d*, against which the short ends of the jaws, *bb*, fit. *g* is a coil spring which keeps the short ends of the jaws tight against the cone.

In use, *d* is turned by means of the knurled knob and as it advances, owing to the threaded portion in *e*, the bent ends of *bb* are spread, causing the jaws to grasp the boat firmly. Before insertion in the furnace, the boat is placed on a flat surface, and the tongs are set on it and tightened. It is then slid into the furnace to some predetermined mark on the rod, the jaws are released, and the tongs are withdrawn. The disk, *a*, guides the tongs. Since the boat is placed in the tongs on a flat surface, it does not drop but is merely released. To remove the boat from the tube the tongs are slid into the tube to the mark and *d* is turned until the tension indicates that the boat is firmly grasped, when the boat may be easily and safely withdrawn.

The advantages of these tongs over the usual hooked wire are: (1) The boat is held firmly and rigidly while being moved in the combustion tube. (2) The position of the boat in the furnace is easily determined and may be reproduced exactly. (3) Boats are placed in opaque tubes with as great facility as in transparent tubes. (4) The tongs expedite the work in combustion analysis, provided that they are not used in furnaces whose temperature is above 500°C ., since at higher temperatures the spring and the brass are affected.

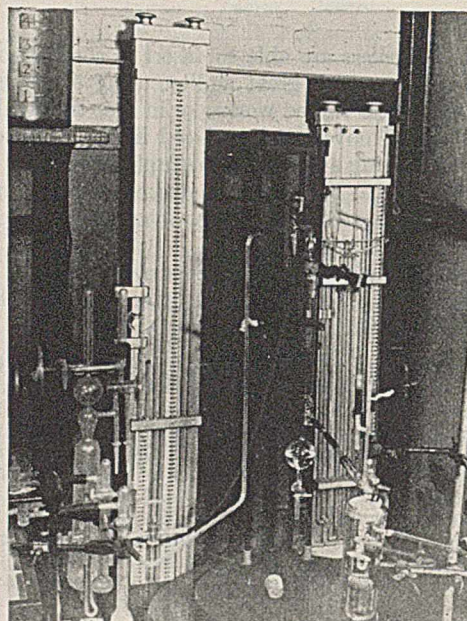
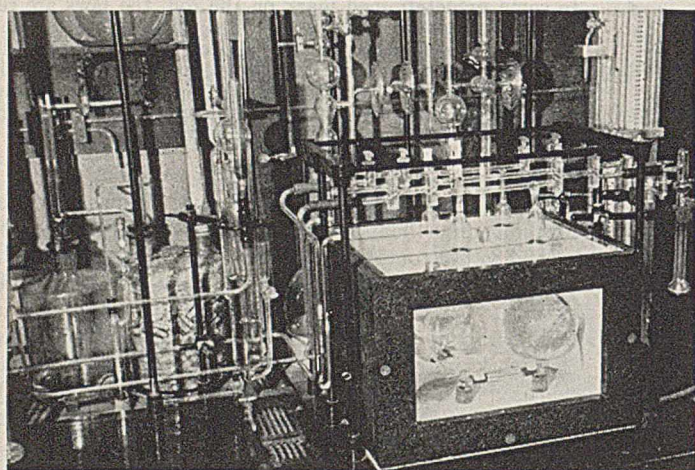
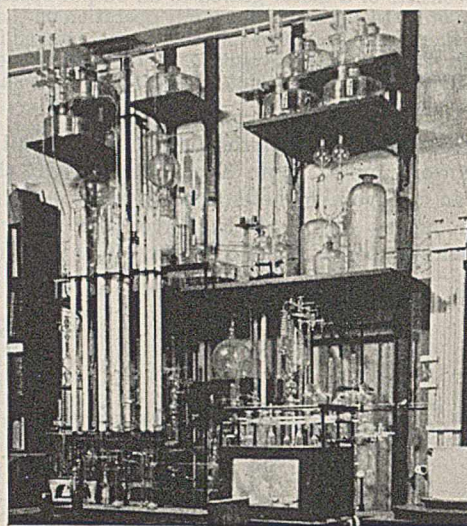
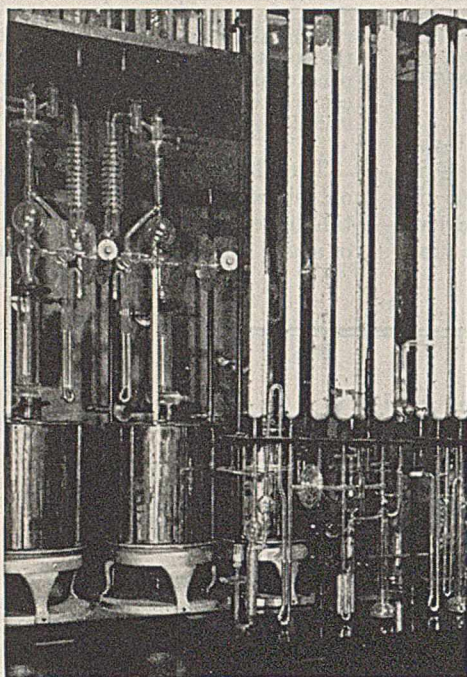


Research in Organometallic Problems

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THE accompanying photographs show research equipment devised and used at the University of Maine for research in organometallic problems. These studies involve preparing and handling the alkyl derivatives of zinc, phosphorus, mercury, and arsenic, as well as nickel carbonyl and various Grignard reagents.

Special precautions are taken to avoid contact with air, which would result in autoxidation, and to secure quantitative reaction studies. The automatic generation of carbon monoxide is especially convenient for metal carbonyl preparation, while nitric oxide is used in making nitrosyl derivatives and in other reactions.

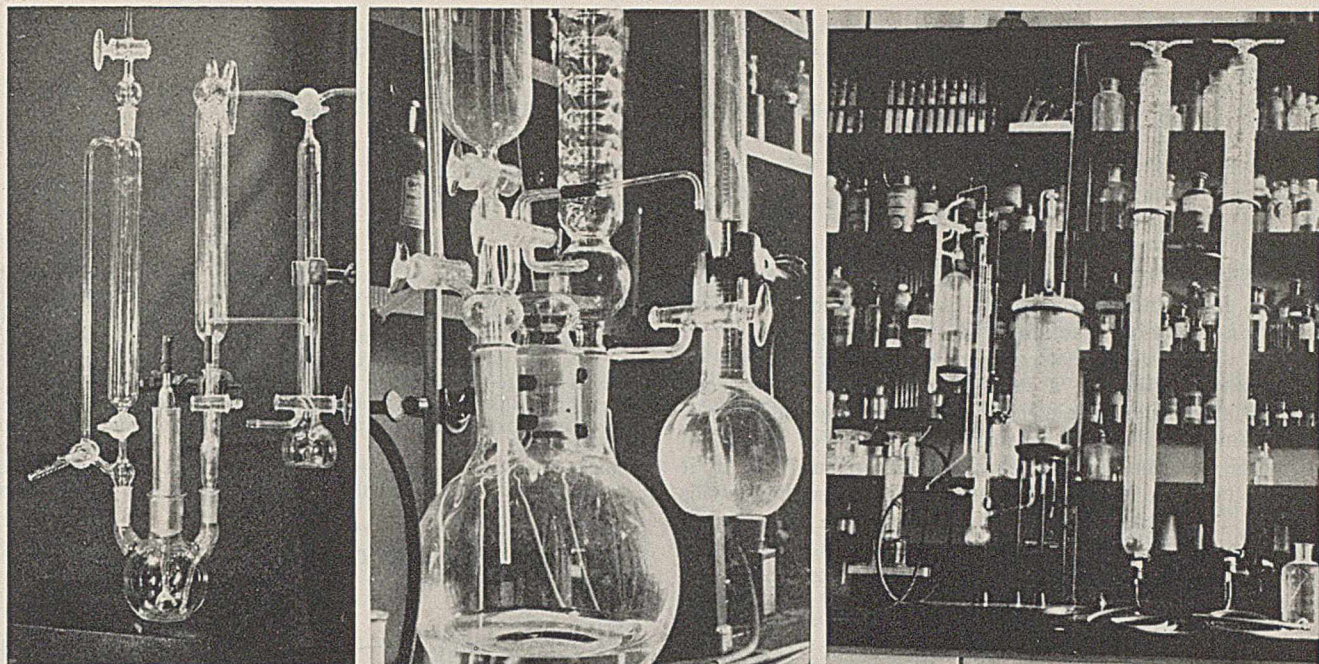


UPPER LEFT. DETAIL OF AUTOMATIC CARBON MONOXIDE GENERATOR; FORMIC ACID FEED INTO GENERATING FLASKS ON RIGHT; PURIFYING TOWERS AND ESCAPE VALVE ON LEFT

UPPER RIGHT. GENERAL VIEW OF GAS GENERATORS; CARBON MONOXIDE ON LEFT, NITRIC OXIDE ON RIGHT, METER BATH IN FOREGROUND

LOWER LEFT. EXTENSION OF GAS-GENERATING APPARATUS AT UPPER RIGHT, SHOWING DISPLACEMENT METERS FOR MEASURING GAS

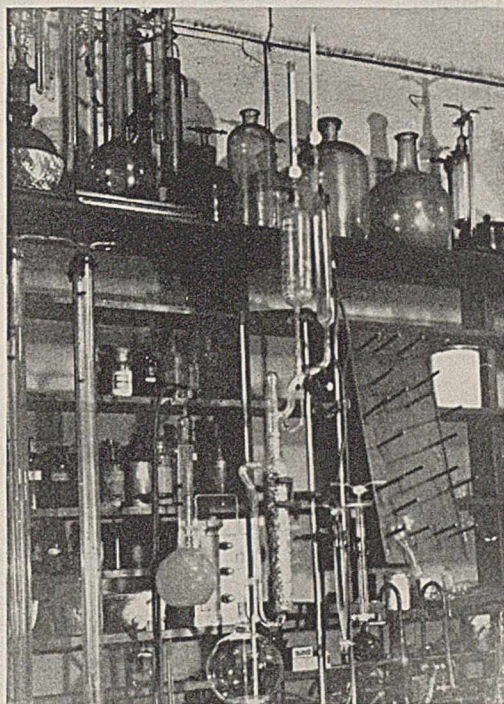
LOWER RIGHT. EXTENSION OF APPARATUS AT LOWER LEFT, SHOWING (RIGHT) MERCURY COMPRESSION PUMP TO REACH 3 ATMOSPHERES' PRESSURE AND (LEFT) MERCURY FALL PUMP. NICKEL CARBONYL IS IN PREPARATION (LIQUID IN BULB IN CENTER)



UPPER LEFT. A 250-ML. REACTION FLASK WITH SPECIAL STOPCOCK SYSTEM TO ALLOW ALL BORES AND CONNECTIONS TO BE SWEEPED WITH INERT GAS BEFORE ADMITTING ACTIVE LIQUIDS

UPPER CENTER. PREPARATION OF TRIMETHYL PHOSPHINE: 470 GRAMS OF ZINC METHYL (RIGHT) ABOUT TO BE ADDED TO REACTION FLASK. NOTE ARRANGEMENTS FOR SWEEPING

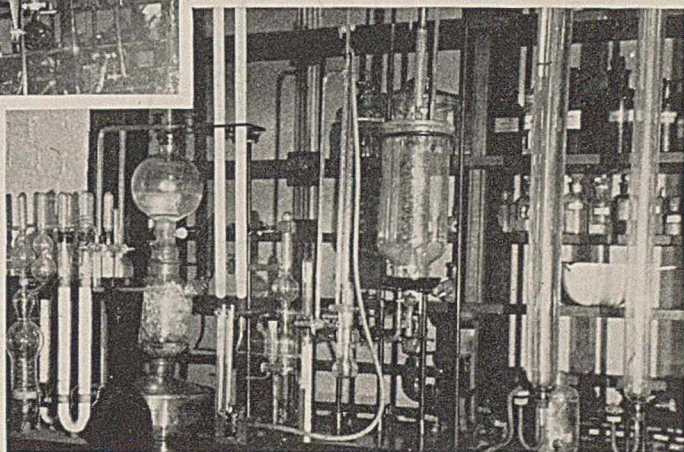
UPPER RIGHT. ZEREWITENOFF SETUP FOR ACTIVE HYDROGEN AND REACTIVE CARBONYL DETERMINATION, USING ETHYL ETHER AS SOLVENT



LEFT CENTER. PREPARATION OF A GRIGNARD REAGENT IN COLUMN OUTFIT. FINISHED REAGENT HAS JUST BEEN SIPHONED TO A REAGENT HOLDER FROM FLASK IN WHICH IT ACCUMULATED

RIGHT CENTER. PHOTOCHEMICAL EFFECT OF REACTION OF NITRIC OXIDE AND NICKEL CARBONYL

LOWER RIGHT. DETAIL OF ZEREWITENOFF OUTFIT, SHOWING PURIFYING JAR FOR REMOVING ETHER VAPORS, AND A MODIFIED REACTION FLASK



The photograph (right center) of W. L. Gilliland was taken in a darkened room by the light of the reaction. The vapors of nickel carbonyl give a slight initial reaction with pure nitric oxide. After this is complete, the resulting mixture will autoxidize on contact with air, producing voluminous white fumes of nickel nitrite; or it will ignite with a brilliant flash upon being

lighted. This flash does not represent oxidation by air, but a reaction between the constituents of the gas mixture, and can be produced in the absence of air. This is the first picture ever taken, using as a source of light this reaction, which was discovered a year ago and reported at the Boston meeting of the AMERICAN CHEMICAL SOCIETY.

Vacuum Tube Voltmeter

Application to Potentiometric Precipitation Titrations

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BIMETALLIC electrodes in potentiometric titrations have so far found their greatest utility in connection with oxidation-reduction reactions. During an investigation of the use of bimetallic electrodes, with particular emphasis on precipitation reactions, a vacuum tube voltmeter was assembled according to the specifications of Kinney and Garman (3). While this apparatus was satisfactory for oxidation-reduction reactions as Kinney and Garman had used it, it was too unstable for precipitation titrations described in this paper. Their circuit was modified to increase the stability of the apparatus to permit such titrations, thus widening the utility of such systems.

Description of Voltmeter

The circuit diagram is shown in Figure 1. A Cunningham Radiotron vacuum tube, type 22, was selected because it seemed to have the most desirable characteristics (5) for the purpose at hand.

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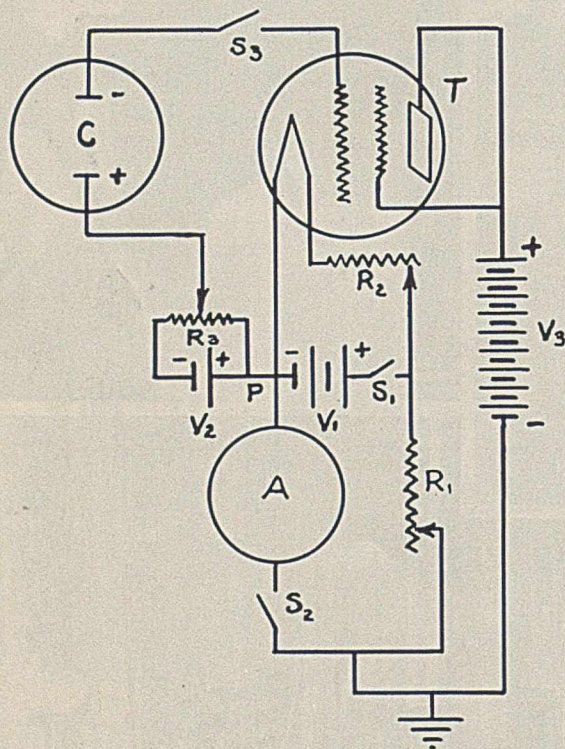


FIGURE 1. VOLTMETER

- A. Microammeter (scale 0-300)
- C. Titration cell
- R₁. 5000 ohms
- R₂. 25 ohms
- P. 10,000-ohm panel-type potentiometer
- S₁, S₂. Switches
- S₃. Control grid switch
- T. Vacuum tube, type 22
- V₁. 4-volt storage A battery
- V₂. 2-volt storage C battery
- V₃. 45-volt dry B battery

The positive pole of the 2-volt battery, V₂, was connected to the negative pole of the 4-volt battery, V₁, thus allowing the 6-volt storage battery to serve a double purpose. As a precaution against drift and instability the vacuum tube and other parts easily affected by stray currents were enclosed in a copper screen-covered box, which was electrically grounded. Controls through a Bakelite panel led into the box to operate the filament rheostat, a battery switch, the panel-type potentiometer, and the control grid switch. The vacuum tube was placed inside the box in a stoppered glass cylinder, in the bottom of which was placed a layer of Desicchlora to maintain a dry atmosphere.

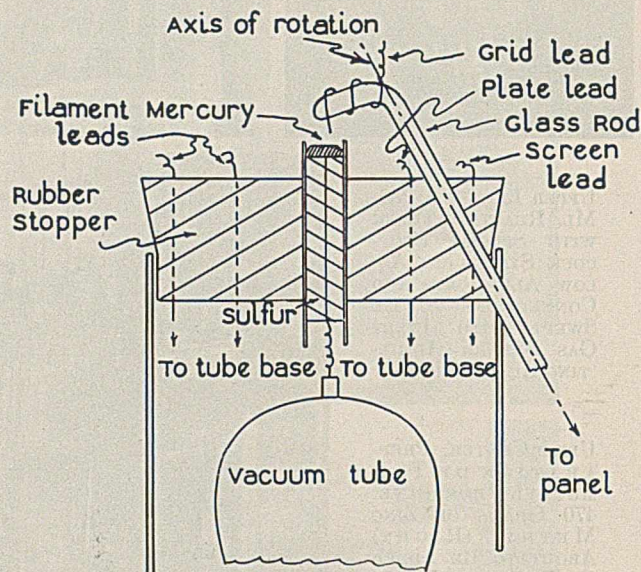


FIGURE 2. CONTROL GRID SWITCH AND MOUNTING

The cylinder was closed with a rubber stopper through which passed the electrical leads from the tube socket terminals. The wire from the grid of the tube also passed through the stopper but was insulated from it by encasing in a 1-cm. glass tube and filling with sulfur. The control grid switch was mounted on the rubber stopper as shown in Figure 2. The top part of the glass tubing which carried the grid lead through the stopper was used as a cup for the mercury grid switch. A flexible insulated wire on the shaft of the switch led out of the box to the titration cell. The length of the grid lead from the tube to the titration cell was less than 15 cm. (6 inches).

Tests with the apparatus showed its free grid potential to be -0.23 volt and its voltage sensitivity to be 3.2 millivolts per microampere. Although this voltage sensitivity was adequate for the determination of the end points for most of the reactions investigated, an increased sensitivity of 1.25 millivolts per unit scale of deflection resulted from substituting a galvanometer (Leeds & Northrup No. 2320 D. current sensitivity 5×10^{-7} ampere) for the microammeter (Weston direct current microammeter Model 1). The maximum current flowing through the grid while operating near the free grid potential was found to be less than 3×10^{-11} ampere.

Operation of Instrument

The electrodes were conveniently mounted upon, and insulated from, the frame of the motor stirrer. The electrodes were connected so that the increasing negative pole was attached to the grid lead of the vacuum tube. With switches S₂ and S₃ (Figure 1) open, S₁ was closed. With the aid of a voltmeter not shown in the figure, R₂ was adjusted so that 3.3 volts were applied to the filament of the tube. Switch S₂ was then closed and by adjust-

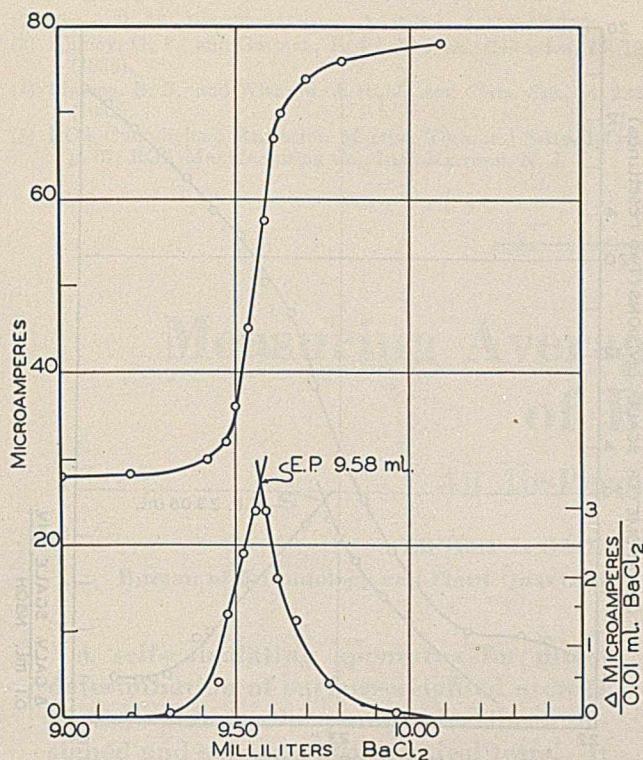


FIGURE 3. TITRATION OF SULFATE WITH BARIUM

ment of R_1 the microammeter needle was set at any convenient value. The grid was then set at free grid potential by closing switch S_3 and adjusting R_3 until the microammeter needle was again at its original setting. By adjusting the grid to free grid potential before titration was begun and by connecting the electrodes in the manner indicated, the grid was prevented from becoming positive during the titration.

Many vacuum tube voltmeters described in the literature are more elaborate, costly, and sensitive than necessary for use with bimetallic electrodes in titrations such as those described in this paper. The apparatus as described here is characterized not only by its simplicity but also by its stability. Its free grid potential with respect to the negative end of the filament is 0.23 volt and at the beginning of a titration adjustment to this voltage is easily made in the manner described. The filament of the vacuum tube operates on only 0.13 ampere. Although the storage cells furnish a current of this magnitude with little fluctuation, the same storage cells are used to balance out the initial steady portion of the plate circuit. Thus any fluctuation in the current from the filament battery is minimized in its effect on the microammeter in the plate circuit. Under the conditions of operation no fluctuation of the microammeter needle could be detected over a 30-minute period. During the course of a titration the change of potential between the electrodes of the titration cell would produce corresponding changes in the microammeter reading. Except near the end point only a few seconds were required for the potential between the electrodes to reach a steady state. If a well-defined end point was not apparent from the titration data, it was obtained graphically by plotting the change in microamperes per unit volume of titrant against the corresponding volume of titrant.

Precipitation Reactions

Bimetallic electrodes have not been extensively used in the potentiometric titration of ions by precipitation reactions. One reason for this has been the small and somewhat variable

potential change at the end point in most titrations. In the titration of the halides with the silver ion various electrode pairs have been used. It has been suggested (6) that in this titration the indicating electrode becomes plated with silver and then acts as a silver electrode. On the other hand, in acid-base titrations French and Kahlenberg (1) believed the potential between the electrodes to be due largely to absorbed gases, that caused the electrodes to function as gas electrodes. In the titration of magnesium (4) or copper (2) ions with sodium hydroxide it is probable that the indicating electrode acts as a gas electrode.

Using the apparatus described above, it was easy to detect the end point of certain precipitation reactions. Not only was chloride titrated with silver ion and magnesium ion with hydroxyl but sulfate was titrated with barium ion. The titration time varied between 5 and 15 minutes, depending upon the titration reaction, the electrodes, and the rate of stirring.

DETERMINATION OF SULFATE. For the titration of sulfate 10 ml. of a standard potassium sulfate solution were placed in a 150-ml. titration beaker and 50 to 60 ml. of water plus 25 ml. of acetone were added. Natural graphite was used as the reference electrode and approximately 7.5 cm. (3 inches) of No. 20 tungsten or platinum wire as the indicating electrode. The solution was vigorously stirred as the barium chloride solution was added. After each addition of barium chloride sufficient time was allowed for the electrodes to reach a steady state as indicated by the microammeter. Table I shows typical data obtained during a titration. The end point can be determined by inspection of the data, but they have been plotted in Figure 3 to show graphically the sharpness of the end point.

The barium chloride solution was prepared 0.5000 *M* by weighing pure barium chloride dihydrate as a primary standard. Analysis of this solution for its barium content by precipitating and weighing barium sulfate verified this concentration at least to within 1 part in 2500. For titration of 10-ml. aliquot portions of the potassium sulfate solution 9.58, 9.57, 9.54, 9.56, 9.56, and 9.60 ml. of the barium chloride solution were required. This indicated 0.383 gram of sulfur trioxide to be present per aliquot, whereas 0.399 gram of sulfur trioxide had been the value obtained by weighing the potassium sulfate as a primary standard as well as by precipitating and weighing barium sulfate.

The precision of the potentiometric titration was satisfactory, but the results were about 4 per cent low. Though its accuracy was such that this method of titration cannot be recommended for quantitative work, the results have considerable theoretical interest because the end point of such a titration can be detected with bimetallic electrodes. However, no theory is presented to account for the manner in which the indicating electrode functioned. The change in

TABLE I. TITRATION OF SULFATE WITH BARIUM

BaCl ₂ ML.	Microamperes	Microamperes 0.01 ML.
9.00	28	0.0
9.20	28	0.1
9.42	30	0.4
9.47	32	1.3
9.50	36	2.2
9.54	45	3.0
9.58	57	3.0
9.61	66	2.0
9.63	70	1.3
9.71	74	0.5
9.82	76	0.1
10.10	78	

End point, 9.58 ml.

potential at the end point was not great but was definite. The potential across the titration cell attained a steady state in the presence of a water-acetone mixture more readily than in a water medium. Thus the presence of the acetone enabled greater speed in titration and it was added for this reason.

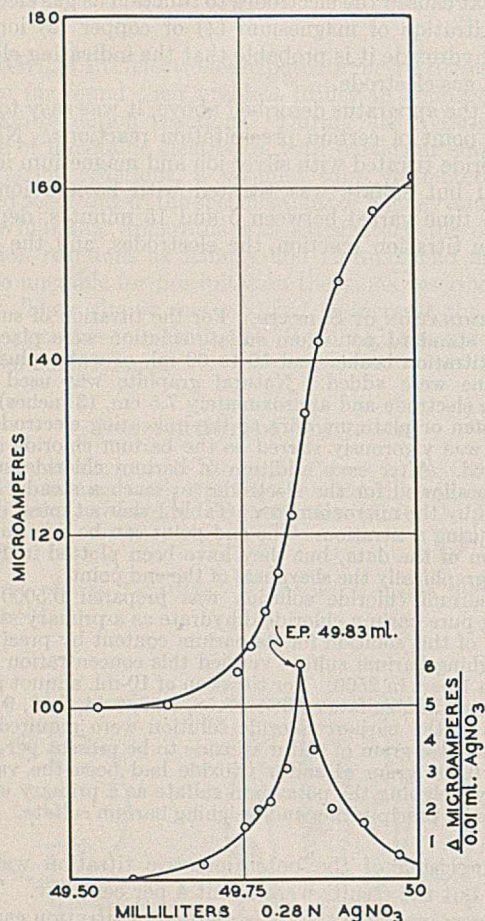


FIGURE 4. TITRATION OF CHLORIDE WITH SILVER

DETERMINATION OF CHLORIDE. Solutions containing chloride were titrated with 0.28 *N* silver nitrate. The same electrodes and titration technique described in the previous section were used except that the addition of acetone was unnecessary. Using 25-ml. aliquots of a sodium chloride solution 49.83 ml. of 0.28 *N* silver nitrate were required for each of three potentiometric titrations. A Mohr titration checked this value to within 0.02 ml. Figure 4 shows the curve for one of the potentiometric titrations. The end point is so sensitive that it is possible to use more dilute silver nitrate solution in the titration of smaller chloride samples. No attempt was made to establish the minimum feasible concentration of silver nitrate, but a very sharp end point resulted with 0.028 *N* solution.

DETERMINATION OF MAGNESIUM. For the potentiometric titration 25 ml. of magnesium chloride solution were diluted to 70 ml. to prevent splattering during titration. In some cases (Table II) 20 ml. of acetone or ethyl alcohol were included in this volume. These solvents allowed the end point to be detected more easily than when using only an aqueous medium. Platinum and tungsten were found to be the best indicating electrodes and a buret electrode (?) was used as a reference electrode because of the protection it offered against absorption of carbon dioxide from the air by the sodium hydroxide solution during titration. The sodium hydroxide solution was prepared carbonate-free by precipitating the carbonate with an excess of barium ions. This solution was determined to be 0.2283 *N* by standardizing against potassium acid phthalate using phenolphthalein as the indicator. The magnesium chloride solution contained 0.0642 gram of magnesium per 25 ml. of sample, as

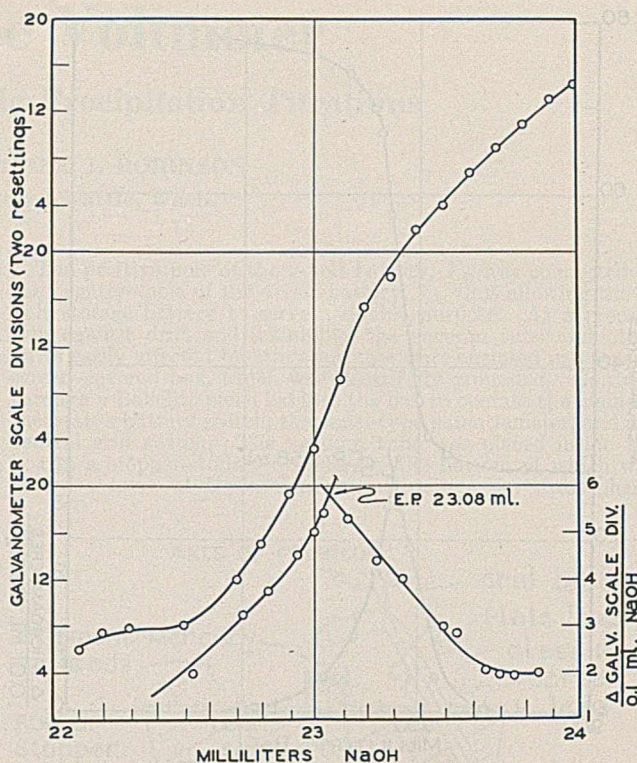


FIGURE 5. TITRATION OF MAGNESIUM WITH HYDROXYL

determined by gravimetric analysis in which $MgNH_4PO_4 \cdot 6H_2O$ was precipitated and $Mg_2P_2O_7$ was weighed. The magnesium chloride solution had a pH of 6.4 as prepared. The data for the titration of magnesium ions with sodium hydroxide are listed in Table II and a typical titration curve is shown in Figure 5.

In passing from an excess of magnesium to an excess of hydroxyl at the end point, the potential change was so small that it was advisable to substitute a galvanometer for the microammeter. The change was only about 10 to 15 microamperes, whereas in the titration of a strong acid with a strong base an abrupt change of about 70 microamperes was noted. Notwithstanding the small change in potential at the end point, it was sufficiently abrupt to be detected with considerable precision and accuracy by the use of the galvanometer.

TABLE II. TITRATION OF MAGNESIUM WITH HYDROXYL
(0.0642 gram of Mg present per sample)

Sample No.	Indicating Electrode	Mg Found Gram	Error %
1	Pt	0.0640	-0.3
2 ^a	Pt	0.0641	-0.16
3 ^a	Pt	0.0640	-0.3
4 ^a	Pt	0.0641	-0.16
5 ^b	Pt	0.0640	-0.3
6 ^b	Pt	0.0640	-0.3
7 ^b	W	0.0640	-0.3
8 ^b	W	0.0640	-0.3

^a 20 ml. of acetone present in 70 ml. total volume.

^b 20 ml. of ethyl alcohol present in 70 ml. total volume.

Summary

A one-tube vacuum tube voltmeter which is inexpensive and easy to operate allows rapid titrations to be performed with simple electrodes. The instrument has been applied to the titration of sulfates, chlorides, and magnesium as well as to the more common oxidation-reduction titrations.

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ABSTRACTED from a thesis by Lloyd E. West submitted to the Graduate Faculty of the University of Washington, 1939, in partial fulfillment of the requirements for the degree of doctor of philosophy. Contribution No. 96 Oceanographic Series.

Measuring Average Particle Diameter of Powders

An Air-Permeation Apparatus

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A self-calculating apparatus for direct determination of surface-weighted average particle diameter of powders has been designed and subjected to practical tests. It consists of a device for determining the average or effective particle diameter of a powder as deduced through Carman's specific surface equation from its permeability to air when the sample is formed into a compact bed. The operation of the device is remarkably convenient, simple, and economical of both time and material. The automatic-calculating feature reduces to a minimum the work of a determination and the chances of making mistakes. In precision and accuracy the method employing this apparatus compares favorably with the usual methods of granulometric analysis for powders.

THE present-day emphasis on particle fineness, in the production of powders for insecticides and for various uses, has increased the need for a rapid, convenient method of evaluating the fineness of powders below the range where sieve measurements are applicable. Because of the great size dispersion found in most commercial samples, and the lack of analytical detail obtained near the fine end of the range, a size-distribution analysis is usually not a sufficient basis for calculating average diameter. This is true because the finer particles are harder to measure accurately, while they have more influence on the surface-weighted average than the coarser particles.

The apparatus here described is a useful adjunct to any equipment for granulometric analysis of powders, in that it indicates the surface-weighted average diameter directly, independently of any distribution analysis, sedimentation experiments, or microscopic measurements. No calculations are required, provided the density of the material is known in advance. Problems of solubility do not enter, as they do in sedimentation, and the sample is not consumed or altered in

the experiment, but may be returned to the stock bottle for use in other work.

The working of the instrument is based on the fact that a current of air flows more readily through a bed of coarse powder than through an otherwise equal bed of fine powder—that is, equal in shape of bed, apparent volume, and percentage of voids, but by reason of difference in general coarseness of material differing in average pore diameter and in total interstitial surface.

This principle, as applied to liquid currents rather than air currents, was used by Carman (1) in many experiments for determining the specific surface of granular materials. The same principle, as applied to air currents, was employed by Traxler and Baum (6) for the determination of average pore diameter, and more recently by Dalla Valle (2) for the determination of surface area in coarse sand. Concurrently with the original drafting of the present paper there appeared a report of air-permeation experiments by Lea and Nurse (5), which lends excellent support to the indications of the authors' experience that the usefulness of air permeation for determining surface functions extends well into the range of fine powders.

The design for the apparatus here described is based largely on the diagram of Traxler and Baum, but embodies several major modifications. The mathematical formulas involved are derived from Carman's specific surface formula, by the conversion of conditions of liquid flow to those of air flow, and by the change from specific surface to surface-weighted average diameter as the dependent variable. By suitable standardization of the conditions of operation the number of independent variables is reduced to a minimum, making possible the plotting of a graph to serve as a sliding scale for the air-flow indicator, such that the evaluation of the sample as to average diameter is read directly, in microns.

Basis for Computing Average Diameter

It has been pointed out by Green (3) and by Carman (1) that, of the many kinds of average particle diameter for a powder, the most important is the average that is equal to the diameter of a sphere equivalent in specific surface to the sample as a whole. For spherical particles this is simply an average diameter by surface weighting; for particles of any shape it is twice the average normal radius by surface weighting. The value of this average diameter, either for a single particle or for a group, is six times the total volume divided by the total surface, regardless of particle shape or size distribution.

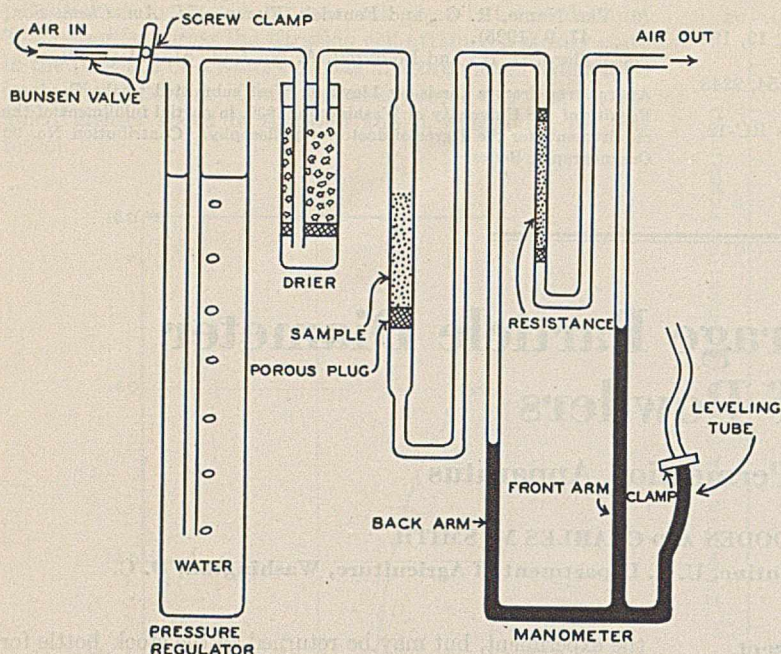


FIGURE 1. DIAGRAM OF MECHANICAL SYSTEM IN AIR-PERMEATION APPARATUS

to be encountered in practice is approximately 40 to 80 per cent.

Method of Calculation

It is obvious that under uniform conditions of observation a coarse powder will cause the manometer indicator to stand at a relatively high level and a fine powder will make it stand at a lower level. A basis for quantitative interpretation is found in the following considerations.

Carman (1), working principally with liquids, has shown that the specific surface of particles forming a granular bed is related to the porosity and permeability of the bed by the equation

$$S_0 = \sqrt{(g/k K \gamma)} [\epsilon^3/(1 - \epsilon)^2] \quad (1)$$

where S_0 = specific surface in sq. cm. per cc., g = the gravitational constant in cm. per second per second, k = a proportionality constant with a value of 5.0, K = a permeability constant, representing apparent linear velocity per unit hydraulic gradient, and expressed in cm. per second, γ = kinematic viscosity of the fluid in stokes (sq. cm. per second), and ϵ = the fractional free volume, or ratio of volume of voids to total volume of bed.

Mechanical System

A diagram of the mechanical system is given in Figure 1. Air is introduced at the connection labeled "air in", near which the rubber tubing constituting the air line of the apparatus is slit to form a Bunsen valve, for protection against danger to the apparatus from excessive pressure. From here the line passes through a screw clamp, which serves as a fine-adjustment control for the air influx. A standpipe, kept filled with water to a certain permanent level, serves to fix the pressure of the air at the point of introduction to the sample, the excess pressure being released in bubbles escaping through the water. The air retained in the main stream flows through a calcium chloride drying tube and then downward through the sample tube, in which the powder is supported by a porous plug formed by a wad of No. 40 copper wire compacted in place. (The resistance of plug and drier is found by observation to be insignificant, and experience indicates that the effect of the plug on the structure of the bottom layer of powder is negligible.)

The air passes thence through a column of compacted fine sand situated between the upper ends of the two arms of a water-filled manometer. The manometer and the resistance formed by the sand column together constitute a flowmeter, while the manometer, in showing the pressure drop across the sand column, gives by difference the pressure drop across the other resistance, the powder sample. The sand column is substituted for the common capillary-tubing type of resistance, because the resistance required is too great for convenient production and reproducibility in the tubing type. The sand is held in place by porous plugs, of the kind described above, one at each end of the column. The manometer is provided with a flexible leveling tube, closed by a suitable clamp such as a pinchcock. Only the rising arm of the manometer, called the "front arm", is used in making readings, the back arm being mounted out of sight within the apparatus housing, along with all the other parts that do not require frequent access.

Mounted on the same base with the above system, but not shown in the diagram, is an electric vibrator, of an inexpensive therapeutic type, used to assist in compacting the sample if necessary. Very free flowing materials may be measured without compaction; those that flow somewhat less freely may be brought to uniformity by a little tapping on the side of the sample tube with a pencil or some light wooden object; samples in which pockets or channels persist must be tapped more vigorously, by hand or by the power vibrator. It is not necessary to obtain any certain degree of compaction, but essential that the porosity be as nearly uniform as possible (6). The porosity may be accepted as uniform when the apparent volume remains constant, or reaches constancy, under some particular system of steady lateral tapping, if at the same time there are no visible pockets, cracks, or other marks of uneven distribution. The magnitude of the lowest obtainable porosity is dependent upon the fineness and type of material. The range of acceptable porosities likely

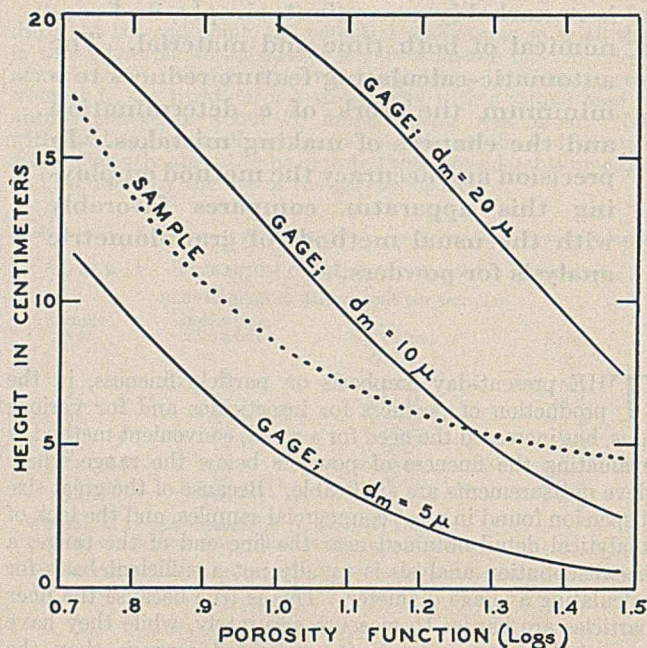


FIGURE 2. METHOD OF PLOTTING CALCULATOR GRAPH

This equation may be put into more convenient form for use with air currents by replacing $K \gamma$ with $K_2 \eta$, in which η = viscosity in poises (grams per cm. per second) and K_2 = permeability expressed as apparent linear velocity per unit pressure gradient (cm.⁴ per gram per second). By apparent linear velocity is meant the volume rate of delivery of air from the apparatus at atmospheric pressure divided by the internal cross-section area of the sample tube.

By substituting for S_0 the equivalent $6/d_m$, expressing K_2 and ϵ in terms of the observational data required for their determination, simplifying terms, and changing the unit of diameter, there is obtained the formula

$$d_m = \frac{60,000}{14} \sqrt{\frac{\eta C F D L^2 M^2}{(V D - M)^3 (P - F)}} \quad (2)$$

in which d_m = average diameter in microns, η = viscosity of air in poises, C = conductance of the flowmeter resistance in cc. per second per unit pressure (gram per sq. cm.), D = density of sample in gram per cc., L = length or height of the compacted sample—i. e., depth of bed—in cm., M = mass of sample in grams, V = apparent volume in cc. of compacted sample, P = over-all air pressure in grams per sq. cm., and F = pressure difference in grams per sq. cm. across the flowmeter resistance.

If a sample weight is chosen numerically equal to the density so that the true volume is 1 cc., and if, as is allowable for practical purposes, the viscosity of air is considered constant and the density of water equal to unity, the last formula may be simplified to the form

$$d_m = \frac{cL}{(AL - 1)^{3/2}} \sqrt{\frac{F}{P - F}} \quad (3)$$

in which c is a new constant and A is the cross-section area of the sample tube. P and A being maintained constant, the dependent variables are now only two, L and F . The right-hand side of the equation consists of two functions. That part coming before the radical, its value varying only with changes in porosity, may for brevity be designated the porosity function; the remainder, in which F is the only variable, may be designated the flow function.

Automatic Calculator

A method of constructing a graphic calculator for the apparatus is illustrated in Figure 2. With an assumed value of d_m , gage heights as ordinates are plotted against porosity-function values as abscissas, by Formula 3, gage height being numerically equal to $F/2$ if the two arms of the manometer are equal in cross-section area. The horizontal scale may be logarithmic to save space. Other curves are plotted in like manner, with suitably chosen values of d_m , to cover the whole range of diameters from 0 to 40 or 50 microns. Three examples of these curves are given in Figure 2, corresponding to 5, 10, and 20 microns. Upon the same graph sample height, L , is also plotted against porosity function; the resulting curve is represented by a dotted line.

For reference purposes the graph is now complete. With a given sample height the value of the porosity function is immediately fixed, and with the porosity-function value thus given the average diameter signified by any gage height is easily obtained by reference to the d_m curves.

For greater convenience in practical use the calculator is further simplified. The sample tube and the upper part of the front manometer arm are mounted side by side in a vertical position on the panel formed by the front wall of the apparatus housing. The manometer arm mounting is permanent; the sample tube is held accurately parallel to the manometer arm by two spring clips. The calculator graph is drawn with the vertical scale actual size, and the sample-height (dotted) curve is given a horizontal shift equal to the center-to-center separation of the sample tube from the manometer arm. All mathematical notations are eliminated, except the average-diameter values, with which the solid curves are labeled, and the porosity-function axis is designated simply as the "base line". The graph is attached to a slide mounted on the instrument panel and just back of the sample tube and gage indicator. The base line serves as a zero line for the gage.

When a determination is to be made, the required amount of material (mass in grams numerically equal to density in grams per cc.) is loaded into the sample tube by pouring in a fine stream, and then examined for uniformity and compacted, if necessary, according to directions given in the last part of the section "Mechanical System". The tube containing the sample is inserted in the air line by rubber-tube connections, and is then placed behind the spring clips, with the bottom of the sample adjusted to the level of the base line on the calculator. The slide is shifted in its track to such a position that the dotted line marks

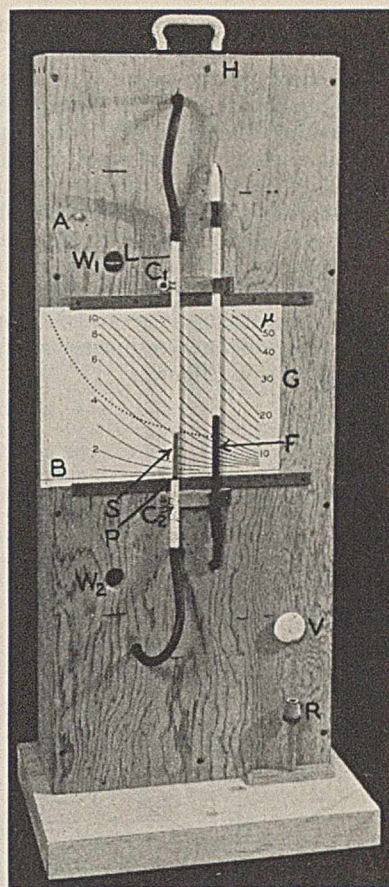


FIGURE 3. AIR-PERMEATION APPARATUS

the top of the sample; the air supply is turned on and adjusted to give gentle bubbling; the gage rises slowly for a few minutes and then comes to rest in a position to indicate directly the average particle diameter of the sample.

Photograph of Apparatus

A front view of the apparatus is given in Figure 3. Here are shown the gage indicator or front manometer arm, F , filled with colored water; a sample, S , supported within the sample tube by the porous plug, P ; the spring clips, C_1 , C_2 , holding the sample tube in place; the calculator graph, G , consisting of the base line, B , and an ample set of curves; the knob, A , of the air-control screw; the windows, W_1 , W_2 , through which the bubbles in the pressure regulator are observed; the water-level mark, L , seen through the upper window; the protruding vibrator head, V , which is activated by an electric mechanism concealed behind the panel; a one-hole rubber stopper, R , which holds the sample tube in place while the vibrator is being used; and the handle, H , by which the apparatus is carried.

In the picture the gage is indicating an average diameter of approximately 12 microns. While there is considerable latitude in the dimensions allowable for various parts of the apparatus, a general idea of the orders of magnitude may be obtained from the fact that the over-all height of the instrument here pictured is approximately 90 cm. (3 feet).

Quality of Performance

With regard to operation and performance, three of the best features of this device are convenience, simplicity, and speed. The total time required for a determination, including weighing out the sample (the density being known in advance), is only a few minutes for coarse or free-flowing fine samples; some extremely fine samples may take an hour because of the difficulty of compacting to uniformity. Results

are reproducible within 5 per cent over the range 1 to 50 microns.

For a practical check on the accuracy of this method, a series of tests was run on size fractions of a silica powder, the results by the air-permeation apparatus being compared with microscopic measurements. In microscopic work for this purpose it is essential to account for the third (vertical) dimension, which is often neglected in microscopic observations. When this dimension is the smallest of the three, as it is likely to be, it has the greatest influence on the surface-weighted average. For example, in the case of a rectangular parallelepiped with its three dimensions in geometric proportion, the surface-weighted average of the three dimensions is smaller than the intermediate dimension (Figure 4).

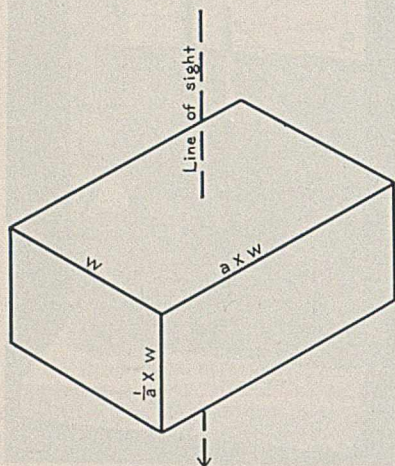


FIGURE 4. RECTANGULAR PARALLELEPIPED WITH DIMENSIONS IN GEOMETRIC PROPORTION

Average of two dimensions by microscope greater than W . Surface-weighted average of three dimensions, equal to diameter of sphere equivalent in specific surface, less than W

When the equivalent spherical diameter (with regard to specific surface) of an irregular granular material is to be determined microscopically, a first approximation can be obtained by considering the particles as spheres, each with a diameter equal to the minor projected axis (probably the intermediate axis) of the corresponding irregular particle. This first approximation, however, is subject to a correction factor dependent on the shape habit of the material, and in the absence of a general tendency toward a rodlike shape the correction factor is likely to be less than unity. The correction factor used for the silica powder was derived from manual measurements on natural rough specimens of massive silica having apparently the same general shape habit as the silica powder. The value thus obtained was $2/3$, and was used in calculating the values obtained by the microscopic method (Table I). This factor does not apply for other systems of microscopic estimation, but it should apply approximately when sieve tests are used, since the intermediate axis is the one that determines whether a particle can go through a given sieve.

Calculation of the corresponding factor based on the screen-test and air-permeation data of Lea and Nurse (5) for a sand of undescribed type, 120–150 B. S. sieve, gives a value of 0.82. Similar calculations on the screening and silver-coating data of Gross and Zimmerley (4) for several fractions of smooth sand give values from 0.72 to 0.76; for crushed or sharp sand the figures would have been lower. It may be accidental that the check between the microscopic and the air-permeation

TABLE I. DIAMETER MEASUREMENTS ON SEPARATE FRACTIONS OF SILICA POWDER

Range Microns	Microscope Method (Original Values Adjusted for Third Dimension) Surface-weighted average Microns	Air-Permeation Method (Original Readings), Sur- face-Weighted Average Microns
33–97	59	52
27–59	43	40
7–27	15	14
5–12	8	7
3–9	5	5
0.3–3	1.2	1.9

TABLE II. DIAMETER MEASUREMENTS ON MIXTURES OF FRACTIONS OF SILICA POWDER

(Equal parts by weight)		Average Diameter of Mixture by Air Permeation Method	
Diameter of Component Fractions Microscope (range) Microns	Air permeation (average) Microns	Calculated Microns	Observed Microns
7–27 3–9	13.6 4.8	7.1	6.9
27–59 0.3–3	40 1.9		
All fractions combined		4.8	4.7

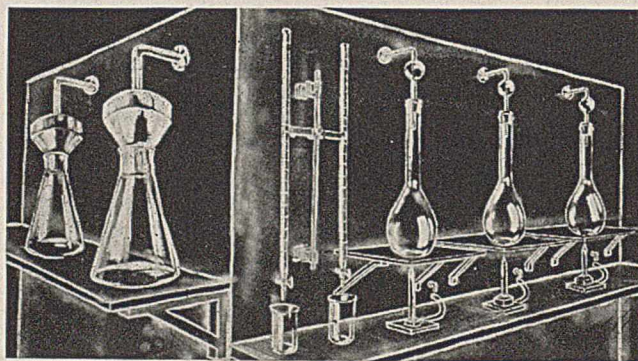
methods is as close as it appears in Table I, for the correction factor is subject to considerable error. Regardless of correction factor, the proportionality of results by the two methods is very good.

No suitable means has yet been found for testing the accuracy of the air-permeation apparatus for particles of extreme shape habits, such as needles and leaves. It has been observed, however, that averages indicated for leafy material are many times as small as the prevalent projected diameters, as would be expected since the surface-weighted average dimension of a leaf can never be more than three times the thickness.

Another series of determinations was made to test the behavior of the apparatus toward mixtures. The results, which are presented in Table II, show a close agreement between the observed values for mixtures and the values calculated from the observations on the component fractions.

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Apparatus for Maintaining Constant Levels in a Water Bath and a Distilling Flask

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TWO modifications of an apparatus for controlling the level of liquid in a bath or other vessel are described here. One form was employed in a metal bath for small serological test tubes, in which distilled water was used to avoid excessive corrosion and deposition of scale, and in which it was desirable to maintain the level within narrow limits. In this case the operation of the apparatus so far exceeded expectation in constancy and sensitivity to minute changes in level that it can be recommended for more ex-

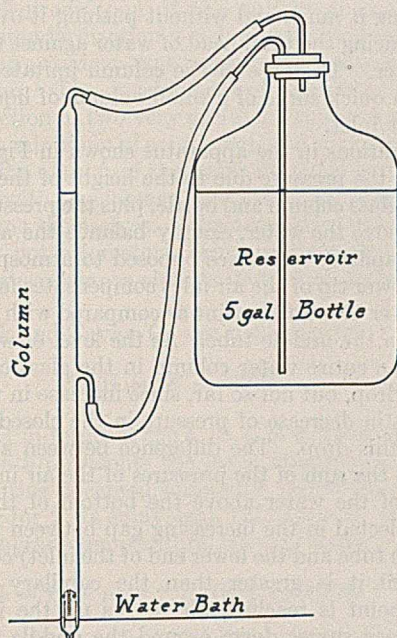


FIGURE 1

acting requirements. The other form, which has been used for more than a year for the preparation of redistilled water, makes it possible to use a small distilling flask in the continuous distillation of a large quantity of material from a reservoir.

Column for Water Bath

The general setup of the apparatus is shown in Figure 1, and the details of the bottom of the column are shown in Figure 2. The outer tube forming the glass column is of 25-mm. tubing and of a length to reach the top of the reservoir (75 cm. in the ones tested). The lower end of this tube is drawn down to a strong tip having an inside diameter of between 1.2 and 1.8 mm. The air inlet of 4-mm. tubing about 45 mm. long is fused into the end of the middle tube, which is of 17-mm. tubing and about 60 mm. long and extends at least 20 mm. below the lower end of the air inlet. The three supporting vent tubes are formed by blowing blebs in the proper places just below the junction of the two tubes, and then blowing out or grinding off the closed tops of the blebs. The assembled air inlet and middle tube is then slid into place and fused to the walls of the outer tube, and the closed centers of the vents are opened by blowing out, grinding, and fusing to a smooth joint, or by any other suitable method.

The only reason for making three tubes venting the middle tube to the outside is to give support to the inner parts. This type of joint is strong if well annealed; otherwise it is fragile, usually cracking spontaneously on cooling. For this reason the entire end of the column is rotated frequently in a bushy flame during this fusing; and as soon as the job is finished, the whole thing is immediately placed in a hot annealing oven. If a large annealing oven is not available, the lower 25 cm. of the column may be made separately, annealed in a small furnace, and joined later to the rest of the column (which does not require such careful treatment) by fusing butt to butt or by using a piece of large rubber tubing.

The finished column is supported in the position shown in Figure 1, with the lower tip of the air inlet about 1 cm. above the desired bath level. A full 19-liter (5-gallon) bottle of water is set on the shelf above the bath, the top of the column is connected with the air space in the top of the bottle, and the siphon is started and connected to the column. If the bottle is nearly full, only a small volume of water will be delivered to the bath before equilibrium is reached. If even this small change of volume is undesirable, it may be prevented during subsequent changing of bottles by clamping off both tubes and drawing a slight vacuum in the top of the fresh bottle before removing the clamps. (Some such device as a short piece of glass tubing in the upper tube for breaking this connection and a clamp between it and the bottle will be required.) Otherwise bottles are quickly changed without interrupting operation merely by clamping the siphon, transferring the rubber stopper, air tube, and siphon to the fresh bottle, and removing the clamp.

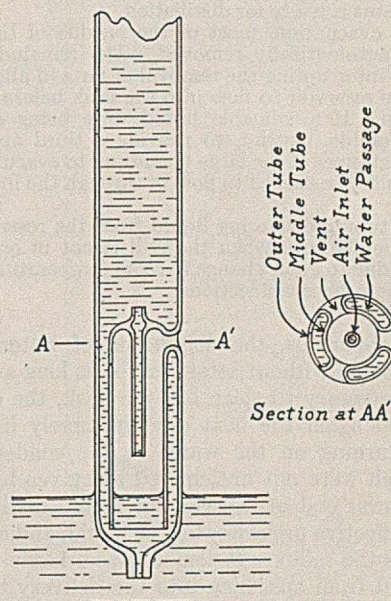


FIGURE 2

This apparatus maintains the level of water in a large bath (area 50 × 50 cm.) within less than 1 mm. The only attention required is the replacement of the empty bottle by a full one as required. This form could also be used, as similar devices (1, 2, 3) have been, in controlling the flow of a large amount of liquid to a filter, or in concentrating large amounts of dilute solutions by evaporation from an open dish.

Column for Distilling Flask

The lower part of the column (of 22-mm. tubing) projects below a standard-taper joint to within about 5 mm. of the bottom of the flask (Figure 3), and above the joint to a height of about 80 mm. The male part of the joint is an integral fused-in part of the column, and the female part forms the top of the neck of the flask. In the center is a tube, the air inlet (of 4-mm. tubing), connecting through an inner seal with a side tube (of 7-mm. tubing) above the glass joint, and extending down to within about 35 mm. of the bottom tip of the column. Air must be taken in above the top of the flask because the atmosphere within the flask is mostly vapor which would condense in the column and fail to displace any liquid from the reservoir. The bottom of the column is constricted to a narrow outlet (about 1.5 mm. in inside diameter) to minimize surge into the flask. To the top of the lower part and the bottom of the upper part of the column are fused short pieces of 8-mm. tubing which are connected closely by heavy rubber tubing. The constriction thus formed serves to restrict the convection of hot liquid in the column. The inlet for liquid from the reservoir is placed below the constriction to aid in forcing the large bubbles of air through the constriction.

To start operation, a bottle of liquid is put in place, the top of the column is connected with the air space in the top of the bottle, and the siphon is started and then clamped. The siphon is connected to the water inlet tube on the column without removing the clamp. At this time, and whenever a fresh bottle of liquid is put in place, it is necessary to evacuate partially the top of the reservoir before starting, to avoid delivery of too much liquid. This is done by plugging the delivery tube of the distilling flask with a stopper and connecting the air inlet tube with a water-suction pump. The rubber tube to the pump is then clamped off and the pump disconnected. By careful manipulation of the two clamps air and liquid are alternately admitted until the system is in equilibrium, the stopper and clamps are removed, and the apparatus is ready for distillation.

During this evacuation, most of the residue of the previous distillation is automatically removed. The remainder may be flushed out by interrupting the removal of air and allowing some liquid from the reservoir to flow into the flask before continuing the evacuation. If a valuable liquid were being distilled, it would be preferable, instead, to provide a third opening with a clamp in the stopper of the large bottle and to evacuate directly through this until air started to flow in through the inlet into the column.

The rubber tubing delivering liquid from the reservoir to the column may be clamped when the still is not in operation, to avoid flooding due to great change in room temperature or to any slow leak in the rubber connections.

With this apparatus, the distillation of water has been allowed to proceed without attention for as long as 15 hours. Unless it is necessary to clean out the flask, the distillation can be started again the next day by merely lighting the burner and turning on the water to the condenser. Advantages which were not anticipated are given by the presence of the lower end of the column in the distilling flask. It acts as an effective preheater for the liquid, and at the same time increases the reflux. It also acts as a baffle to prevent drops of liquid from splashing into the delivery tube. The control is amply close for the purpose of distillation, the change in level in a 250-ml. distilling flask being held within the range of about 5 mm.

Experience has shown that it is a mistake to use a small orifice in the air inlet to restrict the flow of air. The range of change in level is increased instead of being decreased.

Discussion of Operation

The principle involved in the operation of both forms of apparatus is that of some of the oldest and most familiar of

constant-level devices (of which the best known is probably the Mariotte bottle, *S*), in which the main supply of fluid in a reservoir is held back by the partial vacuum in the closed top of the reservoir. For example, in the "drinking fountain" used to supply water for small animals, lowering the level of water in a lower vessel or cup admits air to the reservoir. This displaces water which flows into the small cup and quickly seals the reservoir against further entry of air.

The application of this principle to a large closed bottle equipped with an ordinary siphon necessitates, for ingress of air, a second tube, touching the surface of liquid in the lower vessel. If this tube is of the size ordinarily used for connections in the laboratory, the air entering it will lift the entire column of water ahead of it and rush into the bottle, and a volume of water far in excess of that required to restore the former level in the lower vessel will flow out. The flow of liquid through the small siphon is too slow to close the air inlet before this occurs. To overcome this difficulty in the larger apparatus, the conditions of the smaller drinking fountain have been reproduced outside the bottle in the glass column. In this column the air rises freely through the water without lifting it much and without pushing it over into the bottle or reducing the total head of water against which more air must enter. The base of the column imitates the small cup in which quick surge of a small volume of liquid quickly closes the air inlet.

Static conditions in the apparatus shown in Figures 1 and 2 imply that the pressure due to the height of the column of water in the glass column and bottle, plus the pressure of air in the spaces above the water, exactly balance the atmospheric pressure. Capillary resistance opposed to atmospheric pressure at the lower tip of the air inlet compensates for the lesser height of water above this point as compared with that above the surface in the middle tube. As the level of water in the bath falls, the entire water column in the glass column and bottle must drop, but not so far, since increase in the volume of air results in decrease of pressure in the closed air spaces and lessens this drop. The difference between atmospheric pressure and the sum of the pressures of the air in the closed spaces and of the water above the bottom of the air inlet (which is reflected in the increasing gap between the surface in the middle tube and the lower end of the inlet) continues to increase until it is greater than the capillary resistance. When this point is reached, air moves up the inlet. The water displaced surges down around the middle tube much faster than it can escape through the constricted tip of the column, and therefore up into the middle tube, quickly closing the air inlet. This surge checks the flow of air before equilibrium is reached, so that equilibrium at the desired level of the bath is approached by small steps and is not overreached.

In the apparatus for use with the distilling flask, the changes in pressure and the movements of air and liquid are too complex for brief exposition. Therefore, a bare outline of the cycle must suffice. The major pressure relationships are similar to those of the apparatus for the bath. The vertical distance of the lower end of the air inlet tube above the level in the flask is analogous to the gap between the air inlet and the water in the middle tube of the other apparatus. As air enters the lower part of the column, water can escape through the constriction above, back into the siphon, down into the flask, or up into the air inlet, momentarily blocking the inflow of air. The bubble of air rises to the constriction, where it is temporarily checked. Water flows into the column from the siphon, part going down into the flask, and part going up into the top of the column, apparently aiding in carrying the bubble through the constriction. After several bubbles have entered, and the water level has been restored in the flask, the system comes to rest and remains in equilibrium until the level is again lowered by the distillation.

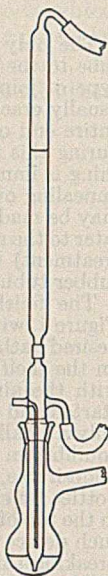


FIGURE 3

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Universal pH Meter and Simplified Vacuum Tube Electrometer

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WHEN confronted with the problem of using standard equipment for determining the pH of solutions with the glass electrode, one of the authors discovered a new method of standardization which greatly facilitated the task of converting a student-type potentiometer into a direct-reading pH meter. The development of this method resulted in the construction of two very useful instruments which can be made with a minimum of equipment, and which are capable of measuring the e. m. f. of the usual electrode systems directly in pH units with an accuracy limited in most cases by the electrode systems themselves. The assemblies can also be used as ordinary potentiometers, being particularly useful in the study of high-resistance circuits, but by no means limited to these.

Hitchcock and Taylor (4) use the equation

$$\text{pH} = (E - E^0)/k \quad (1)$$

to define pH in terms of the e. m. f. of suitable electrode systems, where k represents the usual quantity, $2.3026 RT/F$. By substituting accepted numerical values (6) for R and F and writing for T its equivalent, $(273.15 + t)$, where t stands for the centigrade temperature, we may write

$$k = k_0 + at = 0.05418 + 0.0001983 t \quad (2)$$

where k_0 is $2.3026 \times 273.15 \times R/F$ and a is $2.3026 R/F$.

Any direct-reading pH meter must be so standardized that a change of 1 unit represents a change of k volts. Hemingway (3) accomplishes this in a conventional manner and Wynd and Varney (10) resort to the expedient of inserting a calibrated resistor into the working battery circuit after first standardizing the potentiometer in volts. The authors employ a different principle of standardization which eliminates the need for any precision electrical equipment except the potentiometer and standard cell.

Potentiometer Circuit

The circuit shown in Figure 1 accomplishes the purpose outlined above. The fixed resistor, F_1 , is designed to extend the range of the potentiometer so that when S_1 is in position STD and S_2 is in position pH , the same effect is produced as if the potentiometer range were extended to the value of the standard cell in pH units—i. e., $1.018/k$. When reading the potentiometer in pH units the decimal point is shifted mentally, so that 0.1 volt is read "one pH unit". By this simple expedient it is possible to standardize a potentiometer in pH units by the method commonly used for standardizing in volts.

Since the magnitude of the pH unit changes with temperature, it is necessary to construct a chart or table showing the temperature of the electrode system as a function of the slide-wire setting to be employed when standardizing against the standard cell. The

principle of this calibration is simple and does not depend upon direct measurement of temperature. From the results of two measurements of the same potential, one in volts and one in pH units, and the relation expressed in Equation 2, it is possible to calculate the working temperature corresponding to any selected slide-wire setting. The work is repeated for several different positions of the slide-wire and the results are plotted.

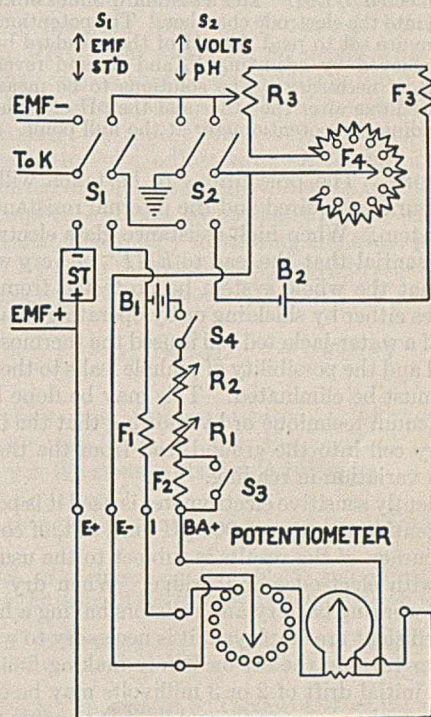


FIGURE 1. POTENTIOMETER CIRCUIT

Batteries. B_1 , 3 volts; B_2 , 1.5 volts (long line +)
 Binding posts. E^+ , E^- , 1, and BA^+ connected to corresponding terminals on potentiometer
 Fixed resistors. F_1 , 17 ohms (depending on temperature range); F_2 , 250 ohms; F_3 , 2500 ohms; F_4 , ten fixed resistors ranging from 100 to 150 ohms with a total resistance of 1200 ohms; F_4 is equipped with a rotary tap switch
 Leads. EMF^- (well insulated) to negative electrode. $To K$, see Figure 2. EMF^+ to positive electrode
 Potentiometer. Leeds & Northrup student-type potentiometer having a total resistance of 160 ohms
 Resistors (variable). All resistors should be straight-line wire-wound. R_1 , 150 ohms; R_2 , 6 ohms; R_3 , 150 ohms
 Standard cell. ST , Weston standard cell having a potential of 1.018 volts
 Switches. S_1 , S_2 , double-pole double-throw (good insulation required); S_3 , S_4 , single-pole single-throw

TABLE I. CIRCUIT ARRANGEMENTS

Arrangement	S_1	S_2	S_3	Use
No. 1	Down (ST'D)	Up (VOLTS)	Closed (VOLTS)	Standardizing for volts
No. 2	Up (EMF)	Up (VOLTS)	Closed (VOLTS)	Reading in volts
No. 3	Down (ST'D)	Down (pH)	Open (pH)	Standardizing for pH units
No. 4	Up (EMF)	Down (pH)	Open (pH)	Reading in pH units
No. 5	Up (EMF)	Down (pH)	Closed (VOLTS)	Calibrating set

The variable resistors, R_2 and R_1 , the fixed resistor, F_2 , and switch S_3 permit necessary adjustment of the working battery current supplied from B_1 . Resistors F_3 , F_4 , and R_3 so divide the potential of the battery, B_2 , as exactly to compensate for the E° portion of the e. m. f. when reading in pH units. F_4 consists of a number of fixed resistors in series. A rotary tap switch serves to change the number of resistors in the circuit. It is important that the resistance between taps shall not exceed the resistance of R_3 . The two double-pole double-throw switches, S_1 and S_2 , permit changing the circuit into different arrangements as shown in Table I.

OPERATION OF CIRCUIT. When measuring the e. m. f. of an electrode system in volts the conventional operations are performed, arrangements 1 and 2 of Table I being required.

If the instrument is to be used as a direct-reading pH meter, arrangements 3 and 4 are employed and the calibration chart is used to determine the proper slide-wire setting in connection with standardization. The glass, hydrogen, or quinhydrone electrode is always connected to EMF^- and a standard buffer of known pH is introduced into the electrode chamber. The potentiometer dial and slide-wire are set to read the pH of the standard buffer and balance is achieved by adjusting F_4 and R_3 and reversing the polarity of B_2 if necessary. The solutions to be measured are then introduced one after the other and the pH of each is determined by reading the potentiometer at the null point.

PRECAUTIONS. The precautions to be taken will depend upon the accuracy required and the internal resistance of the electrode system. When high-resistance glass electrodes are used it is essential that the lead to EMF^- be very well insulated and that the whole system be protected from electrostatic charges either by shielding or by operating in a suitable location. If a water-jacketed cell is used the thermostat must be grounded and the possibility of pinhole leaks to the thermostat water must be eliminated. This may be done by using standard vacuum technique or by showing that the introduction of a dry cell into the ground lead from the thermostat produces no variation in reading.

If a sufficiently sensitive electrometer is used it is possible to read the potentiometer to ± 0.001 pH unit, but, of course, the absolute accuracy of the results is subject to the usual errors associated with electrodes and bridge. When dry cells are used for the working battery and resistors having a high temperature coefficient are employed, it is necessary to wait a few minutes after turning the set on before making final adjustments. An initial drift of 2 or 3 millivolts may be expected, but after the set has been on for awhile it is possible to establish constancy within 0.1 or 0.2 millivolt over a reasonable period of time.

Electrometer Circuit

Figure 2 shows the electrical diagram of the electrometer which was developed by modifying Goodhue's design (2) in accordance with some of the basic principles of thermionic amplification of direct currents discussed by Macdonald (7). The result is an electrometer that has given satisfactory service and can readily be adapted to portable instruments.

Several of the parts shown in the diagram may be omitted as nonessential. The leads to galvanometer G and the switch, S_7 , are unnecessary if a fairly sensitive milliammeter is used in position M . F_8 and S_8 are designed to protect the milliammeter or galva-

nometer against sudden surges when the set is turned on. With a milliammeter of the range specified this protection is not essential. It was found empirically that the set could be stabilized for several hours, so that it behaved as quietly as a galvanometer, by merely momentarily grounding the grid lead of the first tube. The contact point, P , represents a convenient, well-insulated extension of the grid lead which is designed to facilitate this operation. However, the set behaves satisfactorily without this addition and without touching the grid lead.

The other parts are essential. A conventional treatment of the grid circuit of the first tube was tried but it was found that the switch, K , and condenser, C_1 , which are described by Goodhue (2) gave much better results. Condenser C_2 was suggested by Hemingway (3).

USE OF ELECTROMETER. The electrometer is turned on by closing the filament switch, S_5 , with S_6 open. When the milliammeter needle is steady it is brought to about 0.02 ma. by adjusting R_4 ; S_6 is closed and the needle brought to any convenient position for observation. When the set is first constructed it may be necessary to change the value of the resistor, F_7 , to accommodate the individual tube.

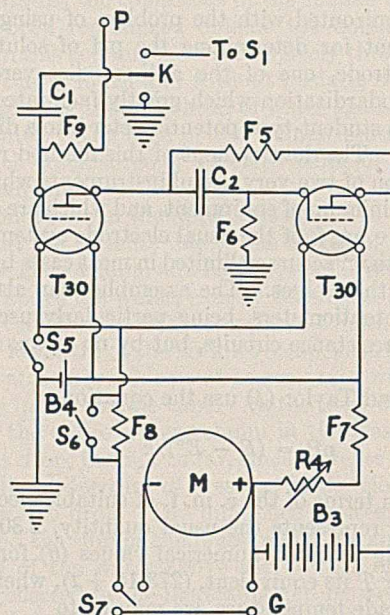


FIGURE 2. DIAGRAM OF ELECTROMETER

Batteries. B_3 , 45 volts; B_4 , 1.5 volts (long line +)

Condensers. C_1 , 0.001-mfd. highest quality mica; C_2 , 0.1-mfd. paper

Fixed resistors. F_6 , 2.5 megohms; F_4 , 5 megohms; F_7 , 500 ohms (depending on particular tube in use); F_8 , 20,000 ohms; F_3 , 25 megohms (exact value not important)

Key (Tap). K , slightly modified form of highly insulated, rapid-action, platinum-contact, single-pole, double-throw switch designed by Goodhue (2). Central element normally contacts grounded element, but is brought into momentary contact with upper element by depressing key

Milliammeter. M , direct current milliammeter range 0 to 1.0 milliamperes

P , Special contact point for momentarily discharging grid

Resistor (variable). "Straight-line" wire-wound, R_4 500 ohms

Switches. S_5 , S_6 , single-pole single-throw switches; S_7 , optional

Tubes. T_{30} , two 30 type tubes having a rated filament voltage of 2 volts. Reduction of this value to 1.5 volts does not decrease efficiency of these tubes in this circuit

The electrometer operates as a null instrument by tapping the key connected with the switch, K , of Figure 2. Fluctuations in thermionic emission or battery potential may cause a momentary shift of the milliammeter needle or an occasional spurious effect on tapping the key. These results never prove troublesome because subsequent trials always show a definite balance point.

Experiments with a dry cell connected in series with resistors ranging from 0 up to 80 megohms showed that the reading was essentially unaffected by increasing the resistance in series, provided that the cell was insulated from the table with glass, or the high-resistance portion of the circuit was connected to switch K through EMF^- . However, with the cell resting on the table and the 80-megohm resistance connected to EMF^+ (Figure 1), an error of 0.27 volt resulted.

Details of Construction

The cost of the equipment, exclusive of cabinet, potentiometer, standard cell, and electrode assembly should not exceed \$20, although set 2 exceeded this estimate because the best available parts were purchased. However, set 1 was produced for less and has been giving continuously satisfactory service under general laboratory conditions for almost 2 years.

When selecting parts, special attention should be given to the excellence of insulation in switches S_1 and S_2 . It is important, of course, that all resistors be free from the possibility of faulty contact and that the variable resistors be wire-wound and smooth in operation, both mechanically and electrically. In general, with the exception of condenser C_1 , which must be of highest quality (but not necessarily designed for high voltage), and switches S_1 and S_2 , moderately priced equipment may be used. A "Triplet" milliammeter (Model 221) has been giving satisfactory service in set 1.

The essential features of switch K are rapid action, excellent insulation, and positive contact. Goodhue (2) obtains the first by using a long mechanical lever attached to the key, the second by mounting the switch elements at the ends of glass rods, and the third by constructing the elements of platinum wire. The central element is soldered to the end of a length of No. 18 steel wire which is attached to the lever by means of silk fishline. The central element is normally grounded and is brought into momentary contact with the upper element on tapping the key. Both of the authors' switches were made according to the above specifications with minor variations in mechanical detail. In designing a switch attention should be given to the possibility of electrical leakage along glass surfaces and the possibility that moving parts may generate electrostatic charge.

Both of the authors' sets were constructed with all the instruments mounted on shielded Bakelite panels. The tubes are mounted on the back of the panels in an inverted position and each cabinet is shielded. It is important to keep the grid lead to the first tube as short as possible, and to make sure that condenser C_1 is satisfactory. Goodhue (2) specifies that the direct current leakage through this condenser shall not exceed 0.01 microampere at 200 volts. A condenser that exceeds this leakage by a factor of ten should be discarded but a certain tolerance is permitted, depending upon the precision desired and the resistance of the glass electrodes.

The required resistance of F_1 will depend upon the temperature likely to be encountered in use and may be calculated by the equation

$$F = \left(\frac{S}{10V(k_0 + at)} - 1 \right) R \quad (3)$$

where F is the proper resistance in ohms of the fixed resistor, F_1 , R is the total resistance of the potentiometer, V is the total range of the potentiometer in volts, S is the value of the standard cell in volts, and t is the lowest Centigrade temperature likely to be encountered in use. The term $(k_0 + at)$ is defined by Equation 2. For the Leeds & Northrup student-type potentiometer used in this work, R is 160 ohms, V is 1.6 volts,

and S was taken as 1.018 volts for the purpose of these calculations.

The method described below for calibrating the complete circuit eliminates the need for accurate adjustment of the resistance of F_1 . The following values are calculated for the equipment listed above.

t ° C.	F_1 Ohms	t ° C.	F_1 Ohms
0-15	28	31-49	9
15-31	18	49-67	0

For temperatures above 67° C. the circuit diagramed in Figure 1 may still be used for direct reading in pH units, provided S_2 is set at the position marked *VOLTS* and the potentiometer is set to the value S/k , when balancing against the standard cell.

It is clear that it will be necessary to insert different resistors and to calibrate each one separately if it is desired to cover a wide range of temperature. An alternative method is to employ a variable resistor and graduated dial. The authors prepared resistor F_1 by soldering copper leads to a length of resistance wire. Wire having a minimum temperature coefficient of resistance should be employed.

Calibration for Use at Different Temperatures

The calibration requires a constant potential which is most conveniently provided from the E° circuit by connecting EMF^- to EMF^+ . The switching arrangement is such that the leads may remain shorted during the entire operation because the E° circuit is automatically disconnected when not needed. Briefly, the calibration consists of balancing the set to read directly in volts, adjusting the E° circuit and measuring its potential in volts, balancing the set to read in whatever pH units happen to result by setting the slide-wire at some arbitrary value, and finally measuring the same potential in pH units. By using the relation expressed in Equation 2 it is possible to derive the equation

$$t = \frac{1}{a} \left(\frac{x}{y} - k_0 \right) = 5042 \left(\frac{x}{y} - 0.05418 \right) \quad (4)$$

where t is the temperature represented by the slide-wire setting used for standardizing, x is the constant potential in volts, and y is the same potential in pH units. a and k_0 are defined by Equation 2.

The following operations are required for calibration:

1. Switch to arrangement 1 (Table I) and adjust R_1 and R_2 after setting the value of the standard cell in volts on the potentiometer.
2. Switch to arrangement 5 (Table I) and read the potential of the E° circuit in volts. It is best to choose a value of about 0.45 volt.
3. Switch to arrangement 3 (Table I) and set the slide-wire at zero. Balance by adjusting R_1 and R_2 .
4. Switch to arrangement 4 and read the same potential in pH units. Each division representing 0.1 volt is taken as one pH unit.
5. Calculate the temperature corresponding to the slide-wire setting used in operation 3 by Equation 4.
6. Repeat the above operations for several different slide-wire settings and plot the results.

Experimental Verification

Two sets were constructed embodying the circuit diagramed in Figure 1. Both sets were first equipped with the electrometer described by Goodhue (2), but later No. 1 was modified to operate with the electrometer diagramed in Figure 2. No. 2 was not changed because the principal advantage of the modification is the elimination of equipment which

was already installed. All results reported below for No. 1 were obtained while using the modified electrometer.

The electrode system diagramed in Figure 3 was used in all the work. Water from a thermostat held at $25^\circ \pm 0.1^\circ \text{C}$. was pumped through jacket *J* and the solutions studied were introduced into compartment *B*. The calomel electrode, *C*, is of the authors' own design and is kept covered with a saturated solution of potassium chloride which is permitted to flow around the stopcock, thus maintaining a liquid junction. A small portion of this solution was discarded after each determination by properly manipulating the stopcock. Different glass electrodes containing Brown's silver-silver chloride electrodes (*I*) immersed in 0.1 *M* hydrochloric acid were used.

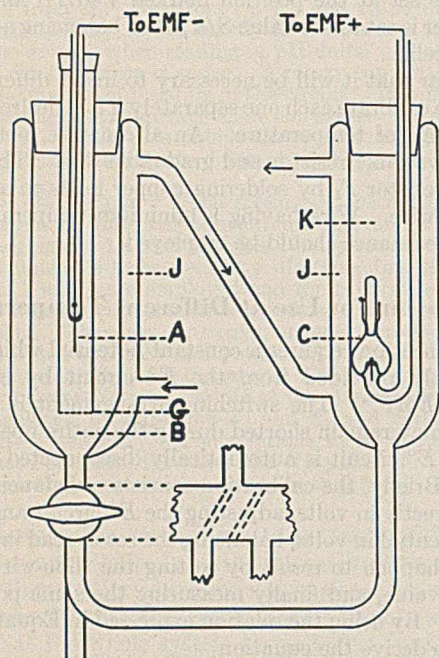


FIGURE 3. ELECTRODE SYSTEM

- A. Silver-silver chloride electrode
 B. Buffer compartment
 C. Calomel electrode (saturated)
 J. Glass electrode
 J. Water jacket
 K. Saturated potassium chloride reservoir
 To EMF⁻. Always true when reading in pH units, but electrodes may be reversed as required when reading in volts

The solutions tested were prepared according to the specifications of Hitchcock and Taylor (4) from salts that had been recrystallized from water two or three times and dried. The potassium dihydrogen phosphate was freed from suspended matter by the addition of purified talc to the hot concentrated solution just before filtration and subsequent recrystallization. The phosphates were analyzed by ignition and the phthalate by titration. The borax was dried to constant weight over a saturated solution of sodium bromide and the hydrochloric acid solution was prepared from constant-boiling acid.

TABLE II. TYPICAL RESULTS WITH SET 1

Solution	pH Given (4)	Glass Bulb Type ^a 124 Meg.	35 Meg.	Hydrogen (B ₂ , Figure 1) Reversed
0.1 <i>M</i> HCl	1.085	1.15	1.11	1.14
0.025 <i>M</i> KH ₂ PO ₄ + 0.025 <i>M</i> Na ₂ HPO ₄	6.857	6.83	6.85	6.85
0.05 <i>M</i> borax	9.180	9.10	9.16	9.19
0.05 <i>M</i> potassium acid phthalate	4.008	Chosen as standard buffer		

^a A small bulb of special glass (Corning .015) about 1 cm. in diameter was blown on end of a length of ordinary soft-glass tubing. Resistance was determined on instrument itself by measuring potential drop across 1-megohm resistor in series with electrode system and dry cell.

TABLE III. TYPICAL RESULTS WITH SET 2

Solution	pH Given (4)	pH Direct	E. M. F. (Volts)	Sign of Glass Electrode	pH Calcd.
0.1 <i>M</i> HCl	1.085	1.10	0.0436	+	1.09
0.025 <i>M</i> KH ₂ PO ₄ + 0.025 <i>M</i> Na ₂ HPO ₄	6.857	6.86	0.2964	-	6.85
0.05 <i>M</i> borax	9.180	9.16	0.4329	-	9.16
0.05 <i>M</i> potassium acid phthalate	4.008	Standard	0.1287	-	Standard

Table II gives typical results of direct reading in pH units with set 1 at 25°C .

The results shown in Table III were obtained at 25°C . with set 2 using a MacInnes and Dole glass electrode (9) having a resistance of 70 megohms. These results are typical of several independent series of determinations made on different days.

The circuit has been further tested in practical use for almost 2 years and has been found entirely satisfactory for routine control and investigation. The potential of the E° circuit can be measured at any time by the method discussed in connection with calibration, thereby eliminating one serious disadvantage of most direct-reading instruments.

In interpreting the results recorded above it should be noted that Hitchcock and Taylor (4) recognize the arbitrary nature of any pH standard in the very acid range. The intrinsic limitations of the glass electrode and the saturated potassium chloride bridge together with the insidious problem of electrical leakage should also be considered. The later work of Hitchcock and Taylor (5) and the work of MacInnes, Belcher, and Shedlovsky (8) should also be taken into account when evaluating the accuracy of pH measurements. However, the older values appearing in the second column of Tables II and III have not been changed sufficiently to affect the present work and for this reason the tables have not been recalculated.

Summary

A circuit capable of transforming a potentiometer and standard cell into a direct-reading pH meter is described. This circuit is self-calibrating and may be used with the glass, hydrogen, quinhydrone, or other electrode systems in connection with a suitable electrometer. The design of a simplified vacuum tube electrometer is also given and some typical results with various electrodes are recorded.

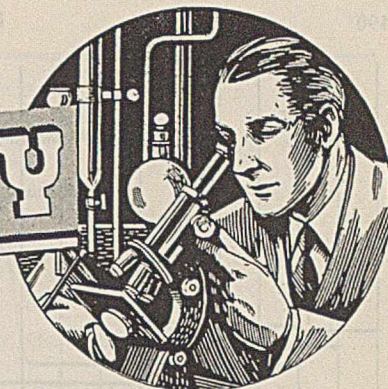
Acknowledgment

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MICROCHEMISTRY



Determination of Zinc in Plant Materials

Using the Dropping Mercury Electrode

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THE importance of zinc in plant nutrition has received considerable attention in recent years, and this has led to investigations of methods of determination of zinc in plant materials and in soils. The most promising have been the colorimetric method suggested by Lott (5), the dithizone separation as used by Hibbard (2), spectrographic methods as outlined by Rogers and Gall (6), and methods involving the use of the dropping mercury electrode, often referred to as polarographic methods. Lott's colorimetric method involves a hydrogen sulfide precipitation and complete separation of zinc from other constituents. The dithizone separation is acknowledged to be neither as precise nor as easy to carry out as the spectrographic or dropping mercury electrode method (1). The apparatus required for quantitative measurement by means of the dropping mercury electrode is much less expensive than for the spectrographic method, and the method should be comparatively simple in the case of zinc in plant materials and soils.

Stout and his co-workers (7) used the polarograph in conjunction with the dithizone chloroform separation in the routine estimation of zinc in plant materials, but Stout reported neither the limits of zinc that may be determined nor the limits of substances other than zinc that may occur in plants without interfering with the use of the method. Some trouble was experienced in this laboratory with the method as outlined, particularly where comparatively large amounts of zinc or of cadmium, lead, copper, nickel, or cobalt were present. In either case it was necessary to extract at least five or six times instead of once as suggested in order to separate the zinc quantitatively from iron, aluminum, and alkali metals. This increase in number of manipulations, besides being troublesome, increases the possibility of introducing contamination.

Accordingly a more satisfactory method has been devised in this laboratory and the limitations have been worked out.

Procedure

The sample of plant material, which may consist of 0.5 to 2.0 grams, is ashed below 450° C. The ash is taken up in 1 to 2 ml. of concentrated hydrochloric acid, evaporated to dryness, taken up in a few milliliters of 1 *N* hydrochloric acid, and transferred with 20 to 30 ml. of water to a 50-ml. beaker. The reaction is then adjusted by means of dilute ammonium hydroxide to a pH of between 4 and 5 using the glass electrode. The solution is filtered and washed, and the filtrate carried to dryness on the steam bath. The residue is taken up in 25 ml. of a solution of

0.1 *N* ammonium acetate of pH 4.6, 0.025 *N* with respect to potassium thiocyanate. The zinc is then determined polarographically. Oxygen is removed from the solution prior to the determination by bubbling in pure nitrogen.

Adjustment of the reaction to a pH of 4 to 5 removes from solution practically all the aluminum and ferric iron. Although the alkali metals and most of the other constituents are not removed, zinc may be determined polarographically in their presence.

Experimental Investigations

The current voltage curves were all obtained by use of the Heyrovsky polarograph, which is designed for automatic photographic recording. The dropping mercury electrode was constructed like that recommended by Kolthoff and Lingane (4), so that it involved no rubber connections. Connection to a manometer permitted reproduction of a constant pressure on the mercury column in the electrode and therefore reproduction of the dropping rate of the electrode. Occasionally after continued use the electrode became clogged and required cleaning. In such cases the method of cleaning suggested by Kolthoff and Lingane was followed.

In all determinations the same dropping mercury electrode was used. A dropping rate of 2.0 to 2.6 seconds per drop was found most satisfactory for the range of galvanometer sensitivities used. The anode potential was measured against the saturated calomel half-cell so as to correct the half-wave potential for it. This varied so little that in routine determinations on plant ash one measurement of the anode potential would probably be sufficient for correction. The corrected half-wave potential for zinc in the regulating solution used was determined as 1.01 volts.

The possibility of contamination by additions of zinc through the reagents used should be recognized, and it is advisable to run a blank for correction purposes. The small number of manipulations involved in the procedure tends to minimize possibility of contamination. In the experimental work outlined below, where synthetic ash extracts were made up to include all the probable constituents of plant ash, reagent grade chemicals were used in every case and particular precautions taken to avoid contamination. A synthetic extract containing all of these except zinc was put through the procedure as a blank. The polarogram showed no measurable zinc at the highest galvanometer sensitivity used in the investigations and therefore no correction was necessary.

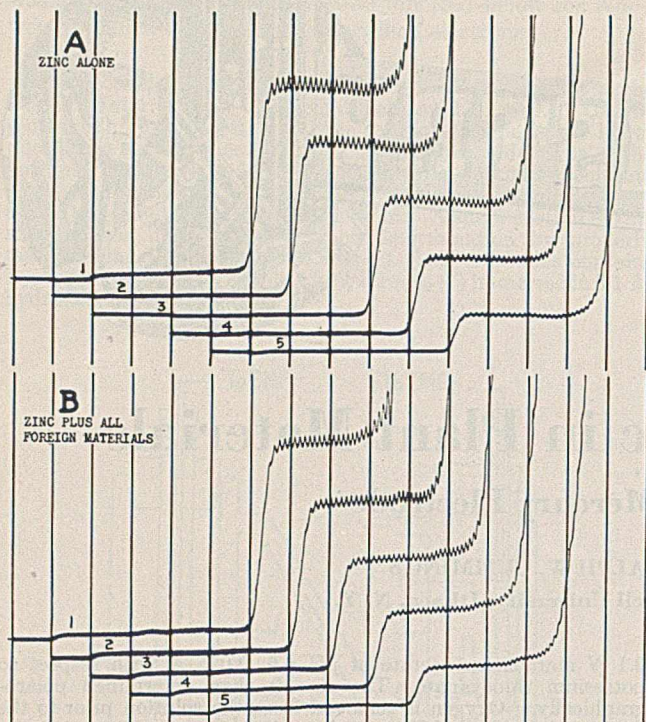


FIGURE 1. COMPARISON OF ZINC ALONE AND ZINC PLUS ALL FOREIGN MATERIALS

PRESENCE OF INTERFERING MATERIALS. To determine the concentration limits of materials other than zinc which may appear in the plant ash without interfering with the determination of zinc by this method, solutions were made up containing all cations and anions that are likely to appear in an extract of ashed sample. The basic synthetic solution which approximates the plant ash extract is listed in Table I.

Now each constituent was varied in concentration, holding the other constituents constant. These solutions were then carried through the procedure outlined above and zinc was determined.

When the concentration of zinc was maintained at 2×10^{-6} gram per ml. (assuming 1.0 gram of plant material ashed and taken up in 25 ml. of regulating solution, this is equivalent to 0.005 per cent of zinc) there was no interference from chloride, sulfate, phosphate, carbonate, sodium, potassium, calcium, magnesium, or manganese at large concentrations. The cations in this group are all reduced at a more negative potential than zinc and no interference would be expected. Iron and aluminum were added in concentrations much larger than would be expected in plant materials. Here no interference was encountered, as they are largely removed by pH adjustment and filtration. Lead, cadmium, and nickel offered no interference when present at a concentration of 2×10^{-5} gram per ml. (equivalent to 0.05 per cent in the plant). This indicates that there is no interference from any of these ele-

ments at concentrations that greatly exceed their normal concentrations in plant material.

Copper and cobalt if present in abnormally high concentrations interfered if the concentration of zinc was low. With the zinc concentration 2×10^{-6} gram per ml., copper interfered if present to the extent of 2×10^{-5} gram per ml. or more. However, if the copper content was 1.6×10^{-5} or the zinc concentration was 2.5×10^{-6} there was no interference.

In the case of relatively high concentrations of copper or any other materials reduced at a lower potential than zinc, interference would be due to a relatively large reduction current produced before the reduction potential of zinc is reached. With such materials the interference is determined not by the actual concentration but by ratio of concentrations of these materials to that of zinc. Zinc could be determined in the presence of any amount of copper, lead, cadmium, nickel, etc., provided the ratio of the total concentrations of these materials to that of zinc does not exceed 10 to 1.

Although cobalt is reduced at a more negative potential than zinc, the zinc and cobalt inflections tend to coalesce when relatively high concentrations of cobalt are present. With the zinc concentration 2×10^{-6} gram per ml., cobalt interfered if its concentration was 1×10^{-5} gram per ml. or greater. Further experimentation showed, however, that when cobalt occurs in concentrations greater than 1×10^{-5} gram per ml., it interferes with the zinc determination only when the ratio of cobalt to zinc exceeds 2 to 1.

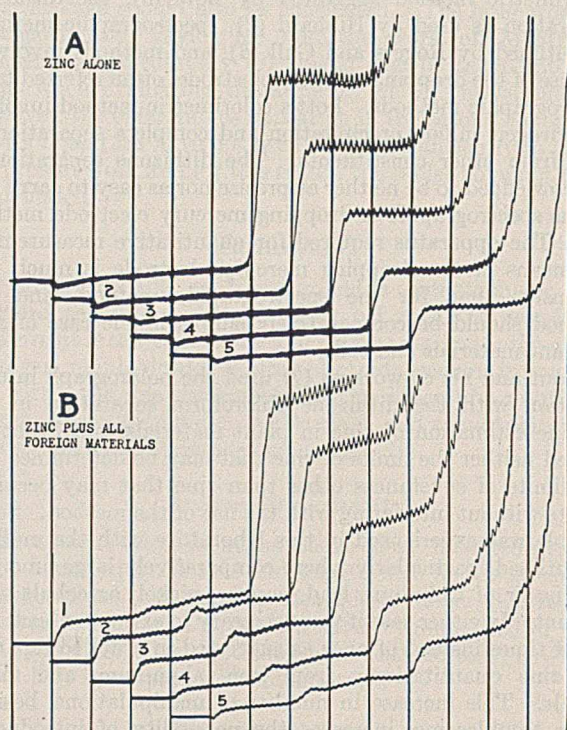


FIGURE 2. COMPARISON OF ZINC ALONE AND ZINC PLUS ALL FOREIGN MATERIALS

TABLE I. BASE MIXTURE

Material	Element Mg.	% in Plant ^a	Material	Element Mg.	% in Plant ^a
KCl	10.0 K	1.0	MnSO ₄	0.2 Mn	0.02
Na ₂ CO ₃	0.5 Na	0.05	NiSO ₄ ·7H ₂ O	0.05 Ni	0.005
CaCl ₂	10.0 Ca	1.0	CoCl ₂ ·6H ₂ O	0.05 Co	0.005
MgSO ₄ ·7H ₂ O	4.0 Mg	0.4	PbCl ₂	0.05 Pb	0.005
H ₂ PO ₄	2.0 P	0.2	CdCl ₂ ·2H ₂ O	0.05 Cd	0.005
FeCl ₂ ·6H ₂ O	1.0 Fe	0.10	CuSO ₄ ·5H ₂ O	0.05 Cu	0.005
Al ₂ Cl ₆ ·12H ₂ O	0.2 Al	0.02	ZnSO ₄ ·7H ₂ O	0.05 Zn	0.005

^a Assuming 1.0-gram plant sample represented in 25 ml. of solution.

The above-mentioned possibilities are not likely to be encountered in practice in plant materials and therefore should not prove a serious limitation in the use of the method.

LIMITS OF METHOD. In order to determine the limits of zinc concentration for which the method is applicable, synthetic solutions of the composition indicated in Table I were again made up, which approximated plant ash extracts and contained all the cations and anions likely to occur or interfere. In this case the zinc content was varied and the solutions were

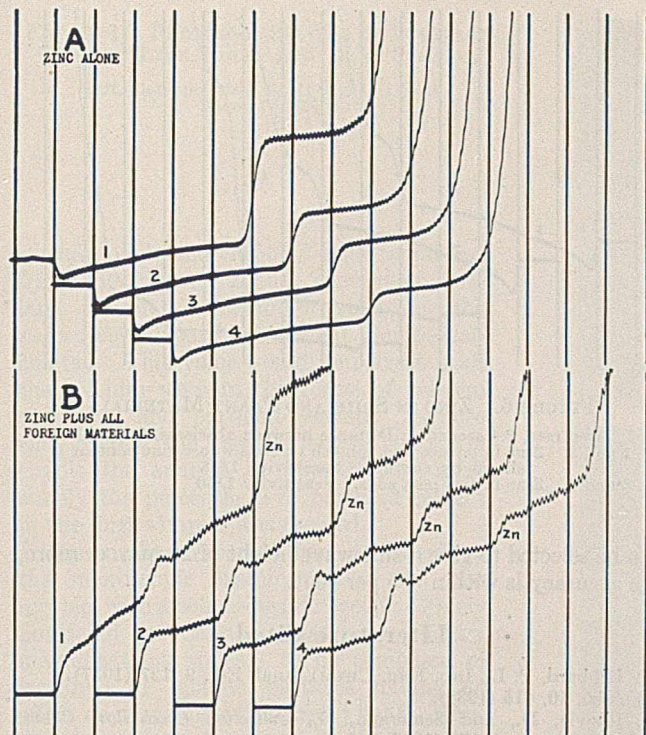


FIGURE 3. COMPARISON OF ZINC ALONE AND ZINC PLUS ALL FOREIGN MATERIALS

analyzed for zinc by the procedure suggested. The polarograms obtained were compared with others obtained at the same time by taking similar concentrations of zinc alone, evaporating to dryness, taking up in the ammonium acetate-potassium thiocyanate solution, and determining polarographically. The results of these determinations are indicated in Figures 1 to 5, data for which are given in Table II. The synthetic ash extracts of Figure 5 involving concentrations of 1×10^{-6} to 2×10^{-7} gram of zinc per ml., where a high galvanometer sensitivity (1/5) was used, contained only half as much nickel, cobalt, cadmium, lead, and copper as the other synthetic extracts. It was evident that reduction of these concentrations was necessary for determination of concentrations of zinc less than 5×10^{-7} gram per ml. With the possible exception of copper, this still represents a greater content of these interfering materials than normally occurs in plant materials.

The range of determinations varies from 2×10^{-4} to 2×10^{-7} gram of zinc per ml. Expressed on a plant basis, if the procedure were carried out as outlined using as a sample 1 gram of plant material and taking up the residue from evaporation in 25 ml. of regulating solution, this would amount to a range of from 0.5 to 0.0005 per cent of zinc in the plant. Higher concentrations than those listed could have been determined by using a lower galvanometer sensitivity or by diluting the solution, but this probably represents the upper limit likely to be encountered in plant material. With the lowest concentrations the measurements become more difficult and less accurate, owing to the appreciable "condenser" current registered at high galvanometer sensitivities. It is possible that still smaller amounts could be determined in plant materials by compensation of the condenser current as suggested by Ilkovic and Semerano (3).

Wave heights were evaluated by measuring at the half-wave potential the vertical distance between straight-line extensions of the principal slopes before and after the current step, placing the slope lines through the centers of the oscillation amplitudes. Several measurements were made of each wave

TABLE II. DATA FOR FIGURES 1 TO 5

(Distance between abscissas, 0.20 volt)

Curve	Zinc Concentrations G./ml.	Difference in Zn Wave Heights between A and B Mm.
Figure 1, Sensitivity 1/200, Drop Rate 2.7 Seconds		
1	2×10^{-4}	0.0
2	1.6×10^{-4}	1.0
3	1.2×10^{-4}	1.0
4	8×10^{-5}	0.2
5	4×10^{-5}	0.0
Figure 2, Sensitivity 1/40, Drop Rate 2.6 Seconds		
1	4×10^{-5}	0.0
2	3×10^{-5}	0.5
3	2×10^{-5}	0.0
4	1.2×10^{-5}	1.5
5	8×10^{-6}	1.0
Figure 3, Sensitivity 1/15, Drop Rate 2.6 Seconds		
1	8×10^{-6}	0.0
2	4×10^{-6}	0.5
3	3×10^{-6}	0.5
4	2×10^{-6}	0.3
Figure 4, Sensitivity 1/10, Drop Rate 2.6 Seconds		
1	2×10^{-6}	0.7
2	1×10^{-6}	0.5
3	5×10^{-7}	0.2
Figure 5, Sensitivity 1/5, Drop Rate 2.3 Seconds		
1	1×10^{-6}	0.8
2	5×10^{-7}	0.0
3	2×10^{-7}	1.0

height. The average of these was used in arriving at the difference in wave height between zinc alone and zinc plus interfering materials and treatment. The accuracy of the method may be judged from the difference in measurements. It is probably governed largely by the linear measurement of wave height, since the wave height can be measured with precision only to within 1 mm. This obviously means a greater relative error in the linear measurements involving small wave heights (2 to 10 mm.). Where possible a sensitivity should be chosen which results in a wave height of 20 mm. or

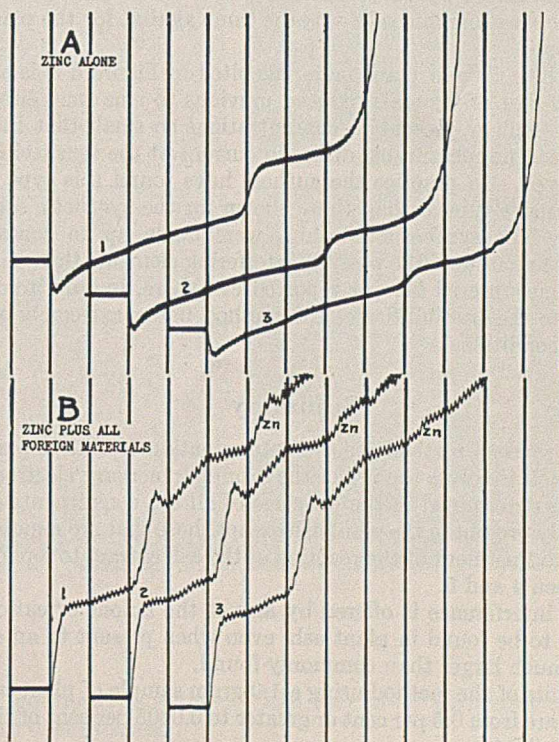


FIGURE 4. COMPARISON OF ZINC ALONE AND ZINC PLUS ALL FOREIGN MATERIALS

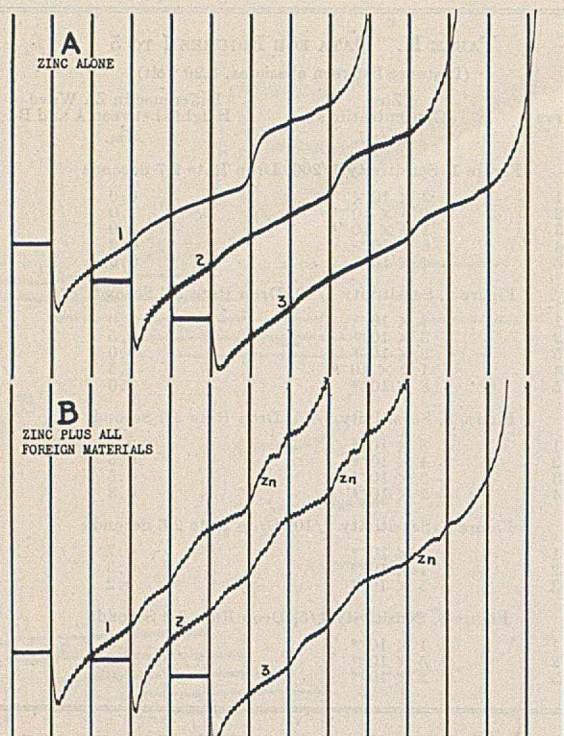


FIGURE 5. COMPARISON OF ZINC ALONE AND ZINC PLUS ALL FOREIGN MATERIALS

more. This reduces the experimental error and assures an accuracy of within ± 5 per cent.

Figure 6 illustrates typical curves obtained with plant material and soils. Curves 3 and 4 show the zinc content of two peat soils, while curves 1 and 2 show the zinc content of lettuce and spinach, respectively, grown on soil whose analysis is indicated by curve 3. The procedure followed in the case of these organic soils was the same as that for the plant materials.

In the soils and plant materials cited in Figure 6 it is apparent that any metals reduced previous to zinc were either not present or present in concentrations so small that they produced no measurable diffusion current at the sensitivities employed. In practice the authors have found this type of curve more typical than those shown for the synthetic solutions. The synthetic solutions were made up to contain higher amounts of the possible interfering elements than have been encountered here or reported elsewhere, in order to determine the possibilities of the method under extremely adverse conditions.

Summary

A proposed method for the determination of zinc in plant materials involves the use of the dropping mercury electrode. Zinc is determined in the presence of all the constituents ordinarily present in the plant ash except those that are removed by an adjustment of the reaction of the ash extract to a pH of between 4 and 5.

No interference is offered by any of the anions or cations likely to be found in plant ash, even when present to an extent much larger than commonly found.

Limits of the method using a 1.0-gram sample of plant material are from 0.5 per cent or greater to 0.0005 per cent of zinc in the plant.

The accuracy of the method is limited largely by the measurement of wave height. If a galvanometer sensitivity

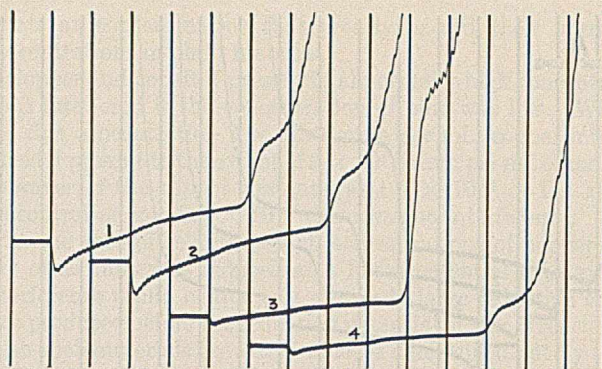


FIGURE 6. ZINC IN SOILS AND PLANT MATERIALS

Drop rate, 2.4 seconds. Distance between abscissas, 0.20 volt
1 and 2. Zinc in lettuce and spinach on soils whose zinc content is
shown by curve 3. Sensitivity 1/15
3 and 4. Zinc in two peat soils. Sensitivity 1/50

can be selected to give a zinc wave height of 20 mm. or more, the accuracy is within ± 5 per cent.

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Microscopic Method for Portland Cement in Dust Samples

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IN SUITS involving alleged damages due to portland cement, the chemist is frequently called to analyze samples of dusts taken in the vicinity of the plant. Because the presence or the absence of cement cannot be determined with certainty by chemical methods, an application of the polarizing microscope has been devised.

In the vicinity of a cement plant the dust is composed of particles from the kiln stacks and from various outside sources. The dust from the kiln stacks may contain unburned limestone, clay, calcium carbonate, calcium oxide, calcium hydroxide, monocalcium silicate, fly ash from the combustion of coal, and the components of portland cement: dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. The dust from other sources is mainly road and earth dust and, if the roads are covered with crushed lime rock, it contains an appreciable quantity of calcite. The calculated values for the cementation and the hydraulic ratios derived from the analytical data are of little use for the determination of cement in dusts because synthetic samples, containing no cement, might easily give the same ratios as portland cement. From the percentages of

FIGURE 1. PHOTOMICROGRAPHS OF PORTLAND CEMENT, LIME ROCK, AND DUST SAMPLES

Left, plane polarized light; right, crossed Nicols ($\times 80$)

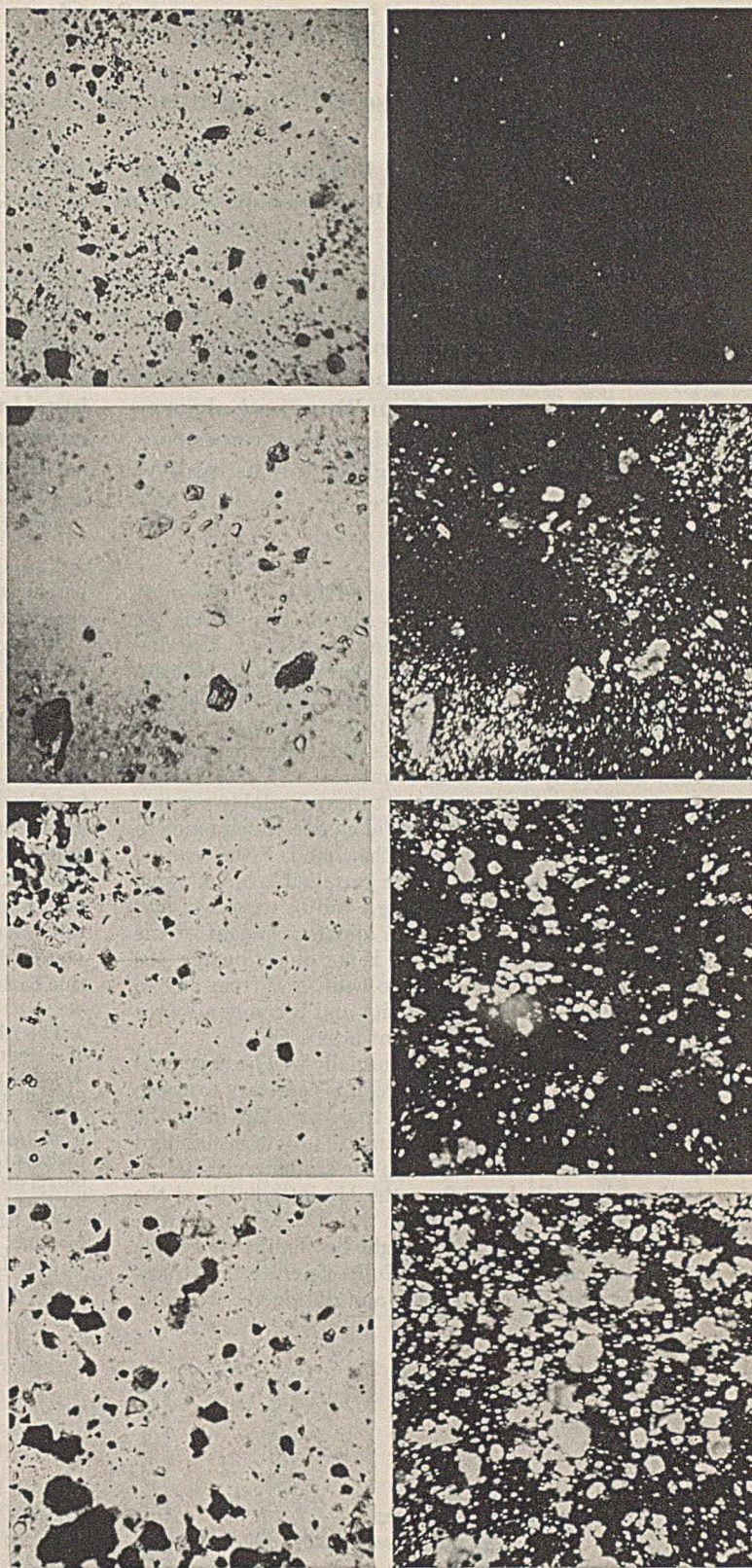
calcium oxide and carbon dioxide found and from the known calcium content of portland cement, a maximum value for the percentage of portland cement can be calculated. This value would be correct if all the calcium were in the forms of calcium carbonate and portland cement. Because this is not the case, a method that will enable the analyst to approximate more closely the percentages of portland cement in the dust samples was devised.

The method reported here is based on the microscopic examination of the dust samples with a polarizing microscope. Finely powdered portland cement at ordinary magnifications appears to be composed of isotropic or opaque particles having no effect on transmitted polarized light. This, together with the fact that anisotropic properties are shown by the other possible components of the dusts except the organic matter, enables the analyst to determine the presence or absence of portland cement in samples of dusts by both visual and photographic microscopy.

The microscopic slides were made by carefully dusting well-mixed dust samples onto melted hard balsam and covering with a cover slide. After the balsam hardened the slides were examined with a polarizing microscope with a visual magnification of $\times 80$. Each slide was first examined with transmitted plane polarized light without the analyzer in place. Then without moving the slide the analyzer was inserted in its crossed position and the slide was again examined. When a dust mixture was examined between crossed Nicol prisms, under suitable conditions of illumination, all the anisotropic particles except those at the extinction angle appeared as brilliantly glistening specks which could readily be distinguished from the black or grayish aggregates of the isotropic and opaque particles such as those of portland cement. By counting the particles between crossed Nicol prisms and comparing with the number of particles in the same field as observed with plane polarized light, the number of isotropic or opaque particles was determined.

For approximate analysis, a visual count can be made in a short time with both plane polarized light and crossed Nicols. For more exact analyses, the counting may be performed according to the method of Seaman (1), who quantitatively determined the amount of anthraquinone-1,8-disulfonic acid in the presence of the 1,5-disulfonic acid and sulfuric acid by precipitation with barium chloride and subsequent examination of the barium salts with crossed Nicols. For permanent record, photomicrographs are easily made.

Figure 1 shows at the top a sample of commercial portland cement, illustrating an isotropic or amorphous substance; the bright specks are due to particles of gypsum for controlling the time of set. The next two photographs, illustrating an anisotropic or birefringent substance, are showings of a sample



of powdered limestone. The four lower photographs show two dust samples.

Literature Cited

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Microdetermination of Carbon and Hydrogen

Use of Abrahamczik Absorption Tubes

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Under routine analytical conditions the Abrahamczik type of absorption tubes, with minor structural modifications, compared favorably with those of Pregl design in accuracy, ease of handling, and absorption capacity. In addition, they were practically unaffected by high or low humidity, changes in temperature, or standing idle

for long periods. The use of Abrahamczik tubes brings about economies of time corresponding to two to three carbon and hydrogen determinations in a normal working day. Experiments leading to these conclusions are described and illustrated, as are the details of the tubes and analytical procedures.

THE Pregl type of absorption tube seems to be used most generally in the combustion of organic compounds for the microdetermination of carbon and hydrogen. The disadvantages of this type of tube are apparent to all who have used them extensively. Unless the atmosphere of the laboratory is controlled in such a way as to place the relative humidity within certain rather close limits, difficulty in weighing the tubes accurately will be encountered. If the relative humidity falls below 45 per cent the tubes invariably assume, as a result of wiping, a static electrical charge which tends to give erratic results (7, 9); on the other hand, if the relative humidity is higher than average, the permissible blank value (12) for the Dehydrite tube (0.05 mg.) will be exceeded, and a correction must be applied to the apparent weight of the water absorbed. While this in itself is not objectionable, the blank correction varies from hour to hour, and from day to day, with changes in relative humidity and becomes a source of error unless determined at frequent intervals.

Finally, since the Pregl tubes are normally weighed and conditioned while open to the atmosphere, it is necessary to sweep the oxygen out of the combustion train with air after the sample has been vaporized and burned. By the standard Pregl procedure air is passed through the system until 100 cc. of water have been displaced from the Mariotte bottle at the rate of 4 cc. per minute, an operation which takes 25 minutes.

It is obvious that these faults might be eliminated by the use of a tube which could be successfully closed to the atmosphere directly after the combustion and during the weighing

period, and by the adoption of a wiping technique less vigorous than that required by Pregl (11).

Tubes which can be closed to the atmosphere have been described in the literature (2, 4, 5, 6, 8) and have found some success. One of the most recent developments was made by Abrahamczik (1). This paper describes experiences in the use of the Abrahamczik absorption tube; no attempt will be made to compare it with others of the sealed type. Except for Abrahamczik's original article there is not, to the authors' knowledge, any published report of experimental work on his apparatus. With certain minor modifications in the Abrahamczik design and procedure, the authors are able to get better results under adverse conditions than with the Pregl tube, many of the faults of the latter are eliminated without sacrificing its virtues, and an appreciable time-saving in routine carbon and hydrogen analyses is effected.

The Abrahamczik absorption tubes were developed from those of Friedrich (4, 5, 6), which are shown in Figure 1 with the Abrahamczik tube for comparison. The grooves (A, Figure 1) encircling the upper and lower edges of the male ground surface of the Abrahamczik version are intended to keep the lubricant from leaking out of the joint into the exposed part of the apparatus (3). When the dots (B, Figure 1) fused into the tube and barrel are aligned, it is possible to pass the gases leaving the combustion tube into the bottom of the absorption chamber through one of the capillary side arms, upward through the absorbing medium, and out through the other capillary. The system may be closed to the atmosphere by merely turning the tube 90° in the barrel.

Structural Modifications in Abrahamczik Tube

The first Abrahamczik tubes used by the authors were purchased from a microchemical supply house and were essentially identical in construction and dimensions (Figure 2) with those described by their designer (1). These tubes were used in routine carbon and hydrogen analyses and gave excellent results.

After thoroughly testing the tubes as originally designed, certain modifications seemed justified. According to Abrahamczik, the Dehydrite tube should absorb approximately 100 mg. of water and the Ascarite tube about 150 mg. of carbon dioxide. Since this was considered inadequate for routine industrial determinations, involving considerable loss of time due to frequent renewing of the tube filling, the

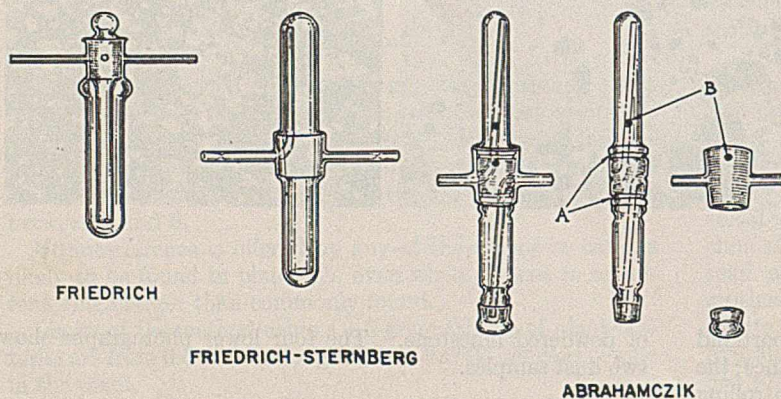


FIGURE 1. ABSORPTION TUBES

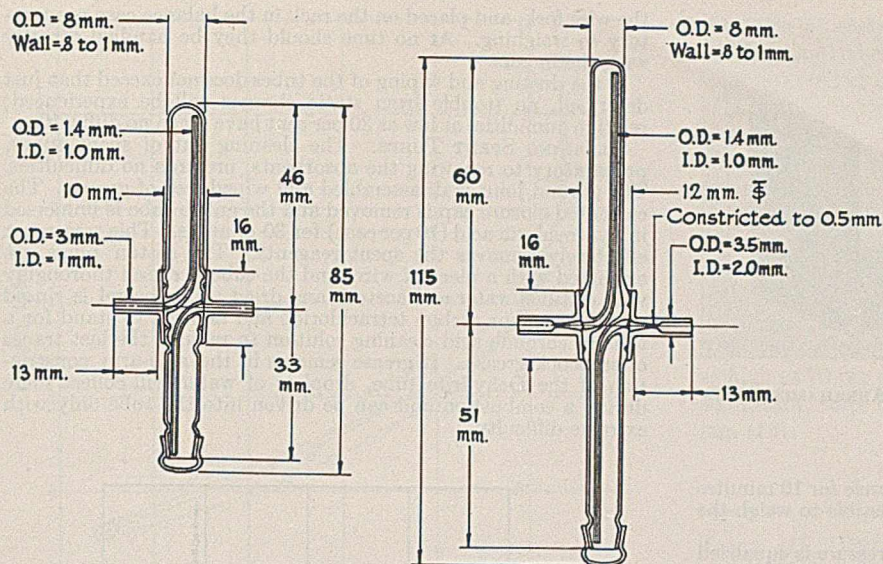


FIGURE 2. ABRAHAMCZIK ABSORPTION TUBE
Original at left, modification at right

length of the tube was increased from 85 to 115 mm. and the diameter of the ground-glass section was increased slightly. The calculated increase in volume indicates that the life of the tubes was approximately doubled. In actual use the modified type absorbed 330 to 400 mg. of water and 500 to 600 mg. of carbon dioxide, with a liberal margin of safety. Although Abrahamczik's figures were not checked by experiment, they appear to be much too conservative. The increase in volume added less than 2 grams to the weight of the improved tubes. A typical modified Ascarite tube weighed 8.2 grams empty and 11.0 grams when filled, ready for use. Besides providing more adequate absorption capacity, lengthening the tubes allows them to be placed on the hooks of the balance-pan suspension for weighing, instead of on the pan itself, as is necessary when the regulation Abrahamczik tubes are used.

In charging the unmodified Abrahamczik tubes it was found that the space at the center of the apparatus was too limited to permit easy filling. This difficulty was completely eliminated by increasing the bore approximately 1 to 1.5 mm. at this point. Moreover, the slightly larger female joint necessitated by this change allows the male joint and tube to be completely removed while the closure cap is in place.

The standard Abrahamczik tube has capillary side arms sealed to the barrel, or female member, of the ground joint. In practice, these side arms are very difficult to clean, an operation which must be performed before the tubes are placed in the balance case preparatory to weighing. On the modified type of apparatus these side arms are replaced by tubes of 2-mm. bore, as compared with 1 mm. for the standard design. The large-bore side arms are constricted to 0.5 mm. approximately 3 mm. from the ground joint to prevent the cotton used for cleaning from coming into contact with grease at the ground joint. Changing the side arms greatly facilitates cleaning and increases the blank value for the Dehydrite tube only 0.010 mg. at a relative humidity of 50 per cent.

Preparing Tubes for Use

The tubes are filled with Ascarite and Dehydrite as directed by Abrahamczik (1). The details of the procedure are apparent from Figure 3.

The Ascarite (12- to 20-mesh) must not be packed tightly, since this will cause the tube to become plugged when approximately 200 mg. of carbon dioxide have been absorbed. It is advisable

to add the reagent in small portions, tapping gently against the hand after each addition. The Dehydrite tube is packed rather firmly to prevent excessive settling. Commercial Dehydrite (Arthur H. Thomas & Company) is ground in a mortar until fine enough for easy filling of the tubes (10- to 30-mesh).

In assembling the tubes and barrels, sufficient grease is applied to ensure a gas-tight seal without filling the grease-retaining grooves or the inlet and outlet openings. "Lefco seal" stopcock grease was found very satisfactory for this purpose. After the tubes are filled and assembled, they are wiped with a cloth moistened slightly with a good grade of benzene, and then with a clean, dry chamois skin to remove grease, finger marks, and dust. Thereafter they are stored in the balance case when not in actual use and are handled only with chamois skin or with the specially constructed wire fork (Figure 4) used for putting the tubes on the balance.

The freshly filled tubes are conditioned for use by connecting them into the standard Pregl carbon and hydrogen outfit (10) and passing oxygen through the system at the rate of 4 cc. per minute for 1 hour. They are connected into the system in such a way that the gas from the combustion tube enters the absorbent from the bottom and passes upward to the exit tube. The tubes are conditioned further by passing through them the combustion products of an unweighed sample of a pure organic compound, maintaining the flow of oxygen at 4 cc. per minute. They are now ready for use in an analysis and need not be conditioned again unless the analyst deems it necessary because of unusual circumstances.

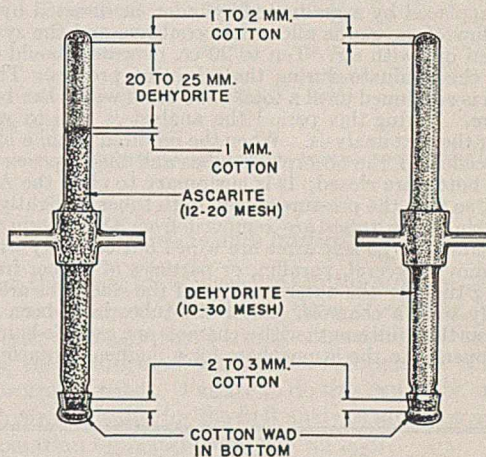


FIGURE 3. ASCARITE TUBE (LEFT) AND DEHYDRITE TUBE (RIGHT)

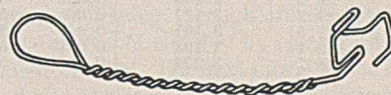


FIGURE 4. WIRE FORK FOR HANDLING ABSORPTION TUBES

WEIGHING. After the absorption tubes have been dusted and wiped as directed below, they are opened momentarily to the atmosphere (Ascarite tube first) and are placed in the balance case by means of the wire fork. A small metal rack (Figure 5) placed inside the balance case is convenient for storing the tubes while not in use or while waiting for them to come to equilibrium.

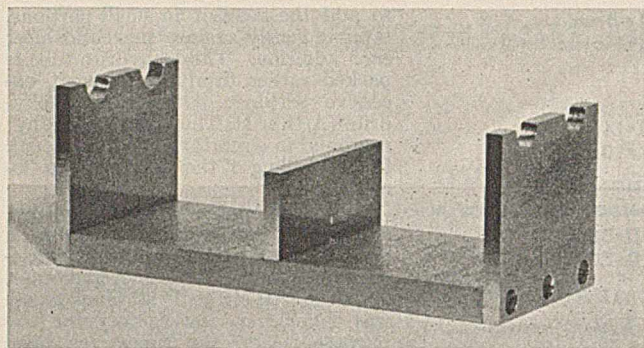


FIGURE 5. ALUMINUM RACE FOR STORING ABRAHAMCZIK ABSORPTION TUBES

When the Ascarite tube has been at the balance for 10 minutes it may be weighed. At 15 minutes it is permissible to weigh the Dehydrite tube.

The procedure just outlined, in which the pressure is equalized immediately after the tubes are wiped, assumes that the temperatures at the absorbing train and at the balance differ by less than 1° C. If the difference is 1° C. or more it will be necessary to equalize the pressure by opening the tubes again for about 1 second just before they are placed on the balance for weighing. This method has been found to give reproducible weights.

COMBUSTION. In carrying out a combustion the absorption tubes are weighed, inserted in the combustion train, and opened to the system by aligning the reference dots on the tube and barrel; there is no preference as to the order in which the two tubes are opened. The regular Pregl combustion procedure (10) is then followed. If the sample is vaporized too rapidly, water will condense in the Dehydrite tube at the constriction in the inlet side arm. It is extremely difficult to drive this condensate into the absorbent.

When the second heating of the combustion tube with the movable burner is begun, the beaker beneath the outlet of the Mariotte bottle is replaced by a graduated cylinder, as directed by Pregl, but the flow of oxygen is allowed to continue and the system is not flushed out with air. Ten to 20 cc. of water should be collected in the graduate during the reheating process. The flow of oxygen is continued until a total of 50 cc. of water has been allowed here. During this period the analyst is free to weigh a sample for the next analysis. When the required volume of water has been collected, the absorption tubes and the stopcock on the Mariotte bottle are closed; it is customary to close the Ascarite tube first, so that the pressure within both tubes is slightly above atmospheric. The tubes are removed from the system with a chamois skin and the side arms are wiped out carefully with cotton to remove glycerol, paraffin, or particles of rubber from the connecting tubing; the outer surfaces of the side arms are wiped thoroughly with a chamois. After the tubes have been dusted lightly over their full length with a chamois or a camel's-hair brush, they are opened to the atmosphere for a moment, transferred to

the wire fork, and placed on the rack in the balance case preparatory to weighing. At no time should they be handled directly with the fingers.

If the dusting and wiping of the tubes does not exceed that just described, no trouble from static charges will be experienced; relative humidities as low as 30 per cent have given no difficulty.

CLEANING SPENT TUBES. The cleaning out of spent tubes, preparatory to renewing the absorbents, presents no difficulties. The ground joint is disassembled and wiped free of grease. The cemented closure cap is removed and the entire tube is immersed in hydrochloric acid (10 per cent) for 30 minutes. This treatment effectively removes the spent reagents. The cotton plugs are extracted with a piece of wire, and the tube is rinsed thoroughly with distilled water and acetone and dried. The barrel is rinsed with benzene or carbon tetrachloride and allowed to stand for a time in chromic acid cleaning solution to remove the last traces of stopcock grease. If grease remains in the side-arm constriction of the Dehydrite tube, droplets of water will collect there during a combustion and can be driven into the tube only with extreme difficulty.

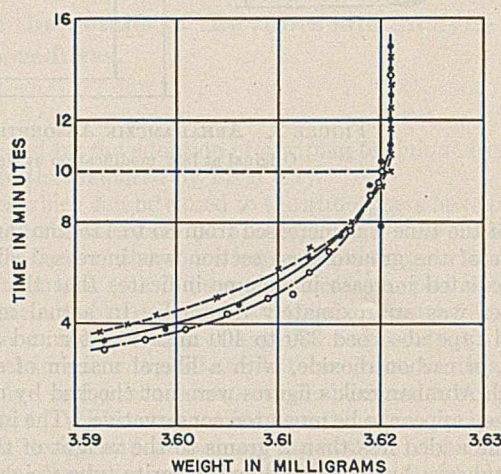


FIGURE 6. OPTIMUM TIME INTERVAL BETWEEN WIPING AND WEIGHING ASCARITE TUBE

Temperature Effects

When the closed Abrahamczik tubes were tested for constancy in weight there was a steady gain throughout the day, with a loss the next morning. The temperature of the microanalytical laboratory, since it was not thermostatically controlled, rose slowly to reach a maximum at the end of the working day. It was suspected, therefore, that the rising temperature was responsible for the gain in weight. This was

TABLE I. EFFECT OF TEMPERATURE ON WEIGHT OF ABRAHAMCZIK ABSORPTION TUBES

Temperature ° C.	Weight against Lead Shot				Weight against Similar Absorption Tube			
	Ascarite tube Mg.	Change of weight Mg.	Dehydrite tube Mg.	Change of weight Mg.	Ascarite tube Mg.	Change of weight Mg.	Dehydrite tube Mg.	Change of weight Mg.
25.8	3.142	5.132	2.396	7.200
26.2	3.165	+0.023	5.153	+0.021	2.394	-0.002	7.194	-0.006
27.2	3.171	+0.006	5.167	+0.014	2.382	-0.012	7.195	+0.001
27.5	3.191	+0.020	5.189	+0.022	2.378	-0.004	7.197	+0.002
28.1	3.198	+0.007	5.198	+0.009	2.378	0.000	7.197	0.000
28.7	3.204	+0.006	5.206	+0.008	2.379	+0.001	7.193	-0.004

TABLE II. EFFECT OF OPENING TUBES TO ATMOSPHERE TO EQUALIZE PRESSURE

Temperature ° C.	Weight, Tubes Closed				Weight, Tubes Opened Momentarily			
	Ascarite tube Mg.	Change of weight Mg.	Dehydrite tube Mg.	Change of weight Mg.	Ascarite tube Mg.	Change of weight Mg.	Dehydrite tube Mg.	Change of weight Mg.
25.5	1.155	0.491	1.155	0.491
26.1	1.184	+0.029	0.499	+0.008	1.146	-0.009	0.485	-0.006
26.6	1.190	+0.006	0.521	+0.022	1.153	+0.007	0.487	+0.002
27.5	1.201	+0.011	0.531	+0.010	1.154	+0.001	0.489	+0.002
28.0	1.210	+0.009	0.540	+0.009	1.154	0.000	0.487	-0.002

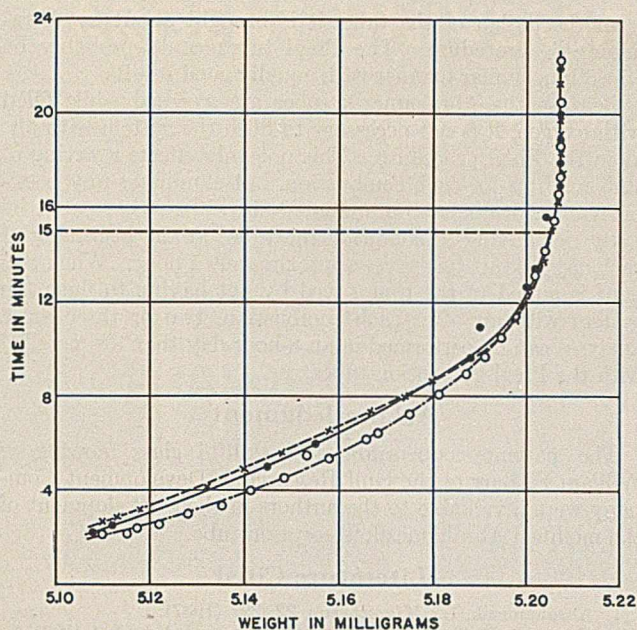


FIGURE 7. OPTIMUM TIME INTERVAL BETWEEN WIPING AND WEIGHING DEHYDRITE TUBE

confirmed by experiment. Conclusive proof was obtained by weighing the tubes with similar tubes for counterpoises. It was found that the maximum deviation between successive readings was 0.006 mg. for the Dehydrite tube and 0.012 mg. for the Ascarite tube (Table I). Tubes weighed against a lead-shot counterpoise on different days, but at identical temperatures, gave results which agreed to within 0.005 mg.

The effect of temperature may be eliminated, as recommended by Friedrich (4), by opening the tubes to the atmosphere for a moment before weighing, in order to equalize their pressure with that of the atmosphere. At varying temperatures this procedure gave consistently uniform values (Table II).

Like the Pregl tubes, the Abrahamczik type must be allowed to stand for a specified time at the balance after removal from the combustion train before they will come to constant weight. Experiment showed that the optimum time in the case of the Ascarite tubes was 10 minutes (Figure 6) and for the Dehydrite tubes, 15 minutes (Figure 7).

Accuracy of Results

The final and most important test in the evaluation of any absorption tube is that of accuracy and reproducibility. It seemed that this test could be accomplished best (1) by the use of the Abrahamczik tubes in the determination of carbon and hydrogen in a pure compound of known composition; and (2) by comparison, under routine analytical conditions, with the Pregl tubes, since the latter have been used extensively by microanalysts for many years and have given very satisfactory results when handled correctly under suitable atmospheric conditions.

The first test was carried out by making three consecutive analyses of salicylic acid. The results, shown in Table III, were excellent.

Next, three pure compounds were analyzed, first with the Abrahamczik and then with the Pregl absorption tubes. All determinations were made under approximately the same conditions over a short time period. The compounds were not chosen for the test alone but were submitted to the micro laboratory for analysis by research workers. Instead of using

one type of absorption tube for two consecutive analyses, the Pregl and Abrahamczik tubes were alternated and both results reported as checks. The results are shown in Table IV.

It is apparent from these two tests run under routine conditions that the Abrahamczik absorption tubes are capable of accurate and reproducible results when judged alone or by comparison with standard Pregl tubes. The hydrogen values obtained with the Pregl tube have been corrected by blank determinations. This correction varies from 0.100 mg. under dry conditions to as high as 0.250 mg. when the humidity is high. A series of blank determinations on the Abrahamczik dehydrite tubes showed the blank value to be approximately 0.020 mg. at various temperatures and at relative humidities, as high as 70 per cent. A blank value of this magnitude is insignificant, since it need not be applied unless it exceeds 0.050 mg. (12).

TABLE III. DETERMINATION OF CARBON AND HYDROGEN IN PURE SALICYLIC ACID, USING MODIFIED ABRAHAMCZIK TUBES

Carbon %	Found		Carbon %	Calculated	
	Hydrogen %	Hydrogen %		Hydrogen %	Hydrogen %
60.85	4.43	4.31	60.78	4.35	..
60.85	4.31	4.32
60.80	4.32

TABLE IV. COMPARISON OF PREGL AND ABRAHAMCZIK TUBES IN ROUTINE ANALYSIS OF PURE ORGANIC COMPOUNDS

Com- pound	Type of Tube Used	Found		Calculated	
		Carbon %	Hydrogen %	Carbon %	Hydrogen %
A	Pregl	80.71	10.31 ^a	80.90	10.15
	Abrahamczik	80.89	10.14		
B	Pregl	80.38	9.91 ^a	80.43	9.84
	Abrahamczik	80.36	9.99		
C	Pregl	82.40	9.34 ^a	82.58	9.27
	Abrahamczik	82.46	9.44		

^a Blank correction applied.

Effect of Tubes Standing Idle

When the Pregl tubes were used in the authors' laboratory it was customary to recondition them after they had stood overnight, or longer, by burning an unweighed sample and passing the products of combustion through the combustion and absorption tubes. Failure to do this generally resulted in a low hydrogen value for the first analysis after the shutdown. The operation took approximately an hour.

The Abrahamczik type of absorption tube gave satisfactory results on the first analysis of the day without any reconditioning. Overnight the tubes were stored, closed to the atmosphere, in the balance case. To avoid partial dehydration of the lead peroxide in the combustion tube filling, the stream of oxygen flowing through the system was stopped after the last analysis of the day by closing off the open end of the combustion tube. The next morning the flow of oxygen was resumed and the combustion furnace was brought up to operating temperature. The absorption tubes were dusted, opened to the atmosphere momentarily, weighed after the usual time interval, and the first analysis was started. The results obtained by following such a procedure are shown in Table V.

Moreover, tubes which had stood for as long as 96 hours gave consecutive results in close agreement with each other and with the calculated values, without reconditioning (Table VI).

TABLE V. RESULTS WITH ABRAHAMCZIK TUBES WHICH HAD STOOD IDLE FOR 12 HOURS

Trial No.	When Analyzed	Found		Calculated	
		Carbon %	Hydrogen %	Carbon %	Hydrogen %
17	End of day	81.15	10.55	81.15	10.50
	Next morning	81.01	10.45		
26	End of day	82.90	12.13	82.94	12.03
	Next morning	82.99	12.21		
34	End of day	80.94	10.14	81.00	10.11
	Next morning	80.98	10.10		
40	End of day	60.82	4.40	60.78	4.35
	Next morning	60.80	4.50		

TABLE VI. PERFORMANCE OF ABRAHAMCZIK TUBES AFTER STANDING 96 HOURS

Trial No.	Found		Calculated	
	Carbon %	Hydrogen %	Carbon %	Hydrogen %
22	80.86	10.16	80.85	10.17
	80.77	10.30		
30	82.26	9.93	82.21	9.90
	82.16	9.78		
52	80.94	10.19	80.85	10.17
	80.98	10.29		

Conclusions

This investigation shows that the Abrahamczik absorption tubes, with minor structural changes, compare favorably with those of the Pregl type in accuracy and reproducibility of results, ease of handling and filling, and capacity for the absorption of carbon dioxide and water. In addition, they have the following advantages over the Pregl tubes:

High atmospheric humidity has no effect upon the results obtained and corrections for humidity need not be applied.

Since the Abrahamczik tubes are not vigorously wiped prior to weighing, the effect of static charges due to low humidity is entirely eliminated. While this advantage does not come

from the design of the tube, it is brought about by Abrahamczik's procedure. The Pregl tubes could probably be wiped in a similar manner with equally good results.

Because the Abrahamczik tubes are weighed while filled with oxygen, it is not necessary to flush the system with air, as in the Pregl procedure. This not only effects a saving of 12.5 minutes for each combustion, but eliminates any possibility of error due to contaminated air.

By not having to condition the tubes at the beginning of each day, the analyst saves approximately 1 hour. When this hour is added to the time saved by not having to flush the system with air after each combustion, two or three more analyses can be performed in an 8-hour day than are possible with the Pregl absorption tubes.

Acknowledgment

The patient cooperation and skillful glass blowing of William E. Barr of the Gulf Research & Development Company were invaluable to the authors in their development of the modified Abrahamczik absorption tube.

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PRESENTED before the Division of Microchemistry at the 98th Meeting of the American Chemical Society, Boston, Mass.

Qualitative Identification of Ferrocyanide Ion

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THE identification of ferri- and ferrocyanides in the presence of each other by means of the colored precipitates obtained with ferrous and ferric ions has always presented difficulty in qualitative analysis. Prussian blue and Turnbull's blue appear alike to most chemists. A solution of this problem is the use of titanium tetrachloride solution for the precipitation of ferrocyanide ions. The slightly yellow solution of titanium tetrachloride in dilute hydrochloric acid gives a reddish-brown, flocculent precipitate with ferrocyanide ions which is insoluble in 6 M hydrochloric acid. Ferri-cyanides give no precipitate over a wide range of acidity. The only interference is from strongly oxidizing anions such as chromate and nitrite, which oxidize the ferrocyanide ions.

The only mention of this or a similar reaction to be found in the literature is that of von der Pfordten (1, 3), who indicates that both ferri- and ferrocyanides give precipitates with a solution of titanium tetrachloride in alcohol and water. This has not been confirmed. An investigation of the nature and constitution of the brown ferrocyanide precipitate is being undertaken.

The following method for the identification of ferrocyanide ions has been used successfully by students at Grinnell College (2).

TITANIUM TETRACHLORIDE REAGENT. Add 10 ml. of liquid titanium tetrachloride to 90 ml. of 1 to 1 hydrochloric acid. Caution, use hood.

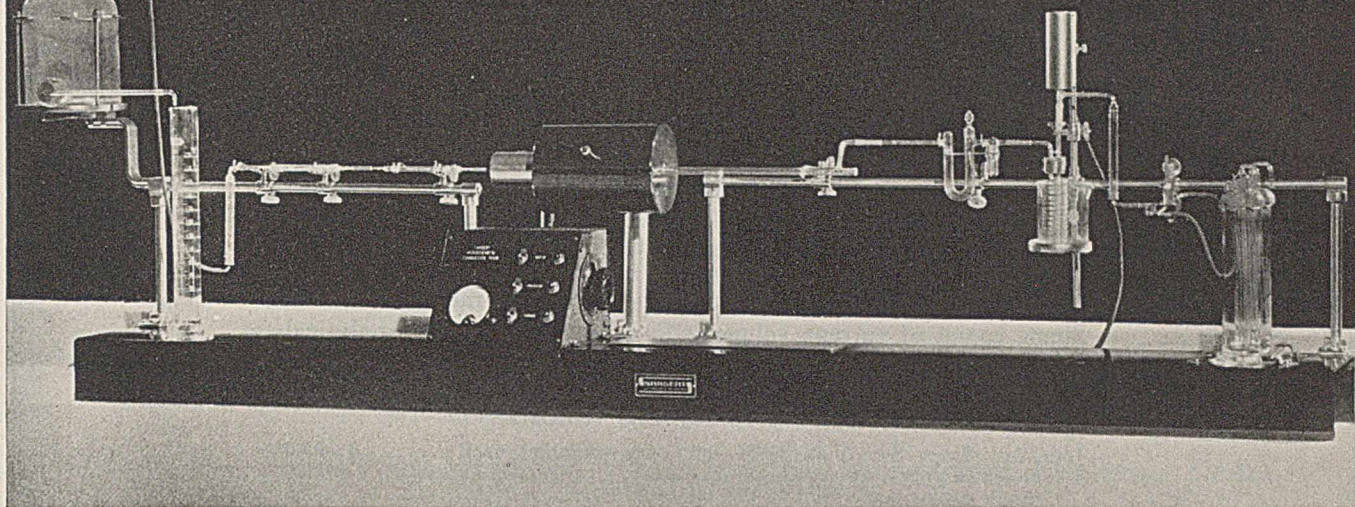
TEST. Place 1 drop of the solution to be tested on a white spot plate. Acidify slightly with dilute hydrochloric acid and add 1 drop of titanium tetrachloride reagent. A slow-forming yellowish or reddish-brown precipitate indicates the presence of ferrocyanide ions. Nitrite, arsenate, chromate, and other strongly oxidizing ions interfere. The limit of sensitivity is about 0.05 mg. of ferrocyanide ion.

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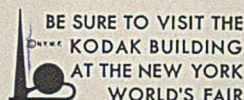
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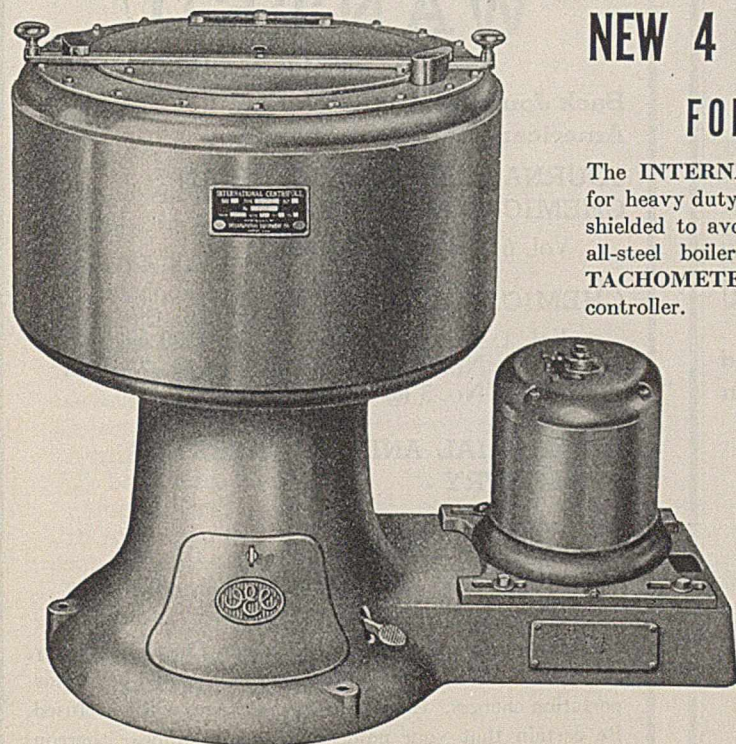
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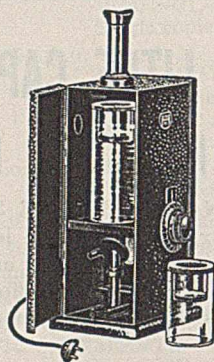
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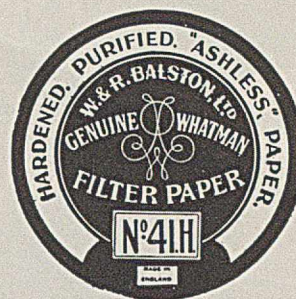
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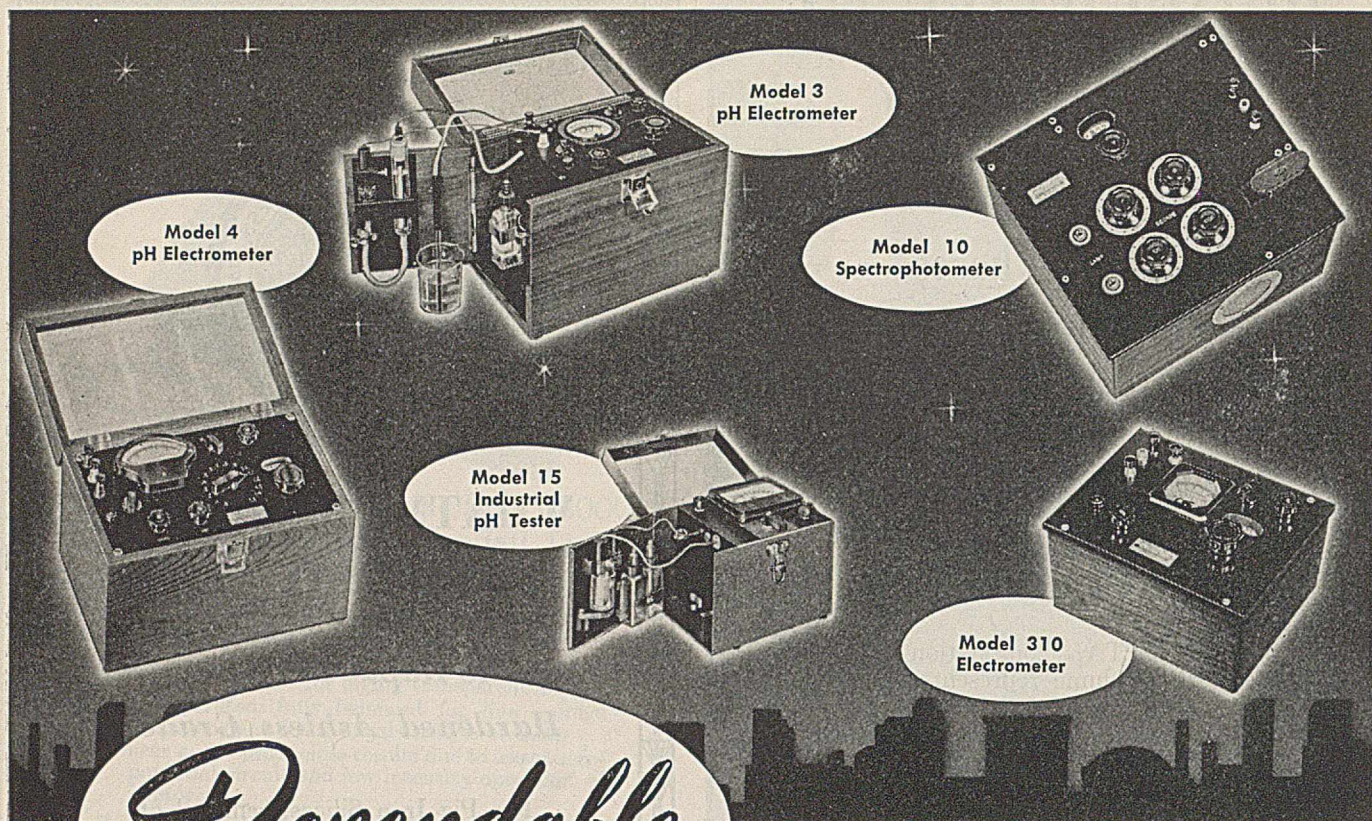
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