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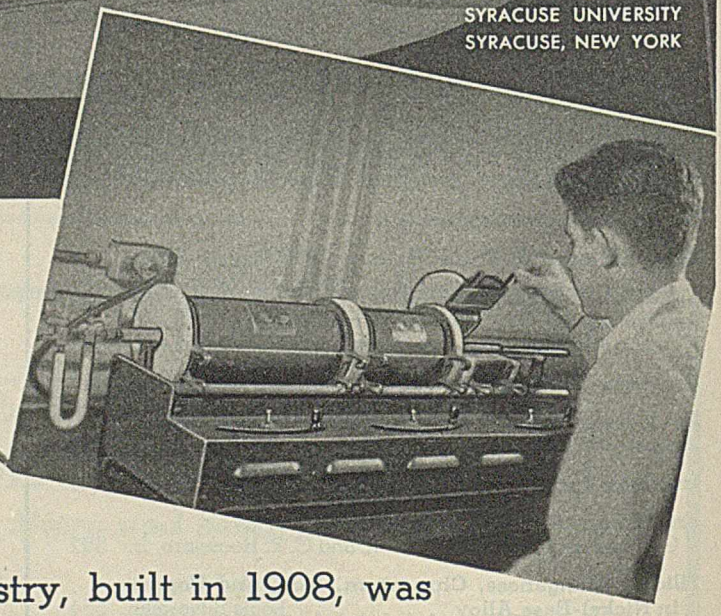

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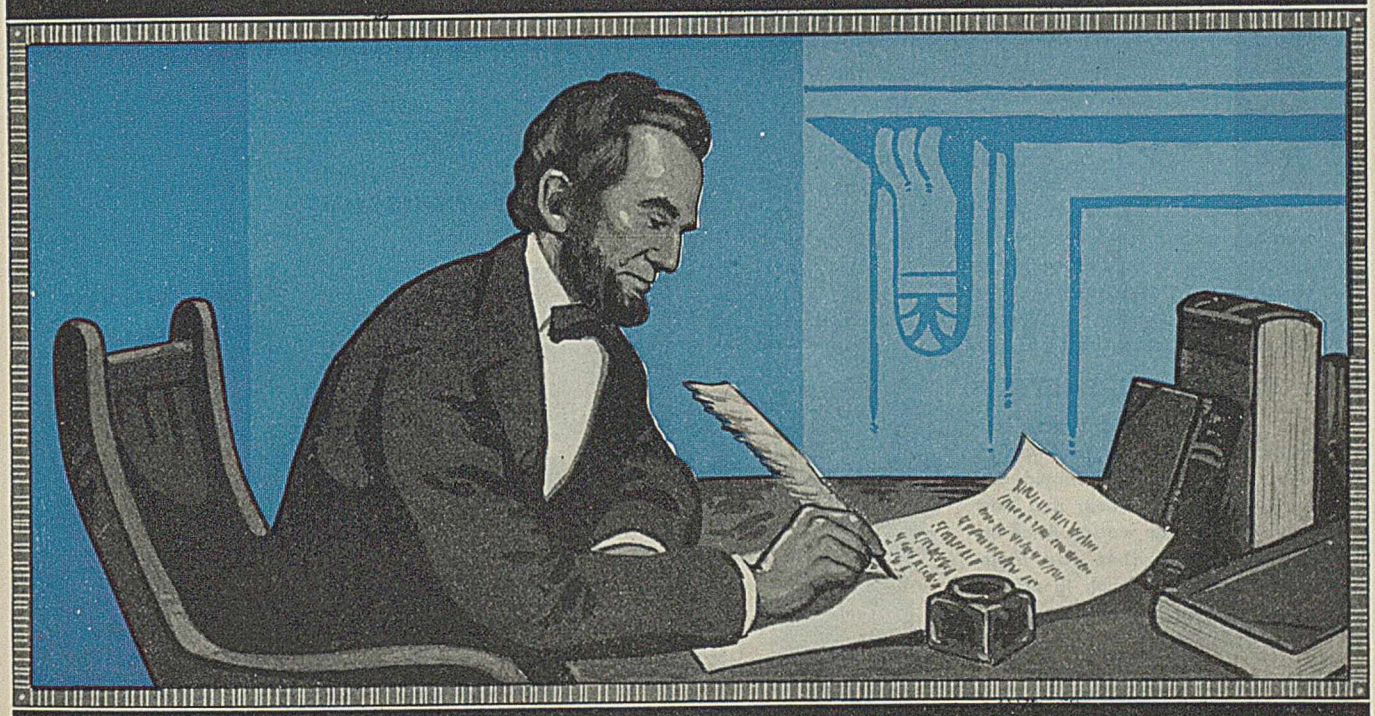

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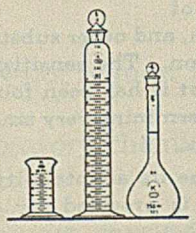

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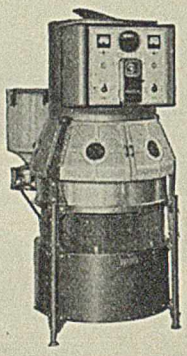

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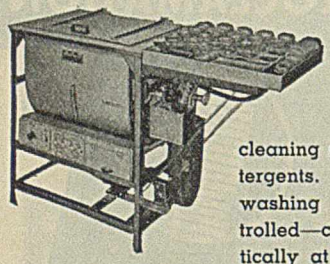

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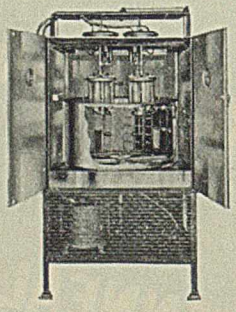

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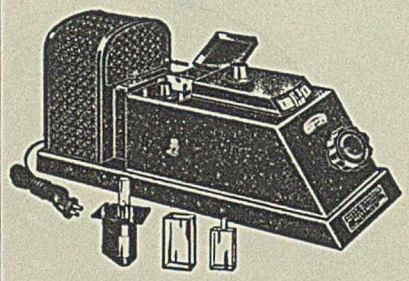

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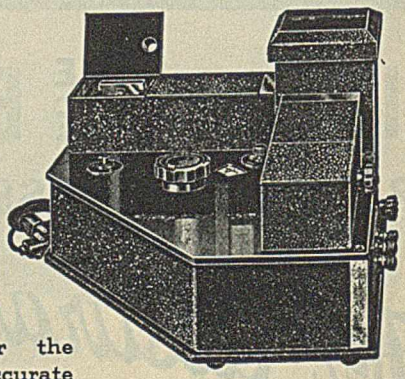

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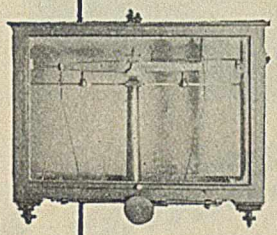

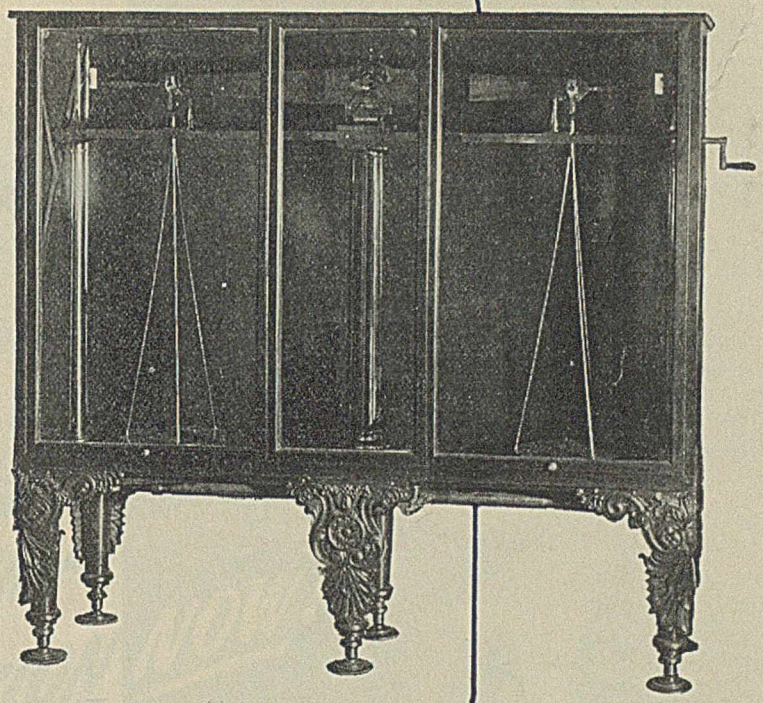

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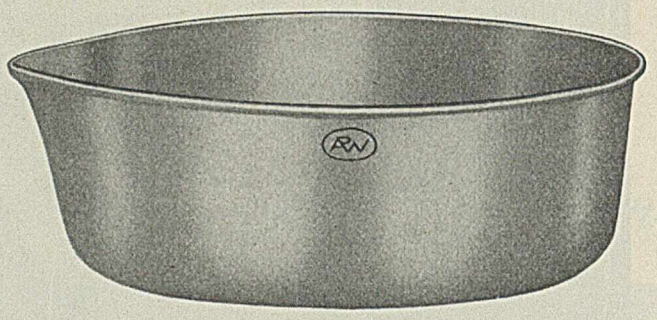

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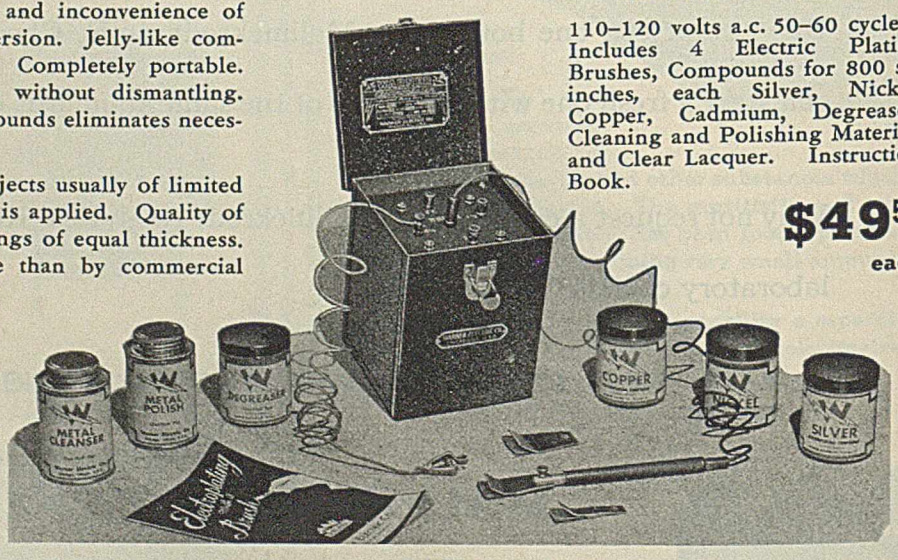

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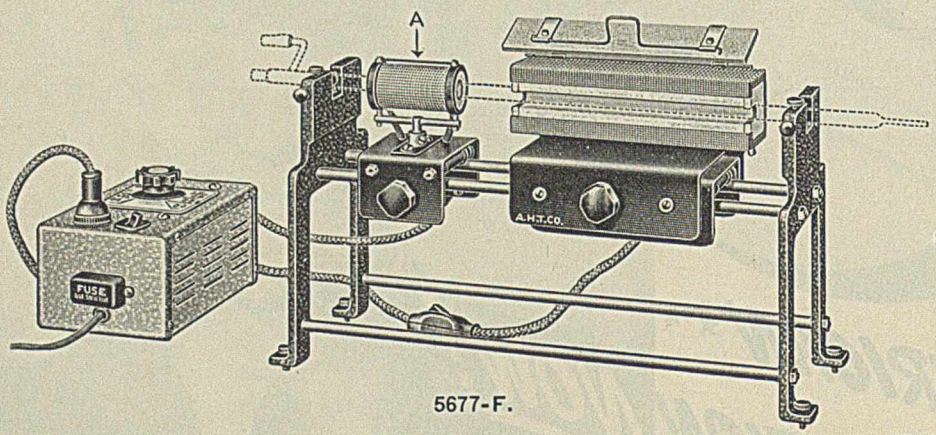

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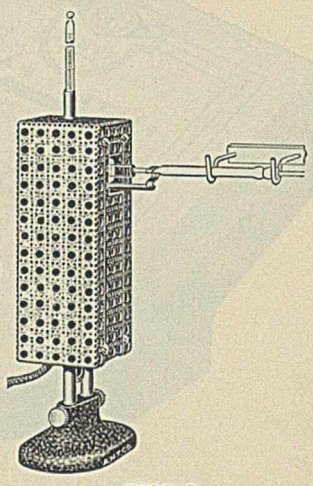

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Field Testing of Mold-Resistant Properties of Interior Oil Paints

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

ALEX M. PARTANSKY

Biochemical Research Laboratory, The Dow Chemical Company, Midland, Mich.

THE object of the present paper is to discuss the problems involved in testing mold-resistant properties of interior oil paints in the field and to describe the author's experience in such work.

The previously reported (*12*) laboratory method for determining mold resistance of oil paints affords a rapid and convenient way for evaluating the relative effectiveness of toxicants under the readily reproducible standardized conditions. However, such effectiveness against fungi is only the first prerequisite for a good paint preservative. In addition, it should be stable, not affect the physical or chemical properties of the paint, and be effective under the conditions of actual use over a fairly long period of time (*2, 3, 14*). In other words, after a quick elimination of ineffective preparations by the laboratory method, the selected compounds should be subjected to a further testing "in the field".

The mold resistance of outside oil paints tested by exposing wooden panels in localities where the prevalent natural conditions are conducive to mold growth (such as certain parts of Florida, Louisiana, Cuba, and the Panama Canal Zone) has been previously reported by various investigators (*1, 4, 5, 6*). However, no systematic study of the mold-resistant properties of interior oil paints under conditions similar to those of actual use could be found in the literature.

As a preliminary step for the investigation, a survey of the occurrence of mold growth on paint at different types of industrial plants was made in the midwestern and eastern states. Results of this survey, supplemented by subsequent experience during the actual testing of fungicidal paints, gave the following picture of the occurrence and cause of mold growth on interior paints:

1. Generally speaking, the prevalence of mold growth on interior painted surfaces (walls, ceilings, window sash, etc.) in the various industrial plants examined was much greater than was originally anticipated. Occurrence of mildew was particularly common in industries where, owing to the nature of the processes involved, a high relative humidity was maintained.
2. In many of the food-processing and packing establishments, such as malt houses, breweries, distilleries, meat and vegetable packing houses, bakeries, and dairies, and in cheese, butter, margarine, pickle, and similar plants, in addition to having high relative humidity, the air also frequently carries dust and water spray and vapors containing organic matter. The latter materials when deposited or adsorbed on the walls and other surfaces provide most favorable conditions for the development of mildew (*9, 13, 14*).

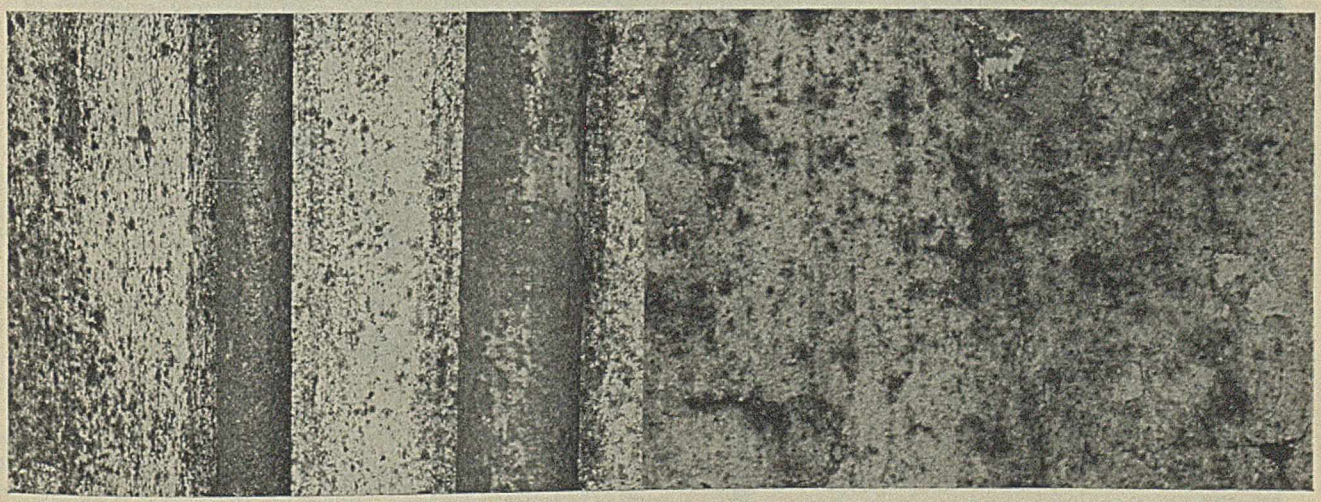

FIGURE 1. TYPICAL MOLD GROWTHS

Left. Unusually heavy growth on wall and pipes repainted less than a year prior to time picture was taken
Right. Interior oil paint, showing fuzzy circular colonies

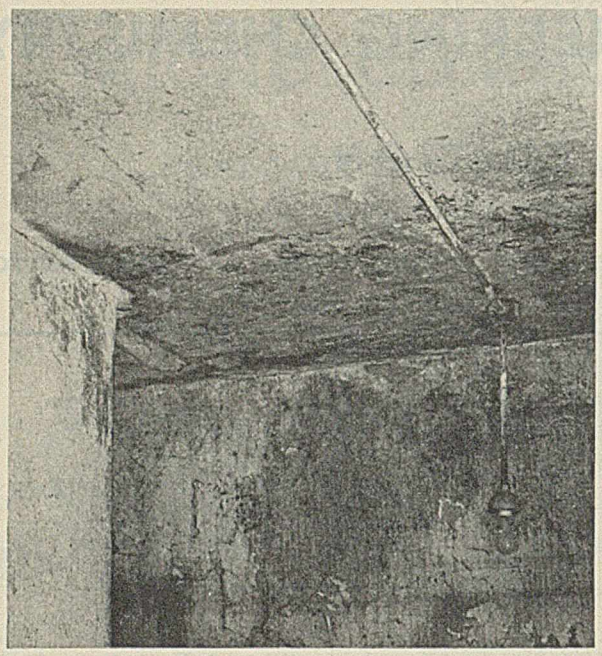

FIGURE 2. DIFFERENCE IN MOLD INFESTATION

Outside wall at back, interior partition at left. Significant gradation in intensity of mold growth on ceiling

3. Mold growth on painted interior surfaces usually manifests itself as black and less frequently as green or red discoloration (*1*, *11*). Although this discoloration is sometimes mistaken by the layman for dirt, the mold growth can be readily distinguished from dirt by the fact that it is usually patchy or blotchy and consists of circular, spreading, and somewhat fuzzy spots (Figure 1).

4. Mold infestation of the painted surfaces is seldom uniform and depends on the local variations in two important factors—moisture content of the paint film and relative humidity of the atmosphere. The following examples illustrate this:

The inner side of a cold outside wall of a building on which moisture is condensing is more apt to have mildew than the inner side of a warmer wall or the interior partitions (Figure 2). For this reason heavier mold growth can be expected during the cold winter months.

For the same reason (moisture condensation), ceilings and portions of the walls near the ceiling have, as a rule, a much heavier mold growth than the lower parts of the walls (Figure 3).

Probably because of the difference in air circulation, corners of the rooms, usually, have more mold growth than the adjacent open wall space.

In selecting a location for testing mold resistance of interior paints, all the above factors should be taken into consideration. Since in indoor testing the conditions conducive to mildew do not, as a rule, vary much from year to year in any one given place, the intensity and uniformity of mold growth on paint from the previous year are one of the best guides in choosing the area for the test.

The uniformity of the conditions throughout the test area is particularly important, since usually only the relative values, such as a comparison between the treated and the untreated paint, are desired. As a further precaution, in a series of test panels every fourth or fifth panel should be painted with an untreated paint. The absence of mold growth on fungicidal paint is considered as a proof of its mold resistance only when the untreated paint panels in the same series show a fair amount of molding. The test paints are best applied to the selected areas during the season when the surfaces to be painted are driest.

From what has been said on the importance of moisture condensation on the surface, it is apparent that the test paint should be applied directly to the walls and ceiling of the building rather than to the separate panels. This fact has been verified by the parallel use of wooden panels and direct painting on ceiling and walls. In all cases, molding of the corresponding untreated or insufficiently preserved paints was less severe on the wooden panels than on the walls.

A typical experiment in testing mold-resistant properties of interior oil paints treated with a selected group of fungicidal agents under actual conditions of usage was as follows:

The 6 × 30 foot test area selected was on the interior of the northern brick wall in a relatively old grain-processing plant in the Middle West. It was located under the fresh-air intake, and at the time of selection had the greatest amount of mildew found anywhere in the plant. For many years previously the walls and ceiling of the building had been whitewashed during the annual summer clean-up period, but in the past 4 years the practice was changed to painting the walls with oil paints and the ceiling with a water-cement paint. The test area was prepared for painting

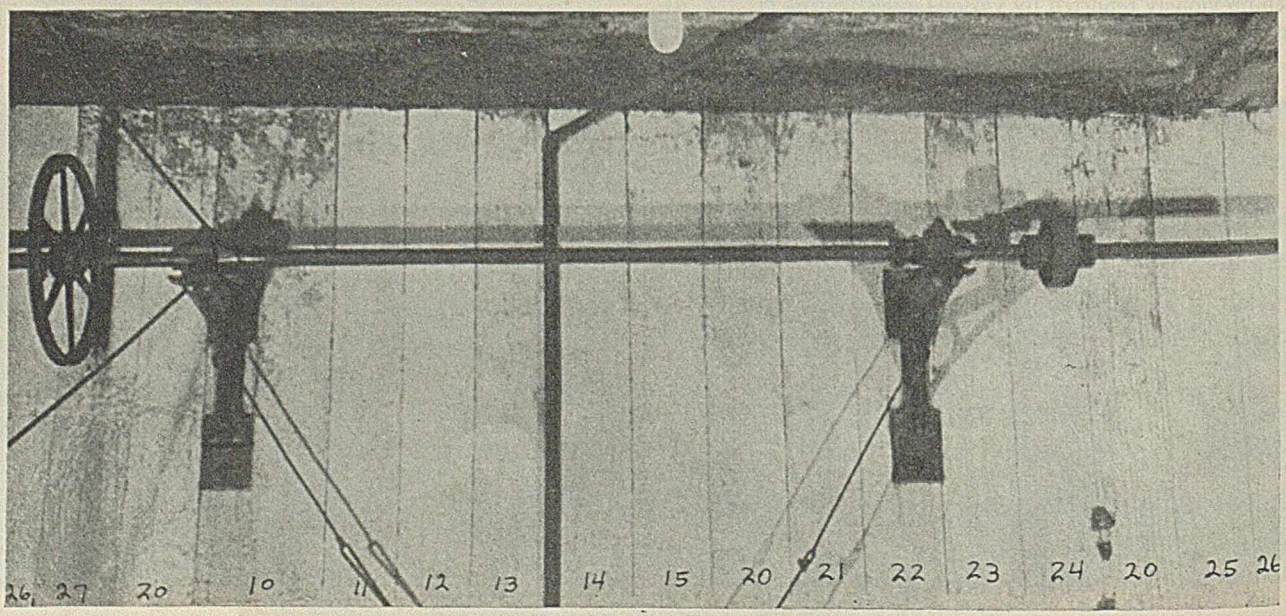

FIGURE 3. GENERAL VIEW OF TEST AREA AFTER EIGHT MONTHS

Note gradation in intensity of mold growth on No. 10, untreated paint, and complete absence of mildew on panels 12, 22, and 26.

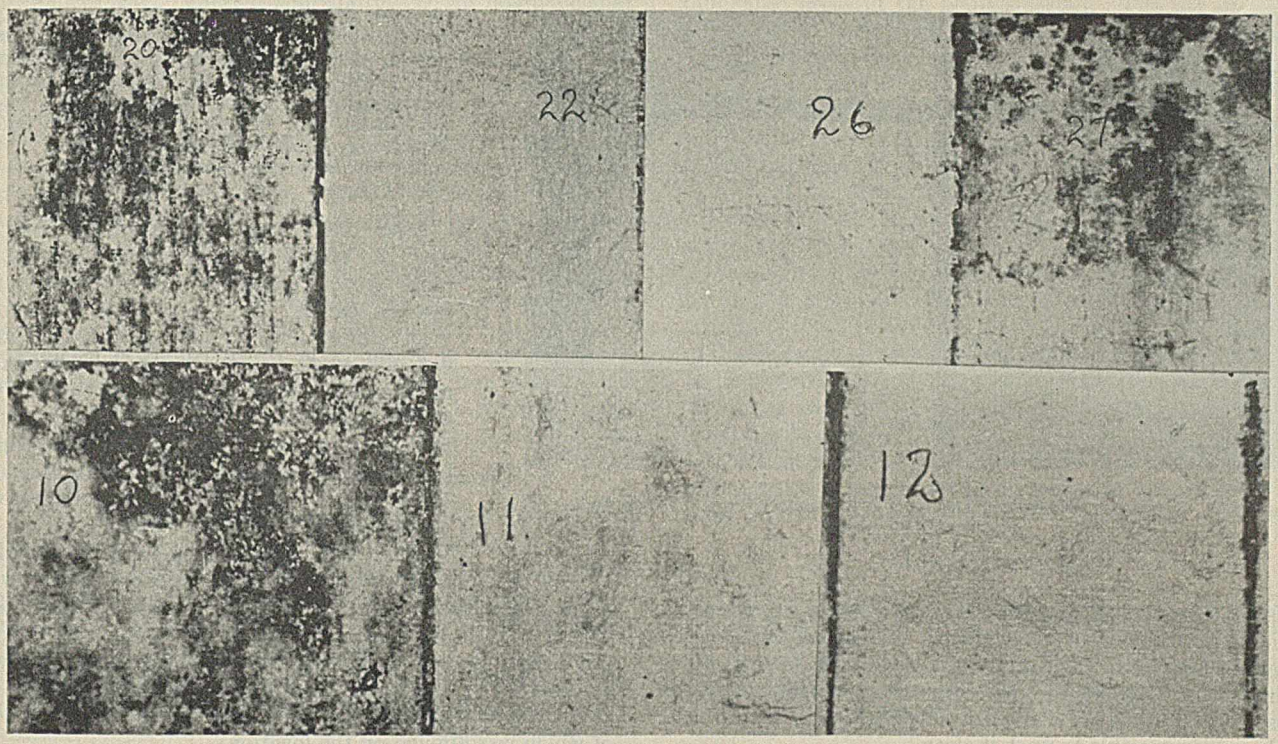

FIGURE 4. CLOSE-UP OF TYPICAL SECTIONS AFTER EIGHT MONTHS' EXPOSURE

10, 11, 12. Painted with mill white paint
10. Untreated paint
11. 1.5 per cent tetrachlorophenol
12. 3 per cent tetrachlorophenol
20, 22, 26, 27. Painted with gloss paint
20. Untreated paint
22. 3 per cent tetrachlorophenol
26. 3 per cent zinc tetrachlorophenate
27. 0.63 per cent calomel

in the usual way—that is, it was scrubbed with soap and phosphate-softened water using a stiff brush, rinsed with fresh water, and the old loose paint was scraped off with a putty knife. The test area was divided into 25 sections, each approximately 12 inches wide and extending 76 inches downward from the ceiling; two coats of test paint were applied. The painting was done in August, 1939, during the summer shut-down when the walls were dry; the plant started operation 2 weeks later.

The paints used were as follows:

Paints 10 to 15 were made up from a widely used flat mill white paint with heat-bodied linseed oil vehicle.

Paints 20 to 27 were made up from a typical interior gloss white paint of a cold-cut Damar resin type.

These paints were treated with preservatives as follows (all percentages are on the original paint weight basis):

Nos. 10 and 20, controls, without preservatives
Nos. 11 and 21, with 1.5 per cent tetrachlorophenol
Nos. 12 and 22, with 3 per cent tetrachlorophenol
Nos. 13 and 23, with 1.5 per cent lead tetrachlorophenate
Nos. 14 and 24, with 3 per cent lead tetrachlorophenate
No. 25, with 1.5 per cent zinc tetrachlorophenate
No. 15, with 2.5 per cent zinc tetrachlorophenate
No. 26, with 3 per cent zinc tetrachlorophenate
No. 27, with 6.3 volume per cent (manufacturer's recommendation) of a commercial antimildew paste containing 8 per cent (by weight) of calomel, giving a total of 0.63 per cent calomel by weight of the total paint, or 3.5 per cent calomel by weight of the nonvolatile portion of the vehicle.

Periodic examination of the test area showed practically complete absence of mildew during the first 3 months. However, with the advent of cold weather, when moisture condensation on the wall kept the paint surface continuously wet, the mold growth began to make its appearance.

The original untreated paints, 10 and 20, and the calomel-containing paint, 27, were the first to show mold growth. Paints 13 and 23 with 1.5 per cent of lead tetrachlorophenate were next, and 8 months later, on April 3, 1940, when photographs shown in Figures 3 and 4 were taken, a small amount of mold growth was also noted on paint 21 (gloss white with 1.5 per cent tetrachlorophenol). At the same time, all paints containing 3 per cent of toxicants and the mill white paint containing 1.5 per cent tetrachlorophenol were still mold-free.

In all cases the mold growth started on the upper end (near the ceiling) of the test sections and with time gradually spread downward (Figure 3). The same photograph gives the general view of the setup and the appearance of a part of the test area and the surroundings at that time. Note particularly the severity of mold infestation of the ceiling (painted with a cement paint) and the very interesting gradation in the intensity of mold growth on section 10. Close-ups of the upper portions of the two sets of typical test sections are given in Figure 4.

The next set of photographs was taken on August 26, 1940, after one year of exposure. By that time the plant had been shut down for cleaning and redecoration; thus, the walls had already been repainted with an oil paint and the ceiling sprayed with a cement-water paint. These operations resulted in some damage to the test area, both from the water during cleaning and from the spraying of the cement paint. In addition to this, dirt accumulation from April to August was rather severe. The general view of the test area, photographed after a light washing with water to remove surface dirt, is shown in Figure 5. The paints containing tetrachlorophenol (except for the upper portions of the sections splattered with the cement paint) washed practically clean, indicating that their original dark color was due primarily either to the surface dirt or to the loose readily washable mold growth on the dirt film. In contrast to this, the mold growth on the untreated paint, No. 10, could not be washed off with the same effort, indicating that in this case the mildew had grown into the paint itself.

The above-described test area was allowed to remain undisturbed for another year. During the second season dirt deposition on the walls was again heavy. The general view of the test area, taken July 15, 1941, after a light washing,

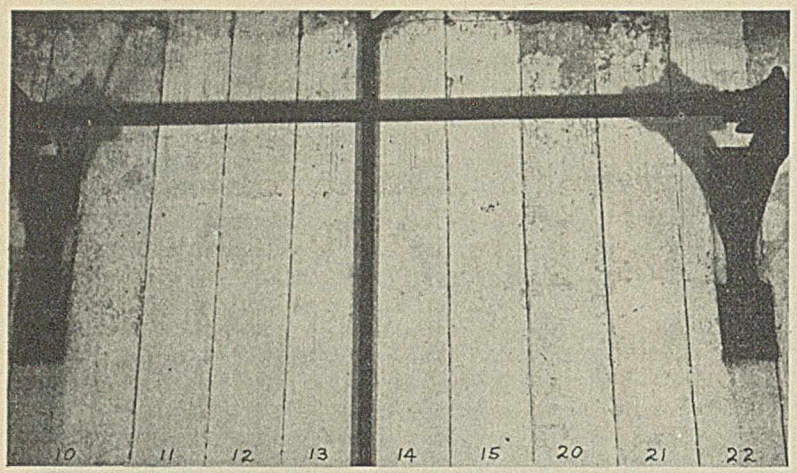

FIGURE 5. GENERAL VIEW OF PART OF TEST SECTION (ONE-YEAR EXPOSURE) AFTER WASHING

(Figure 6, above), shows that after two years' exposure the general distribution of mold growth was about the same as after the first year. The sections painted with flat mill white paint washed almost to their original whiteness, while the gloss paint, both treated and untreated, acquired a gray cast, making it impossible to wash it clean.

In May, 1939, two sets of 12 × 24 × 0.5 inch white pine panels were prepared in the laboratory, in which one half (6 × 24 inch areas) of each panel was painted with the untreated paints, No. 10 or 20, and the other half of each with treated paints (same as previously listed). Two coats of each paint were applied at the laboratory, and in addition one set of panels received a third coat of paint applied on the location just before the panels were exposed. The wooden panels were hung on the wall near the ceiling in the same room and just east of the test area described above.

After one season's exposure, in contrast with the wall tests, only a small amount of mold growth could be seen on any of the wooden panels. However, after the second year, panel sections painted with untreated flat mill white paint developed considerable mold growth, while on the treated paints the growth was small or absent. Photograph of the back side (toward the wall) of these panels is given in Figure 6 (below). The front side of the panels (toward the room) accumulated too much dirt for the observation to be of value. The 2-year results with the flat mill white paints on wooden panels were in good agreement with those obtained with the wall tests The gloss paint on the wooden panels of the same set molded but lightly except in places where dirt accumulation was considerable. There was no difference in mold growth between the two-coat and the three-coat panels (the third coat of which was applied on the location).

The difference in the results obtained with the wooden panels and the painted wall area, after one season's exposure, is accounted for by the difference in moisture condensation

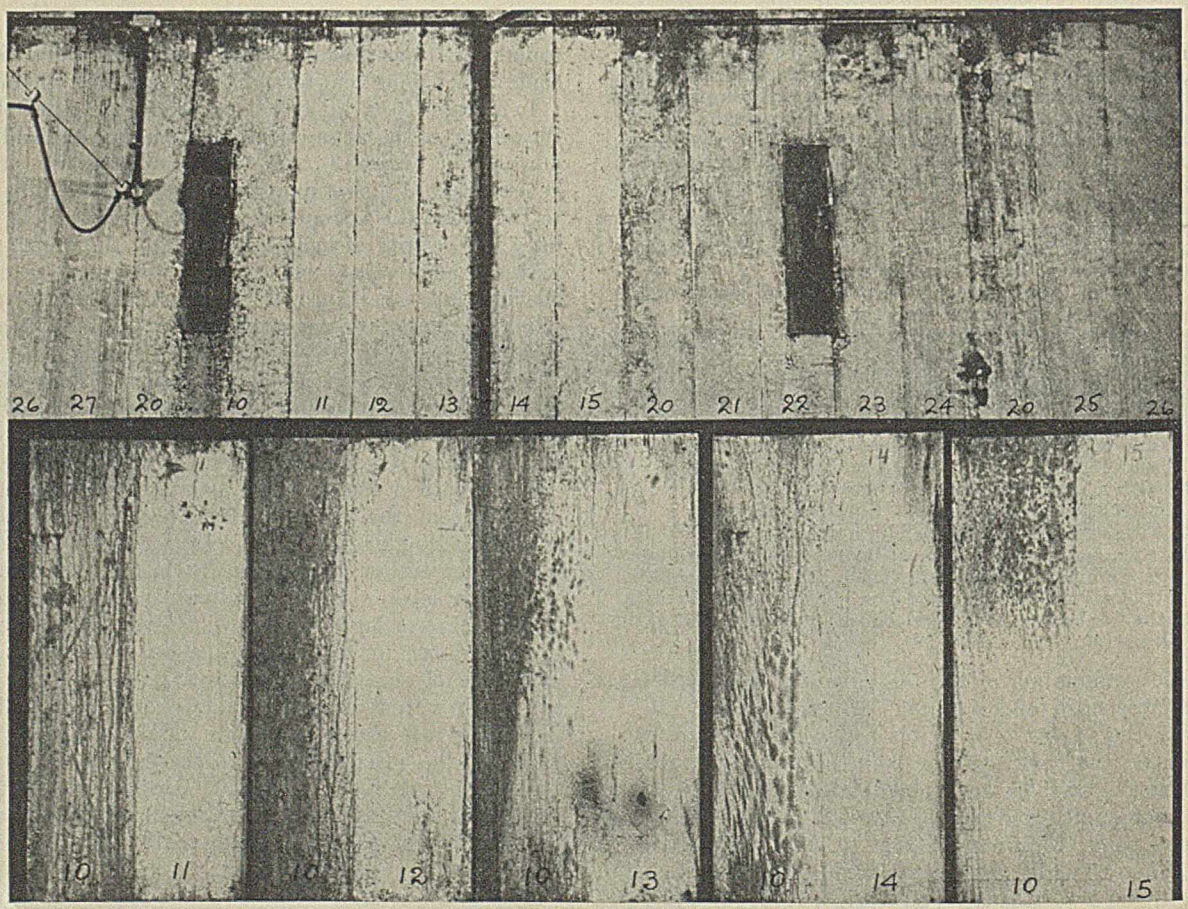

FIGURE 6. PANELS AFTER TWO-YEAR EXPOSURE

Above. General view of test area after washing. Note clearness of Nos. 11 and 12, containing tetrachlorophenol in mill white.
Below. Back side of "half and half" wooden panels. Left-hand portion of each was painted with untreated paint, No. 10.

on the surfaces. Another contributing factor might be that the wood used in the panels was new, while the painted wall area had a previous mold growth. This mold growth, although partially scraped and washed off in preparing the surface for repainting, nevertheless provided a ready-made source of mold infection for the new paint. A considerable volume of evidence is now at hand which suggests that under favorable conditions certain types of mold growth, when painted over, can and will come through a nontoxic paint film. This has also been pointed out by Findlay (*1*).

For the above reason, cleaning and disinfection of old moldy surfaces prior to repainting are important and should be made a part of the repainting procedure (*1, 7, 8, 10*). This contention is confirmed by actual tests in which identical paints were applied to a contaminated area, one half of which was first washed with a disinfectant solution while the other half was not.

Summary and Conclusions

Mold growth on interior oil paints is common in industrial plants where a high relative humidity is maintained.

The mold growth is never uniform even in any one room, but is heaviest on surfaces where moisture condensation takes place, such as the interior side of cold outside walls, locations near refrigeration pipes, ceilings, etc.

Organic matter, vapors, and dust are conducive to mold growth but interfere somewhat with the testing of the mold-resistant properties of paints. However, where mold growth develops on the dust deposited over an oil paint, a preserved paint can be relatively easily washed clean, while on a nonfungistatic paint the mold growth becomes established in the paint itself and cannot be washed off.

Mold resistance of interior paints should be tested by applying the test paints to carefully selected sections of walls and ceiling on which water condensation is continuously taking place and which are found to be the most heavily contaminated areas in the plant selected. The use of wooden panels, even when most advantageously exposed, may give erroneous results due to the difference in conditions between them and the painted surfaces of the building.

In preparing moldy surfaces for repainting, disinfection of the cleaned surface is beneficial, since some molds can grow through a paint film.

Without an adequate preservative the paint with a cold-cut resin type of vehicle molded as readily as the paint with a vegetable oil type of vehicle.

Tetrachlorophenol and zinc tetrachlorophenate were found to be the most effective paint preservatives among those tested.

Under extremely severe conditions of testing 3 per cent of tetrachlorophenol and 3 per cent of zinc tetrachlorophenate preserved both an oil and a cold-cut resin type of interior paint for 2 years.

The field test confirmed earlier conclusions on the relative effectiveness of fungicides in oil paints as determined by the rapid laboratory method.

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Determination of Small Amounts of Benzene in the Presence of Cyclohexane

And of Toluene in the Presence of Methylcyclohexane

B. B. CORSON AND L. J. BRADY, Mellon Institute, Pittsburgh, Penna.

THE method described in this paper consists in measuring the temperature rise (ΔT) caused by the interaction of benzene or toluene with nitrating acid under definite conditions, and reading the percentage of aromatic from a curve relating ΔT with hydrocarbon composition. Benzene, up to 12 per cent, can be determined by this empirical method without diluting the sample. For higher concentrations the sample must be diluted with cyclohexane, so that ΔT will not exceed 20° C.

This thermometric method, which depends specifically upon the heat of reaction of benzene with nitrating acid, is especially suitable for the analysis of benzene-cyclohexane mixtures resulting from the hydrogenation of benzene. Analysis by refractive index or density is unreliable, owing to the fact that cyclohexane is usually contaminated with methylcyclopentane (*1*) (C_6H_{12}: n_D^{20} 1.4264, d_4^{20} 0.7781; $CH_3C_5H_9$: n_D^{20} 1.4099, d_4^{20} 0.7488). Also, open-chain paraffins often contaminate benzene and the cyclohexane produced from it. The thermometric method gives results which are at least as accurate as those obtained from freezing point data. In the analysis of a series of synthetic benzene-cyclohexane mixtures, in which the benzene concentrations varied from 0 to 12 per cent, the average deviation from the mean was 0.06 per cent.

The thermometric method works equally well with toluene-methylcyclohexane mixtures; but in the case of xylene-dimethylcyclohexane mixtures ΔT is dependent upon the isomeric composition of the xylene, and therefore, the relationship between ΔT and aromatic content must be determined for each sample of xylene in question.

Development of Method

The variables of acid strength, period of stirring, water content, size of stirrer, initial temperature, and change of ΔT with time have been studied.

The procedure was to add 50 cc. of a mixture of benzene and cyclohexane (containing 5.2 per cent of benzene) to 100 cc. of nitrating acid contained in a small-necked pint thermos bottle

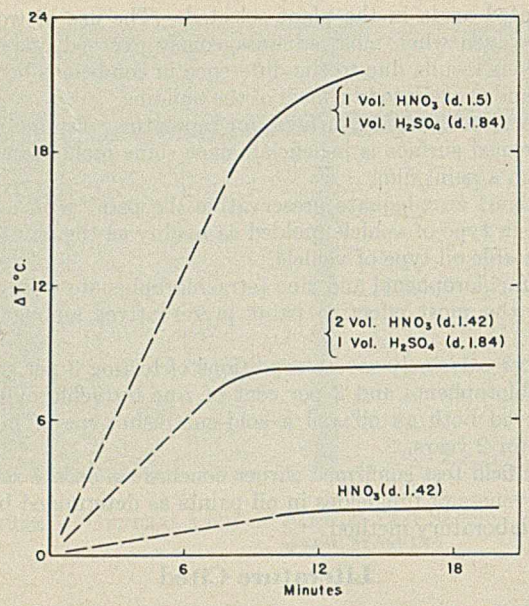

FIGURE 1. VARIATION IN ΔT WITH COMPOSITION OF ACID

Broken lines, temperature during stirring period
Solid lines, temperature after stirring period

whose metal collar was coated with paraffin to protect it against the acid. Both solutions, acid and hydrocarbon, were initially at room temperature, as was the thermos bottle. After stirring for different lengths of time, the stirring was stopped, and the temperature of the acid-hydrocarbon mixture was measured with a 50° thermometer graduated in 0.1° C.

EFFECT OF STRENGTH OF NITRATING ACID. Nitrating acid containing 1 volume of nitric acid (density 1.5) and 1 volume of sulfuric acid (density 1.84) was unsatisfactory, for ΔT continued to increase long after the stirring had been stopped (Figure 1), owing to slow de-emulsification of the acid-hydrocarbon mixture. Only 40 cc. of hydrocarbon were used with this acid because 50 cc. of hydrocarbon raised the temperature to such an extent that the nitric acid rapidly decomposed. The finally accepted nitrating acid contained 2 volumes of nitric acid (density 1.42) and 1 volume of sulfuric acid (density 1.84). This acid gave a definite end point with a sufficiently large ΔT. Nitric acid alone (density 1.42) yielded a ΔT of only 2° C., whereas mixed acid containing one third as much nitric acid produced a ΔT of 8.5° C. (Figure 1).

EFFECT OF STIRRING PERIOD. Figure 2 shows the effect of varying the length of the stirring period. The mixed acid contained 2 volumes of nitric acid (density 1.42) and 1 volume of sulfuric acid (density 1.84). The ΔT was recorded 10 minutes after the end of the stirring period. Evidently the length of the stirring period is critical up to 9 minutes, but after 9 minutes ΔT is essentially independent of small changes in the stirring time ($\Delta T/t$ being 0.03° C. per minute, which corresponds to an analytical uncertainty of less than 0.02 per cent of benzene per minute).

EFFECT OF WATER. A mixture of 5.2 per cent of benzene and 94.8 per cent of cyclohexane was analyzed after drying, and also after saturating with water. The ΔT of the dry sample was 0.1° C. lower than that of the wet sample. Wet cyclohexane gave the same ΔT as dry cyclohexane (0.1° C.). It is recommended that the hydrocarbon under examination be dried by anhydrous calcium chloride before analysis.

EFFECT OF STIRRER. The recommended stirrer is a glass rod, 7 mm. in outside diameter and 24 cm. long, with a flattened end ±13 mm. wide × 19 mm. long (Figure 3); it is operated by a 3000 r. p. m. electric motor. Using a stirrer with a blade twice as large raised ΔT by 0.3° C. with a benzene-cyclohexane mixture containing 5.2 per cent of benzene, and this difference corresponds to an apparent increase in the benzene content of about 0.2 per cent.

EFFECT OF INITIAL TEMPERATURE. It is to be noted that ΔT for the reaction of benzene with nitric acid is greater at 20° C. than at 30° C., which is opposite to the thermodynamic prediction, because $\frac{(d\Delta H)}{(dT)_p} = \Delta C_p$, and ΔC_p is negative. The effect is less with toluene-methylcyclohexane, but is in the

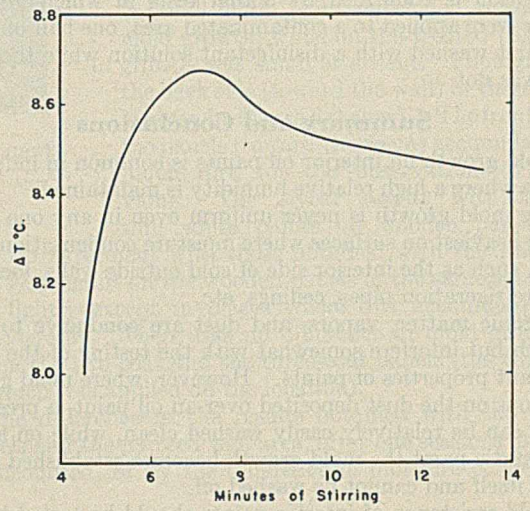

FIGURE 2. VARIATION IN FINAL ΔT WITH TIME OF STIRRING

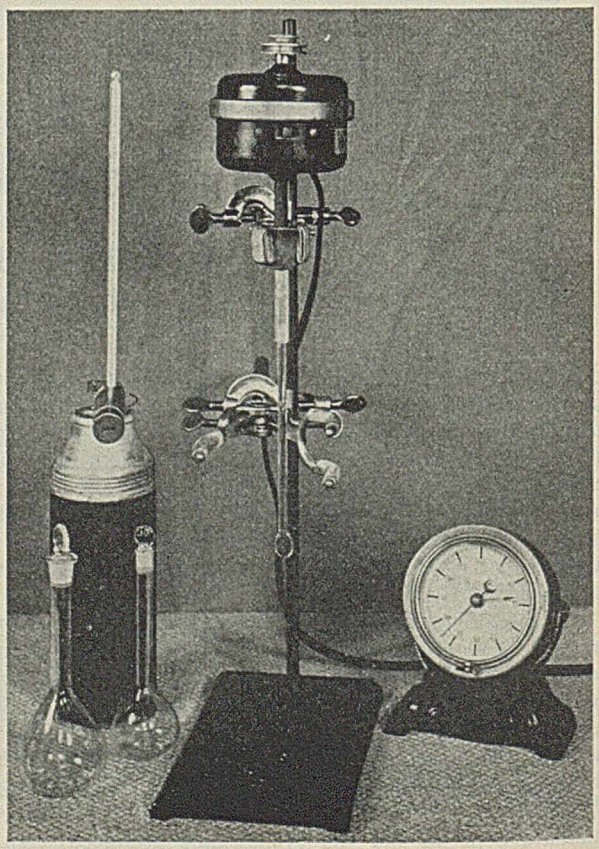

FIGURE 3. EQUIPMENT FOR ACID HEAT TEST

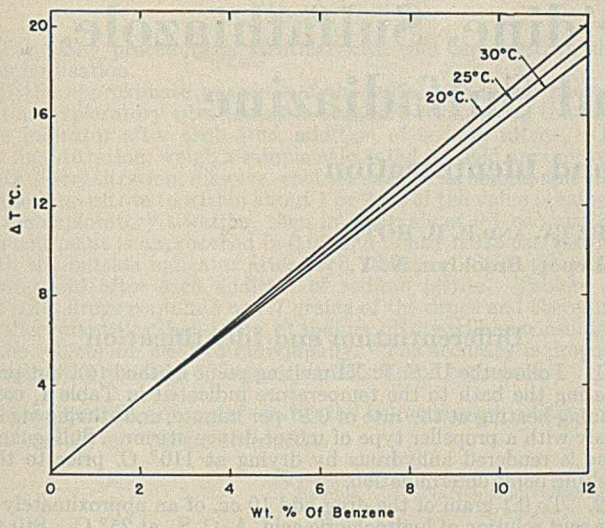

FIGURE 4. ACID HEAT TEST DATA FOR BENZENE-CYCLOHEXANE
Initial temperature, 20°, 25°, and 30° C.

same direction. Presumably this anomalous relationship of ΔT to initial temperature is attributable to the relative speeds of demulsification at the different temperatures.

PURITY OF HYDROCARBONS. The benzene was of reagent quality; the cyclohexane was made from it by catalytic hydrogenation under pressure at about 135° C. The cyclohexane was shaken with nitrating acid, washed with water, and distilled. Its freezing point of 5.9° C. indicated a purity of 99.7 per cent.

TABLE I. ACID HEAT TEST DATA FOR BENZENE-CYCLOHEXANE (FIGURE 4)

Weight Percentage of Benzene	ΔT from Initial Temperatures of 20° C.	25° C.	30° C.
0.00	0.10	0.10	0.10
0.56	1.10	1.10	1.09
1.08	2.07	2.04	2.00
1.56	2.87	2.79	2.70
3.29	5.59	5.40	5.22
6.38	10.82	10.44	10.07
10.15	17.13	16.55	16.00
12.01	20.13	19.44	18.75

TABLE II. ACID HEAT TEST DATA FOR TOLUENE-METHYLCYCLOHEXANE (FIGURE 5)

Weight Percentage of Toluene	ΔT from Initial Temperatures of 20° C.	25° C.	30° C.
0.00	0.32	0.32	0.32
1.34	3.96	3.95	3.95
3.50	9.71	9.64	9.58
5.49	15.00	14.89	14.80

Determination of Benzene in Cyclohexane

One hundred cubic centimeters of nitrating acid (1 volume of sulfuric acid, d. 1.84, plus 2 volumes of nitric acid, d. 1.42), measured in a 100-cc. volumetric flask, are poured into a thermos bottle, the flask being allowed to drain 15 seconds. The thermometer is placed in the thermos, the bulb resting on the bottom of the latter, and the temperature is read after 2 to 3 minutes (with a magnifying lens). Fifty cubic centimeters of hydrocarbon sample (measured in a 50-cc. volumetric flask and at the same temperature as the acid) are added to the acid in the thermos. An interval timer is started and the flask is allowed to drain 15 seconds.

The stirrer is placed in the thermos, with the bottom of the stirring blade about 1.25 cm. (0.5 inch) from the bottom of the thermos, and when the timer reaches 30 seconds the motor is started. The stirrer is run 9.5 minutes and then removed from the mixture. The thermometer is placed in the thermos (bulb resting on bottom of thermos) and the temperature is read 10 minutes after stopping the stirrer—i. e., 20 minutes after the addition of the hydrocarbon. The mixture is not shaken nor stirred during the last 10 minutes.

For precise work, not only should the acid and hydrocarbon be thermostated to the same temperature, but the thermos bottle should also be at that temperature (although its heat capacity is small).

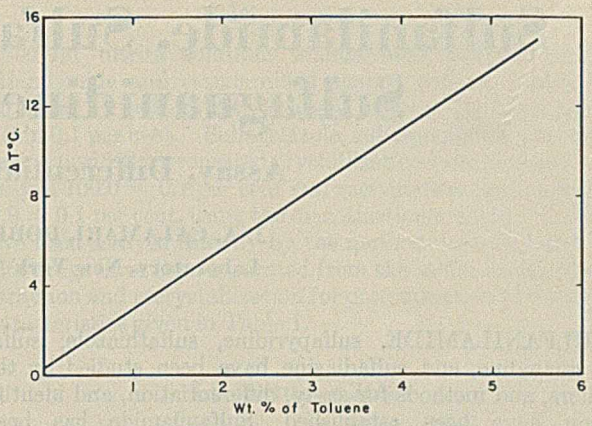

FIGURE 5. ACID HEAT TEST DATA FOR TOLUENE-HEXAHYDROTOLUENE
Initial temperature, 20°, 25°, and 30° C.

The benzene content is read from the family of curves corresponding to the data in Table I, and it is to be noted that ΔT is essentially independent of the initial temperature (20° to 30° C.) up to 1.5 per cent of benzene.

Table II presents acid heat data for toluene-methylcyclohexane mixtures.

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CONTRIBUTION from the Koppers Multiple Fellowship on Tar Synthetics, Mellon Institute, Pittsburgh, Penna.

Cleaning Porcelain Crucibles

JOHN E. D. CARWARDINE
55 Donald St., Winnipeg, Manitoba, Canada

THE method described here can save considerable time and confusion by cleaning "burner grime" and marking inks such as ferric chloride from porcelain crucibles. It does not injure the glaze in any manner, but leaves the crucible with a perfectly clean surface.

Place the crucible in a dish of fused potassium bisulfate for about 5 minutes. Remove, allow to cool, and wash with hot water.

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Sulfanilamide, Sulfapyridine, Sulfathiazole, Sulfaguanidine, and Sulfadiazine

Assay, Differentiation, and Identification

J. A. CALAMARI, ROBERT HUBATA, AND P. B. ROTH
Laboratory, New York Medical Depot, Brooklyn, N. Y.

SULFANILAMIDE, sulfapyridine, sulfathiazole, sulfaguanidine, and sulfadiazine have been studied by the authors, and methods for assay, differentiation, and identification have been established. Sulfanilamide has been adopted as a primary standard for the standardization of the nitrite solution used in the assay of the sulfa drugs, because of the ease with which it may be purified and its stability in air. Rapid differentiation of the sulfa drugs from each other is accomplished by means of the solubility of the original compounds and the solubility and color of some of the easily prepared derivatives. The identity of the sulfa drugs is established by determining the melting points of both the original drugs and the 2-amino hydrolysis products in the case of sulfapyridine, sulfathiazole, and sulfadiazine. The melting points of sulfanilamide and sulfaguanidine and the presence of ammonia in their hydrolysis products identify them.

The authors have selected the diazotization reaction for the assay of the sulfa drugs in preference to an element analysis such as that depending on the estimation of sulfur (*1*), because the former is based on the presence of a characteristic group—the aryl amino group—and because of the greater rapidity of the assay. Using the easily purified sulfanilamide as a primary standard for the standardization of the sodium nitrite volumetric solution, the possibility of error is less than in assay methods employing volumetric solutions standardized by more indirect methods such as the sulfanilamide assay of the U. S. Pharmacopoeia (*4*). Furthermore, the assay method is applicable to all five sulfa drugs either as pure compounds or in tablets, and since the standardization reaction and procedure are identical with those of the assay method, the possibility of an end-point error is minimized.

The information necessary for the differentiation and identification of the sulfa drugs is given in Table I. The methods employed in establishing these characteristics are described below, in following paragraphs numbered to correspond with those in the table.

Table I shows that sulfanilamide can be differentiated from the other sulfa drugs by its solubility in water; sulfaguanidine by its insolubility in sodium hydroxide solution; sulfathiazole by the insolubility of its diazonium chloride at 0° to 4° C.; and sulfadiazine by the insoluble compound formed with stannous chloride.

Differentiation and Identification

1. Follow the U. S. P. XI melting point method (*6*), but preheating the bath to the temperature indicated in Table I, continuing heating at the rate of 0.5° per minute, and stirring vigorously with a propeller type of motor-driven stirrer. Sulfaguanidine is rendered anhydrous by drying at 110° C. prior to the melting point determination.

2. To 0.1 gram of the drug add 10 cc. of an approximately 5 per cent solution of hydrochloric acid, A. C. S., at 25° C. Stir to effect solution.

3. To 0.1 gram of the drug add a 5 per cent solution of sodium hydroxide, reagent grade, at 25° C. and stir.

4. To 0.1 gram of the drug add 20 cc. of distilled water at 25° C. and stir vigorously. The numerical values offered have been obtained from the literature (*3*).

5. Reflux 1 to 2 grams of the drug with 50 cc. of hydrochloric acid, A. C. S., for 1 to 2 hours. Cool and make strongly alkaline with a 25 per cent solution of sodium hydroxide. Cool and extract with ether. Collect the ether extractions, filter, and evaporate. Determine the melting point by the U. S. P. XI (*6*) method, employing vigorous stirring as in paragraph 1.

6. Place 0.50 gram of the drug in a test tube and dissolve in 7 cc. of hydrochloric acid, A. C. S., and 35 cc. of distilled water. Cool in an ice water bath. Add 20 cc. of 0.1 *M* sodium nitrite solution slowly with constant stirring and cooling. Cool the contents of the tube to 0° to 4° C.

7. Dissolve 0.1 gram of the drug in 5 cc. of a 5 per cent solution of hydrochloric acid, A. C. S., and add 1 cc. of stannous chloride–hydrochloric acid reagent. Cool to 20° C. and allow to stand for 10 minutes.

8. Add 20 cc. of acetone, A. C. S., to 0.1 gram of the drug and agitate.

9. Add 20 cc. of ether, U. S. P., to 0.1 gram of the drug and agitate.

REAGENTS. Sodium nitrite solution. Dissolve 7.0 grams of sodium nitrite, A. C. S., to make 1 liter of 0.1 *N* or 0.1 *M* solution. Standardize as directed below.

Stannous chloride–hydrochloric acid reagent. Dissolve 50 grams of stannous chloride, reagent grade, in 50 cc. of hydrochloric acid, A. C. S.

Sulfanilamide (for primary standard). Recrystallize once from acetone and twice from water.

Starch iodide paper, U. S. P. XI (*7*), and starch iodide paste (*2*).

STANDARDIZATION. Dissolve 0.52 gram of pure sulfanilamide (see reagents) in 7 cc. of hydrochloric acid, A. C. S., and 35 cc. of water. Add 30 grams of ice and titrate with 0.1 *M* sodium nitrite volumetric solution, using starch iodide paper or paste as an outside indicator. Each cubic centimeter of 0.1 *M* sodium nitrite is equivalent to 0.01722 gram of sulfanilamide.

TABLE I. IDENTIFICATION OF SULFA DRUGS

	Sulfanilamide	Sulfapyridine	Sulfathiazole	Sulfaguanidine	Sulfadiazine
Melting Point, ° C.	165.5–166.0°	191–192° (decomposed)	201–202° (decomposed)	190.5–191.5°	251–252° (decomposed)
1. Temperature of preheated bath, ° C.	150°	170°	180°	170°	225°
2. Solubility in 5% HCl	Soluble	Soluble	Soluble	Soluble	Soluble
3. Solubility in 5% NaOH	Soluble	Soluble	Soluble	Insoluble	Soluble
4. Solubility in water, mg. per 100 cc. (*5*)	Soluble. Very soluble in hot water. 800 at 25° C.	Insoluble, 49.5 at 37° C.	Insoluble, 94 at 37° C.	Insoluble, 190 at 37° C.	Insoluble, 12.3 at 37° C.
5. Basic hydrolysis product, melting point	NH_3	56°	90°	NH_3	126°
6. Diazonium chloride, color of solution and solubility	Colorless Soluble	Yellow Soluble	Yellow Insoluble at 0–4°	Colorless Soluble	Pale yellow Soluble
7. $SnCl_2$-HCl	No ppt.	No ppt.	No ppt.	No ppt.	White ppt.
8. Solubility in acetone	Soluble	Soluble	Soluble	Soluble	Soluble
9. Solubility in ether	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

Assay

The assay procedure is identical with that employed in the standardization.

If the approximate quantity of the sulfa drug is not known, run an exploratory titration as in standarization, using the outside indicator after each 1-cc. addition of sodium nitrite. On the final titration, weigh a sample calculated to yield an approximate 30-cc. titration, dissolve, cool the sample as before, and add the sodium nitrite to within about 1 or 2 cc. of the value obtained in the exploratory titration, then in intervals of 0.1 cc., and as the end point is approached in 0.05 and finally 0.025 cc., testing with the outside indicator after each addition. Stir vigorously during and after each addition of sodium nitrite. Tablets of the sulfa drugs contain 5 or 7.7 grains of the drugs and therefore smaller quantities than 30 cc. of sodium nitrite will be consumed if the tablets are assayed individually. The accuracy is proportional to the quantity of sodium nitrite solution consumed.

If the quantity of sample indicated below is used, a titration of about 30 cc. will be obtained:

	Quantity of Sample	Each Cc. of 0.1 *N* $NaNO_2$ Equivalent to:
	Gram	*Gram*
Sulfanilamide	0.52	0.01722
Sulfapyridine	0.75	0.02492
Sulfathiazole	0.75	0.02553
Sulfaguanidine, anhydrous	0.64	0.02142
Sulfadiazine	0.75	0.02501

Discussion

Sodium nitrite solutions standardized against purified sulfanilamide and standardized against sodium oxalate by the U. S. P. sodium nitrite assay method (*5*) have agreed within 0.1 per cent. Sulfathiazole, sulfaguanidine, and sulfadiazine purified by repeated crystallization from acetone have assayed 100.0 ± 0.1 per cent and recrystallized sulfapyridine 99.9 ± 0.1 per cent, using the diazotization method. Tablets have been assayed directly by the method described and the sulfa drugs have been separated from the tablet excipients by extraction and recrystallization for determination of the other characteristics given in Table I.

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Rapid Detection of Gold by the Electrographic Method

J. A. CALAMARI, ROBERT HUBATA, AND P. B. ROTH
Laboratory, New York Medical Depot, Brooklyn, N. Y.

GOLD in alloys and in plating may be detected rapidly by spot tests (*3–7*) and by electrographic methods (*1*), the latter being the more rapid. The authors have discovered a rapid test for gold in alloys and plating which may be completed in about one second and is apparently specific for gold.

When gold is made the anode in a neutral or slightly acid solution of nitrate ion, using an e. m. f. of 6 to 9 volts and a current of about 0.5 to 1.0 ampere, it enters solution as Au^{+++} and reacts with water to form auric hydroxide which deposits on the anode. Hydrogen peroxide added to the solution reduces the auric hydroxide to purple aurous hydroxide and colloidal gold.

APPARATUS AND TEST SOLUTIONS. The equipment and procedure are identical with those described for the electrographic test (*2*). The test solution is prepared by dissolving 30 grams of sodium nitrate, reagent grade, in sufficient hydrogen peroxide, U. S. P., to make 100 ml., and filtering.

METHOD. Ashless filter paper is folded to form a wad three to four layers thick and then dipped into the sodium nitrate–hydrogen peroxide solution. The moistened filter paper is placed on the test metal anode and a graphite cathode about 7.5 cm. (3 inches) long and 0.6 cm. (0.25 inch) in diameter is firmly applied to the free side of the moistened section of the filter paper for about one second. An e. m. f. of about 6 to 9 volts is employed and may be obtained by using 4 to 6 No. 6 dry cell batteries connected in series. The current is about 0.5 to 1 ampere. An e. m. f. of 4.5 to 6 volts, a current flow of 0.1 to 0.5 ampere, and about a 5-second contact are recommended for plating.

If gold is present, a purple stain appears on the paper adjacent to the test metal anode. The intensity of the color increases with the percentage of gold present in the test metal when current density and time remain constant. The stain also increases in intensity upon standing. Very thin or porous plating yields a faint purple to purple stain; heavy plating, a purple stain.

A strong positive test for gold has been obtained with a series of dental alloys ranging from 25 per cent, to pure gold, and with 14- and 18-karat jewelry golds. Copper and silver in the gold alloys tested did not interfere. Numerous other metals and alloys have been tested by this method and negative results have been obtained in each case: nickel-silver, platinum-ruthenium, platinum-iridium, solders, brasses, white metals, 15 per cent silicon steel, bronzes, copper-nickel alloys, carbon steels, platinum, palladium, nickel, copper, manganese, molybdenum, tantalum, tungsten, mercury, cadmium, aluminum, tin, zinc, vanadium, silver, and lead. Chromium yields a blue spot which fades rapidly. Vanadium yields a red spot and silver a black spot.

It is believed that the test is applicable to alloys containing less than 25 per cent of gold, because the purple stain obtained with the alloys containing 25 to 30 per cent of gold is intense.

Heavy gold plating can be detected readily. Thin or porous gold plate on sterling silver yields a spot, faint purple to purple in color, often interspersed with dark areas, due to silver. The characteristic gold stain, however, has been clearly discernible in all tests performed.

Very thin gold plate on copper or brass cannot be detected by this method.

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Estimation of Ortho-, Pyro-, Meta-, and Polyphosphates in the Presence of One Another

LOREN T. JONES, The Solvay Process Company, Syracuse, N. Y.

Procedures for the estimation of ortho-, pyro-, hexameta-, trimeta-, and polyphosphates have been developed. Hexametaphosphate is separated as barium hexametaphosphate in an acid solution, and pyrophosphate is precipitated as manganous pyrophosphate at pH 4.1 in the presence of a small amount of acetone after removal of the hexametaphosphate radical. Orthophosphate is precipitated in the cold filtrate after removal of barium phosphates from a solution just acid to methyl red. Trimetaphosphate is obtained in the filtrate from an alkaline precipitation of all other phosphates as their barium salts. Total phosphorus pentoxide is determined so that polyphosphates may be obtained by difference. A qualitative test to identify the polyphosphate as tetraphosphate is given. Alkalinity determination is made by a standard acid titration to phenolphthalein and bromocresol green indicators to aid in calculating the probable form in which the phosphates may be present.

Data on application of method to analysis of samples of glassy metaphosphate, tetra- and tripolyphosphates, and synthetic mixtures of phosphates, carbonates, and silicates, as well as unknowns of these substances, are given.

USE of alkali ortho-, pyro-, meta-, and polyphosphates has recently become widespread, and a suitable method for their estimation in the presence of one another is of considerable importance. This investigation started with the development of a method for the analysis of mixtures of ortho-, pyro-, and metaphosphates, but was later expanded to include polyphosphates such as tripolyphosphate ($Na_5P_3O_{10}$) and tetraphosphate ($Na_6P_4O_{13}$). This work has not been concerned with the controversial question of the existence of additional polyphosphates, but rather with the development of a procedure which can be used analytically to estimate ortho-, pyro-, and metaphosphates as well as the more common commercial polyphosphates. Several published methods for analysis of mixtures of ortho-, pyro-, and metaphosphates were investigated and found more or less unsatisfactory when applied to commercial products. A brief résumé of the published methods and some of the difficulties encountered in their use are presented below.

In the analysis of a mixture of ortho-, pyro-, and metaphosphates, Aoyama (*1*) and Dworzak and Reich-Rohrwig (*6*) first precipitated the phosphates with a measured excess of silver nitrate in the presence of 50 per cent alcohol and determined the excess silver after filtering off the precipitated silver phosphates. Aoyama (*1*) treated the silver phosphates with hydrogen sulfide, while the others (*6*) used hydrochloric acid to form the phosphoric acids, which after separation by filtration, they titrated with sodium hydroxide to both the methyl orange and phenolphthalein end points. From these two titrations and the silver determination they calculated the amounts of ortho-, pyro-, and metaphosphates.

When tests were made in this laboratory on the analysis of known mixtures of phosphates according to these directions, the author found that, in the precipitation of phosphates with silver nitrate, as much as 10 per cent of the total phosphorus pentoxide of the metaphosphate either singly or in mixtures of all three remained in solution. The metaphosphate used in these tests was the glassy variety which is the general commercial type and was prepared by rapid cooling of a molten mass of metaphosphate. Based on the best information available at this time, metaphosphate prepared in this manner is composed mainly of sodium hexametaphosphate, $(NaPO_3)_6$, with a small amount of sodium trimetaphosphate, $(NaPO_3)_3$. As trimetaphosphate is not capable of repressing calcium and magnesium hardness, it may be regarded as an impurity when present in commercial products. Mellor (*12*) points out that trimetaphosphate is not precipitated by any metallic ion, including silver and barium. The author prepared some trimetaphosphate and confirmed this. In addition, he found that in the presence of alcohol some silver trimetaphosphate was precipitated but that a large part of the trimetaphosphate remained in the filtrate. Even though an additional step for the determination and calculation of the unprecipitated phosphorus pentoxide in an aqueous filtrate to trimetaphosphate might be included in the method, other difficulties, such as the conversion of the silver phosphates to the acids, the separation of the acids by filtration, and the neutralization of the acids, which were recognized by these workers, proved to be rather serious. It was desirable to find refinements in the method or an entirely different approach to the analysis.

Certain refinements in neutralization procedures were presented by Lum, Malowan, and Durgin (*11*) in determining the composition of strong phosphoric acid. They employed modifications of the Britzke and Dragunov (*4*), Travers and Chu (*13*), and Gerber and Miles (*7*) methods. The first method included in addition to a neutralization titration to both methyl orange and phenolphthalein end points, a second titration with bromophenol blue as the indicator to the first distinct blue color, followed by the addition of 2.5 to 3 times the amount of zinc sulfate necessary to precipitate the pyrophosphoric acid as the neutral zinc pyrophosphate. The sulfuric acid liberated was then titrated. The second method consisted of a titration by sodium hydroxide with bromocresol green, continued titration after the addition of silver nitrate solution and methyl red as the indicator, and titration of a second aliquot by sodium hydroxide with thymol blue as the indicator in the presence of sodium nitrate to prevent hydrolysis. The titrations were made to pH color standards of pH 4.2, 4.4, and 4.6 to bromocresol green and to pH 8.4, 8.8, 9.0, and 9.2 to thymol blue to aid in determining the exact end points. Although Gerber and Miles' titration of the acids allowed greater refinement in that step of the procedure, the combined procedures were still not generally applicable.

The present investigation has for its purpose the development of procedures intended primarily for the determination of mixtures of phosphates in commercial products such as cleaners and detergents. The volumetric procedures of the new method appear to be reliable and sufficiently accurate to meet the usual requirements in the analysis of such products. They overcome many of the weak points of the previous

methods and also include polyphosphates in the analytical scheme. For greater accuracy longer gravimetric procedures should be used. The present paper describes the new volumetric method, its development, and application to commercial products.

Reagents and Solutions

Disodium Orthophosphate. C. P. disodium orthophosphate was thrice recrystallized from distilled water and dried at 110° C. overnight. The sample, analyzed by magnesia mixture, indicated the presence of 100 per cent disodium hydrogen orthophosphate. Pyro- and metaphosphates (*9*, *10*) were absent.

Tetrasodium Pyrophosphate. C. P. tetrasodium pyrophosphate was thrice recrystallized from distilled water and was dried to constant weight at 250° C. The sample, analyzed by magnesia mixture after conversion to orthophosphate in nitric acid, indicated the presence of 100 per cent tetrasodium pyrophosphate. Ortho- and metaphosphates (*2*, *10*) were absent.

Sodium Hexametaphosphate. C. P. monosodium dihydrogen orthophosphate was heated to about 900° C. for 3 hours in a platinum dish and then the molten mass was cooled rapidly. Different batches of the resulting glassy product contained from 90 to 95 per cent sodium hexametaphosphate and, since ortho-, pyro-, and polyphosphate were absent, the balance of the phosphorus pentoxide must be present as trimetaphosphate. A solution of sodium hexametaphosphate with only 0.10 per cent of trimetaphosphate was prepared by separating the hexametaphosphate from the trimetaphosphate by precipitating the former with silver nitrate in a nitric acid solution acid to methyl orange. The soluble trimetaphosphate was washed out of the silver hexametaphosphate precipitate by decantation until the filtrate showed only a trace of phosphate. The silver hexametaphosphate was then suspended in water and stirred while sodium iodide solution was added slowly. The filtrate from the removal of silver iodide contained the hexametaphosphate.

Sodium Trimetaphosphate. C. P. monosodium dihydrogen orthophosphate was heated for 1 hour at 300° C. The temperature was increased to 610° C. and held there for 3 hours and then slowly decreased to 390° C. where it was held for 14 hours. The phosphorus pentoxide determination indicated that the sample must be 100 per cent $(NaPO_3)_x$. The sample yielded no precipitate to silver nitrate or barium chloride at any pH, thereby indicating the absence of hexametaphosphate, pyrophosphate, and orthophosphate (*12*). Furthermore, tripoly- and tetraphosphate precipitate with either silver nitrate or barium chloride in an alkaline solution.

Sodium Tripolyphosphate. Quantities equivalent to 1 $NaH_2PO_4.H_2O$ and 2 $Na_2HPO_4.12\ H_2O$ were heated in a platinum dish in an oven at 110° C. The salts first dissolved in the water of hydration, and after evaporation to dryness the mixture was transferred to a muffle furnace at 250° C. for 2 hours before increasing the temperature to approximately 800° C. The mixture was allowed to remain at this temperature until the entire mass became molten, then the temperature was lowered to about 650° C. and maintained at this temperature for 18 hours. At the end of this time the temperature was lowered gradually from 650° C. to 250° C. over a period of 8 hours and then was transferred to a desiccator to cool. The white crystalline solid mass disintegrated into a fine white powder upon cooling to room temperature. Analysis of the material by the procedure given below indicated the following composition: $(NaPO_3)_3$ 4.4%, Na_2HPO_4 1.7%, $Na_4P_2O_7$ 16.0%, $Na_5P_3O_{10}$ 77.9%.

A sample of a commercial sodium tripolyphosphate was also obtained, which analysis indicated to have the following composition: $(NaPO_3)_3$ 0.4%, Na_2HPO_4 3.0%, $Na_4P_2O_7$ 10.6%, $Na_5P_3O_{10}$ 86.0%.

Sodium Tetraphosphate. A commercial sodium tetraphosphate made by a large producer was the source of the sample used in this work. Analysis by the current procedure indicated a composition of $(NaPO_3)_3$ 3.8%, NaH_2PO_4 3.8%, and $Na_6P_4O_{13}$ 92.4%.

Standard Sodium Hydroxide, 1 *N* and 0.1 *N*. Prepare a carbonate-free solution of sodium hydroxide and standardize against standard hydrochloric acid with phenolphthalein indicator. Use in determining the phosphomolybdate volumetrically.

Standard Hydrochloric Acid, 1 *N* and 0.1 *N*. Prepare solutions from C. P. hydrochloric acid (sp. gr. 1.18) and standardize against pure sodium carbonate. Use in titrating the excess sodium hydroxide in the phosphomolybdate and alkalinity determinations.

Ammonium Molybdate Solution. Dissolve 100 grams of pure molybdic acid in a mixture of 400 ml. of cold distilled water and 80 ml. of C. P. ammonium hydroxide (sp. gr. 0.90). When solution is complete, pour slowly with constant stirring into a mixture of 400 ml. of C. P. nitric acid (sp. gr. 1.42) and 600 ml. of distilled water. Do not reverse the order of procedure, as nitric acid poured into ammonium molybdate will cause the precipitation of a difficultly soluble molybdic oxide and render the solution practically worthless. Add 0.05 gram of sodium ammonium phosphate dissolved in a little water and agitate. After 24 hours decant the clear solution through a filter paper into a reagent bottle. Sixty milliliters of the reagent are sufficient for 0.1 gram of phosphorus pentoxide.

Barium Chloride Solution. Dissolve 25 grams of C. P. barium chloride dihydrate in 1 liter of distilled water. Use to precipitate the hexametaphosphate radical.

Potassium Nitrate Solution. Dissolve 10 grams of C. P. potassium nitrate in 1 liter of water. Use as a wash solution for the phosphomolybdate precipitate.

Manganous Chloride Solution. Dissolve 100 grams of C. P. manganous chloride tetrahydrate in 1 liter of distilled water. Use to precipitate the pyrophosphate radical.

Phenolphthalein Indicator, 0.5 per cent solution. Dissolve 0.5 gram of C. P. phenolphthalein in 60 ml. of 95 per cent ethyl alcohol, and dilute to 100 ml. with previously boiled and cooled distilled water. Neutralize with 0.1 *N* sodium hydroxide.

Methyl Orange Indicator, 0.1 per cent solution. Dissolve 0.1 gram of methyl orange in 100 ml. of distilled water.

Bromocresol Green Indicator, 0.4 per cent solution. Dissolve 0.4 gram of bromocresol green in 5.75 ml. of 0.1 *N* sodium hydroxide and a few milliliters of alcohol. Dilute with water to 100 ml.

Analytical Procedure

Preparation of Solution for Analysis. Run a rough preliminary test by the method given below for the determination of the approximate total phosphorus pentoxide. Then prepare a solution of the sample in a standard volumetric flask such that a convenient size of aliquot will contain about 0.05 gram of total phosphorus pentoxide.

Conversion of Phosphates to the Ortho Form. This conversion of the phosphates, isolated by the various analytical steps, makes possible application of the volumetric molybdate method for determination of their phosphorus pentoxide content. It is accomplished by boiling gently for 15 minutes the acidified phosphate solution containing a 25-ml. excess of C. P. nitric acid per 100 ml. of solution. Before adding the ammonium molybdate, cool the solution to room temperature, and neutralize the excess acidity with ammonium hydroxide, so that the solution is just acid to litmus paper.

Total Phosphorus Pentoxide. Transfer a suitable aliquot of the prepared solution to a beaker and dilute to 75 to 100 ml. Convert all phosphates to the ortho form as directed above and precipitate the phosphorus pentoxide with 50 ml. of ammonium molybdate. Wash the precipitate with a minimum volume of 1 per cent potassium nitrate wash solution cooled to 10–12° C., until 5 ml. of the wash solution turn alkaline to phenolphthalein indicator with not over 3 drops of 0.1 *N* sodium hydroxide. One hundred milliliters of wash solution should be sufficient. Determine the phosphorus pentoxide content of the phosphomolybdate volumetrically, using 1 *N* or 0.1 *N* reagents depending on the amount of precipitate.

Hexametaphosphate. This procedure should be carried out soon after the solution has been prepared, so that the metaphosphate ion, which undergoes hydration particularly in strongly acid or alkaline solutions, will not have time for conversion.

Transfer an aliquot of the prepared solution of the size used for total phosphorus pentoxide to a beaker and dilute to 50 ml. with distilled water. Add 1 drop of methyl orange indicator, make the solution just acid to the indicator with 1 *N* hydrochloric acid, then add 0.5 ml. of the acid in excess. If the solution is already acid, make slightly alkaline to the indicator, then make final acid adjustment as indicated above. Add slowly with constant stirring 15 ml. of barium chloride solution and let the precipitate settle before filtering. If the solution clouds up without the precipitate separating within a minute, stir vigorously for 15-second intervals until a precipitate commences to separate when stirring is stopped. Filter and wash precipitate by decantation with a small amount of cold barium chloride solution (1 gram per liter), then transfer the precipitate to the filter paper and wash four or five times with small portions of the cold barium chloride wash solution. Save the filtrate for the determination of trimetaphosphate. Dissolve the precipitate in 1 to 1 nitric acid and convert the metaphosphate to orthophosphate as above and determine the phosphorus pentoxide as for total phosphorus pentoxide.

TABLE I. CONVERSION OF PYRO-, META-, AND POLYPHOSPHATES TO ORTHOPHOSPHATE

Phosphate	P_2O_5 by Molybdate After 15 minutes' boiling	P_2O_5 by Molybdate After 30 minutes' boiling	P_2O_5 by Mg Mixture after 2 Hours' Boiling
	Gram	*Gram*	*Gram*
Hexameta 95% Trimeta 5%	0.0472	0.0473	0.0472
Pyro	0.0482	0.0481	0.0483
Hexameta 60% Trimeta 2% Pyro 33% Ortho 5%	0.0798	0.0798	0.0799
Tetra	0.0624	0.0624	....
Tripoly	0.0576	0.0576	....

TRIMETAPHOSPHATE. To the filtrate from the separation of hexametaphosphate add 1 *N* sodium hydroxide with stirring until the mixture remains definitely alkaline to phenolphthalein indicator. Filter off the precipitated barium phosphates and determine the phosphorus pentoxide of the trimetaphosphate on the resulting filtrate as for total phosphorus pentoxide.

ORTHOPHOSPHATE. Transfer a suitable aliquot of the prepared solution to a beaker, dilute to 100 ml., make just acid to methyl red indicator with 1 *N* hydrochloric acid, then add 25 ml. of barium chloride solution, and filter off any barium phosphate precipitate. To the filtrate cooled to 20–25° C. add 8 to 10 grams of ammonium nitrate before precipitating the orthophosphate radical with ammonium molybdate and determining it volumetrically as above. Allow only 15 minutes for precipitation. Phosphates other than orthophosphate are not precipitated under these conditions.

PYROPHOSPHATE. Transfer a suitable aliquot of the freshly prepared solution to a beaker and make just acid to methyl orange indicator with 1 *N* hydrochloric acid before adding barium chloride 10 per cent in excess of the stoichiometric amount needed for the hexametaphosphate present. In absence of hexametaphosphate add no barium chloride. Stir vigorously to hasten separation and settling out of the barium metaphosphate. Filter off the precipitate, dilute filtrate to approximately 125 ml. with distilled water, and add 5 ml. of manganous chloride solution. Adjust the pH of the solution with the aid of a glass electrode or other suitable pH-meter by adding 0.1 *N* sodium hydroxide drop by drop with stirring until the pH remains 4.1. Then add with stirring 7 to 8 ml. of acetone and allow to stand 12 to 16 hours at 20° to 30° C. to permit the manganous pyrophosphate to precipitate. Filter off the precipitate and wash with a 1 gram per liter manganous chloride solution. Reserve filtrate for polyphosphate qualitative test. Dissolve precipitate in 1 to 1 nitric acid, convert to orthophosphate, and determine the phosphate as for total phosphorus pentoxide.

POLYPHOSPHATE. Qualitative test. This test must be performed on the filtrate immediately after removal of manganous pyrophosphate which has been previously precipitated from a freshly prepared solution.

Add 25 ml. of barium chloride solution to the filtrate from the pyrophosphate determination. The formation of a cloudiness or precipitate within 15 minutes, a behavior found to be characteristic of tetraphosphate, is considered indicative of the presence of this compound. Tripolyphosphate gives no visible change under these conditions.

The phosphorus pentoxide of the polyphosphates is taken as the difference between the total phosphorus pentoxide and the sum of the phosphorus pentoxide values of ortho-, pyro-, and the metaphosphates, and is calculated to tripoly- or tetraphosphate as dictated by the qualitative test. The calculation of polyphosphate is subject to an accumulation of additive errors; however, results from numerous experiments indicate that they are satisfactory for the purpose for which the method is intended.

For greater accuracy, the total phosphate may be determined gravimetrically by precipitating with magnesia mixture, igniting the precipitate, and weighing as magnesium pyrophosphate. The barium hexametaphosphate and manganous pyrophosphate precipitates may be fused with sodium carbonate, the fusion extracted with cold water, and the phosphorus pentoxide in the filtrate determined gravimetrically by the magnesium pyrophosphate method. Before adding magnesia mixture, the filtrates must be acidified with nitric acid and boiled to eliminate carbon dioxide and convert the meta- and pyrophosphate radicals to orthophosphate.

Experimental Development

CONVERSION OF PYRO-, META-, AND POLYPHOSPHATE TO ORTHOPHOSPHATE. Since ammonium molybdate does not precipitate the phosphorus pentoxide of pyrophosphate, the metaphosphates, and polyphosphates, it is necessary to convert them to the ortho form before determining total phosphorus pentoxide. Results of numerous experiments indicate that gentle boiling for 15 minutes in the presence of nitric acid is sufficient for complete conversion.

SEPARATION OF METAPHOSPHATE. In hydration studies of metaphosphoric acid, Holt and Myers (*8*) precipitated the hexametaphosphate ion with barium chloride in the presence of ortho- and pyrophosphoric acids. In ascertaining the composition of the barium metaphosphate, they decomposed it with nitric acid, determined the barium as sulfate, and found the precipitate to have a practically constant composition corresponding to the empirical formula $Ba(PO_3)_2$. In this laboratory the author analyzed the precipitate for the phosphorus pentoxide content according to the above procedure, and confirmed their conclusions.

TABLE II. COMPOSITION OF METAPHOSPHATE USED

Hexameta	Trimeta	Total Hexameta + Trimeta Found	Hexameta	Total P_2O_5 by Mg Mixture	P_2O_5 Found (H + T)
Gram	*Gram*	*Gram*	%	*Gram*	%
0.1187	0.0065	0.1246	94.7	0.1253	99.4
0.0704	0.0039	0.0743	94.7	0.0750	99.1
0.0473	0.0028	0.0501	94.4	0.0502	99.8
0.0078	0.0004	0.0082	95.2	0.0082[a]	100.0
0.0025	0.0001	0.0026	96.1	0.0025[a]	104.0

[a] Calculated from size aliquot used.

Kiehl and Wallace (*10*) tested for metaphosphates qualitatively in mixtures of the three phosphates by adding 0.1 *M* barium chloride solution to the phosphates in a 1 *M* nitric acid solution. Tests made in strongly acid solution showed that the precipitation of barium hexametaphosphate was either prevented or incomplete. However, some acidity is necessary to avoid the formation of insoluble barium ortho-, pyro-, and polyphosphates. No barium phosphate precipitate formed when barium chloride was added to solutions of ortho-, pyro-, and polyphosphates when acidified according to directions given in the procedure. This indicated that a solution of this acidity was sufficient to prevent the precipitation of these phosphates. A precipitate did form when a solution of tetraphosphate was just acid to methyl orange, but tripolyphosphate did not produce a precipitate in a solution just acid to either methyl orange or methyl red with barium chloride in the proportions given in the analytical procedure. On the other hand, results of tests carried out on equal volumes of solutions of glassy metaphosphate of widely different concentrations indicated that the hexametaphosphate was precipitated quantitatively. Although the total phosphorus pentoxide content of the sample was not precipitated completely with barium chloride, the amount of unprecipitated phosphorus pentoxide in the filtrate was approximately 5 per cent of the total on the sample under consideration here, even though the concentration of the samples was varied greatly. This lack of complete precipitation in widely varying concentrations points to the presence of another phosphate rather than to errors resulting from solubility of the barium hexametaphosphate.

As the results of the acid and alkaline precipitation with barium chloride were in good agreement with each other, this indicated the absence of ortho-, pyro-, and polyphosphates. The unprecipitated phosphorus pentoxide in the alkaline filtrate is considered to be trimetaphosphate, as its behavior corresponded with that given for it in Mellor (*12*). After development work on the procedure for determining trimetaphosphate had been completed, an article (*14*) applying a similar procedure for it was published. Results of analyses based on the proposed method are given in Table II.

Hexametaphosphate may be determined gravimetrically by drying the barium metaphosphate precipitate and weighing (*8*). The presence of other ions, such as sulfate, which form insoluble barium compounds under the conditions of precipitation, will interfere with such a gravimetric determination. The method described in this paper for the treatment of barium hexametaphosphate avoids such interferences.

Strontium and calcium chlorides were tried in place of barium chloride as a precipitating agent for the separation of hexametaphosphate, but were discarded either because of undesirable physical properties of the precipitate or inability to obtain satisfactory check determinations.

PRECIPITATION OF ORTHOPHOSPHATE IN THE PRESENCE OF PYROPHOSPHATE AND SILICATE. Courtois (*5*) suggested that orthophosphate could be determined with ammonium molybdate in the presence of pyrophosphate but stated that it was necessary to work rapidly. Boratynski (*2*) applied the same test at 25° C. and 15 minutes' standing to the colorimetric determination of small amounts of orthophosphate in the presence of pyro- and metaphosphates. Experiments, carried out in this laboratory on the precipitation of various amounts of orthophosphate alone with ammonium molybdate at 25° and 60° C. and 15 to 30 minutes' standing, indicated that satisfactory results could be obtained at 25° C. and 15 minutes' standing. When ammonium molybdate was added to pyrophosphate solutions at 60° C., considerable phosphomolybdate precipitated because of the accelerated hydration of pyro- to orthophosphate, but at 25° C. no precipitate formed after 15 minutes. Although the silicate radical forms a silicomolybdate, it does not interfere with the phosphate determination since the yellow complex remains in the filtrate. The results of the analysis of ortho- and pyrophosphate and silicate under various conditions indicate that 25° C. and 15 minutes' standing are satisfactory conditions for the determination of orthophosphate. A few precipitations of orthophosphate which were carried out on solutions chilled in an ice bath were found to be incomplete at the end of 15 minutes.

TABLE III. ORTHOPHOSPHATE PRECIPITATED WITH MOLYBDATE UNDER DIFFERENT CONDITIONS

Ortho Added	Pyro Added	$Na_2SiO_3 \cdot 5H_2O$ Added	P_2O_5 Found: 60° and 15 min.	P_2O_5 Found: 25° and 15 min.	P_2O_5 Found: 25° and 30 min.
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0586	0.0000	0.0000	0.0585 0.0586	0.0585 0.0585	0.0586 0.0585
0.0586	0.0534	0.0000		0.0586 0.0585	0.0584 0.0586
0.0586	0.0000	0.1250	0.0586 0.0584	0.0584 0.0584	0.0585 0.0586
0.0586	0.0534	0.1250		0.0586 0.0587	0.0585 0.0584
0.0000	0.0000	0.2500	0.0000	0.0000	0.0000

DETERMINATION OF PYROPHOSPHATE IN THE PRESENCE OF ORTHO-, TRIMETA-, AND POLYPHOSPHATES. Were it not for the existence of polyphosphates, pyrophosphate could be obtained satisfactorily by calculating it from the difference between the total phosphorus pentoxide and the sum of the phosphorus pentoxide values of ortho- and the metaphosphates. However, the possibility of the presence of polyphosphates in such mixtures makes it necessary to find a selective precipitant either for pyrophosphate or for the polyphosphates. Zinc salts have been used to separate pyrophosphate from ortho- and metaphosphates at a pH of 3.8 but polyphosphates were found to precipitate also under these conditions, and precipitation at even lower pH values did not furnish a means of separation. Other precipitating agents investigated for this purpose included salts of cadmium, mercurous and mercuric mercury, ferrous iron, nickel, cobaltous and luteo-cobaltic cobalt, and manganous manganese.

TABLE IV. DETERMINATION OF PYROPHOSPHATE IN PRESENCE OF POLYPHOSPHATES

Sample	P_2O_5 as $Na_4P_2O_7$ Found	Net $Na_4P_2O_7$ after Deducting Pyro
Gram	*Gram*	*Gram*
0.10 tripoly + 0.00 pyro	0.0161	....
0.09 tripoly + 0.01 pyro	0.0250	0.0105
0.075 tripoly + 0.025 pyro	0.0365	0.0244
0.10 tetra- + 0.00 pyro	0.0004	....
0.09 tetra- + 0.01 pyro	0.0099	0.0096
0.075 tetra- + 0.025 pyro	0.0270	0.0267
0.00 poly + 0.01 pyro	0.0098	0.0098
0.00 poly + 0.025 pyro	0.0242	0.0242

Of these salts manganous chloride was the only one found to precipitate pyrophosphate from a solution just acid to methyl red soon after its addition without doing likewise in the polyphosphate solutions. After several hours' standing at about 25° C. a small amount of precipitate settled out of both the tripoly- and tetraphosphate solutions, but the phosphorus pentoxide in each case was but a small portion of the total of the samples. In solutions containing from 25 to 100 mg. of pyrophosphate, the precipitate formed readily upon addition of manganous chloride, but the formation of a precipitate from solutions of less than 25 mg. of pyrophosphate was slow, requiring several minutes to a few hours for very small amounts. In the presence of polyphosphates the precipitation of pyrophosphate was retarded even longer. Chilling the solution in an ice bath delayed the precipitation still longer. When solutions of polyphosphates acid to methyl red indicator, to which manganous chloride had been added, were heated, not only was the rate of precipitation accelerated but the amount was greatly increased. This action appeared to be dependent on both the temperature and the length of time of heating at any given temperature, and may have been a result of decomposition of the polyphosphates. The most satisfactory conditions of temperature and time for precipitation of pyrophosphate in either the presence or absence of polyphosphate were found to be 20° to 30° C. and 12 to 16 hours.

The volume of manganous chloride solution (100 grams per liter of $MnCl_2 \cdot 4H_2O$) necessary for best precipitation of pyrophosphate alone was determined by varying the amount of manganous chloride solution from 2 to 50 ml. The minimum amount for optimum precipitation was 20 ml., but in the presence of polyphosphates the pyrophosphate results were abnormally high even after correcting for the pyrophosphate known to be present in the polyphosphate samples. In order to reduce this precipitation error of pyrophosphate in the presence of polyphosphates, the volume of manganous chloride solution was progressively reduced and it was shown that a total of 5 ml. was sufficient. At the same time to compensate for the increased solubility of manganous pyrophosphate in solutions not containing polyphosphates, a small amount of acetone was added which appeared to have overcome the solubility problem without affecting the precipitation when polyphosphates are present. As a further aid in establishing best conditions of precipitation, a series of pH control tests from 2.5 to 4.4 was made with the use of a glass electrode pH-meter. In each case manganous chloride was added to the solutions at a lower pH than prevails after final adjustment with 0.1 *N* sodium hydroxide. The results of these experiments indicated that a pH of 4.0 to 4.1 in combination with the other conditions already mentioned were the most satisfactory. Table IV gives data on analysis of pyrophosphate according to the directions given in the procedure.

TABLE V. ANALYSIS OF PHOSPHATE MIXTURES

Sample		Ortho %	Pyro %	Hexa-meta %	Trimeta %	Tripoly %	Tetra %
1	Present	10.6	78.9	9.6	0.9	....	....
	Found	11.2	78.2	9.9	0.7	....	....
	Difference	+ 0.6	− 0.7	+ 0.3	−0.2	....	....
2	Present	31.9	29.9	....	1.5	....	36.6
	Found	31.1	31.1	....	2.3	....	35.7
	Difference	− 0.8	+ 1.2	....	+0.8	....	− 0.9
3	Present	25.9	27.7	22.8	2.2	21.4	....
	Found	25.5	26.6	25.0	0.7	22.3	....
	Difference	− 0.4	− 1.1	+ 2.2	−1.5	+ 0.9	....
4	Present	26.2	25.0	22.9	3.1	....	22.9
	Found	25.8	25.6	25.5	1.0	....	22.2
	Difference	− 0.4	+ 0.6	+ 2.6	−2.1	....	− 0.7
5	Present	80.5	9.9	....	0.4	....	9.1
	Found	79.7	9.2	....	0.4	....	10.8
	Difference	− 0.8	− 0.7	....	0.0	....	+ 1.7
6	Present	80.1	9.9	9.1	0.8	....	....
	Found	79.9	9.3	9.8	0.9	....	....
	Difference	− 0.2	− 0.6	+ 0.7	+0.1	....	....
7	Present	0.3	91.1	....	0.04	8.6	....
	Found	0.3	91.7	....	0.1	7.9	....
	Difference	0.0	+ 0.6	....	+0.06	− 0.7	....
8	Present	0.5	90.0	....	0.4	....	9.2
	Found	0.8	91.8	....	0.4	....	7.0
	Difference	+ 0.3	+ 1.8	....	0.0	....	− 2.2
9	Present	0.8	2.7	68.6	6.4	21.5	....
	Found	1.8	0.8	68.7	5.6	23.1	....
	Difference	+ 1.0	− 1.9	+ 0.1	−0.8	+ 1.6	....

As manganous ion also precipitates hexametaphosphate radical, although incompletely, the hexametaphosphate radical must be removed before precipitating the pyrophosphate radical with manganous chloride. In the procedure for the analysis of hexametaphosphate, the filtrate free of the hexametaphosphate radical might be used, were it not for the presence of a large excess of barium ions which might precipitate other phosphates when the pH is increased for the pyrophosphate precipitation. The removal of this interference by precipitation of barium as barium sulfate was unsuccessful as a considerable amount of pyrophosphate was found to precipitate with the barium sulfate. Although this difficulty can be reduced greatly in a strong hydrochloric acid solution, an uncertainty still exists as to the extent that pyrophosphate precipitation might occur. It would be desirable then to be able to reduce the excess of barium chloride used in the regular analysis of hexametaphosphate, so as to avoid removal of barium ion and yet effect a satisfactory separation of the hexametaphosphate radical.

In an attempt to accomplish this, stoichiometric quantities of barium chloride were added to hexametaphosphate solutions just acid to methyl orange. Instead of precipitating, the barium hexametaphosphate remained as a cloudy suspension which was almost impossible to filter. However, when barium chloride 10 per cent in excess of the calculated amount was used, the barium hexametaphosphate separated readily upon stirring vigorously and approximately 98 per cent of the hexametaphosphate was removed. These conditions appeared to obviate the difficulties from both the hexametaphosphate and barium, since pyrophosphate determinations, made on the filtrates from the removal of hexametaphosphate by this method, were in good agreement with the actual amounts of pyrophosphate present.

POLYPHOSPHATES. Chemically pure polyphosphates were found not to be available and because of the absence of other independent methods of analysis, the composition of the samples of tripoly- and tetraphosphates has been based on analyses according to the procedures developed in this investigation. This procedure may be open to questioning, especially because of the complex nature of these materials. Therefore, a brief discussion of the nature of the tests is given.

First, it appears that free hexametaphosphate is not present in the samples of polyphosphates used in this work, since no precipitate was obtained when samples were treated with barium chloride according to the directions for determination of hexametaphosphate. Furthermore, upon addition of known amounts of hexametaphosphate to the different polyphosphates, only the amount added was obtained on analysis.

With respect to the phosphorus pentoxide recovered as trimetaphosphate, it might be claimed that this was due to solubility of the barium polyphosphates in the alkaline precipitation. There may be a slight solubility, but the percentages of phosphorus pentoxide calculated to trimetaphosphate from different size samples were in too close an agreement with each other to be considered due essentially to solubility, and according to Bornemann and Huber (*3*) sodium trimetaphosphate, $(NaPO_3)_3$, may be present in polyphosphates depending on the proportions of sodium oxide and phosphorus pentoxide which are fused together and on the manner in which the melts are cooled.

The filtrates from the orthophosphate determinations remained free of phosphomolybdate precipitate too long after filtration to attribute the orthophosphate found to hydration. Both trimeta- and orthophosphate might be considered present as impurities.

Finally, the pyrophosphate determination appears to be open to question. In the case of the tripolyphosphate samples, a manganous phosphate precipitate, corresponding to 16.0 and 10.6 per cent, respectively, as tetrasodium pyrophosphate on samples from two different sources, was obtained consistently regardless of size of sample up to 0.1 gram or with the addition of known amounts of pyrophosphate. However, the tetraphosphate sample gave no or, at best, a very slight amount of precipitate alone, but with pyrophosphate added approximately 15 per cent of the tetraphosphate sample calculated as tetrasodium pyrophosphate was precipitated consistently with the pyrophosphate. This may actually be pyrophosphate not precipitating in absence of added pyrophosphate, or it may be a manganous polyphosphate equivalent of 15 per cent sodium pyrophosphate. Even with this discrepancy, the combined procedures go a long way in enabling one not only to find out whether polyphosphates are present but also to provide a good estimation of the amount. And, as pointed out in the procedures, solutions of tetraphosphate produced a cloudiness or precipitate upon addition of barium chloride to the filtrate from the pyrophosphate determination while tripolyphosphate gave none.

Generally, it was found that the qualitative test for distinguishing between tetraphosphate and tripolyphosphate could be applied satisfactorily even though the solutions had been prepared for several days. However, in one instance a phosphate mixture, containing about 9 per cent tripolyphosphate along with 35 per cent sodium carbonate, gave a qualitative test similar to that for tetraphosphate when carried out on solutions which had been made up a few days before analyzing. But tests on freshly prepared solutions of this phosphate mixture gave no indication of cloudiness or precipitate characteristic of tetraphosphate. Hence, this test must be performed on fresh solutions so as to avoid misinterpretation. In the analysis of several unknowns, the qualitative test was applied correctly to the detection of the presence of tetraphosphate.

At the conclusion of the development of the various procedures, a series of several mixtures of phosphates in widely different proportions was made up and analyzed to check the combined procedures. Data on these results are given in Table V.

Application to Commercial Products

ANALYSIS OF COMMERCIAL METAPHOSPHATES AND PYROPHOSPHATE. The procedures have been applied to the analysis of two different commercial metaphosphates and a pyrophosphate, with the results shown in Table VI.

COMMERCIAL PRODUCTS CONSISTING OF PHOSPHATES AND OTHER MATERIALS. Commercial products may be composed of mixtures of ortho-, pyro-, meta-, and polyphosphates not only in the presence of one another, but also in combination with various other materials, such as sodium hydroxide, sodium carbonate, sodium silicate, abrasives, and soap. Standard procedures of analysis of these materials may be found in reference books. If the mixture contains such soluble substances as sodium hydroxide, sodium carbonate, or sodium

TABLE VI. ANALYSIS OF SAMPLES OF COMMERCIAL PYRO- AND METAPHOSPHATES

Constituent	1 Meta	2 Meta	3 Pyro
	%	%	%
$(NaPO_3)_6$	63.8	67.4	...
$(NaPO_3)_3$	7.2	7.0	...
Na_2HPO_4	3.7	3.7	1.1
$Na_4P_2O_7$	...	...	98.9
$Na_2H_2P_2O_7$	5.2	6.6	...
$Na_6P_4O_{13}$	20.1	9.8	...
$NaHCO_3$	...	5.5	...
Total	100.0	100.0	100.0

TABLE VII. ANALYSIS OF PHOSPHATES IN PRESENCE OF CARBONATE AND SILICATE

Phosphate Present					Phosphate Found		
Ortho	Pyro	Hexametа	$Na_2SiO_3 \cdot 5H_2O$	Na_2CO_3	Ortho	Pyro	Hexametа
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0586	.....	....	0.125	...	0.0586	.....	.....
0.0586	.....	....	0.125	0.5	0.0585	.....	.....
0.0293	0.0267	....	0.125	0.5	0.0290	0.0270	.....
0.0293	0.00284	0.0250	0.125	0.5	0.0295	0.00280	0.0252
0.04814	0.0267	....	1.0	0.5	0.04806	0.0270	.....
0.02407	0.00284	0.0250	1.0	0.5	0.02392	0.00280	0.0252
0.02407	0.00142	0.0125	1.0	0.5	0.02422	0.00139	0.0125
0.00481	0.0341	0.0125	1.0	0.5	0.00494	0.0344	0.01235

silicate, the procedures for the phosphates may be applied directly to the solution. If soap or insoluble material such as abrasives is present, it should be removed first. Abrasives may be separated by filtration and washed well to remove completely the soluble phosphates. Mixtures containing soap should be dissolved in the smallest amount of cold distilled water necessary for solution of the soap, then made just acid to methyl orange, and the insoluble fatty acids filtered off and washed well with cold water. The phosphates may then be determined in the filtrate by the indicated procedures.

It would be difficult to evaluate the accuracy of the method by the analysis of commercial products, since there are no standard references on which to base any conclusions. It seems preferable to analyze known mixtures. Hence, samples of various phosphates in combination with sodium silicate and sodium carbonate were prepared and analyzed.

ALKALINITY DETERMINATION. An alkalinity determination is an aid in enabling one to calculate a probable combination of the sodium oxide with the phosphate radicals in solution.

According to Gerber and Miles (*7*) the pH values at the equivalence points of the phosphates under consideration for titration are:

Phosphate	pH
$Na_4P_2O_7$	9.1
Na_2HPO_4	8.5
NaH_2PO_4	4.6
$Na_2H_2P_2O_7$	4.2

For solutions containing only mixtures of phosphates, the alkalinity is determined by a standard acid titration to a light pink phenolphthalein end point in the presence of sodium nitrate or sodium chloride, which titrates the alkalinity of trisodium orthophosphate to disodium orthophosphate. The titration is then continued to the greenish yellow end point of bromocresol green, which titrates the alkalinity of the disodium ortho- and tetrasodium pyrophosphates to monosodium ortho- and disodium acid pyrophosphates, respectively. From the alkalinity values and the values of phosphate radicals, combinations of the phosphates may be calculated.

If desired, a glass electrode may be used for this titration, but in this case, it will be necessary to determine empirically the actual pH values of the various conversion points in the presence of approximately the same salt concentration as the sample to be analyzed.

If the mixture of phosphates contains sodium hydroxide, sodium carbonate, or sodium silicate, the alkalinity determination is made to methyl orange and the carbonate and silicate determinations must be made also. The sodium oxide must then be adjusted to satisfy the pH of the solution for the different acid radicals present.

ANALYSIS OF UNKNOWN MIXTURES. After each step of the procedure had been checked separately, and the entire method had been applied satisfactorily to the analysis of mixtures of phosphates of known composition, two sets of "unknowns", one of mixtures of phosphates only and the other with sodium carbonate and sodium silicate in addition to phosphates, were prepared by a disinterested chemist and submitted for analysis. Actual titration values and compositions of the phosphate unknowns and the condensed summary of the sodium carbonate–sodium silicate unknowns are given in Table VIII.

TABLE VIII. ANALYSIS OF UNKNOWNS

	Phosphate	NaOH Used	Phosphate Found	Phosphate Found	Present	Difference
		Ml.	*Gram*	%	%	%
I.	Total P_2O_5	16.98, 17.00 Av. 16.99 (1 *N*)	....	..	..	...
	$(NaPO_3)_6$	37.8, 37.9 Av. 37.85 (0.1 *N*)	0.0168	17.4	16.7	+0.7
	$(NaPO_3)_3$	2.40, 2.50 Av. 2.45 (0.1 *N*)	0.0011	1.1	1.5	−0.4
	Na_3PO_4	29.80, 30.00 Av. 29.90 (0.1 *N*)	0.0213	22.1	22.1	0.0
	$Na_4P_2O_7$	10.01, 10.03 Av. 10.02 (1 *N*)	0.0579	60.1	59.7	+0.4
	Polyphosphate	(by difference)	None			
II.	Total P_2O_5	18.18, 18.22 Av. 18.20 (1 *N*)	....	..	..	...
	$(NaPO_3)_6$	84.70, 84.80 Av. 84.75 (0.1 *N*)	0.0376	39.7	38.8	+0.9
	$(NaPO_3)_3$	5.7, 5.9 Av. 5.80 (0.1 *N*)	0.0026	2.7	3.6	−0.9
	Na_3PO_4	20.90, 21.1 Av. 21.00 (0.1 *N*)	0.0150	15.8	15.5	+0.3
	$Na_4P_2O_7$	54.7, 54.8 Av. 54.75 (0.1 *N*)	0.0312	32.9	33.4	−0.5
	$Na_3P_3O_{10}$	1.53 (1 *N*) (by difference)	0.0084	8.9	8.7	+0.2
III.	Total P_2O_5	18.37, 18.38 Av. 18.38 (1 *N*)	....	..	..	...
	$(NaPO_3)_6$	None	....	..	..	...
	$(NaPO_3)_3$	1.3, 1.6 Av. 1.45 (0.1 *N*)	0.0006	0.5	1.2	−0.7
	Na_3PO_4	85.8, 85.4 Av. 85.6 (0.1 *N*)	0.0610	53.8	53.4	+0.4
	$Na_4P_2O_7$	39.4, 38.8 Av. 39.1 (0.1 *N*)	0.0226	19.9	14.9	+5.0
	$Na_6P_4O_{13}$	5.76 (1 *N*) (by difference)	0.0294	25.9	30.5	−4.6

Composition	IV Found	IV Present	IV Difference	V Found	V Present	V Difference	VI Found	VI Present	VI Difference
$(NaPO_3)_6$	..	..	...	10.4	10.1	+0.3	20.8	20.8	0.0
$(NaPO_3)_3$	0.6	0.8	−0.2	1.1	0.9	+0.2	2.3	2.0	+0.3
Na_3PO_4	12.6	12.2	+0.4	..	..	...	24.5	24.2	+0.3
$Na_4P_2O_7$	23.6	19.0	+4.6	16.2	16.4	−0.2	23.2	22.3	+0.9
$Na_3P_3O_{10}$	..	..	...	..	..	...	17.5[a]	18.2	−0.7
$Na_6P_4O_{13}$	15.7[a]	19.9	−4.2	..	..	...	..	..	...
Na_2CO_3	47.8	48.1	−0.3	57.3	56.7	+0.6	0.1	0.1	0.0
Na_2SiO_3	..	..	...	14.8	15.6	−0.8	11.1	12.2	−1.1
SiO_2	..	..	...	0.3	0.3	0.0	0.2	0.2	0.0

[a] By difference.

The titration values given in Table VIII are typical of those one might expect with the method, and indicate that good precision can be obtained. They also show that the method can be applied to the analysis of phosphate mixtures containing sodium carbonate and sodium silicate. The method can be applied to mixtures of phosphates in any proportion, but at the discretion of the analyst use of larger aliquots of the prepared solutions may be desirable for small amounts of any constituent.

Summary

A method has been worked out for the analysis of mixtures of phosphates in which hexameta-, trimeta-, pyro-, and orthophosphates are separated and determined. Polyphosphates are obtained from the difference between the total phosphorus pentoxide and the sum of the phosphorus pentoxide values of the other mentioned phosphates. Data on application of the procedures to synthetic phosphate and carbonate and silicate mixtures, commercial phosphates, and "unknowns" are included.

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Pressure-Measuring Device for Moderate Vacua

ERNEST R. KLINE

University of Connecticut, Storrs, Conn.

THE increasing use of moderate vacua in distillations requires a pressure-measuring device having its maximum utility in the range of 0.05 to 2 mm. of mercury pressure. This range is below that at which the ordinary mercury-filled manometer is accurate and somewhat above that at which the conventional McLeod gage is designed to operate. Efforts to increase sensitivity by the use of lighter liquids of low vapor pressures in closed-end manometers yield unsatisfactory results, since such liquids wet glass and have a most persistent habit of sticking in the closed arm of the manometer. A serious objection to the use of mercury as the working liquid at these pressures is that a substantial amount of distillate vapor is present in the system and pressure variations eventually result in fouling the mercury surface. This is especially serious in McLeod gages where capillary tubes are used.

These difficulties have been overcome in this laboratory by the use of the modified McLeod gage shown. The operating liquid which has been found to give best results is olive oil which has been subjected to prolonged evacuation at 100° C. to remove volatile solvents and moisture. This is introduced through the trap, T, to fill the reservoir, R_1, and the by-pass tube, B, to the level, A-A'. An additional quantity of the oil is added to fill the supplementary reservoir, R_2 to its effective capacity. The effective capacity of R_2 is approximately the capacity of the compression tube, C. The device is attached to the distillation system by a length of pressure tubing forced over the outlet, S, which is bent at right angles to the plane of the figure and away from the operator.

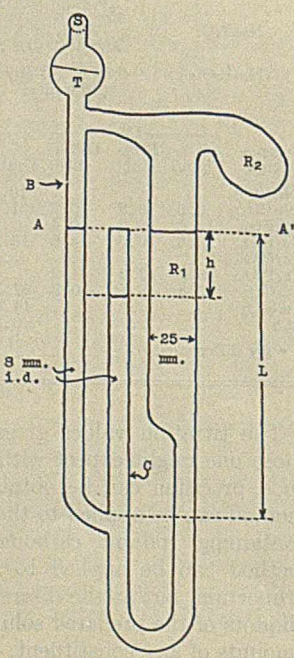

TABLE I. CALIBRATION OF MODIFIED MCLEOD GAGE

(Conversion: h in millimeters to millimeters of mercury pressure)

Units	Tens 0	1	2	3	4	5	6	7	8	9
0	...	0.038	0.163	0.390	0.740	1.24	1.93	2.84	4.05	5.66
1	0.0004	0.047	0.181	0.419	0.784	1.30	2.00	2.94	4.20	5.85
2	0.0015	0.056	0.200	0.450	0.828	1.36	2.09	3.05	4.34	6.06
3	0.0033	0.066	0.220	0.482	0.873	1.43	2.17	3.17	4.49	6.23
4	0.0060	0.077	0.241	0.515	0.921	1.49	2.26	3.28	4.64	6.44
5	0.0094	0.089	0.263	0.548	0.970	1.56	2.35	3.41	4.80	6.65
6	0.0135	0.102	0.286	0.583	1.02	1.63	2.44	3.53	4.96	6.86
7	0.0185	0.116	0.310	0.620	1.07	1.70	2.54	3.66	5.13	7.08
8	0.0244	0.130	0.336	0.659	1.13	1.77	2.64	3.78	5.30	7.30
9	0.0309	0.142	0.363	0.699	1.18	1.85	2.74	3.91	5.48	7.55

This rubber pressure tubing should be of sufficient length to permit rotation of the gage through a 90° arc about S as a center.

During evacuation of the system and between pressure readings this device is supported with tubes B and C nearly horizontal but with sufficient slope to permit drainage into reservoir R_1. Measurements are made by rotating the gage to the vertical with trap T uppermost. The level of the meniscus in B is adjusted to point A by the addition of oil from R_2. The depression, in millimeters, h, of the meniscus in C is a function of the pressure in the system

$$p_0 = \frac{h^2}{(L - h)r}$$

where r is the ratio of the density of mercury to that of the oil and p_0 is expressed in millimeters of mercury. A scale may be attached to bridge the space between B and C. This scale may be graduated in millimeters or to read directly in millimeters of mercury pressure. In actual use in this laboratory no such scale is used. The value of h is determined by the use of a millimeter rule and the value of p_0 is read off a chart which is mounted in a convenient location.

Great precision is not claimed for this apparatus but it is sufficiently accurate for vacuum distillations. While the idea of a rotary gage is not original with the author, the use of a nonvolatile liquid of low density in such a gage does not appear to be mentioned in available literature.

For the benefit of those who do not care to prepare a calibration chart, Table I is given. The gage for which the chart was prepared has L = 188 mm., and for the olive oil used r = 14.6.

Optical Activity of Some Cinchona Alkaloids and Some of Their Salts

In Mixtures of Water and Ethyl Alcohol

JAMES C. ANDREWS, School of Medicine, University of North Carolina, Chapel Hill, N. C.

Optical activity can be used as a criterion of the purity of cinchona alkaloids only if exact data are available as to the relationship between this property and such conditions as composition of solvent and degree of neutralization of the cinchona base. Such data are presented for a representative series of the more common quinine derivatives. For each compound studied, data are recorded showing the variation in optical activity in progressively varied mixtures of water and ethyl alcohol of the free base, the sulfate, and the dihydrochloride, as well as the change in optical activity as the free base is progressively neutralized with sulfuric and hydrochloric acids. Studies were made on quinidine, dihydroquinidine, cinchonine, and cinchonidine.

IN A recent paper (*2*), Andrews and Webb reported the results of a systematic investigation of the optical activity of quinine as the free base, the sulfate ($B_2.H_2SO_4$), and the hydrochloride (B.2HCl) in various mixtures of water and ethyl alcohol. At the same time there was reported the effect on optical activity of progressive neutralization of the free base with both sulfuric and hydrochloric acids. The purpose of this work was to establish optimum conditions for the use of optical activity as a criterion of purity of these alkaloids and to fill some of the many gaps in our knowledge of the stereochemistry of these compounds.

It has been found desirable to extend these investigations to other cinchona alkaloids. The present paper records the results of investigations, previously reported for quinine, applied to quinidine, dihydroquinidine, cinchonine, and cinchonidine. This series, while very limited, provides examples of the effect on optical activity of stereochemical isomerism, of the removal of the ethoxy group from quinine, and of hydrogenation of the vinyl group. The procedure used was identical with that described by Andrews and Webb (*2*). In the case of each compound the following data were determined:

1. The specific rotation of the free base, the sulfate, and the dihydrochloride in varying percentages of water and alcohol.
2. The effect on specific rotation of progressive neutralization of the free base with both sulfuric and hydrochloric acids.

The second of the above series was, in each case, carried out at that percentage of ethyl alcohol which had given the maximum rotation when the water-alcohol curve for that particular salt was determined. All figures for $[\alpha]_D$ were determined at 25° C. and refer to the free base, regardless of the salt used. These values are all rounded off to the nearest unit. In the opinion of the writer the reporting of specific rotations in tenths of a unit is usually not justified by the accuracy of the reading, particularly when, as is often the case in the present paper, solubility limitations compel the use of comparatively dilute solutions.

Quinidine

Kahlbaum's quinidine (base) was recrystallized four times by dissolving in 95 per cent alcohol and adding about five

TABLE I. SPECIFIC ROTATION OF CINCHONA ALKALOIDS

(In varying percentages of water and ethyl alcohol)

Free Base Alcohol (by volume) %	$[\alpha]_D^{25}$	Sulfate Alcohol (by volume) %	$[\alpha]_D^{25}$	Dihydrochloride Alcohol (by volume) %	$[\alpha]_D^{25}$
Quinidine Free Base, Quinidine Sulfate, and Quinidine Dihydrochloride					
20.0	216	0.0	230	0.0	312
28.0	227	7.4	240	10.8	315
36.0	237	19.4	260	18.8	317
44.0	243	27.4	267	26.8	317
52.0	248	35.4	272	34.8	315
60.0	252	43.4	275	42.8	312
68.0	257	51.4	277	50.8	307
76.0	260	67.4	275	58.8	302
84.0	260	75.4	272	66.8	295
92.0	258	83.4	267	74.8	287
100.0	255	91.4	262	82.8	280
		100.0	258	90.8	272
				98.8	265
				100.0	263
Dihydroquinidine Free Base, Dihydroquinidine Sulfate, and Dihydroquinidine Dihydrochloride					
0.	190	0.	219	0.	277
20.0	203	17.4	230	9.0	281
40.0	215	27.4	241	17.6	285
50.0	219	35.4	248	26.8	287
60.0	225	43.4	252	34.8	287
70.0	231	51.4	252	42.8	285
80.0	235	59.4	251	50.8	277
90.0	234	67.4	250	58.8	270
100.0	228	75.4	249	66.8	262
		83.4	246	74.8	258
		91.4	244	82.8	250
		99.4	238	90.8	242
				98.8	230
Cinchonine Free Base, Cinchonine Sulfate, and Cinchonine Dihydrochloride					
32.0	150	0.8	195	0.	245
40.0	175	7.8	210	10.6	250
48.0	200	19.4	225	18.6	255
56.0	215	27.4	230	34.6	255
64.0	225	35.4	232	50.6	250
72.0	225	43.4	233	66.6	245
80.0	230	51.4	235	74.6	240
88.0	240	59.4	235	82.6	232
96.0	245	67.4	235	90.6	222
100.0	225	75.4	237	94.6	217
		83.4	235	98.6	210
		87.4	232		
		91.4	227		
		95.4	222		
		99.4	217		
Cinchonidine Free Base, Cinchonidine Sulfate, and Cinchonidine Dihydrochloride					
	$-[\alpha]_D^{25}$		$-[\alpha]_D^{25}$		$-[\alpha]_D^{25}$
20.0	44	0.1	140	0.	180
28.0	88	5.9	150	10.6	185
32.0	100	18.7	165	18.6	187
44.0	115	38.7	180	26.6	187
56.0	127	58.7	185	42.6	185
68.0	125	70.7	190	58.6	175
76.0	122	78.7	195	70.6	165
84.0	120	82.7	190	78.6	157
92.0	117	86.7	185	82.6	152
96.0	115	90.7	180	86.6	147
100.0	108	94.7	170	90.6	140
		98.7	155	94.6	130
				98.6	120

volumes of water. The product was dried at 110° C. A constant specific rotation $[\alpha]_D^{25} = +255.0$ in absolute ethyl alcohol was obtained.

This is somewhat higher than the usually accepted figure reported by Rabe (*5*), +243.5, but the ease of contamination of quinidine with dihydroquinidine and resulting lowering of its optical activity have already been commented on by Butler and Cretcher (*3*). On the other hand, the author has never succeeded in obtaining a figure for the anhydrous free base in absolute alcohol as high as that reported by Butler and Cretcher (+262), but they do not specify temperature and the author employed a concentration of 0.300 gram per 100 ml. as compared with 2.0 grams per 100 ml. used by them. The author has found only small concentration effects with the optical activity of these alkaloids and has not investigated the effect of temperature variations. His sample melted at 167.5° C. (corrected). Butler and Gretcher report 162° to 163° C. for U. S. P. quinidine and 170° to 171° C. for their product made by rearrangement of quinine.

The sulfate and dihydrochloride were both made by adding the calculated amount of standard acid to the recrystallized free base, and diluting to volume with absolute ethyl alcohol to make the stock solution. The necessary correction was made for the amount of water introduced with the standard acid.

Neutralization curves were run as described by Andrews and Webb. In all cases, these curves were determined in that concentration of ethyl alcohol which had produced the highest specific rotation when the alcohol-water curve of that particular salt was run. Some deviations from this procedure were dictated by considerations of solubility of the salt. The actual percentage of alcohol used is recorded with each part of Table II.

Table I shows the variation in specific rotation of quinidine free base, quinidine sulfate ($B_2.H_2SO_4$), and quinidine dihydrochloride (B.2HCl). Table II shows the variation in specific rotation of quinidine (as free base) during progressive neutralization with sulfuric and hydrochloric acids at the specified concentrations of ethyl alcohol.

Dihydroquinidine

A sample of dihydroquinidine base (kindly furnished by the laboratories of Merck & Co., Inc.) was dried at 110° C. to constant weight and gave in absolute alcohol a value of $[\alpha]_D^{25} = +228.0$ (concentration of base = 1.852 grams per 100 ml. of solution). Since a recrystallized sample produced no measurable difference in optical activity, the original dried sample of the base was used. The value given by Rabe (*5*) is +237.5 at 15° C. and by Henry (*4*) is +230. In neither case is the concentration of alcohol specified. Using the author's sample of the base, the same determinations were made as described above for quinidine. The results for the alcohol-water curves of the free base, the sulfate ($B_2.H_2SO_4$), and the dihydrochloride (B.2HCl) are shown in Table I and the data concerning neutralization of the free base with sulfuric and hydrochloric acids in Table II.

Cinchonine

The fact that commercial samples of cinchonine, as usually obtainable, are highly contaminated with quinine makes necessary special precautions for obtaining a pure product. The sample used as a starting point for purification showed, in absolute ethyl alcohol, a specific rotation of +177 as compared with the figure of +224.4 reported by Rabe and +229 (at 17° C.) by Henry. In substantial agreement with Rabe's figure, the author's highest rotation in absolute ethyl alcohol, reached after successive purification, is +224.0.

The procedure used is based on the fact that the chief contaminant, quinine, is much more soluble in ether than is cinchonine and can therefore be removed by successive extractions. These were repeated until the ether extracts showed a constant optical activity and a constant amount of solid residue on evaporation. As the quinine content of the sample approaches zero, the amount of alkaloid dissolved by the ether and the optical activity shown by the solution gradually approach that produced by the very limited solubility of cinchonine base in ether. This is listed by Allen (*1*) as 0.27 gram of cinchonine per 100 ml. of ether. The specific rotation of +177 for this sample indicates, by interpolation, the presence of about 12 per cent of quinine, assuming no other alkaloids to be present.

A 25-gram sample was shaken mechanically for some hours with 100 ml. of ether. The filtered ether solution was read in a 4-dm. polariscope tube and 25-ml. portions were evaporated to dryness and the residues weighed. Twenty-six such extractions were made before constancy of rotation and of solubility was obtained. During this series the observed rotation changed progressively from −2.90 to +1.20 as the quinine was removed. The last three extractions gave satisfactorily constant values averaging 0.170-gram residue per 100 ml. of ether solution.

Assuming cinchonine to be the only solid phase present, this indicates an ether solubility of this alkaloid at 25° C.

TABLE II. EFFECT ON OPTICAL ACTIVITY OF PROGRESSIVE NEUTRALIZATION WITH SULFURIC AND HYDROCHLORIC ACIDS

Sulfuric Acid		Hydrochloric Acid	
Molar ratio of H_2SO_4 to base	$[\alpha]_D^{25}$	Molar ratio of HCl to base	$[\alpha]_D^{25}$
Quinidine Base[a]			
0.	245	0.	216
0.235	260	0.190	220
0.470	276	0.572	235
0.706	291	0.954	257
0.941	300	1.335	280
1.177	306	1.525	294
1.412	310	1.905	316
1.647	312	2.480	338
1.882	313	2.860	339
2.352	315	3.240	346
3.293	316	3.810	345
Dihydroquinidine Base[b]			
0.	219	0.	208
0.177	232	0.415	225
0.355	244	0.830	248
0.532	253	1.245	269
0.710	261	1.660	283
0.888	270	2.075	292
1.065	273	2.490	295
1.242	276	2.905	296
1.420	278	...	...
1.775	280	...	...
Cinchonine Base[c]			
0.	226	0.	150
0.205	230	0.747	230
0.410	235	1.493	251
0.615	240	2.240	260
0.820	243	2.990	265
1.025	247	3.735	267
1.435	252	5.230	268
2.05	255	7.470	267
3.28	255	...	...
Cinchonidine Base[d]			
	$-[\alpha]_D^{25}$		$-[\alpha]_D^{25}$
0.	121	0.	110
0.160	137	0.584	142
0.320	164	1.168	166
0.480	191	1.752	182
0.640	199	2.336	187
0.800	202	2.920	189
1.120	206	4.380	187
1.600	207	5.84	186
2.400	209	7.30	184
3.200	207	...	...

[a] Sulfuric acid neutralization run in 50% ethyl alcohol by volume; hydrochloric acid in 20% ethyl alcohol by volume.
[b] Sulfuric acid neutralization run in 50% ethyl alcohol by volume; hydrochloric acid in 30% ethyl alcohol by volume.
[c] Sulfuric acid neutralization run in 75% ethyl alcohol by volume; hydrochloric acid in 30% ethyl alcohol by volume.
[d] Sulfuric acid neutralization run in 80% ethyl alcohol by volume; hydrochloric acid, in 40% ethyl alcohol by volume.

of 0.170 gram per 100 ml. of solution, a figure much lower than that of Allen (*1*). This also gave a specific rotation in ether of $[\alpha]_D^{25} = +176$. The residual cinchonine when dried gave a specific rotation of +224.0. This sample of the base was used for all optical activity determinations as described above under quinidine. The results for the alcohol-water curves of the free base, the sulfate ($B_2.H_2SO_4$), and the dihydrochloride (B.2HCl) are shown in Table I, and data concerning neutralization with sulfuric and hydrochloric acids in Table II. Because of the more limited solubility of cinchonine base in water, the data for the former in Table I could not be extended to alcohol concentrations below 32 per cent. Even at this point only 0.02 gram of base per 100 ml. was possible. The error of the determination is therefore correspondingly large.

Cinchonidine

A commercial sample of the free base was recrystallized from solution in 95 per cent ethyl alcohol by addition of sufficient water to reduce the alcohol percentage to 25 per cent. The resulting precipitate was filtered, washed with 25 per cent ethyl alcohol, and dried. Three such treatments gave a product showing, in absolute ethyl alcohol, a constant optical activity of $[\alpha]_D^{25} = -107.3$. A value of −111.0 was reported by Rabe. Since further recrystallization did not alter the author's figure (−107.3), it was taken as representing the pure base under the conditions specified. Using this sample, the determinations were made as described above for quinidine. The results for the alcohol-water curves of the free base, the sulfate ($B_2.H_2SO_4$), and the dihydrochloride (B.2HCl) are shown in Table I, and data concerning neutralization of the free base with sulfuric and hydrochloric acids in Table II.

It is obvious that the curves of all of these alkaloids follow the same pattern. As in the case of quinine, the water-alcohol curves of optical activity of free base, sulfate, and dihydrochloride all rise to flat maxima at intermediate percentages of water and alcohol, giving lower values of specific rotation in both pure water and pure ethyl alcohol. The position of these maxima varies with the different cinchona derivatives examined, but it may be said that for the free bases, the maxima lie between 60 and 95 per cent alcohol by volume, for the sulfates between 50 and 75 per cent, and for the dihydrochlorides between 20 and 30 per cent.

Using, in each case, the percentage of alcohol giving maximum rotation for that salt, the neutralization curves shown in Table II were run. These follow the course previously reported for quinine: a smooth curve with no breaks corresponding to any stoichiometric ratios. In some cases, particularly with the hydrochlorides, addition of excess acid causes a slight drop in the maximum rotation attained. Some examples of this will be noted in the table.

Acknowledgment

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Oil Absorption of Pigments

M. A. AZAM[1], Industrial Research Laboratory, Calcutta, India

At a certain point in oil absorption of pigments the paste in oil is very easily taken off on the palette knife. This marks the point of saturation and the indication is sharp within 1 drop of oil (0.05 cc.) from an ordinary standard buret.

When pastes, fully or partly saturated with oil according to the above standard, are immersed in a bath of oil stock used for absorption, saturated pastes absorb no more oil, while unsaturated pastes absorb oil almost equal to the calculated deficiency for saturation in one to two days (24 to 48 hours).

THE term "oil absorption" has been vaguely defined and the method of determining its value has not been truly standardized. In view of the circumstances, a rigorous study of oil absorption with strictly accurate and reproducible results has not yet been possible.

Oil absorption has been defined in various ways: as nothing but the filling of a void (*5*) or the filling of interspaces of the pigment particles with oil, the wetting power of the liquid (*3*), or the maximum quantity of oil required with any pigment for an intimate mixture in liquid state with minimum tendency to flow. A point which does not appear to be appreciated and which adds to the difficulty of attaching significance to oil-absorption measurement is the problem of defining experimentally the condition of complete wetting of the pigment. The criterion usually adopted by specifications depends on a rather vague visual judgment of consistency at the end point, which although it may afford a fairly accurate basis for comparing samples of the same pigment, does not necessarily serve well for comparison between different pigments.

Apart from such interpretations, there is in general neither a fixed method nor a sharp finishing point in the determination of oil absorption. The current methods of locating the end point have more or less the common flow of a rule-of-thumb experiment and, as such, the end point determined by these methods is scarcely reproducible with exact precision.

[1] Present address, Plastics Industries Technical Institute, Los Angeles, Calif.

TABLE I. ABSORPTION OF OIL BY UNSATURATED PIGMENT PASTES

Pigment	Quantity Taken	Degree of Saturation	Oil Absorbed 24 hours	36 hours	48 hours	Calculated Deficiency of Oil for Saturation
	Grams	%	*Cc.*	*Cc*	*Cc.*	*Cc.*
Red oxide of iron	10	50	0.8	0.8	0.8	1.0
		75	0.4	0.4	0.4	0.45
White lead	20	50	1.2	1.2	1.2	1.3
		90	0.2	0.2	0.2	0.26
Lithopone	10	50	0.7	0.7	0.7	0.75
		90	0.05	0.09	0.09	0.15

TABLE II. PERCENTAGE OF OIL ABSORPTION BY COMMON PIGMENTS

Pigments	Quantity Taken for Each Experiment[a], Grams		Raw Linseed Oil	Double-Boiled Linseed Oil	Castor Oil	Tung Oil
		Specific gravity	0.930	0.931	0.953	0.936
		Acid value	2.7	6	7	6.6
		Saponification value	192	198	186	200
		Iodine (Hanus) value	170	145	83	165
			Mean Oil Absorption Values			
White lead	20		12.15	12.32	12.12	12.17
White zinc	10		17.89	16.81	17.63	16.85
Lithopone	10		14.18	13.02	13.34	13.1
Whiting	20		19.65	19.29	19.77	19.07
Barytes	20		11.16	10.35	10.48	10.18
Yellow ochre	10		27.9	..	23.83	23.4
Red ochre	10		22.39	18.83	20.1	18.25
Ultramarine blue	10		33.48	33.48	35.26	31.82
Prussian blue	5		56.27	..	53.37	..
Red oxide	10		16.74	14.88	16.20	15.68
Red lead	20		7.44	7.44	7.15	7.02

[a] According to recommendations of I. S. D. specifications.

The Gardner-Coleman method which determines the "oil absorption factor" is accurate within 0.2 cc. (of oil added). The elimination of grinding and incorporation of certain precautions make it easier to duplicate the results within that limit of accuracy. But, unfortunately, the oil-absorption factor does not work out a paste of the conventional consistency approved by painters; and the method, apart from its theoretical importance, has not much to recommend itself to the paint maker in his everyday practice. Obviously, the standard rub-out method and the Gardner-Coleman method give results wide apart, one using much less oil than the other (*2*).

The author of the present communication, after a prolonged search, has observed definite indications locating a sharp end point. The results provide a dependable basis for a comparative study of oil absorption of pigments.

It has been consistently observed by the author that at a certain point, on gradual addition of oil to the pigment with constant rubbing for thorough incorporation of the oil with the pigment, the paste sticks to the palette knife with very little effort. The difference in the coherence of the mass is clearly distinguishable before and after this definite stage is reached. The results are reproducible with very close coincidence.

Following the A. S. T. M. procedure (*1*), using a buret and taking about 20 minutes for each experiment for comparable extent and pressure of grinding, oil absorption of pigments was determined using raw linseed oil of known specifications. The quantity of pigment varied according to its nature from 5 grams in the case of Prussian blue to 20 grams in the case of white lead, following the recommendations of the I. S. D. specifications (*4*). This limits the amount of oil added, in most cases to approximately 40 drops (1 drop = 0.05 cc.). The variation in the results did not exceed 1 drop of oil from a standard buret or 1 per cent in the value of oil absorption.

There is, however, another aspect of the end-point determination by this method. The results have supplied a newer definition of oil absorption of pigments. The smooth pigment pastes which absorbed oil up to the sharp end point located by the author did not absorb more oil when immersed in a bath of the oil stock used for absorption, whereas pastes with lesser oil did actually absorb more oil almost equal to the calculated deficiency of saturation. A graduated cylinder, used as an oil bath, was filled up to a certain point with the paste carefully scraped into, and totally immersed in, oil. The depression in the level of oil in the cylinder was noted after 24, 36, and 48 hours (Table I).

Thus comes a new interpretation of oil absorption, which might now be defined as the minimum quantity of oil required to saturate a pigment by grinding. The end point as located is not only supported on logical and scientific grounds, but also throws a flood of light on the true approach to this obscure problem of a very well-known practice.

Table II gives oil-absorption values for some common pigments with different oils, as determined by the author at the Paint and Varnish Section, Industrial Research Laboratory in Calcutta, Bengal, India. Each result represents a mean of 70 duplications, mostly concurrent. In the few cases where variations were noted, the difference did not exceed 1 per cent. A steel spatula (Sheffield, London) with a 8.75 × 2.5 cm. (3.5 × 1 inch) blade and a marble slab 30.0 cm. (1 foot) square were used for grinding. The temperature ranged from 23.89° to 29.44° C. (75° to 98° F.) and humidity varied between 52 and 67 per cent.

The author's attention has lately been drawn to a recent U. S. Navy Department Specification, 52-Z-7 (int.), September 1, 1941, Bureau of Ships ad interim specification, advocating a method identical with the author's. Incidentally, the experiments by the author were conducted towards the end of 1940. This happy coincidence is in itself a very strong argument in favor of the method for location of the end point.

Conclusion

In view of the fact that pastes produced by various pigments with oil show a considerable difference in characteristics, the end point is better located at the point of saturation as described. The saturated paste is invariably a coherent, stiff, puttylike mass which does not break or separate and which lends itself conveniently for further operation in the preparation of mixed paint.

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Determination of Thiosulfate in Used Doctor Solution

KARL UHRIG AND HARRY LEVIN, The Texas Company, Beacon, N. Y.

A method for determining thiosulfate in used doctor solution is based on the observation that carbon dioxide precipitates the lead and simultaneously converts any sulfite present to bisulfite, which subsequently is bound to formaldehyde to render it inactive toward iodine. Under these conditions, thiosulfate is titrated alone.

ONE of the finishing steps in the refining of gasoline and other light petroleum fractions is the "sweetening" operation in which mercaptans, the compounds responsible for the "sour" odor of the product, are converted to less obnoxious disulfides. A process widely used for this purpose is the doctor treatment, in which gasoline is agitated with doctor solution (sodium plumbite in an excess of caustic soda solution) with subsequent addition of free sulfur in carefully controlled amounts. The conversion from mercaptans to disulfides is believed to occur according to the following equations:

$$2RSH + Na_2PbO_2 \longrightarrow (RS)_2Pb + 2NaOH \quad (1)$$

$$(RS)_2Pb + S \longrightarrow R_2S_2 + PbS \quad (2)$$

The disulfides remain in the hydrocarbon fraction, which is separated from the used doctor solution containing lead sulfide.

The usual practice is to regenerate the spent doctor by oxidation (air blowing); the reaction proceeding, it is believed, according to the following equation:

$$2PbS + 2O_2 + 6NaOH \longrightarrow 2Na_2PbO_2 + Na_2S_2O_3 + 3H_2O \quad (3)$$

Since sodium thiosulfate, which is the principal by-product of this process, remains in the reactivated doctor solution and reflects its further utility for sweetening operations (*8*), a method for its analytical determination was desired.

The effect of this increasing thiosulfate concentration is to further the tendency to emulsification, decrease the solubility of lead, and increase the specific gravity, so that gravity is no longer an index of the caustic concentration in doctor solution (*6*). A number of methods are available in the literature for determining it in the presence of other reducible sulfur salts, but none of these can be applied directly to the analysis of doctor solution because lead interferes.

Kalmann (*4*) determines thiosulfate plus sulfite by titration with iodine. In the titrated solution hydriodic acid, equivalent to the sulfite,

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$$

is titrated with alkali. Thiosulfate is calculated from the two titrations.

Autenrieth and Windaus (*1*) determine thiosulfate by titration with iodine after removing sulfite as strontium salt. A similar method, removing sulfite as barium salt, is described by Scott (*7*).

Giberton (*2*) describes a method based on rapid conversion of silver thiosulfate to silver sulfide, the sulfur of which is determined colorimetrically.

Heinemann and Rahn (*3*) describe a method for determining reducible sulfur in caustic soda, based on reduction of such sulfur compounds to hydrogen sulfide which is determined iodometrically.

Several promising methods were investigated after it was observed that in doctor solution carbon dioxide quantitatively precipitates lead and converts sulfites to bisulfites. When sodium sulfite is added to fresh doctor solution and an excess of carbon dioxide is passed through it and filtered, the filtrate gives no evidence of lead to hydrogen sulfide. When formaldehyde is added to another portion of the filtrate and this is titrated with iodine the latter is immediately in excess, indicating the absence of sulfite.

Most of these procedures, though capable of giving accurate results on knowns, are too long and tedious for routine use. In this class belong such methods as that of Autenrieth and Windaus (*1*) which, involving separation of sulfite as its strontium salt, requires too much time for settling and filtering.

The method of Kurtenacker and Wollak (*5*), which is based on the fact that bisulfite is rendered inactive toward iodine by binding it to formaldehyde, formed the basis of the following method, which has been adopted for determining thiosulfate in used doctor solutions.

Apparatus and Reagents

Apparatus required includes 500-ml. and 250-ml. volumetric flasks, 50-ml. pipet, 50-ml. buret divided in 0.1 ml., 1000-ml., 500-ml., and 250-ml. Erlenmeyer flasks, glass funnels, carbon dioxide reducing valve, and Whatman filter paper No. 4, 11 cm.

The reagents are carbon dioxide, 0.1 *N* iodine, 0.1 *N* sodium thiosulfate, C. P. formaldehyde (35 to 40 per cent), 10 per cent acetic acid, starch indicator, and phenolphthalein indicator.

Procedure

Pipet 50 ml. of sample into a 500-ml. volumetric flask, dilute with water to 500 ml., mix, transfer the entire solution to a 1000-ml. Erlenmeyer flask, add a few drops of phenolphthalein indicator, and pass carbon dioxide through the solution until the pink phenolphthalein color is discharged. The lead is thus precipitated and any sulfite present is converted to bisulfite. As a precaution continue the passage of carbon dioxide for 5 minutes longer.

Filter this solution through Whatman No. 4 filter paper and collect 250 ml. of filtrate in a 250-ml. volumetric flask. For each test put 50 ml. of this filtrate into a 250-ml. Erlenmeyer flask and add 5 ml. of 35 to 40 per cent formaldehyde, followed after 5 minutes by 20 ml. of 10 per cent acetic acid. Titrate the solution with 0.1 *N* iodine immediately after addition of the acetic acid, using starch as indicator.

The 0.1 *N* iodine solution should be checked daily against 0.1 *N* thiosulfate.

Calculations

1 ml. of 0.1 *N* iodine $\simeq$ 0.01582 gram of sodium thiosulfate. 20 $\times$ ml. of 0.1 *N* iodine $\times$ grams of thiosulfate per ml. of standard iodine = grams of sodium thiosulfate per 100-ml. sample.

Discussion

The weight-volume manner of reporting results is in accord with the plant practice of expressing constituents of doctor solution in pounds per barrel.

Frothing usually occurs on passing carbon dioxide through the sample, but subsides after a few minutes, during which a little shaking of the flask will prevent serious difficulty.

The end point fades after a little standing but is sufficiently stable for recognition without difficulty.

After the precipitation of lead by carbon dioxide, the used doctor solution usually is still colored and has a phenolic odor, indicating that not all phenolic compounds have been removed. These compounds, however, do not interfere with the iodine titration. This was demonstrated by comparing

TABLE I. THIOSULFATE DETERMINATIONS IN USED DOCTOR SOLUTIONS

(Known amounts of thiosulfate added)

Sample	Thiosulfate in Original G./100 ml.	Thiosulfate Added G./100 ml.	Total Thiosulfate Found G./100 ml.	Added Thiosulfate Found G./100 ml.
1	2.55	3.12	5.60	3.05
		6.23	8.65	6.10
		9.34	11.76	9.21
2	1.74	2.49	4.38	2.64
		4.98	6.80	5.06
		7.48	9.34	7.60
3	1.94	1.25	3.10	1.16
		2.49	4.38	2.44
		3.74	5.45	3.51

results obtained by the proposed method with those obtained by a long gravimetric procedure in which organic matter does not interfere. The latter involved the separation of sulfate and sulfite as barium salts and the oxidation of the thiosulfate to sulfate which was determined gravimetrically. Results obtained by the two methods agreed very well.

The time required for a thiosulfate determination is approximately one hour for the proposed volumetric method as compared to approximately 12 hours' elapsed time for the gravimetric method.

The precision and accuracy of the proposed method, applied in a routine manner, are evident from Table I.

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PRESENTED before the Division of Petroleum Chemistry at the 103rd Meeting of the AMERICAN CHEMICAL SOCIETY, Memphis, Tenn.

Apparatus for Continuous Concentration of a Solution under Reduced Pressure

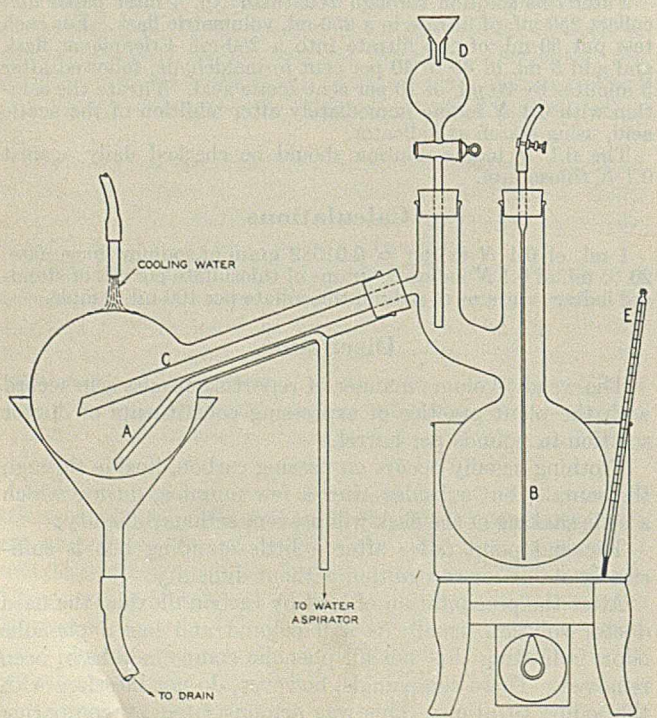
BENJAMIN L. DAVIS

Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture, Washington D. C.

IN THIS laboratory, it is frequently necessary to concentrate large volumes of dilute sugar solutions resulting from the hydrolysis of polysaccharides, the solvent—water or alcohol—being discarded. Because of the danger of decomposition at higher temperatures, distillation at reduced pressure with a maximum bath temperature of 50° C. is used. A water aspirator lowers the pressure enough to obtain rapid distillation. With the usual apparatus (consisting of two side-arm distilling flasks, one being the boiling flask and the other the receiver, cooled with a stream of water), however, the process of concentration must be frequently interrupted in order to empty the receiver and to add more of the dilute solution to the boiling flask.

A modified concentration apparatus, which has been in use in this laboratory for over two years, is described here. It may be operated continuously until the concentration is completed, the receiver being automatically emptied and the dilute solution being added from time to time, or continuously, without breaking the vacuum or stopping the boiling.

A cursory search of the literature shows that a somewhat similar apparatus was reported by Burger (*1*), but it is believed that the apparatus here described necessitates much less manipulation in operation for the purpose outlined above.



The receiving flask was made by sealing a piece of 6-mm. tubing, *A*, into an ordinary 2-liter, side-arm, distilling flask. Another modification of this arrangement consists of a close-fitting rubber tube pushed through the side arm and extending to the bottom of the receiving flask. While not suitable for use with all solvents, this arrangement has been used for several years in this bureau for concentrating sugar solutions. *B* is a fine capillary, to help prevent bumping, with a short rubber tube and screw clamp at its upper end for regulation. Replacing the usual side arm, *C*, of the Claisen distilling flask with a tube of larger diameter (15-mm. outside diameter) hastens the distillation. The dilute solution to be concentrated is added through the funnel, *D*, either intermittently or by a continuous slow drip as the liquid boils out. *E* is a thermometer to indicate the bath temperature. The vapors are condensed in the receiving flask, then drawn off by the aspirator through tube *A* to the drain. The rest of the equipment is obvious from the drawing.

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AGRICULTURAL Chemical Research Division Contribution No. 54.

A Dropping Mercury Electrode

GEORGE J. KAHAN
University of Minnesota, Minneapolis, Minn.

A NUMBER of suggestions have been made for constructing the dropping mercury electrode (*1–6*). The trend is to avoid the use of rubber tubing, since it reacts with the mercury. The rubber connections can be eliminated by a very simple siphon system.

The mercury storage vessel has the form shown in *a*, Figure 1, the capillary itself is *b*, and the glass tubing, *c*, dips into the storage vessel. The height of the mercury can be varied by moving *a* up or down. A mark on the side arm, *d*, makes it easy to reproduce the mercury pressure for every polarogram. The capillary itself is connected to the siphon with an interchangeable ground joint 10/30, held in place by a couple of springs. This makes it easy to clean the capillary separately.

The capillary should be sealed to the glass tubing of the ground joint. To blow out a capillary as used in polarography it is necessary to use the pressure of a gas cylinder. To make such a seal without a cylinder, the capillary tubing is filled with mercury, using an ordinary leveling bulb with mercury connected to the capillary with rubber tubing. The open end of the capillary is closed with one finger and the capillary disconnected from the rubber tubing. One end of the capillary is brought into a very hot flame to close the capillary on this side, the other end being closed with the finger; then the other end is also sealed. The capillary should now be nearly full of mercury. If the glass is heated with a moderately hot flame, the pressure of the mercury will blow it out to a bulb large enough to be sealed to ordinary glass tubing. The sealed end of the capillary is now broken off.

A ground joint 12/18 is sealed to the electrode (Figure 2). The cell to be used with this electrode has a corresponding ground joint, and *g* and *h* are inlet and outlet for the gas. Contact to the mercury pool in the bottom is made through *k*. The capillary tubing between *k* and the cell should have a diameter of approximately 1.5 mm. If an outside anode or reference electrode is to be used, a two- or three-necked cell should be made.

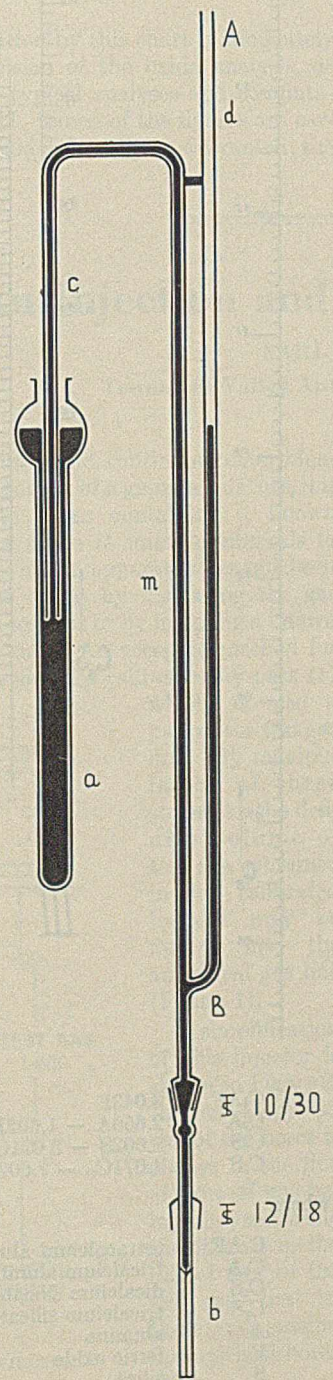

FIGURE 1

Such a capillary should be cleaned before being put into service. Concentrated nitric acid, which is mostly used for this purpose, is not very suitable, as salts form in the reaction of the acid with the mercury left in the capillary and clog it. A solution of iodine in potassium iodide proved to be very effective in cleaning.

To fill the capillary with mercury, *c* is dipped into the storage vessel filled with mercury, and using suction cautiously at *A*, some mercury is brought into *m*. The tapping of *m* causes the mercury to fall and fill out the tubing up to point *B*, where the side arm starts out. Now, using pressure at *A*, all mercury over *B* is driven back into the storage vessel so that the siphon will be free from air bubbles in the end. Then the mercury is brought over by using full suction for a moment. It is necessary to use a safety bottle to save any mercury carried over by the suction.

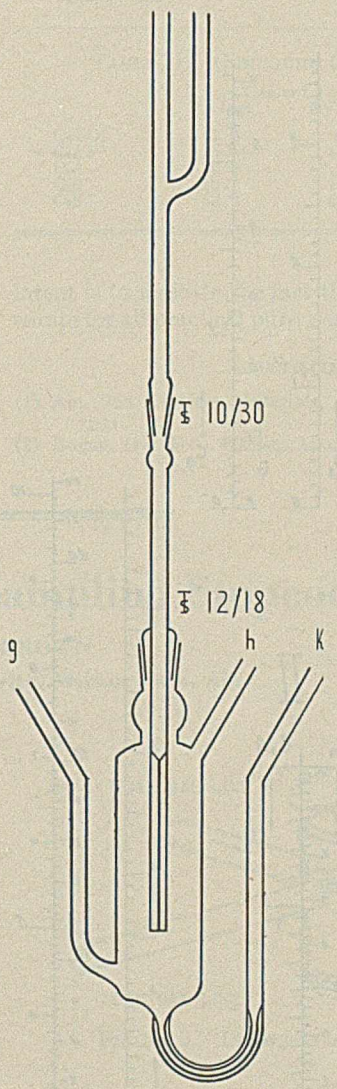

FIGURE 2

This construction allows the side arm with the capillary to be pivoted about the storage vessel as center, and swung away from the polarographic cell. When not in use, it is dipped into a test tube, which is provided with the same ground joint as the polarographic cell. This test tube should be filled with pure mercury. The pressure in the test tube, which is closed tightly by the ground joint of the capillary, increases as the mercury flows into the test tube, and this back pressure will soon stop the flow of mercury completely.

An electrode and cell of this design have been in use for more than six months, and they have worked very satisfactorily.

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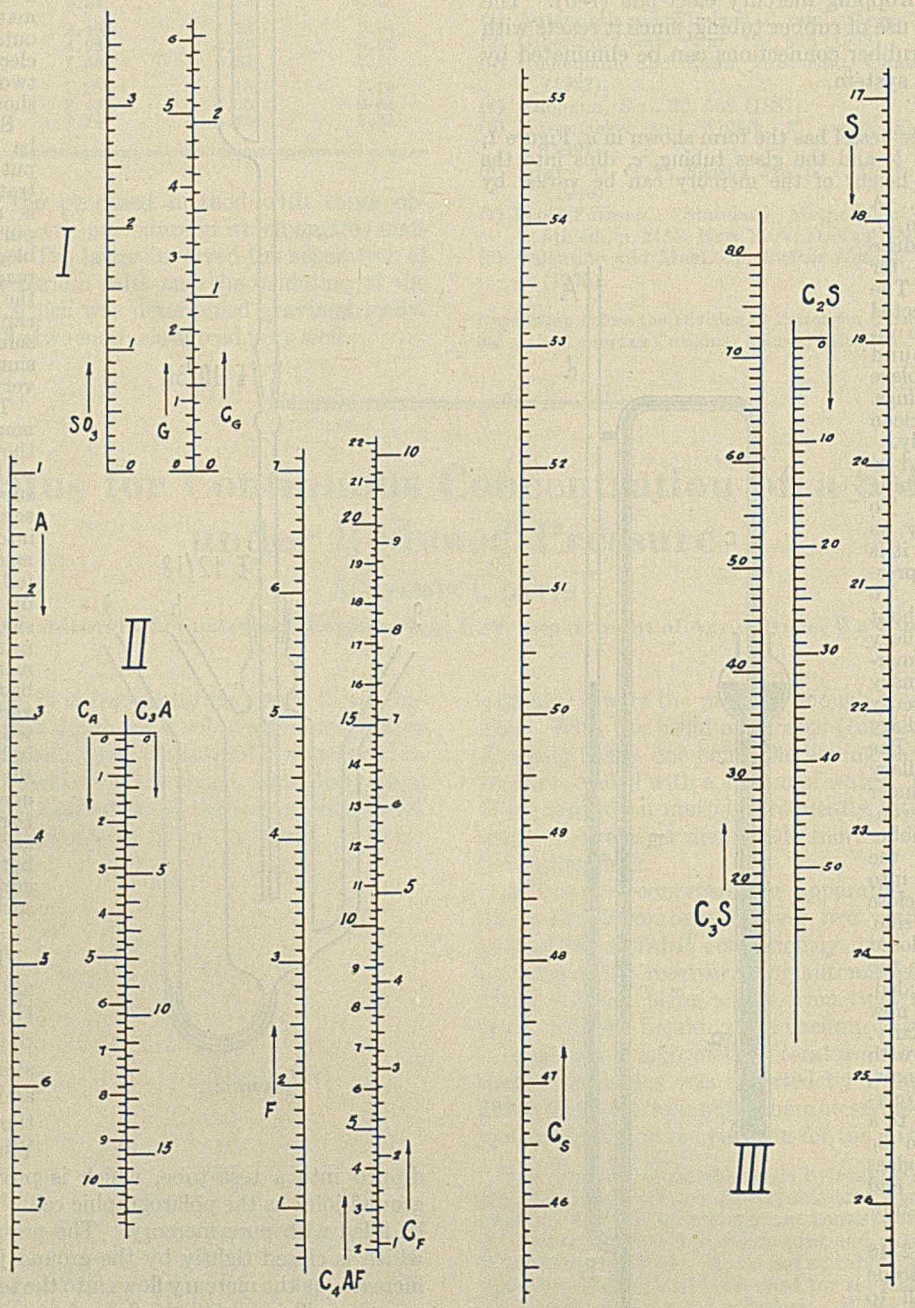
Nomograph for Computing Compound Compositions of Portland Cements

BENJAMIN JANER, Department of Borough Works, Borough of Manhattan, New York, N. Y.



CONSTRUCTION departments of government agencies, federal, state, and municipal, are showing an increasing tendency to specify portland cements on the basis of the computed compound composition (*2*). The latest revision of the specifications for portland cement of the American Society for Testing Materials reflects this trend (*1*). The nomographic chart submitted herewith simplifies considerably the necessary computations from the oxide analyses.

For the values of tetracalcium aluminoferrite, tricalcium aluminate, dicalcium silicate, and tricalcium silicate, we have the following equations:

$$C_4AF = 3.043F$$
$$C_3A = 2.650A - 1.692F$$
$$C_2S = 8.602S - 3.071C_S$$
$$C_3S = 4.071C_S - 7.602S$$

where

C_4AF = tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$)
C_3A = tricalcium aluminate ($3CaO.Al_2O_3$)
C_2S = dicalcium silicate ($2CaO.SiO_2$)
C_3S = tricalcium silicate ($3CaO.SiO_2$)
A = alumina
F = ferric oxide
S = silica

C_S = net calcium oxide available for silicates
= $C - (C_G + C_F + C_A + C_{free})$
C = total calcium oxide
C_A = calcium oxide in tricalcium aluminate
C_G = calcium oxide in calcium sulfate (gypsum)
C_F = calcium oxide in tetracalcium aluminoferrite

and

C_{free} = free calcium oxide, if the analysis has included this determination

The steps in using the nomographic chart would be:

At I, from the value for sulfuric anhydride, a straightedge parallel to the base line gives the values for calcium sulfate (G) and C_G. At II, a straightedge at the value for F parallel to the base line gives to the right the values for C_4AF and C_F. A straightedge from the value for F to the left for the value for A gives C_3A and C_A, as indicated. From the values of C, C_G, C_F, C_A, and C_{free} (if known), C_S is computed and used at III. A straightedge between the values of C_S and S intersects the lines indicated to give at once C_2S and C_3S.

The accuracy of the calculation by this chart is adequately commensurate with the precision of the oxide analysis, as is readily apparent from two typical analyses and computations shown in Tables I and II. Some of the figures are carried to more decimals than would ordinarily be warranted; the intent is to indicate the fact that the chart is sufficiently accurate for all practical purposes.

TABLE I. OXIDE ANALYSIS

	Cement 1	Cement 2
SiO_2	19.8	22.0
Al_2O_3	5.8	5.35
Fe_2O_3	5.07	4.95
CaO	62.6	61.7
MgO	3.60	3.41
SO_3	1.50	1.37
Ignition loss	0.86	0.80

TABLE II. COMPOUND COMPOSITION, COMPUTED

	Cement 1		Cement 2	
	By logs	By chart	By logs	By chart
$CaSO_4$	2.6	2.6	2.3	2.3
C_4AF	15.5	15.4	15.1	15.1
C_3A	6.8	6.8	5.8	5.8
C_2S	16.1	16.0	35.0	34.9
C_3S	53.9	53.8	37.2	37.1

Literature Cited

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An Injection and Sampling Stopcock

EARL H. BROWN
Tennessee Valley Authority, Wilson Dam, Ala.

IN APPARATUS for the automatic, continuous determination or detection of a component of a gaseous mixture, it is imperative that checks with gases containing a known amount of that component be made at suitable intervals to make sure that the sensitivity of the apparatus has not been impaired. This can be done either by displacing the gas being analyzed by a stream of test gas or by injecting a known quantity of test gas into the line. An accepted method for accomplishing the latter is the use of a calibrated by-pass (*1*) which is also a part of the test gas line. By manipulation of three stopcocks the definite volume of test gas contained in the calibrated by-pass may be flushed into the analytical gas line (Figure 1).

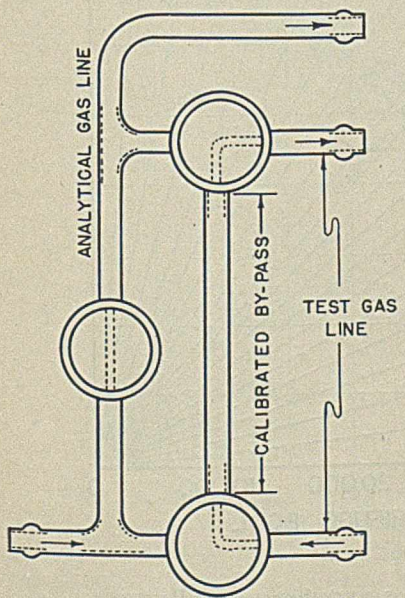

FIGURE 1. BALDEWYNS' INJECTOR

A simplification of this injector is shown in Figure 2. In this stopcock, one of the bores is always in the line of flow of gas being analyzed, while the other is in the line of flow of the test gas—that is, there is gas passing through both bores at the same time. To inject a small amount of test gas into the analytical gas line, the stopcock is turned 90 degrees. The quantity of test gas that was in the test gas line stopcock bore just prior to turning is thus transferred to the analytical gas line. By means of calibrated bores, the amount of each injection can be determined. Larger quantities of the test gas may be injected into the analytical gas line by either manual or mechanical rotation of the stopcock plug.

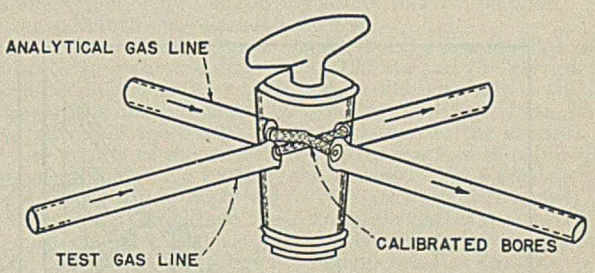

FIGURE 2. INJECTION AND SAMPLING STOPCOCK

The single stopcock injector, when compared with Baldewyns' injector, thus represents a real saving of material and a simplification of manipulations.

By passing an inert carrier gas through the analytical gas line and the gas to be tested through the other line, small samples may be periodically taken for analysis.

In addition to the application mentioned, the device should be useful for mixing and proportioning various fluid combinations.

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Fractionation of Colloidal Systems

Selection of Operating Conditions for the Supercentrifuge

GEORGE FANCHER, S. C. OLIPHANT[1], AND C. R. HOUSSIERE, JR.[2], The University of Texas, Austin, Texas

THE application of the Sharples supercentrifuge to the determination of the size of particles and the distribution of the particles in colloidal and semicolloidal systems has been presented previously (*1–4*). It is possible to operate the machine under such conditions as to separate from a suspension particles varying in size from 1 micron in diameter or larger to particles which approach the size of larger molecules. Compared to other methods of separation, the supercentrifuge method has been found to have the advantages of larger capacity, rapidity of determination, simplicity of operation, and low cost of maintenance and operation. Therefore, it has been adapted to the study of the particle size distribution of oil-well drilling muds and has become a routine operation in the authors' laboratories.

Hauser, Lynn, Reed, and Schachman (*1*, *2*, *3*) developed methods for calculating the size of particles separated by the supercentrifuge under definite conditions of operation, basing the mathematical analysis upon two assumptions—namely, that the flow parallel to the axis of rotation is streamline or viscous, and that Stokes' law holds for dilute suspensions. The effect of the first assumption is to require a rate of feed of the suspension to the centrifuge which is small in comparison to the outward centrifugal force.

[1] Present address, Stanolind Oil & Gas Company, Houston, Texas.
[2] Present address, U. S. N.

It is desirable, therefore, to be able to predict the operating conditions for a particular machine which will result in the separation of particles of definite size or range of size, and Hauser devised a special slide rule to facilitate determination of operating conditions. The expression developed by Hauser and co-workers (for a monodispersed film, *4*) may be used to develop a simpler and less tedious way of accomplishing this desideratum.

Their equation is

$$Y = \frac{18QK_1\eta}{\pi(R_2^2 - R_1^2)D^2\omega^2\,\Delta\rho}\left[\frac{R_2^2}{2}\ln\frac{R_2}{X_0} - \frac{R_1^2}{2}\left(\ln\frac{R_2}{X_0}\right)^2 + \frac{X_0 - R_2^2}{4}\right] \quad (1)$$

in which

$$K_1 = \frac{R_2^2 - R_1^2}{3/4\,R_1^2 + 1/4\,R_2^4 - R_2^2R_1^2 - R_1^4\ln\frac{R_1}{R_2}} \quad (2)$$

Q = rate of feed of suspension
η = viscosity of dispersion fluid
R_1 = distance of overflow weir from axis of rotation
R_2 = inner radius of bowl less thickness of liner
D = equivalent spherical diameter of solid particle
ω = angular velocity of bowl in radians per second
$\Delta\rho$ = density of dispersed phase minus density of dispersing phase at test temperature
X_0 = distance from axis of rotation at which particle begins to settle
Y = vertical distance from bottom of centrifuge bowl

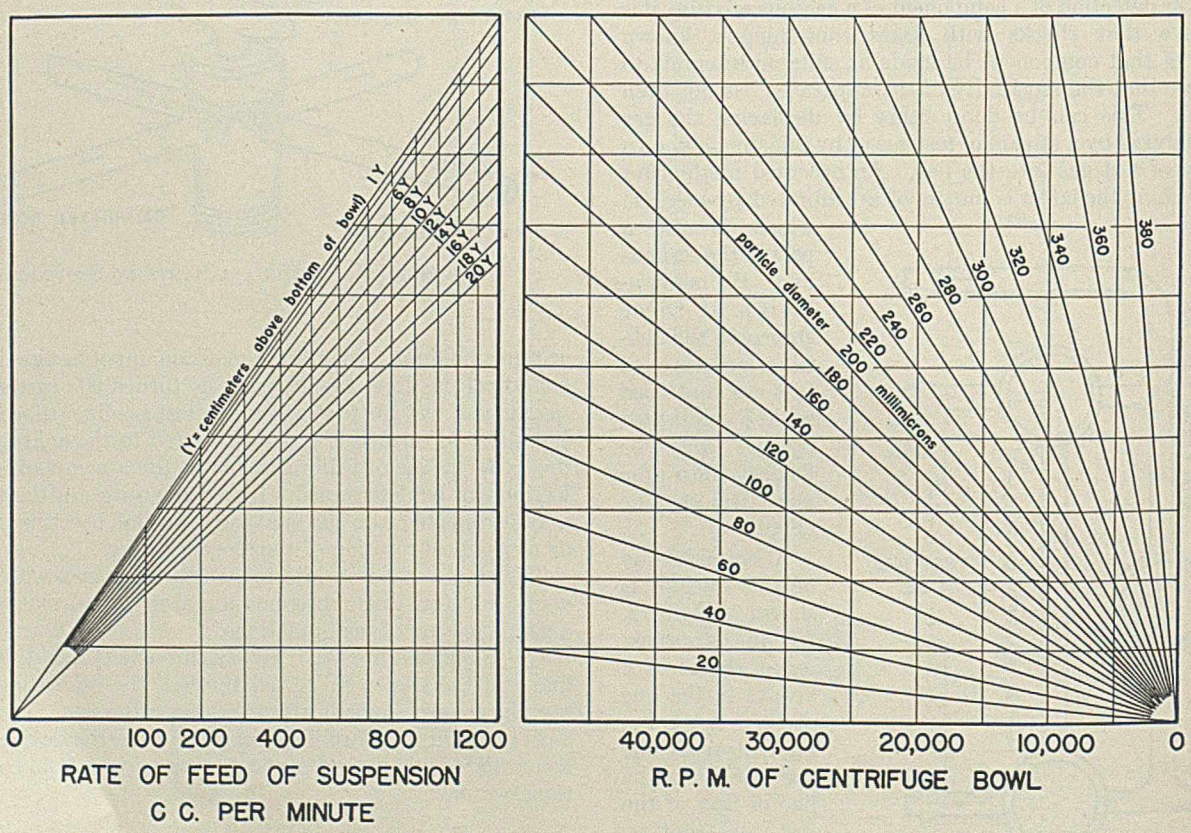

FIGURE 1. ALIGNMENT CHART FOR SELECTION OF R. P. M. AND RATE OF FEED NECESSARY TO SEPARATE A PARTICLE OF DEFINITE SIZE

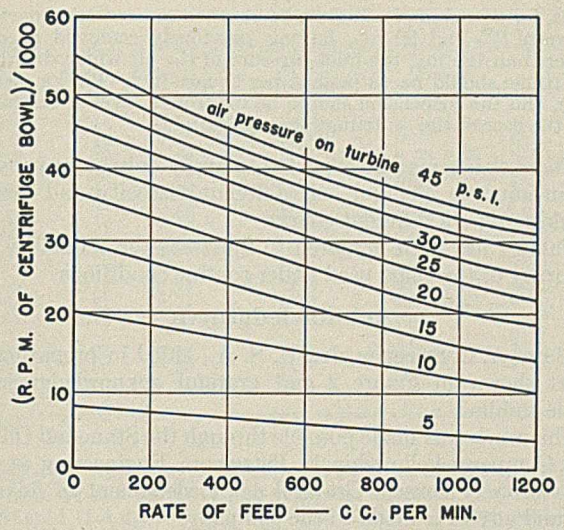

FIGURE 2. AIR PRESSURE REQUIRED TO DRIVE SUPERCENTRIFUGE AT DESIRED R. P. M.

The equation has three variables (Q, ω, D) and is implicit in X_0. This makes the equation soluble only by means of determinants, a family of curves, or some similar method. If, for definite values of Q and in Equation 1, values of X_0 are calculated for any fixed value of D and Y, it is then possible to represent the equation as:

$$Y = \frac{M}{D^2}(C) \tag{3}$$

$$M = \frac{18QK_1\eta}{\pi(R_2^2 - R_1^2)\omega^2\ \Delta\rho} \tag{4}$$

$$C = \left[\frac{R_2^2}{2}\ln\frac{R_2}{X_0} - \frac{R_1^2}{2}\left(\ln\frac{R_2}{X_0}\right)^2 + \frac{X_0^2 - R_2^2}{4}\right] \tag{5}$$

Because Equation 1 is based upon the deposition of a monodispersed film, it follows that values of D at definite values of Y are unique for the particular conditions of operation which prevail, or, in other words, C is only a function of Y and no longer a function of D. The validity of this conclusion was checked by determining independently the range in values of D between the top and bottom of the bowl with the slit-ultramicroscope. Therefore, if dilute enough systems are maintained for fractionation, there is a constant value of C for every value of Y. However, D remains dependent upon Q, ω, and Y. Through readjustment of Equation 3 by bringing Q and ω outside the constant M, we obtain

$$D^2 = \frac{QM'C}{Y\omega^2} \tag{6}$$

$$M' = \left[\frac{18K_1\eta}{\pi(R_2^2 - R_1^2)\Delta\rho}\right] \tag{7}$$

It is then possible for any definite value of Y to establish the relation

$$\frac{D_1^2}{D_2^2} = \frac{Q_1\omega_2^2}{Q_2\omega_1^2} \tag{8}$$

$$D_2 = \left(\frac{Q_2}{Q_1}\right)^{1/2}\left(\frac{\omega_1}{\omega_2}\right)D_1 \tag{9}$$

Using Equation 6 and values of C at various values of Y from independent observation, the diameters of particles were calculated for various r. p. m.'s, ω, and rates of flow, Q. The results of these calculations are graphically illustrated in Figure 1, which provides a rapid and convenient method for determining the diameter of the particles deposited at a definite value of Y for a definite value of Q and of ω. Such a chart can be conveniently used to determine the specific conditions under which the supercentrifuge must be operated to ensure the separation of particles of a definite size.

Further to simplify the operation of the supercentrifuge, the air pressure required to maintain a definite r. p. m. of the centrifuge and the liquid head resulting in definite rates of feed of suspension were determined. Figure 2 shows a plot of the r. p. m. of the centrifuge bowl versus the rate of feed of the suspension at various constant pressures on the air-driven turbine. Figure 3 is a plot of the height of liquid level above the base of the centrifuge versus the air pressure on the turbine for constant rates of feed with three sizes of feed nozzles. The air is supplied to the turbine through two needle valves and a pressure regulator in series. The two valves assure much finer control of pressure than can be obtained with only one valve. The suspension is fed into the bowl through one of three nozzles of different sizes, which can be interchanged while the machine is running. A constant rate of feed is maintained by keeping a definite hydrostatic head on the inlet to the bowl. An automatic overflow siphon, which is adjustable to give any desirable height of liquid level above or below the base of the centrifuge, assures a constant rate of feed. Figures similar to 2 and 3 probably must be determined for each machine because of characteristics inherent in the machine, but they are easily prepared and greatly facilitate routine operation of the machine. The following example is presented to illustrate the use of the chart:

It is desired to obtain from an aqueous suspension containing 1 per cent solids by weight, particles between 125 and 80 millimicrons (mμ) in diameter. Obviously, it is necessary to eliminate from the suspension all the particles larger than 125 mμ by sedimentation or by centrifuging before this can be done. It is assumed that this has already been done.

Using Figure 1, from the intersection of the diagonal line corresponding to a particle diameter of 125 mμ and the vertical line corresponding to 45,000 r. p. m., proceed horizontally to the left; intersect the diagonal line corresponding to $Y = 1$ (1 cm. above the bottom of the bowl); and read below on the abscissa 400 cc. per minute as the rate of feed of the suspension required for the separation. In a like manner, it is seen that a particle of 80 mμ diameter will be deposited at 20 Y (the top of the bowl). It has now been established that, to obtain particles from 125 to 80 mμ in diameter from a suspension containing no particles larger than 125 mμ, the centrifuge is to be operated at 45,000 r. p. m. and the suspension must be fed at a rate of 400 cc. per minute.

Using Figure 2, it is found that 43 pounds per square inch (126 kg. per sq. cm.) air pressure on the turbine are required to drive the bowl at 45,000 r. p. m., when the rate of feed is 400 cc. per minute. Caution should be exercised here in order to prevent the selection of an r. p. m. or flow rate that exceeds the operating limits of the

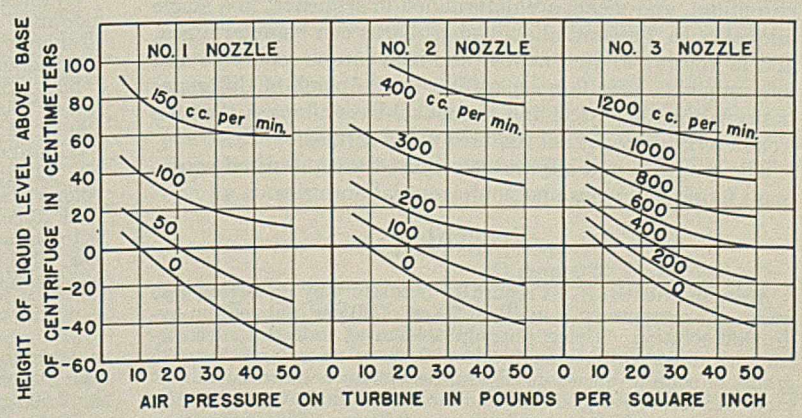

FIGURE 3. CONTROL CHART FOR SELECTION OF FEED NOZZLE AND FLUID HEAD REQUIRED TO MAINTAIN DESIRED RATE OF FEED

Table I. Comparison of Particle Diameter Values Predicted by Calibration Curves and Observed Microscopically

Sample No.	Portion of Liner Represented, Y	Equivalent Spherical Diameter[a] of Particles: Calibration Curves Maximum	Calibration Curves Minimum	Slit-Ultramicroscope (Av. D) Observer 1	Slit-Ultramicroscope (Av. D) Observer 2
	Cm.	*Millimicrons*			
1	0–20	215	150	195	208
2	0–2	150	147	155	158
3	0–20	90	55	...	82

[a] Diameter equivalent to that of a sphere which would settle at a rate equal to that of the actual particle.

centrifuge. From Figure 2 this limit is seen to be 200 cc. per minute at 50,000 r. p. m. and 1000 cc. per minute at 35,000 r. p. m. However, this limit may be altered for the air-driven turbine by adjusting the pressure regulator on the air supply line to a higher driving pressure. If a higher driving pressure is used, care must be exercised never to exceed 50,000 r. p. m. (maximum r. p. m. specified for the supercentrifuge by manufacturer). This might easily be done if a pressure in excess of 45 pounds per square inch (132 kg. per sq. cm.) were applied when the bowl was empty. At the higher rates of feed the basic formula used here for particle size determination may not apply rigidly, owing to the possible development of turbulence within the centrifuge bowl.

From Figure 3, it is seen that to attain a rate of feed of 400 cc. per minute while using 43 pounds per square inch (126 kg. per sq. cm.) it is necessary to use nozzle 3 and keep the liquid feed level at 15 cm. below the base of the centrifuge, or to use nozzle 2 with the liquid level 77 cm. above the base of the centrifuge. Thus, for this example, in order to obtain a separation of particles between 125 and 80 mμ, having previously removed particles larger than 125 mμ, the inlet pressure of the air which drives the centrifuge should be 43 pounds per square inch (126 kg. per sq. cm.), and the suspension should be fed from a level of 15 cm. below the base of the centrifuge through nozzle 3.

These charts may be expected to apply only to suspensions in an aqueous medium and different viscosity and density would require a different chart.

Table I has been prepared to illustrate the reliability and accuracy of the chart used under routine conditions.

Acknowledgment

Major A. E. Sweeney, Jr., U. S. A., aided in preparing the chart shown in Figure 2 and grateful acknowledgment is made to him.

This work was made possible through the Stanolind Oil and Gas Company Fellowship in Petroleum Engineering at The University of Texas. Grateful acknowledgment of financial aid and advice is made to the company.

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Silicon, Manganese, Chromium, Iron, and Copper in a Nickel-Base Alloy

An Aliquot Method for Routine Analysis of an Electrical Heat-Resisting Alloy

LOUIS SILVERMAN, United States Navy Chemistry Laboratory, Munhall, Penna.

NEWER techniques developed for the analysis of chromium steels (*5*) may be applied to certain nickel-base alloys. This paper outlines an aliquot method adapted to the rapid routine determination of the important elements in electrical heat-resisting alloys.

As with high chromium-nickel steels, the alloy is dissolved in acid and the silica dehydrated in boiling perchloric acid. From the silica-free filtrate aliquots are taken for determination of the elements present. Similarly, the manganese, chromium, and nickel are determined in sequence, in a single aliquot. In a second aliquot phosphorus can be determined, and in another aliquot copper and iron can be separated and determined. This last separation is the point of difference between the alloy steel and the nickel-base alloy, in that the iron determination is not required in the former.

The reagents and apparatus required are the usual equipment found in ferrous and nonferrous laboratories.

Reagents

Copper powder, 325-mesh (*2*).

Arsenite-Nitrite (*3*). Prepare 0.1 *N* arsenite by dissolving 4.95 grams of arsenious oxide in about 20 cc. of 20 per cent sodium hydroxide solution. Using phenolphthalein as indicator, decolorize with dilute sulfuric acid, add 500 cc. of water and 20 to 25 grams of sodium bicarbonate, and decolorize with acid if necessary. Dissolve 7.0 grams of sodium nitrite in 200 cc. of water. Mix arsenite and nitrite, and dilute to 2 liters. This is the stock 0.1 *N* solution. For use, dilute to 0.02 *N*, standardize on a steel of about 1 per cent manganese, to which 20 per cent chromium has been added, and check with Bureau of Standards sample No. 101a or No. 121.

Ferrous Ammonium Sulfate. Dissolve about 46.0 grams (0.117 *N*) of ferrous ammonium sulfate in 500 cc. of water containing about 5 cc. of sulfuric acid. Dilute to 1 liter.

Citric Acid Solution. To 380 grams of ammonium sulfate add 270 cc. of concentrated ammonium hydroxide, 1430 cc. of water, 5 grams of ammonium chloride, and 240 grams of citric acid. Use 35 cc. on a 0.2-gram aliquot.

Standard Silver Nitrate Solution. 2.885 grams of silver nitrate per liter. Use 5 ± 0.1 cc.

Cyanide Solution. Dissolve about 7.5 grams of sodium cyanide and 7 grams of sodium hydroxide in 1000 cc. of water. Dilute to analyst's convenience.

Potassium Iodide. 200 grams per 1000 cc. of water. Use 2 cc.

Silver–Sulfuric Acid–Phosphoric Acid Solution. Mix 500 cc. of water, 1000 cc. of sulfuric acid, 5.77 grams of silver nitrate, and 120 cc. of phosphoric acid. Dilute to 2 liters. Use 5 cc.

Titanium Standard. Dissolve 1 gram of Bureau of Standards No. 121 (titanium 0.394 per cent) in 50 cc. of (1 + 1) hydrochloric acid, cool to 10° C., and dilute to 200 cc. with water. Add 20 cc. of 6 per cent aqueous cupferron solution. Continue with the separation and solution of the titanium, as directed below. Dilute to 200 cc. with 5 per cent sulfuric acid. Preserve as a permanent standard. Add peroxide whenever color fades.

Procedure

Solution of Alloy. The nickel alloy is decomposed by direct attack with hot 70 per cent perchloric acid (*1*). Use 20 cc. for 2.500 grams in a 300-cc. beaker.

If the drillings are contaminated by oil or contain high carbon, or if phosphorus is required, treat a 2.500-gram sample in a 300-cc. tall-form beaker with 25 cc. of mixed acids (300 cc. of hydro-

TABLE I. ANALYSIS OF A HEAT-RESISTING NICKEL-BASE ALLOY

Carbon	Silicon	Manganese	Chromium	Copper	Iron
%	%	%	%	%	%
0.04	0.16	0.17, 0.18	12.2	0.34, 0.34	8.35
	0.16	0.17	12.25	0.31	8.15
0.06	0.17	0.23, 0.23	13.1, 13.1	0.32, 0.32	8.40, 8.44
	0.18		13.0	0.32	8.40
0.09	0.12	0.13	13.4	0.27	7.24
	0.12	0.15	13.3	0.28	7.25
0.08	0.12	0.12, 0.12	13.5, 13.5	0.12	7.35
	0.12			0.13	7.40
0.04	0.15	0.08, 0.08	13.4, 13.4	0.24, 0.26	7.13
	0.17			0.25	7.24
0.05	0.18	0.16	12.8	0.05, 0.05	6.71
0.09	0.27	0.14	13.3	0.28, 0.27	6.70, 6.71
0.07	0.18	0.14	13.9	0.23	6.75
				0.25	6.71
0.04	0.24	0.11	13.4	0.60, 0.59	7.43, 7.45
0.07	0.30	0.19	16.7	0.14	7.51
			16.8		

chloric acid, 100 cc. of nitric acid, and 400 cc. of water). Cover, and heat at 80° to 90° C. to complete solution. Add 5 cc. of nitric acid (1.4 specific gravity) and 20 cc. of 70 per cent C. P. perchloric acid.

Heat at the boiling point of perchloric acid (204° C.) until the green spot under the cover glass is changed to yellow. Cool, add about 100 cc. of water and 10 cc. of (1 + 1) sulfuric acid, shake to dissolve soluble matter, and heat to boiling. Cool.

SILICON. Filter through a No. 40 Whatman paper into a 250-cc. volumetric flask. Wash 10 times with a hot (1 + 99) sulfuric acid solution, then with hot water. (Change the receiver, and wash with (1 + 4) hydrochloric acid if the precipitate is green.) Burn the paper and weigh as silica. For a 2.500-gram sample, the factor is 0.1864.

Cool the filtrate to room temperature, dilute to the mark, and shake well.

MANGANESE, CHROMIUM, AND NICKEL (*5*). Transfer 20 cc. (0.20-gram aliquot) to a 400-cc. low-form beaker. Add 5 cc. of the silver–sulfuric acid–phosphoric acid solution and 75 cc. of hot water. Heat to about 80° C., add 20 cc. of 6 per cent ammonium persulfate solution, and maintain at this temperature until persulfate bubbles cease to form. Cool to 10° to 15° C. Titrate with the arsenite-nitrite reagent (approximately 0.02 *N*).

Dilute to 200 cc. with cold water, and titrate chromium potentiometrically with standard ferrous ammonium sulfate (approximately 0.117 *N*).

For nickel, add 35 cc. of the citric acid solution; add ammonium hydroxide (0.9 specific gravity) till blue; make acid to litmus with (1 + 1) sulfuric acid; dissolve the silver chloride precipitate with ammonium hydroxide, add 2 cc. of potassium iodide solution, and titrate with cyanide solution.

For manganese and chromium standards, a 0.2-gram aliquot of Bureau of Standards No. 101a (0.47 per cent manganese, 18.33 per cent chromium, 8.99 per cent nickel) is used; but a larger portion of a strong nickel sulfate solution, gravimetrically standardized, is required for nickel.

COPPER (*6*). Transfer 100 cc. (1.000-gram aliquot) to a tall-form 200-cc. beaker, add 4 cc. of (1 + 1) sulfuric acid, and electrolyze at 4 volts and 0.6 to 0.8 ampere, without agitation. About 90 minutes is sufficient for an electrolyte of 14 per cent chromium, 6 per cent iron, and 0.6 per cent copper. Without any unnecessary agitation, remove the electrolyte. Wash the electrode with water, dry, and weigh for copper.

IRON (*2*). To the electrolyte add about 0.4 to 0.5 gram of powdered copper (325-mesh), sufficient to remain momentarily suspended when stirred. Three 15-second agitations are necessary. Filter through paper (Whatman No. 40, or similar roughened paper) that will not permit fine copper to "creep", and wash with water. To the filtrate add 5 cc. of (1 + 1) sulfuric acid and 5 cc. of 85 per cent phosphoric acid. Add ice, and titrate with 0.1 *N* permanganate, potentiometrically or visually. The first darkening of color corresponds to the potentiometric end point, but for routine visual titration it is best to proceed 0.1 cc. further and subtract the blank.

TITANIUM (*4*). Transfer 100 cc. (1.000-gram aliquot) to a 400-cc. beaker. Add 20 cc. of (1 + 1) sulfuric acid and about 10 cc. of sulfurous acid (or sulfuric acid plus sodium sulfite) to reduce sexivalent chromium, cool to 10° to 15° C., and dilute to 200 cc. Add 20 cc. of 6 per cent cupferron solution. Let stand in the ice box, stirring occasionally, till the precipitate settles. Filter on No. 40 Whatman paper, and wash with cold (1 + 99) hydrochloric or sulfuric acid. Return the paper to the beaker, add 25 cc. of nitric acid (1.4 specific gravity), mix, then heat to destroy organic matter. Add 15 cc. of 70 per cent perchloric acid, and fume. Cool, dilute, and add 10 cc. of (1 + 1) sulfuric acid and 5 cc. of 3 per cent hydrogen peroxide. Compare with standard titanium solution, or with Bureau of Standards No. 121 (0.4 per cent titanium) which has been prepared as in (*4*).

PHOSPHORUS (*5*). If phosphorus is to be determined instead of titanium, transfer 100 cc. (1.000-gram aliquot) to a 300-cc. beaker. Add 5 cc. or more of ammonium hydroxide (specific gravity 0.9) till a precipitate forms, dissolve with nitric acid (specific gravity 1.4), and add 8 cc. excess. Warm to 40° C., and precipitate with ammonium molybdate as usual.

Results

In Table I, accumulated data are given. Two lines of figures indicate that aliquots were obtained from separately weighed samples.

Copper was determined either on a Sloman analyzer, or on an electrolytic board of stationary electrodes. Duplicates of the iron values were obtained, in some cases, from different standard permanganate solutions, accounting for the odd figures.

Titanium and phosphorus averaged 0.2 and 0.008 per cent, respectively.

Discussion

Dissolution of the nickel-base alloy directly in 70 per cent perchloric acid is much more rapid than by preliminary attack with mixed acids. Only in the case of the high-silicon, high-chromium alloys is the direct attack by perchloric acid likely to fail, since these two elements often prevent complete disintegration of the alloy. Loss of phosphorus is not appreciable for the usual amounts present. Too high a temperature will cause volatilization of nickel from fuming perchloric acid.

The silica residues have been found to retain about 0.02 per cent chromium, but no nickel, iron, or manganese.

Manganese and chromium are determined (*5*) as in steel, but the acidity of the nickel solution must be carefully adjusted, as indicated in the procedure. The nickel result is increased by 0.1 per cent for each 0.3 per cent of copper present. Because of the expected accuracy of the nickel titration, the copper error can ordinarily be disregarded. If, however, copper is present in large amounts (1.0 per cent), another procedure is suggested (*6*).

The unusually long time (90 minutes) required to deposit about 0.003 gram of copper is necessitated by the preliminary reduction of sexivalent chromium and trivalent iron. The platings are firm and adherent, and have the same color as copper depositions from sulfuric acid alone. Phosphoric acid is not required.

Since the reduction of iron is not completed during the electrodeposition of copper (*6*) the method of Percival (*2*) is used; and since beakers are used instead of stoppered flasks, more powdered copper is required (0.4 gram), and the stirring must be vigorous enough to keep the reductant momentarily suspended in the solution. Inadequate agitation is the cause of poor results. After reduction, the copper is filtered off; and the paper selected must not be too smooth, lest some powdered copper creep and be washed into the filtrate. Phosphoric acid does not prevent complete reduction of the iron by copper.

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A Graphic Method of Studying the Separation of Mixtures by Immiscible Solvents

LILA F. KNUDSEN AND DONALD C. GROVE
Food and Drug Administration, Federal Security Agency, Washington, D. C.

A graphical procedure is described by which it is possible to predict the ratio of the volumes of the solvents and the number of funnels and separations required to give the best separation of the components of a mixture by the use of immiscible solvents.

THE separation of mixtures by means of immiscible solvents is customarily based on the insolubility of one of the components in one of the solvents. For some mixtures, however, it is not possible to find a pair of solvents which will fulfill this condition. If the distribution coefficients of the components of such a mixture between two solvents differ sufficiently, a separation may be made by passing a solution of the mixture in one solvent through a series of separatory funnels containing the other solvent and repeatedly washing the solution remaining in the funnels with portions of the first solvent. Calculating the proper volume ratio of the solvents, and the number of funnels and washings to give a satisfactorily quantitative separation, is so laborious as to be almost prohibitive. The same results may be obtained rather quickly by a graphical procedure.

The distribution of any solute between two immiscible solvents, where the molecular weight of the solute is the same in both solvents, is expressed by the formula:

$$\frac{x}{1-x} = k\frac{u}{v} \qquad (1)$$

where, considering the amount of solute as unity:

x = fraction of solute dissolved in solvent 1
$1-x$ = fraction of solute dissolved in solvent 2
u = volume of solvent 1
v = volume of solvent 2
k = distribution coefficient

Solving Equation 1 for x,

$$x = \frac{k\frac{u}{v}}{1 + k\frac{u}{v}} \qquad (2)$$

Thus, the fraction present in solvent 1 may be calculated for any ratio of volumes of solvents.

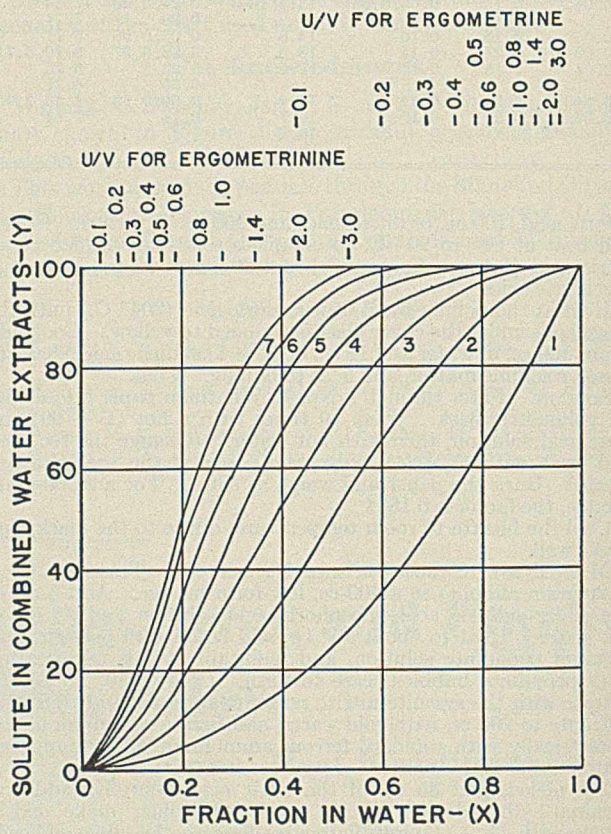

FIGURE 1. SEPARATION OF ERGOMETRINE AND ERGOMETRININE
Using two separatory funnels and one to seven separations

The specific problem used in the development of this method was the separation of the stereoisomeric ergot alkaloids, ergometrine and ergometrinine, wherein it was desired to obtain the ergometrine as free as possible from its stereoisomer. This was accomplished by their distribution between water and ether, and is here used as an example of the general application of the method.

For the purposes of this presentation, the term "separation" indicates the passing of a given volume of one solvent

TABLE I. DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS

Separation	First Funnel: Total solute	First Funnel: Fraction in water	First Funnel: Fraction in ether	Second Funnel: Total solute	Second Funnel: Fraction in water	Second Funnel: Fraction in ether	rth Funnel: Total solute	rth Funnel: Fraction in water	rth Funnel: Fraction in ether
1st	1	x	$1-x$	x	x^2	$x(1-x)$	x^{r-1}	x^r	$x^{r-1}(1-x)$
2nd	$1-x$	$x(1-x)$	$(1-x)^2$	$2x(1-x)$	$2x^2(1-x)$	$2x(1-x)^2$	$rx^{r-1}(1-x)$	$rx^r(1-x)$	$rx^{r-1}(1-x)^2$
3rd	$(1-x)^2$	$x(1-x)^2$	$(1-x)^3$	$3x(1-x)^2$	$3x^2(1-x)^2$	$3x(1-x)^3$	$ax^{r-1}(1-x)^2$	$ax^r(1-x)^2$	$ax^{r-1}(1-x)^3$
4th	$(1-x)^3$	$x(1-x)^3$	$(1-x)^4$	$4x(1-x)^3$	$4x^2(1-x)^3$	$4x(1-x)^4$	$bx^{r-1}(1-x)^3$	$bx^r(1-x)^3$	$bx^{r-1}(1-x)^4$
5th	$(1-x)^4$	$x(1-x)^4$	$(1-x)^5$	$5x(1-x)^4$	$5x^2(1-x)^4$	$5x(1-x)^5$	$cx^{r-1}(1-x)^4$	$cx^r(1-x)^4$	$cx^{r-1}(1-x)^5$
nth	$(1-x)^{n-1}$	$x(1-x)^{n-1}$	$(1-x)^n$	$nx(1-x)^{n-1}$	$nx^2(1-x)^{n-1}$	$nx(1-x)^n$	$dx^{r-1}(1-x)^{n-1}$	$dx^r(1-x)^{n-1}$	$dx^{r-1}(1-x)^n$

$$a = \frac{r(r+1)}{2!} \qquad c = \frac{r(r+1)(r+2)(r+3)}{4!}$$

$$b = \frac{r(r+1)(r+2)}{3!} \qquad d = \frac{n(n+1)(n+2)\ldots(n+r-2)}{(r-1)!}$$

2!, 3!, etc. = factorial 2, factorial 3, etc.

successively through each of the entire series of funnels containing the other solvent. Let us assume a series of funnels containing equal volumes of ether through which a water solution of the alkaloids is shaken successively. This is followed by successive portions of water, each equal to the volume of water used as the original solvent for the alkaloids. The distribution of the alkaloids in the various layers in the separatory funnels is shown in Table I.

From the data in this table, a series of curves are prepared as illustrated for two funnels (Figure 1) and four funnels (Figure 2). Since we are concerned only with the total amount of solute in the combined water extracts, which is expressed as per cent of the original amount of solute and called "y", the curve for one separation, Figure 1, represents a graph of the values of $y = 100\ x^2$ (see column 6, Table I, first separation), that for two separations represents the values of $y = 100\ [x^2 + 2x^2(1-x)]$ (sum of first and second separations, column 6, Table I), that for three separations represents the values of $y = 100\ [x^2 + 2x^2(1-x) + 3x^2(1-x)^2]$, etc. Only two sets of curves are illustrated, but similar graphs may be prepared for any number of funnels and separations required. Since these values are independent of the nature of the solute and solvents, they can be applied to any combination.

For the application of these curves to any specific problem, a scale, as shown above the curves in Figures 1 and 2, must be constructed for the two substances to be separated. This scale consists of the values of x for various ratios of the solvents as calculated from Equation 2. For example, the distribution coefficients, k, for ergometrine and ergometrinine between water and ether were determined experimentally to be 7.55 and 0.39, respectively. By substituting these values of k independently in Equation 2, together with a volume ratio (u/v = water to ether) of 0.3, the values of x for ergometrine and ergometrinine are calculated to be 0.694 and 0.105, respectively. The values of x thus obtained are marked off on the x scale above the graph, each mark being identified by its appropriate u/v ratio as indicated by the figures above the scale.

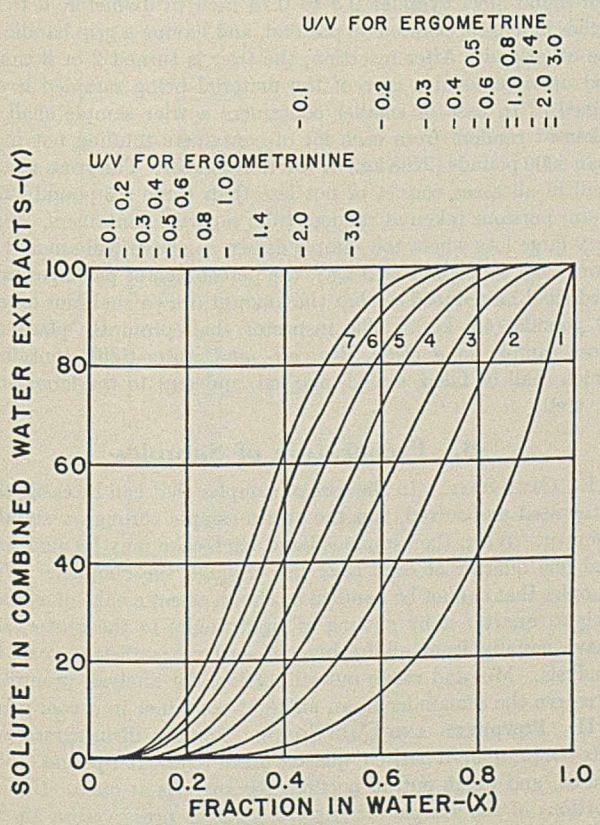

FIGURE 2. SEPARATION OF ERGOMETRINE AND ERGOMETRININE

Using four separatory funnels and one to seven separations

TABLE II. SEPARATION OF ERGOMETRINE AND ERGOMETRININE

u/v	1 Separation		3 Separations		5 Separations		7 Separations	
	A %	B %	A %	B %	A %	B %	A %	B %
				Using Two Funnels				
0.1	18	0	57	1	82	3	93	6
0.4	56	2	94	9	99	19	100	28
1.0	78	8	99	32	100	55	100	72
3.0	93	28	99	74	100	93	100	100
				Using Four Funnels				
0.1	3	0	22	0	48	0	70	0
0.4	33	0	83	0	97	2	100	5
1.0	60	0	97	5	100	17	100	30
3.0	84	9	100	43	100	72	100	89

The intersection of a vertical line projected from these points and each of the curves gives the per cent of the original amount of these alkaloids which has been carried into the combined water extracts for the number of separations indicated. Table II gives a tabulation of some of these values obtained from Figures 1 and 2, where A and B represent the amount of ergometrine and ergometrinine, respectively, in the water extracts from two and four funnels with varying numbers of separations. It is obvious that an optimum separation calls for the highest possible recovery of A and at the same time the lowest possible contamination with B.

An inspection of Table II shows that no separation of these alkaloids approaching quantitative proportions can be obtained with only two funnels. In Table II, however, at a u/v ratio of 0.4, five and seven separations, using four funnels, give practically complete recoveries of ergometrine with only slight amounts of ergometrinine. A more detailed survey of the points in this region on Figure 2 reveals that, at a u/v ratio of 0.3, seven separations give a 99 per cent recovery of ergometrine and 2 per cent of ergometrinine.

It is possible that the use of more funnels would give an even more quantitative separation. The accuracy of the separation to be desired will be dictated by the nature of the problem, and with a set of curves, as illustrated here, it is possible, knowing only the distribution coefficients of the components of a mixture, to determine the optimum ratio of solvents and the least number of funnels and separations required to give the desired results.

In practice, these curves, which are applicable to any situation and need be prepared only once, should be plotted on a fairly large scale to facilitate their use. The single x scale prepared for the specific mixture, if plotted on the same scale on a strip of graph paper, may be applied to all the series of graphs.

To assure sufficient shaking time for the various extractions, it is usually well to determine experimentally the time required for the distribution of the solutes between the solvents to reach equilibrium.

Acknowledgment

The authors are indebted to F. H. Wiley for continued encouragement and assistance and to P. A. Clifford also for helpful suggestions and criticisms.

Standard Methods for the Sampling and Analysis of Commercial Soaps and Soap Products, Revised

R. E. DIVINE, J. E. DOHERTY, C. P. LONG, E. B. MILLARD, M. L. SHEELY, H. P. TREVITHICK, AND F. W. SMITHER, Chairman

THE Committee on Soap and Soap Products of the AMERICAN CHEMICAL SOCIETY has given careful consideration to comments on the methods published in 1937 (*8*), and to cooperative studies carried out by the Soap Analysis Committees of the American Oil Chemists' Society (*18*) and the American Society for Testing Materials (*2*), with the result that the following report was unanimously adopted March 11, 1941.

A. Sampling

The seller shall have the option of being represented at the time of sampling, and when he so requests shall be furnished with a duplicate sample.

I. CAKE SOAPS, FLAKE AND POWDERED SOAP PRODUCTS WHEN PACKED IN CANS OR CARTONS. One cake (can or carton) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds (22.7 kg.). In the case of smaller containers, a cake (can or carton) shall be taken at random from each lot of containers totaling not more than 5000 pounds (2268 kg.) or fraction thereof. The gross sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 pounds (9.1 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds (9.1 kg.).

Wrap the individual cakes (cans or cartons) tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or carton), record its weight and the date of weighing on the wrapper, place the wrapped cakes (cans or cartons) in an air-tight container, which should be nearly filled, sealed, marked, and sent to the laboratory for test. Samples should be kept cool until tested.

II. FLAKE AND POWDERED SOAP PRODUCTS WHEN IN BULK. A grab sample of not less than 0.5 pound (227 grams) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 100 pounds (45.4 kg.). In case of smaller containers, a grab sample of not less than 0.5 pound (227 grams) shall be taken at random from each lot of containers totaling not more than 10,000 pounds (4536 kg.) or fraction thereof. The gross sample shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 pounds (9.1 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds (9.1 kg.). The inspector shall rapidly mix the gross sample and place it in an air-tight container, which shall be filled, sealed, marked, accurately weighed, its weight and date of weighing recorded on the package, and sent to the laboratory for test. Samples shall be kept cool until tested.

III. LIQUID SOAP. A sample of not less than 0.5 pint (236.6 ml.) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 10 gallons (37.9 liters) each. In case of smaller containers, a sample of not less than 0.5 pint (236.6 ml.) shall be taken at random from each lot of containers totaling not more than 1000 gallons (3785.4 liters). The gross sample shall in all cases consist of not less than three portions of 0.5 pint (236.6 ml.) each taken at random from separate containers. Before drawing the sample from the container selected, the contents of the container shall be thoroughly agitated. The inspector shall thoroughly mix the gross sample drawn, and place it in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps, then sealed, marked, and sent to the laboratory for test.

IV. PASTE SOAP PRODUCTS. (1) *When packed in cans or cartons of 5 pounds (2.27 kg.) or less.* One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds (22.7 kg.). In case of smaller containers, a can or carton shall be taken at random from each lot of containers, totaling not more than 5000 pounds (2268 kg.) or fraction thereof. The gross sample shall in all cases consist of not less than 3 cans or cartons taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 pounds (9.1 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds (9.1 kg.). Wrap, seal, mark, and send to the laboratory for test.

(2) *When packed in bulk.* Take a "trier" sample at random of not less than 0.5 pound (227 grams) from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds (22.7 kg.). (A trier sample is obtained by inserting a trier into the material. A trier is a half-round steel cylinder 0.5 to 0.75 inch in diameter, 6 to 36 inches in length, pointed on one end, and having a grip handle on the other end. After insertion, the trier is turned 2 or 3 times, and upon removal a core of the material being sampled is obtained.) In case of smaller containers a trier sample shall be taken at random from each lot of containers totaling not more than 5000 pounds (2268 kg.) or fraction thereof. The gross sample shall in all cases consist of not less than three 0.5-pound (227-gram) portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 pounds (4.5 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 pounds (4.5 kg.). The inspector shall promptly place the gross sample in a clean, dry, air- and water-tight container, which shall be filled, sealed, marked, and sent to the laboratory for test.

B. Preparation of Samples

I. CAKE SOAP. In the case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one quarter of each cake run through the chopper. With samples that cannot be handled as above, select a cake of average weight, quarter it by cutting at right angles in the center, and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an air-tight container in a cool place.

II. POWDERED AND CHIP SOAPS. Rapidly disintegrate and mix the sample; if desired, quarter down to about 1 pound (453.6 grams) and weigh out all portions for analysis at once. Unused portions of the sample for analysis shall be preserved in an air-tight container in a cool place.

III. LIQUID SOAP. No preparation of the sample, other than thorough mixing, is necessary unless it is received during very

cold weather, when it should be allowed to stand at least 1 hour after it has warmed up to room temperature (20° to 30° C.) before it is tested, particularly for its lathering qualities.

IV. Paste Soap Products. Mix thoroughly by kneading and quarter down to about 1 pound (453.6 grams). Weigh out all portions for analysis promptly and preserve remainder in an air-tight container in a cool place.

C. Methods of Analysis

When a determination shows nonconformity with the specifications, a duplicate shall be run.

I. Moisture. The oven method given here is generally applicable to all soaps. Experience has shown, however, that certain exceptions to this method must be made if accurate results are desired. These exceptions include: (*a*) For soaps containing appreciable amounts of sodium silicate the distillation method is preferred. (*b*) Soaps of linseed and other oxidizing oils absorb oxygen and if the oven method is used may gain in weight near the end of the test. Therefore, either an inert atmosphere or vacuum oven should be used. The distillation method is also applicable to these types of soaps. (*c*) Soaps containing appreciable amounts of glycerol, such as cold made and semiboiled (including paste soaps), usually give higher results by the oven method. The distillation method is preferred for most accurate results on these types of soaps.

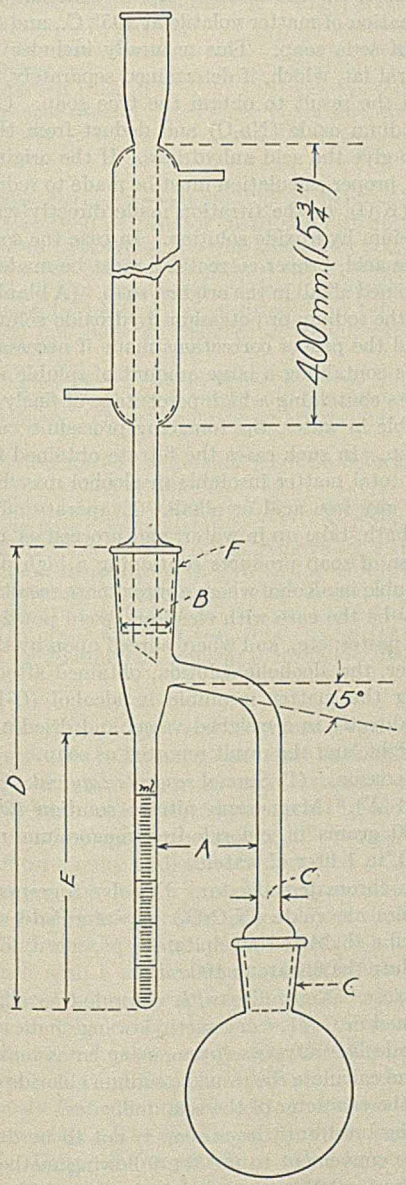

Figure 1. Assembly of Distillation Apparatus

A. 45 to 55 mm.
B. 22 to 24 mm., inside diameter
C. 9 to 11 mm., inside diameter
D. 235 to 240 mm.
E. 146 to 156 mm.
F, G. Interchangeable joints, standard taper 24/40

(1) *Matter volatile at 105° C. (oven method)*. Procedure. Weigh 5 grams (±0.01 gram) of the sample in a porcelain or glass dish about 6 to 8 cm. in diameter and about 2 to 4 cm. deep, and dry to constant weight in an air oven at a temperature of 105° ± 2° C. Constant weight is attained when successive heating for 1-hour periods shows a loss (or gain) of not more than 0.1 per cent.

(2) *Distillation method (9)*. Apparatus. The apparatus required consists of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask. A suitable assembly of the apparatus is illustrated in Figure 1.

Flask. A 500-ml. flask of either the short-necked, round-bottom type or the Erlenmeyer type shall be used.

Heat source. The source of heat may be either an oil bath (stearic acid, paraffin, etc.) or an electric heater provided with a sliding rheostat or other means of heat control.

Condenser. A water-cooled glass reflux condenser (Figure 1), having a jacket approximately 400 mm. (15.75 inches) in length with an inner tube 9.5 to 12.7 mm. (0.375 to 0.5 inch) in outside diameter, shall be used. The end of the condenser to be inserted in the trap may be ground off at an angle of 30 degrees from the vertical axis of the condenser. When inserted into the trap, the tip of the condenser shall be about 7 mm. (0.25 inch) above the surface of the liquid in the trap after the distillation conditions have been established. Figure 1 shows a conventional sealed-in type of condenser, but any other condenser fulfilling the detail requirements above may be used.

Trap. A trap made of well-annealed glass constructed in accordance with Figure 1 and graduated as shown to contain 5 ml. at 20° C. shall be used. It shall be subdivided into 0.1-ml. divisions, with each 1-ml. line numbered (5 ml. at top). The error in any indicated capacity may not be greater than 0.05 ml.

Special reagent required. Xylene or toluene. For soaps containing 1 per cent or more of glycerol, toluene shall be used instead of xylene. Saturate the solvent with water by shaking it with a small quantity of water and distill. Use the distillate for the determination.

Procedure. For soaps containing from 5 to 25 per cent of moisture and volatile matter use a 20-gram (±0.04 gram) sample. For soaps containing more than 25 per cent of moisture and volatile matter use a 10-gram (±0.02 gram) sample. Carefully transfer the weighed sample to the 500-ml. flask. Add approximately 10 grams of anhydrous fused sodium acetate to prevent violent frothing, and then follow with 100 ml. of solvent which has been saturated with water. Attach the flask to the trap which is connected to the condenser. Prior to starting the determination, fill the receiver with saturated solvent by pouring it in through the reflux condenser.

So that the refluxing will be under better control, wrap the flask and the tube leading to the receiver with asbestos cloth. Heat the oil bath with a gas burner or other source of heat, or apply heat directly to the flask with an electric heater and distill slowly. The rate at the start should be approximately 100 drops per minute. When the greater part of the water has apparently distilled over, increase the distillation rate to 200 drops per minute until no more water is collected. Purge the reflux condenser during the distillation with 5-ml. portions of solvent to wash down any moisture adhering to the walls of the condenser. The

water in the receiver may be made to separate from the solvent by using a spiral copper wire. Move the wire up and down in the condenser occasionally, thus causing the water to settle at the bottom of the receiver. Reflux for at least 2 hours, and shut off the heat at the end of this period. Adjust the temperature of the distillate to 20° C. Read the volume of water and calculate the percentage of moisture in the soap, as follows:

$$\text{Moisture, per cent} = \frac{V \times 0.998}{S} \times 100$$

where V = volume of water in milliliters at 20° C. and S = weight of sample in grams.

II. Total Matter Insoluble in Alcohol. *Procedure.* Digest a 2- to 10-gram (±0.01 gram) sample with 200 ml. of freshly boiled ethyl alcohol (94 per cent or higher and neutral to phenolphthalein) in a covered vessel on a steam bath until the soap is dissolved. (Formula 3-A or 30 specially denatured alcohol may be used instead of straight ethyl alcohol.) Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution from carbon dioxide and other acid fumes during the operation by covering with a watch glass. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap and reserve the filtrate and washings. Dry the filter paper or crucible with residue at 100° to 105° C. for 3 hours, cool, and weigh the total matter insoluble in alcohol. (The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates, and sulfates, as well as starch, and may be used for the approximate determination of these constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used. For determination of carbonates see C-XVIII; phosphates, C-XIX; sulfates, C-XX; silicates, C-XVII; borax, C-XVI; starch, C-XXI, C.)

III. Free Alkali or Free Acid. *Procedure.* Heat the reserved filtrate from the determination of total matter insoluble in alcohol (C-II) to incipient boiling, add 0.5 ml. of a 1 per cent solution of phenolphthalein, titrate with standard acid or alkali solution, and calculate to sodium hydroxide (or potassium hydroxide) if alkaline, or to oleic acid if acid.

Note. In the analysis of soaps known to contain little or no alkaline salts, it is unnecessary to filter the hot alcoholic soap solution as described in C-II. However, the filtration should be carried out in all cases where alkaline salts such as silicates, phosphates, borates, and similar salts are present, since these are known to affect the free alkali determination. The presence of carbonates up to 0.5 per cent as Na_2CO_3 does not appreciably affect this determination and filtration may be omitted if the carbonate on a separate sample is not in excess of this amount.

IV. Matter Insoluble in Water. *Procedure.* Proceed as in the determination of matter insoluble in alcohol (starting with a fresh sample of soap and omitting the drying and weighing of matter insoluble in alcohol, C-II). After filtering and thoroughly washing the residue, change the receivers, extract the residue with water at 60° C., and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Reserve the water solution. Dry the filter and residue at 100° to 105° C. for 3 hours, cool, and weigh the matter insoluble in water. The nature of this matter may be determined by further examination.

V. Total Alkalinity of Matter Insoluble in Alcohol (Alkaline Salts). *Procedure.* Titrate the water solution obtained in C-IV with standard acid, using methyl orange as indicator. Calculate the alkalinity to sodium oxide (Na_2O), and, if desired, to any other basis agreed upon by the purchaser and the seller.

VI. Combined Alkali. Total Anhydrous Soap. *Procedure.* Dissolve 5 to 10 grams (±0.01 gram) of the sample, depending upon the anhydrous soap content, in 100 ml. of water in a 250-ml. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid (1 to 1) in slight excess, insert a small funnel in the neck of the flask, and heat the flask at a temperature not exceeding 60° C. until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel, and shake the acid aqueous liquid with two 20-ml. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10-ml. portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing and shake with 20 ml. of ether. Wash this ether until the wash water is neutral to methyl orange. Reserve the acid water for determination of chloride (C-VII).

Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 ml. of neutral alcohol free from carbon dioxide, add phenolphthalein, and titrate to exact neutrality with standard 0.5 N sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105° C., and calculate the percentage of soda soap. This naturally includes any mineral oil and neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide (Na_2O) and deduct from the weight of soda soap to give the acid anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide (K_2O), or the titration made directly with standard 0.5 N potassium hydroxide solution. In case the soap shows an excess of free acid, proper corrections must be made in calculating the combined alkali in the original soap. (A blank test should be made on the sodium or potassium hydroxide solution for neutral salts and the proper corrections made if necessary.) In the case of soaps containing a large amount of soluble silicates, and soap products containing a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol may be used after neutralizing any free acid or alkali. Evaporate off the alcohol on a steam bath, take up in water, and proceed as above.

In the case of soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as may be the case with cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the purchaser and the seller, the alcoholic solution, obtained after filtering off and washing the matter insoluble in alcohol (C-II), may be evaporated directly in a weighed vessel and dried at 105° C. to constant weight, and the result reported as soap.

VII. Chloride. (1) *Special reagents required.* Silver nitrate solution (0.1 N). Magnesium nitrate solution (20 per cent). Dissolve 200 grams of chloride-free magnesium nitrate, $Mg(NO_3)_2.6H_2O$, in 1 liter of water.

Potassium chromate indicator. Dissolve 5 grams of chloride-free potassium chromate (K_2CrO_4) in water, add silver nitrate solution until a slight red precipitate is produced, filter the solution, and dilute the filtrate to 100 ml.

(2) *Procedure.* Neutralize with chloride-free alkali the acid water obtained in C-VI, using methyl orange indicator. Titrate with standard silver nitrate solution, using potassium chromate as indicator, and calculate the result to sodium chloride or potassium chloride as the character of the soap indicates.

In case the total anhydrous soap is not to be determined, it will be more convenient to use the following method (*6*): Dissolve 5 grams (±0.01 gram) of the sample in 300 ml. of water, boiling if necessary to effect solution. Add an excess of neutral chloride-free magnesium nitrate solution [about 25 ml. of 20 per cent $Mg(NO_3)_2.6H_2O$ solution]. Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator. One milliliter of 0.1 N silver nitrate solution is equivalent to 0.00585 gram of sodium chloride (NaCl).

VIII. Unsaponified Plus Unsaponifiable Matter. (1) *Apparatus.* Extraction cylinder. The extraction cylinder shall be a 250-ml. graduated, glass-stoppered cylinder about 39 mm. (1.5 inch) in diameter and about 35.5 cm. (14 inches) in length.

(2) *Special reagents required.* Ethyl alcohol, 50 per cent, 95 per cent, and 10 per cent. Sodium hydroxide solution 0.1 *N* and 0.04 *N*.

Petroleum ether. The solvent used shall be of the pentane type, containing a minimum amount of isopentane, isohexane, and hexane, and conforming to the following requirements:

Distillation test (Note *a*)	
Initial boiling point	35° to 38° C.
Dry flask end point	52° to 60° C.
Distilling under 54° C., minimum	95 per cent
Distilling under 40° C., maximum	60 per cent
Specific gravity at 15.5°/15.5° C. (60°/60° F.)	0.630 to 0.660
Color	Water white
Doctor test	Sweet
Evaporation residue, 100 ml., maximum	0.0011 gram
Copper-strip corrosion test (Note *b*)	Noncorrosive
Unsaturated compounds (Note *c*)	Trace only permitted
Residue in distilling flask	Neutral to methyl orange
Blotter-strip odor test (Note *d*)	Odorless within 12 minutes
Aromatic compounds (Note *e*)	No nitrobenzene odor
Saponification value	Less than 1.0 mg. of KOH per 100 ml.

Note *a*. The distillation test shall be made in accordance with the standard method of test for distillation of natural gasoline of the American Society for Testing Materials (*1*). As a check on the evaporation residue, 250 ml. of the petroleum ether and 0.25 gram of stearin or other hard fat (previously brought to constant weight by heating) when dried as in the actual determination shall not show an increase in weight exceeding 0.003 gram.

Note *b*. The copper-strip corrosion test shall be made by inserting a small polished copper strip into the petroleum ether in the distilling flask. There should be no appreciable darkening of the copper.

Note *c*. Unsaturated compounds shall be determined by the method for determining olefins (*20*, p. 154).

Note *d*. Odor test. Immerse 1 inch of a strip of white, unglazed blotting paper, approximately 1 × 4 × 0.166 inch in size, in the petroleum ether for 30 seconds, remove the strip, and allow it to dry at room temperature in still air for 12 minutes.

Note *e*. Aromatic compounds. Add 5 drops of petroleum ether to 40 drops of sulfuric acid (sp. gr. 1.84) and 10 drops of nitric acid (sp. gr. 1.42) in a test tube, warm for 10 minutes, allow to cool for 30 minutes, transfer to a shallow dish, and dilute with water.

(3) *Procedure* (*21*). (*a*) Weigh 5 grams (±0.2 gram) of the prepared sample into a 250-ml. Erlenmeyer flask or beaker which contains approximately 0.1 gram of bicarbonate of soda, and dissolve in 100 ml. of redistilled 50 per cent ethyl alcohol. Warm and shake to effect solution, keeping the temperature under 60° C., and filter off any undissolved residue on a Gooch crucible with an asbestos pad or in a funnel, using an asbestos pad deposited on a perforated porcelain disk. Wash three times with hot 50 per cent alcohol and then with 5 ml. of hot 95 per cent alcohol. Wash with a small amount of petroleum ether to remove any traces of unsaponified and unsaponifiable matter. Transfer the entire alcohol-water-and-ether filtrate to the extraction cylinder and make up to the 160-ml. mark with redistilled 50 per cent ethyl alcohol. Add 50 ml. of petroleum ether, shake vigorously for 1 minute (Note 1), and allow to settle until both layers are clear. The volume of the upper layer should be about 40 ml. Draw off the petroleum ether layer as closely as possible, by means of a slender glass siphon, into a separatory funnel of 500-ml. capacity.

(*b*) Repeat the extraction at least six times using 50 ml. of petroleum ether each time (Note 2). Wash the combined ether extracts first with a mixture of 15 ml. of 0.1 *N* sodium hydroxide solution and 15 ml. of 95 per cent alcohol, and then three times with 25-ml. portions of 10 per cent alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a beaker and evaporate the petroleum ether on a steam bath by the aid of a current of air.

(*c*) Test the residue for solubility by treating with 50 ml. of petroleum ether at room temperature. Filter, and wash free from the insoluble residue, if any. Evaporate and dry in the same manner on a steam bath, and finally in an air oven at 100° to 101° C. for 30 minutes. Weigh, and return to the oven, reweighing at 15-minute intervals until constant weight is reached. Take up the residue in 50 ml. of warm ethyl alcohol, neutralized to phenolphthalein, titrate to the same color as the original neutral alcohol with 0.04 *N* sodium hydroxide solution, and calculate to oleic acid. Deduct this figure from the gross weight previously found and report as "unsaponified and unsaponifiable matter".

(*d*) Run a blank test on the petroleum ether by evaporating 250 ml. of the ether with about 0.25 gram of stearin or some other hard fat previously brought to constant weight by heating and drying as in the actual determination. The blank must not exceed a few milligrams [see Note *a* under C-VIII (2)] (Note 3).

Note 1. Thorough and vigorous shaking is necessary in order to secure accurate results. The two phases must be brought into the most intimate contact possible; otherwise low and disagreeing results may be obtained.

Note 2. This method will not remove all the unsaponifiable matter in soaps to which lanolin has been added. More extractions are required when substances of this nature are present.

Note 3. Any blank from the petroleum ether must be deducted from the gross weight of the "unsaponified and unsaponifiable" before calculating the percentage of unsaponified and unsaponifiable matter.

IX. Unsaponifiable Matter. (1) *Apparatus.* Extraction cylinder. See cylinder described for the determination of unsaponified plus unsaponifiable matter [C-VIII (1)].

(2) *Special reagents required.* See the special reagents required for the determination of unsaponified plus unsaponifiable matter [C-VIII (2)]. Potassium hydroxide, 50 per cent.

(3) *Procedure.* Weigh 5 grams (±0.2 gram) of the prepared sample into a 200-ml. Erlenmeyer flask. Add 30 ml. of redistilled 95 per cent ethyl alcohol and 5 ml. of aqueous 50 per cent potassium hydroxide, and boil the mixture for 1 hour under a reflux condenser. Transfer to the extraction cylinder and wash to the 40-ml. mark with redistilled 95 per cent ethyl alcohol. Complete the transfer, first with warm and then with cold water, until the total volume is 80 ml. and finally with a small quantity of petroleum ether. Cool the cylinder and contents to room temperature and add 50 ml. of petroleum ether; then proceed with the extraction as outlined in the procedure for "unsaponified plus unsaponifiable matter" [C-VIII (3); also Notes 1 and 2], except that the alkaline wash may be omitted; weigh the residue and correct for fatty acids in the usual manner. Report the result as "unsaponifiable matter".

X. Unsaponified Matter. From the total unsaponified plus unsaponifiable matter determined in C-VIII (3), deduct the unsaponifiable figure obtained in C-IX (3), and report the difference as "unsaponified matter".

XI. Rosin. McNicoll method (*14*). (1) *Apparatus.* The apparatus required consists of a glass flask connected, preferably by a ground-glass joint, to a reflux condenser.

Esterification flask. A 150-ml. flask of either the round-bottom or Erlenmeyer type shall be used.

Reflux condenser. Any suitable water-cooled, glass reflux condenser may be used.

(2) *Special reagents required.* Potassium hydroxide (0.2 *N*). Accurately standardize a 0.2 *N* solution of potassium hydroxide in neutral redistilled alcohol (owing to volatility of alcohol, this solution should be restandardized frequently).

Naphthalene-β-sulfonic acid solution. Dissolve 40 grams of Eastman grade or equivalent reagent in 1 liter of C. P. absolute methyl alcohol.

Phenolphthalein indicator. Prepare a 0.5 per cent solution in neutral redistilled alcohol.

(3) *Procedure.* Preparation of Fatty and Rosin Acids. For the preparation of the sample for this determination, follow the procedure described in C-XII (2).

Esterification and Titration. Weigh about 2 grams (±0.001 gram) of the fatty acids into the esterification flask. Add 25 ml. of naphthalene-β-sulfonic acid solution. Add a few glass beads to ensure smooth boiling, attach the reflux condenser, and boil for 30 minutes; also, run a blank test using 25 ml. of the reagent. At the end of the boiling period cool the contents of the flask, add 0.5 ml. of phenolphthalein indicator, and titrate immediately with 0.2 *N* alcoholic potassium hydroxide.

Calculations. Calculate the results as follows (Note 1):

$$R = \frac{(S - B) \times N \times 0.346 \times 100}{W}$$

$$R_1 = R - 1.0$$

$$R_2 = \frac{R_1 \times F}{100}$$

$$R_s = \frac{R_1 \times 1.064 \times A}{100}$$

where

R = percentage of rosin in fatty acids
R_1 = corrected percentage of rosin in fatty acids (Note 2)
R_2 = percentage of rosin on basis of original sample
R_s = percentage of rosin soda soap on basis of original sample
S = milliliters of potassium hydroxide required to titrate sample
B = milliliters of potassium hydroxide required to titrate blank
N = normality of potassium hydroxide
W = weight of sample
F = percentage of total fatty acids in soap
A = percentage of total anhydrous soap

If true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap.

Note 1. In all cases where the rosin content is found to be less than 5 per cent, the actual presence or absence of rosin should be checked qualitatively by the Liebermann-Storch test, which is as follows:

Transfer 1 to 2 ml. of the sample of fatty acids to a test tube, treat with 5 to 10 ml. of reagent grade acetic anhydride, and warm on a steam bath. After cooling, pour 1 to 2 ml. into a white porcelain dish and allow a drop or two of sulfuric acid (sp. gr. 1.53) to run down the side of the vessel. If rosin is present, a fugitive violet coloration changing to a brownish tinge is immediately produced at the margin of contact of the reagents. The test should be checked with a sample of fatty acids to which a small amount of rosin has been added.

Sulfuric acid of 1.53 specific gravity is prepared by diluting 34.7 ml. of sulfuric acid (sp. gr. 1.84) with 35.7 ml. of distilled water.

Note 2. Cooperative studies have shown that the McNicoll method gives results approximately 1 per cent higher than the amount of rosin present. Consequently, the committee recommends deducting 1 per cent from the percentage of rosin found in the fatty acids.

XII. Preparation of Total Fatty Matter (Fatty and Rosin Acids and Unsaponified Matter). (1) *Special reagent required.* Sulfuric acid (30 per cent by weight of sulfuric acid). Slowly add 650 grams of sulfuric acid (sp. gr. 1.84) to 1400 ml. of distilled water.

(2) *Preparation for rosin and titer tests and iodine and acid numbers.* Dissolve about 50 grams of the sample in 500 ml. of hot water. (If soaps to be tested contain alcohol, the alcohol should be completely removed by evaporation from the soap solution.) Add 100 ml. of 30 per cent sulfuric acid and heat gently until the fatty matter collects in a clear layer.

Siphon off the aqueous acid layer, add 300 ml. of hot water, and boil gently for a few minutes, making sure that all of the fatty acids are melted and clear. High melting point fats are sometimes slow to melt and clear. The fatty acid layer should be carefully inspected while it is quiet, to be sure all has melted. Siphon off the aqueous acid layer.

Wash the acids in this manner three times, or until wash water is neutral to methyl orange. Complete this acidification and washing in a very short period of time, and keep the beaker covered to prevent oxidation of the acids.

After the last washing, remove the last traces of water from the beaker with a pipet, filter the fatty acids through one or two thicknesses of filter paper, and dry at a temperature of 105° C. for 45 to 60 minutes or heat rapidly to 130° C. and allow to cool. Do not hold at 130° C., but if water is present decant the clear fatty acids into another beaker, and again reheat them momentarily to 130° C. These acids may then be used for the titer and rosin determinations.

In preparing the acids for the iodine and acid number determinations, the washed acids should be filtered through one or two thicknesses of filter paper at a temperature not exceeding 15° C. above the titer point of the fatty acids. If the acids are not perfectly clear and dry, refilter.

XIII. Titer Test (Solidification Point of the Fatty Acids (7). (1) *Apparatus.* A 2-liter Griffin low-form beaker.

A wide-mouthed bottle, capacity 450 ml., height 190 mm., inside diameter of neck 38 mm.

Test tubes, length 100 mm., diameter 25 mm., with or without rim. These tubes may have an etched mark extending around the tube at a distance of 57 mm. from the bottom to show the height to which the tube is to be filled.

Laboratory thermometer, 0° to 150° C.

Stirrer, 2 to 3 mm. in outside diameter, one end bent in the form of a loop of 19-mm. diameter. Glass, Nichrome, stainless steel, or Monel wire may be used. The upper end can be formed to accommodate hand stirring or be attached to a mechanical stirrer.

Titer thermometer.

Type, etched stem glass.

Liquid, mercury.

Range and subdivision, −2 to +68° C. in 0.2 degree graduations.

Total length, 385 to 390 mm.

Stem to be constructed of suitable thermometer tubing of either the plain or lens front type.

Diameter, plain front type, 6 to 7 mm.

Thickness of stem, lens front type. The cross section of the stem to be such that it will pass through an 8-mm. ring gage but will not enter a 5-mm. slot gage.

Bulb, Corning normal or equally suitable thermometric glass. Length, 15 to 25 mm. Diameter, 5.5 mm. to not greater than that of stem.

Distance from bottom of bulb to −2° mark, 50 to 60 mm.

Distance to 68° mark from top of thermometer, 20 to 35 mm.

Length of unchanged capillary between the highest graduation and the expansion chamber, 10 mm.

Expansion chamber, to permit heating to at least 85° C. Space above mercury to be evacuated or filled with nitrogen or other suitable gas.

Top finish, glass ring.

Graduations. All lines, figures, and letters to be clear-cut and distinct. Each degree mark to be longer than the remaining lines. Graduations to be numbered at zero and at each multiple of 2 degrees.

Immersion, 45 mm.

Marking. "FAC Titer Test", a serial number, and the manufacturer's name or trade-mark shall be etched on the stem. The words "45-mm. immersion" shall also be etched on the stem, and a line shall be etched around the stem 45 mm. above the bottom of the bulb.

Scale error. The error at any point on the scale shall not exceed 0.2° C.

Standardization. The thermometer shall be standardized at the ice point and at intervals of approximately 20° C., for the condition of 45-mm. immersion, and for an average stem temperature of the emergent mercury column of 25° C.

Case. The thermometer shall be supplied in a suitable case on which shall appear the markings "FAC Titer Test, −2° to 68° C. in 0.2°".

Note. For the purpose of interpreting these specifications, the following definitions shall apply:

The total length is the over-all length of the finished instrument.

The diameter of the plain front round-stem type is that measured with a ring gage or micrometer.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

(2) *Preparation of the fatty acids.* Follow the procedure described in C-XII (2).

(3) *Procedure (solidification of fatty acids).* Fill the water bath so that the level of the water reaches the neck of the wide-mouthed bottle. Adjust the temperature of the water bath. The temperature of the water should be 20° C. for all samples having titers of 35° C. or higher, and 15° to 20° C. below the titer point for all samples with titers below 35° C.

Heat the filtered acids on a hot plate to 130° C. to remove traces of moisture and pour into the test tube. Fill the latter to a height of 57 mm. from the bottom. (The sample should not be held at 130° C. nor should it be reheated to this temperature more than once. If excessive moisture is present, the acids should be decanted after having stood for a few minutes, refiltered and reheated. The acids must be thoroughly dry.) Place the test tube in the assembly as shown in Figure 2. Insert titer thermometer and place in a position equidistant from the sides of the tube, and so that the immersion mark on the thermometer coincides with the upper level of the sample.

Stir with the glass stirring rod in a vertical manner at the rate of 100 complete up and down motions per minute, beginning the stirring at a point 10° C. above the expected titer point. The stirrer should travel through a vertical distance of about 3.8 cm. The stirring may be performed by mechanical means by attaching a small motor with suitable reducing gears to the stirring rod.

Stir at the directed rate and read the thermometer every 15 seconds until the temperature remains constant for 30 seconds or starts to rise. Discontinue stirring immediately and observe the increase in temperature. Report as the titer the highest temperature reached by the thermometer. Duplicate determinations should not differ by more than 0.2° C.

Note. The Committee on Analysis of Commercial Fats and Oils of the American Chemical Society makes the following recommendations:

The committee has approved vertical stirring. The advantages of this over horizontal stirring are that it gives a sharper end point, is more convenient, and can easily be made mechanical by adapting a suitable motor and coupling arrangement to the stirrer.

The committee wishes to emphasize the fact that no changes have been made in the titer determination which will give results different from those that might be obtained with the horizontal stirring method, providing the latter is correctly performed. The committee believes that the proposed modification will make it easier for different chemists to obtain uniform and consistent results.

XIV. Acid Number of Fatty Acids. (1) *Preparation of fatty acids.* Follow the procedure described in C-XII (2).

(2) *Procedure.* In a 250-ml. Erlenmeyer flask dissolve 2 grams of the fatty acids, accurately weighed, in 20 to 30 ml. of neutral 95 per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (milligrams of potassium hydroxide per gram of fatty acids).

XV. Iodine Number (Wijs Method). (1) *Special reagents required.* Wijs iodine solution. Dissolve 13.0 grams of resublimed iodine in 1 liter of reagent grade glacial acetic acid and pass in washed and dried chlorine gas until the original thiosulfate titration of the solution is not quite doubled. There should be no more than a slight excess of iodine, and no excess of chlorine. When the solution is made from iodine and chlorine, this point can be ascertained by not quite doubling the titration (Note). For preparation of the Wijs solution use glacial acetic acid of 99.0 to 99.5 per cent strength. For glacial acids of somewhat lower strength, freezing and centrifuging or draining as a means of purification is recommended. Preserve the solution in amber, glass-stoppered bottles, sealed with paraffin until ready for use. Mark on the bottles the date on which the solution is prepared; do not use Wijs solution that is more than 30 days old.

Note. For preparation of the solution, McIlhiney (*13*) gives the following details:

The preparation of the iodine monochloride solution presents no great difficulty, but it must be done with care and accuracy in order to obtain satisfactory results. There must be in the solution no appreciable excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary; then setting aside a small portion of this solution, while pure and dry chlorine is passed into the remainder until the halogen content of the whole solution is doubled. Ordinarily, it will be found

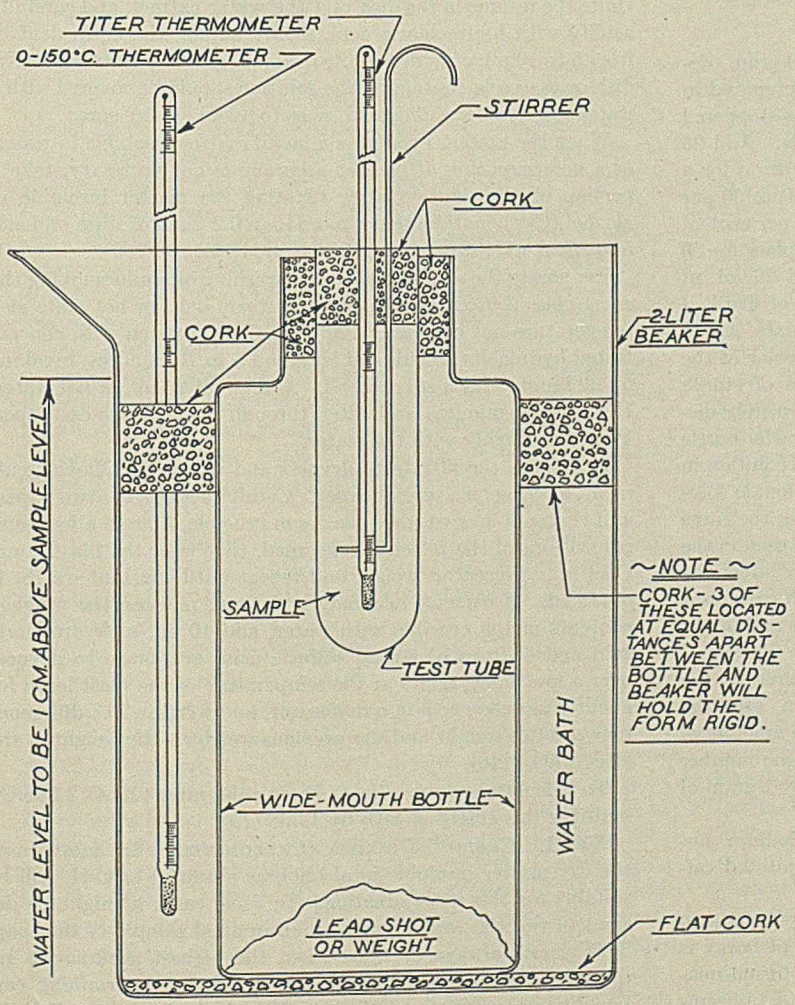

Figure 2. Assembly for Stirring Titers

that on passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged there will be a slight excess of chlorine which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

Sodium thiosulfate solution (0.1 *N*). Dissolve 24.8 grams of reagent grade sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in freshly boiled distilled water and dilute to 1 liter at the temperature at which the titrations are to be made. To standardize, place in a glass-stoppered flask 40 ml. of potassium dichromate solution (0.1 *N*) to which have been added 10 ml. of the solution of potassium iodide, add 5 ml. of hydrochloric acid (sp. gr. 1.19), dilute with 100 ml. of water, and allow the 0.1 *N* sodium thiosulfate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and while shaking constantly, continue to add the 0.1 *N* sodium thiosulfate solution until the blue color just disappears.

Potassium dichromate solution (0.1 *N*). Dissolve 4.903 grams of reagent grade potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1 liter at the temperature at which titrations are to be made.

Potassium iodide solution (15 per cent). Dissolve 150 grams of potassium iodide in water and dilute to 1 liter.

Starch paste. Boil 1 gram of starch in 200 ml. of distilled water for 10 minutes, and cool to room temperature.

Note. An improved starch solution may be prepared by autoclaving 2 grams of starch and 6 grams of boric acid dissolved in 200 ml. of water at 15-pound pressure for 15 minutes. This solution has good keeping qualities.

(2) *Procedure.* Weigh accurately from 0.10 to 0.50 gram (depending on the iodine number) of the fatty acids as prepared in C-XII (2) into a clean, dry, 450-ml. (16-ounce) glass-stoppered bottle containing 15 to 20 ml. of carbon tetrachloride. Add 25 ml. of the Wijs solution from a pipet, allowing it to drain for a definite time. The excess of iodine should be from 50 to 60 per cent of the amount added—that is, from 100 to 150 per cent of the amount absorbed. Let the bottle stand in a dark place for 30 minutes at a temperature of 25° ± 2° C., then add 20 ml. of potassium iodide solution (15 per cent) and 100 ml. of distilled water. Titrate the iodine with 0.1 *N* sodium thiosulfate, added gradually while shaking constantly, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake vigorously, so that any iodine remaining in solution in the tetrachloride may be taken up by the potassium iodide solution. Make two determinations on blanks, employing the same procedure as used for the sample, except that no fat is used in the blanks. Slight variations in temperature appreciably affect the titer of the iodine solution, since acetic acid has a high coefficient of expansion. It is therefore essential that the blanks and determinations on the sample be made at the same time. The number of milliliters of standard thiosulfate solution required by the blank, minus the amount used in the determination, give the thiosulfate equivalent of the iodine absorbed by the amount of sample used in the determination. Calculate the iodine number of the sample tested (centigrams of iodine absorbed by 1 gram of sample) (percentage of iodine absorbed).

XVI. Borax. (1) *Special reagents required.* Sodium hydroxide solution (0.1 *N*); silica, fine powder; precipitated calcium carbonate; and glycerol, reagent grade.

(2) *Procedure* (*16*). Weigh 10 grams (±0.02 gram) of the soap [or 5 grams (±0.01 gram) if more than 5 per cent of borax is present] into a platinum dish and add 2.15 grams of fusion mixture (consisting of 200 grams of sodium carbonate and 15 grams of silica in fine powder). To this mixture add 15 ml. of alcohol, mix with the aid of a glass rod and, after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil, and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-ml. round-bottomed flask. Acidify with 20 ml. of dilute hydrochloric acid (1 to 1), heat nearly to boiling, and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 minutes. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 100 ml.

Return the filtrate to the flask, add a pinch of calcium carbonate, and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 ml. of neutral glycerol, and titrate the solution with 0.1 *N* sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end point is reached, add 10 ml. more of glycerol and again titrate. Repeat this process until the addition of glycerol causes no further action on the end point. The number of milliliters of sodium hydroxide required multiplied by 0.00955 will give the equivalent of borax ($Na_2B_4O_7.10H_2O$) present in the solution.

XVII. Silica Present as Alkaline Silicates. *Procedure.* When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not to exceed 0.2 gram of silica in a platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish, and complete the ignition. Unite the residue in the dish and the water extract, and carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 ml. of hydrochloric acid (sp. gr. 1.19) in excess. The dish or casserole containing the solution should be covered with a watch glass while adding acid, so as to avoid loss by spray.

When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol (C-V) containing not more than 0.2 gram of silica and add 5 to 10 ml. of hydrochloric acid (sp. gr. 1.19).

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on a steam bath or hot plate at a temperature not exceeding 120° C. Cool, moisten with concentrated hydrochloric acid, and let stand 5 to 10 minutes, breaking up all lumps with a stirring rod. Add about 25 ml. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, then over the blast lamp. Cool in a desiccator, weigh, and repeat until constant weight is obtained. If extreme accuracy is desired, moisten the weighed contents of the crucible with water, add 10 ml. of hydrofluoric acid and 4 drops of strong sulfuric acid, evaporate to dryness over a low flame, ignite at the temperature of the blast lamp for about 2 minutes, cool in a desiccator, and weigh. The difference between this weight and the previous weight is the weight of the silica (SiO_2) (*10*).

To calculate sodium silicate having the ratio $1Na_2O:3.25SiO_2$, multiply the weight of SiO_2 by 1.308 (*19*).

XVIII. Carbon Dioxide (Carbonates). In most cases the dry matter insoluble in alcohol, as obtained in C-II, will be suitable for this determination. In some cases it might be desired to run the test directly on an original sample of the soap. This should always be done when the highest accuracy is required. Any reliable absorption method for determining carbon dioxide may be used (*4*). A method which has proved satisfactory is described in the following paragraphs.

(1) *Apparatus assembly.* Place a 250-ml. Erlenmeyer flask on a gauze over a burner. Fit the flask with a two-hole rubber stopper, one opening to carry a 25-cm. (10-inch) reflux condenser and the other a thistle tube equipped with a three-way stopcock. Draw out the end of the thistle tube to a small point, and place it in the stopper so that the point is very close to the bottom of the flask. Attach a small funnel to the straightaway end of the stopcock for the introduction of acid into the flask. Attach the other opening of the stopcock (which is to receive air) to a purifying tube containing soda-asbestos (Ascarite) or any other suitable carbon dioxide absorbent. Attach to the top of the reflux condenser a train consisting of the following: (*a*) a drying tube containing a dehydrating agent such as sulfuric acid (sp. gr. 1.84) or magnesium perchlorate, (*b*) a weighed tube containing Ascarite and magnesium perchlorate, and a second weighed tube containing concentrated sulfuric acid. Attach to this train a protective U-tube containing calcium chloride; attach the U-tube to an aspirator.

(2) *Procedure.* Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon dioxide–free air until the apparatus is free of carbon dioxide. Insert the train and continue to aspirate for 30 minutes. Check the weight of the train to determine whether the air is passing through too fast, or whether the system is free of carbon dioxide. The system must be free from leaks. Weigh a sufficient amount of the sample to yield approximately 0.2 gram of CO_2, transfer to the Erlenmeyer flask, cover with 20 ml. of freshly boiled distilled water, and close the apparatus with the train in place. Add 20 ml. of dilute hydrochloric acid (1 to 1) very slowly through the funnel; do not apply heat to the flask. The rate of adding acid should be carefully controlled, so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to slacken, start heating gently and continue until the contents of the flask have boiled 15 to 20 minutes. Stop heating and continue aspirating until the flask has cooled down. Remove the train and weigh. The increase in weight represents carbon dioxide. The amount of this increase multiplied by 2.41 equals sodium carbonate, or by 3.14 equals potassium carbonate.

XIX. Phosphates. If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol (C-II) or the ash from the incineration of an original sample may be used. An original sample should always be used when the highest accuracy is desired.

(1) *Special reagents required.* Molybdate solution. Dissolve 100 grams of molybdic acid in dilute ammonium hydroxide [144 ml. of ammonium hydroxide (sp. gr. 0.90) and 271 ml. of water]; pour this solution slowly and with constant stirring into dilute nitric acid [489 ml. of nitric acid (sp. gr. 1.42) and 1148 ml. of water]. Keep the final mixture in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

Ammonium nitrate solution. Dissolve 100 grams of phosphate-free ammonium nitrate in distilled water, and dilute to 1 liter.

Magnesia mixture. Dissolve 55 grams of crystallized magnesium chloride ($MgCl_2.6H_2O$) in water, add 140 grams of ammonium chloride and 130.5 ml. of ammonium hydroxide (sp. gr. 0.90), and dilute to 1 liter.

Dilute ammonium hydroxide for washing. Dilute 100 ml. of ammonium hydroxide (sp. gr. 0.90) to 1 liter.

(2) *Procedure* (*3*). Weigh out a 2-gram (±0.01 gram) sample of the alcohol-insoluble or ash, and proceed as described in C-XVII for removal of silica (a platinum dish should not be used), using nitric instead of hydrochloric acid. Boil the covered solution 30 minutes to convert other phosphates that may be present to orthophosphate, wash off and remove cover glass, and evaporate as described. Save the filtrate. Make up to 250 ml., concentrating if necessary. Pipet an aliquot corresponding to 0.50 or 1 gram of the original material into a 250-ml. beaker, add ammonium hydroxide in slight excess, and barely dissolve the precipitate formed with a few drops of nitric acid, stirring vigorously. Add about 15 grams of dry ammonium nitrate or a solution containing that amount. Heat to about 60° C., and add 70 ml. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) present.

Digest at about 65° C. for an hour, and determine if the phosphoric acid has been completely precipitated by adding more molybdate solution to the clear supernatant liquid. Filter, and wash with cold water, or preferably, ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide (1 to 1) and hot water, and wash into a beaker, keeping the volume under 100 ml. Neutralize with hydrochloric acid, using litmus paper or bromothymol blue as an indicator, cool, and from a buret add slowly (about 1 drop per second), stirring vigorously, 15 ml. of magnesia mixture for each decigram of phosphoric acid (P_2O_5) present. After 15 minutes add 12 ml. of ammonium hydroxide (sp. gr. 0.90). Let stand till the supernatant liquid is clear (2 hours is usually enough), filter, wash the precipitate with the dilute ammonium hydroxide until the washings are practically free from chlorides; dry, burn first at a low heat (platinum should not be used), and then ignite to constant weight, preferably in an electric furnace, at 1050° to 1100° C.; cool in a desiccator, and weigh as $Mg_2P_2O_7$. Calculate and report the result as percentage of P_2O_5 or alkaline phosphate known to be present.

XX. Sulfates. *Procedure.* For most determinations the matter insoluble in alcohol (obtained in C-II) may suffice. If a determination of the highest accuracy is desired, ignite a 10-gram (±0.1 gram) sample of the soap and use the ash from the ignition. Digest with 100 ml. of water, cover with a watch glass, and neutralize carefully with hydrochloric acid. When neutralized, add 5-ml. excess of hydrochloric acid, filter, and wash the residue thoroughly. (Evaporation to dryness is unnecessary unless gelatinous silica has separated, and should never be performed on a bath heated by gas, *11*). Make up the filtrate to 250 ml. in a beaker, and boil. To the boiling solution add 15 to 20 ml. of 10 per cent barium chloride solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam bath overnight. Set aside overnight or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate. Calculate to sodium sulfate, or the alkaline sulfate known to be present.

XXI. Glycerol, Sugars, and Starch. *A. Glycerol in the absence of sugars.* (1) Special Solutions Required. Potassium dichromate solution. Dissolve 74.553 grams of potassium dichromate in 500 ml. of water in a 1-liter volumetric flask. Dilute to the mark with water. Sodium thiosulfate solution (0.1 *N*). Potassium iodide solution (10 per cent).

(2) Procedure. (*a*) Weigh a portion of the sample equivalent to not more than 3.0 grams of glycerol and dissolve in 200 ml. of hot water in a 600-ml. beaker. If starch is present, it will be necessary to remove the matter insoluble in water as described in C-II and C-IV. Combine the alcohol and water solutions, evaporate off the alcohol, and proceed. Decompose with 25 ml. of sulfuric acid (1 to 4). If alcohol is present, volatilize it by boiling for 20 to 30 minutes. Cool, remove, and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500-ml. graduated flask, and add about 0.25 gram of silver sulfate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

(*b*) Transfer a filtered, accurately measured 50-ml. aliquot of the solution obtained in (*a*) to a 400-ml. beaker, add 75 ml. of accurately measured potassium dichromate solution, followed by 25 ml. of sulfuric acid (sp. gr. 1.84), cover with a watch glass, and oxidize by heating to 90° to 100° C. for 3 hours. Conduct a blank in like manner but using 100 ml. of water, 25 ml. of sulfuric acid (sp. gr. 1.84), and 25 ml. of accurately measured potassium dichromate. Cool and dilute the solutions to 1000 ml. in graduated flasks. The excess of potassium dichromate is determined by taking 50-ml. aliquots of the above, adding 50 ml. of water and 20 ml. of potassium iodide solution (10 per cent), and titrating the liberated iodine with 0.1 *N* thiosulfate, using starch solution as indicator.

(*c*) Calculate the percentage of glycerol (1 ml. of the potassium dichromate solution is equivalent to 0.0100 gram of glycerol).

B. Glycerol in the presence of sugars. Procedure (*12*). Proceed as in the determination of glycerol in the absence of sugar [C-XXI, A (2)], taking a sample so that the sum of the glycerol and sugar is not more than 3.0 grams. If starch is present, this must first be removed as described in C-XXI, A (2). The solution must be boiled in all cases at least 20 minutes to ensure complete inversion of sucrose as in C-XXI, D (2). Determine the amount of potassium dichromate solution required to oxidize both the sugar and glycerol. Determine also the sugar by the method given in C-XXI, D (2).

Calculate the percentage of glycerol after deducting the amount of potassium dichromate required by the sugar.

1 ml. of potassium dichromate equals 0.0100 gram of glycerol
1 ml. of potassium dichromate equals 0.01142 gram of invert sugar

C. Starch. Procedure (*5*). Separate the matter insoluble in water as described in C-II and C-IV, using a sample of soap that will give not more than 3 grams of starch. Transfer the insoluble matter, without drying, to a 500-ml. flask provided with a reflux condenser, and boil for 2.5 hours with 200 ml. of water and 20 ml. of hydrochloric acid (sp. gr. 1.125). Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 ml., filter, and determine the reducing sugars by the gravimetric method as given for the determination of sugar [C-XXI, D (2)].

Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained. This multiplied by 0.90 equals the amount of starch.

D. Sugars. (1) Apparatus and Reagents Required. The apparatus and reagents used shall be the same as those described in the standard Munson-Walker method (*15*).

(2) Procedure. Dissolve 10 grams (±0.01 gram) of the soap in 200 ml. of hot water in a 600-ml. beaker. Decompose with 25 ml. of sulfuric acid (1 to 4), boil gently for 20 minutes to invert the sucrose completely. Cool, remove, and rinse the cake of fatty acids. Extract the acid liquid with 25 ml. of ether. Neutralize the acid liquid with sodium hydroxide solution, transfer to a 500-ml. graduated flask, make up to volume, and mix thoroughly. Determine invert sugar in 50 ml. of this solution by the Munson-Walker method (*15*). To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95. [If starch is present, first remove as described in C-XXI, A (2) and then proceed as above.]

XXII. Volatile Hydrocarbons. This method (*17*) requires a source of dry, oil-free steam which is passed through the sample treated with acid, sufficient to liberate the fatty acids from the soap. The steam is next passed through strong caustic solution to scrub out any volatile fatty acids, while the volatile hydrocarbons are condensed with the steam in a suitable arrangement which allows the excess water to flow away, leaving the volatile hydrocarbons in the measuring buret. The method may be applied to samples containing substances immiscible with water and volatile with steam. [For solvents heavier than water the trap as shown in Figure 1 for determining water by the distillation method, C-I (2), should be used.]

(1) *Apparatus.* The apparatus and its arrangement are shown in Figure 3. The following are the important items:

Steam trap, *A*. A 1-liter round-bottomed ring-necked flask equipped with a siphon tube to the drain from the bottom of the flask and provided with a means of regulating the steam flow into the flask.

Evolution or sample flask, *B*. A 1-liter round-bottomed ring-necked flask. In case large samples are desirable the size of this flask may be increased.

Caustic scrubber flask, *D*. A steam-jacketed metal flask is preferred, but a 1-liter Florence flask provided with a steam coil of 0.32 cm. (0.125-inch) copper tubing around the upper half may be used. If the glass flask is used it should be provided with a safety bucket below it and should be renewed frequently, since

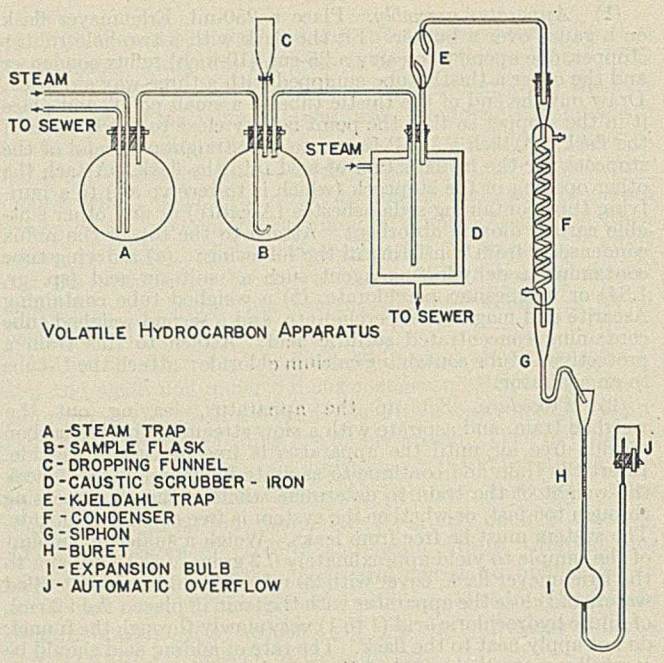

Figure 3. Volatile Hydrogen Apparatus

the strong caustic dissolves the glass rather rapidly. This flask should be connected to the condenser by a Kjeldahl connecting tube, *E*, or similar safety device.

The inlet for the steam into the evolution and scrubber flasks should extend nearly to the bottom of the flasks and be bent at right angles and parallel to the sides of the flask.

Condenser, *F*. A 30.5-cm. (12-inch) or longer spiral condenser of sufficient bore so the condensate will not readily close it.

Measuring buret, *H*. A 10-ml. buret calibrated to 0.1 ml. and carrying a bulb, *I*, of approximately 100-ml. capacity, at the lower end. If desired, an ordinary 10-ml. Mohr-type buret may be used, having attached to it by rubber tubing a bulb of proper capacity which has been blown in the laboratory. An ordinary buret funnel may be placed in the top of the buret in place of the special flared-out top shown in Figure 3.

The stoppers used should be of a good grade of rubber and should have been thoroughly cleaned free from any surface sulfur and should be given a steam-distillation in position for several hours before use on a sample.

Insulating the flasks and tubing to reduce condensation aids distillation and its control.

(2) *Procedure.* Place 150 ml. of sodium hydroxide solution (about 1.47 sp. gr.) and several sticks of solid sodium hydroxide to provide against dilution in the scrubber flask. Rinse out the condenser and buret with acetone. Attach a rubber tubing to the lower end of the buret, fill the buret and tubing with water, and raise the outer end of the tubing so that the water level in the buret is near the top of the scale when the water is flowing to the drain from the automatic overflow, *J*. Be sure the connections are tight and that the tubing contains no air bubbles. Place the condenser in position so that the lower end extends directly into the upper end of the buret just above the water level, or connect to an adapter siphon, *G*, which discharges into the buret. The cooling water should be 15.5° C. or colder. Ice water may be desirable for low-boiling hydrocarbons.

Weigh 100 grams (±0.5 gram) of the soap (cut into cubes of about 1-cm. edges) or 50 grams (±0.3 gram) of soap powder and transfer to the evolution flask. Add about 10 grams of gum arabic (commercial) and 100 ml. of distilled water. Place the flask in position with 100 ml. of sulfuric acid (1 to 3) in a dropping funnel, *C*, carried in the stopper. Connect with the steam line and with the wash flask and the condenser, making sure that the stoppers are tightly fitting and held in place by wiring. Rubber

connections in the lines between the evolution flask and condenser should be avoided.

Add the acid to the sample slowly to avoid excessive frothing. While adding the acid, turn on the steam cautiously, so adjusting the pressure by a bleeder valve that just enough steam flows to prevent any liquid from backing into the steam trap flask.

When all the acid has been added, turn on enough steam to cause brisk distillation, taking care that no liquid is carried over from the evolution and wash flasks and that the condenser water does not become warm.

Continue the distillation until there is no increase in the volume of the upper layer for 45 minutes or no small droplets can be noted in the condensate.

When distillation is completed, shut off and drain the condenser water, and allow the steam to heat up the condenser to drive out the last traces of volatile hydrocarbon. Shut off the steam as soon as vapor begins to issue from the lower end of the condenser. Immediately open the stopcock of the dropping funnel to prevent caustic being drawn into the evolution flask.

Stopper the buret and allow its contents to come to room temperature or bring them to a definite temperature by immersing the buret for 1 to 2 hours in a water bath held at 25° C.

Read the volume of the upper layer to the nearest 0.01 ml. The volume multiplied by the specific gravity equals the weight of the volatile hydrocarbon. The specific gravity should be determined at the temperature at which the volume is read. A small Sprengel tube made of 3-mm. glass tubing is convenient for this purpose.

Calculation. Calculate the percentage of volatile hydrocarbons as follows:

$$V = \frac{M \times \text{sp. gr.}}{S} \times 100$$

where V = per cent of volatile hydrocarbons, M = milliliters of volatile hydrocarbons, and S = weight of sample in grams.

Note. For some samples the volatile hydrocarbon content may be so low that a larger sample than 50 or 100 grams is desirable. The size of the evolution flask may need to be increased if larger samples are used. The amount of water in the evolution flask and acid used should also be correspondingly increased.

XXIII. Combined Sodium and Potassium Oxides. The total combined alkali present in the soap is determined by the method described in C-VI, and calculated as sodium oxide (Na_2O). Determine the combined potassium oxide (K_2O) by the following method, calculate it to the equivalent sodium oxide (Na_2O), and subtract this from the total combined alkali calculated as sodium oxide (Na_2O); the remainder is the combined sodium oxide (Na_2O).

(1) *Special reagents required.* Ammonium chloride solution. Dissolve 100 grams of ammonium chloride in 500 ml. of distilled water, add 5 to 10 grams of pulverized potassium chloroplatinate (K_2PtCl_6), and shake at intervals for 6 to 8 hours. Allow the mixture to settle overnight and filter. (The residue may be used for the preparation of a fresh supply of ammonium chloride solution.)

Platinum solution. Prepare a solution containing the equivalent of 1 gram of metallic platinum (2.1 grams of chloroplatinic acid, H_2PtCl_6) in each 10 ml. of solution. For materials containing less than 15 per cent of potassium oxide (K_2O), a solution containing 0.2 gram of metallic platinum (0.42 gram of H_2PtCl_6) in each 10 ml. of solution is recommended.

(2) *Preparation of sample.* Weigh a 10-gram (±0.01 gram) sample and sinter it in an evaporating dish below a dull red heat. Leach the ash with hot water, filter into a 100-ml. volumetric flask, and wash the paper with three 5- to 10-ml. portions of hot water. Complete the ashing after returning the filter paper and residue to the original dish and sintering as before. Excessive heating should be avoided. Removal of most of the alkali present by thoroughly washing the ash with hot water before completion of the ashing will aid in preventing overheating of the greater portion of the sample. Add a few drops of hydrochloric acid (1 to 1) to the ash and wash the contents of the dish into the volumetric flask. Acidify the solution in the volumetric flask with hydrochloric acid, dilute to 100 ml., mix thoroughly, and pass through a dry filter.

(3) *Procedure.* Acidify an accurately measured 10-ml. aliquot of the solution obtained in Section 2 with a few drops of hydrochloric acid and add 10 ml. of the platinum solution. Evaporate the solution on a water bath to a thick paste which will become solid on cooling to room temperature. Avoid exposure to ammonia fumes while heating the solution. Treat the residue with approximately 6 ml. of alcohol (80 per cent) and add 0.6 ml. of hydrochloric acid (sp. gr. 1.19). Filter on a Gooch crucible and wash the precipitate thoroughly with alcohol (80 per cent) both by decantation and on the filter, continuing the washing until after the filtrate is colorless. Then wash the residue five or six times with 25-ml. portions of the ammonium chloride solution to remove the impurities from the precipitate. Wash again thoroughly with alcohol (80 per cent), dry the precipitate at 100° C. for 30 minutes, and weigh. Calculate the result to potassium oxide (K_2O).

Note. For the conversion of K_2PtCl_6 to K_2O the factor 0.19376 may be used.

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A Dye Extremely Sensitive to Copper

E. I. STEARNS, Research Department, Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

DURING spectrophotometric measurements of dyestuffs the sensitivity of Benzo Fast Yellow 5GL to the presence of copper was found to be 40 times as great as the carbamate method of test. While not necessarily proposed as an analytical method, it was thought that this sensitivity would be of interest.

Figure 1 compares the curve shapes of a solution of Benzo Fast Yellow 5GL (C. I. 346, diphenylurea-*p,p'*-disazo-bis-salicylic acid) at pH 9.0, temperature 23° C., and concentration of 30 mg. per liter with and without 0.1 mg. per liter of cupric ion added. Both solutions are stable over a 24-hour period.

Analysis of the curve shows that the extinction coefficient of the pure dye and the metallized complex is the same at 397 millimicrons, while the extinction coefficient has increased about 150 per cent at 487 millimicrons (from 2.9×10^3 to 7.4×10^3 sq. cm. per gram). Using magnifying cams, it is possible to get a sensitivity of 0.5 per cent extinction coefficient, which means that a small fraction of this amount of copper can be detected.

In order to determine the sensitivity to a small amount of copper, the data shown in Figure 2 were obtained. Figure 2 shows the curves obtained using a magnifying cam with and without 10^{-6} gram per liter of copper divalent ion present in a Benzo Fast Yellow 5GL solution. Since the linear distance

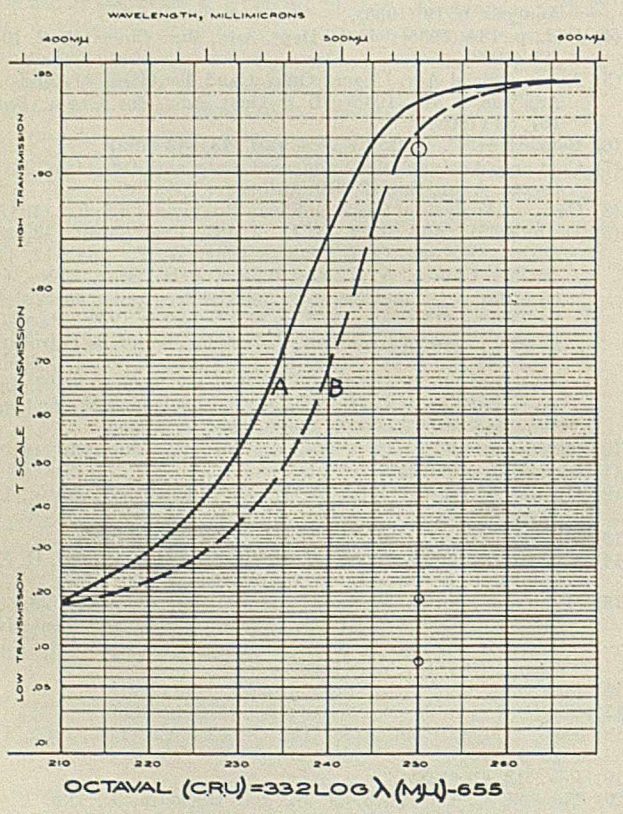

FIGURE 1. EFFECT OF ADDED COPPER ON BENZO FAST YELLOW 5GL

Normal cams
A. 30 mg. per liter of dye in water at pH 9.0, 23° C., measured in 1-cm. cell
B. Same as *A* but with 0.1 mg. per liter of Cu^{++} added

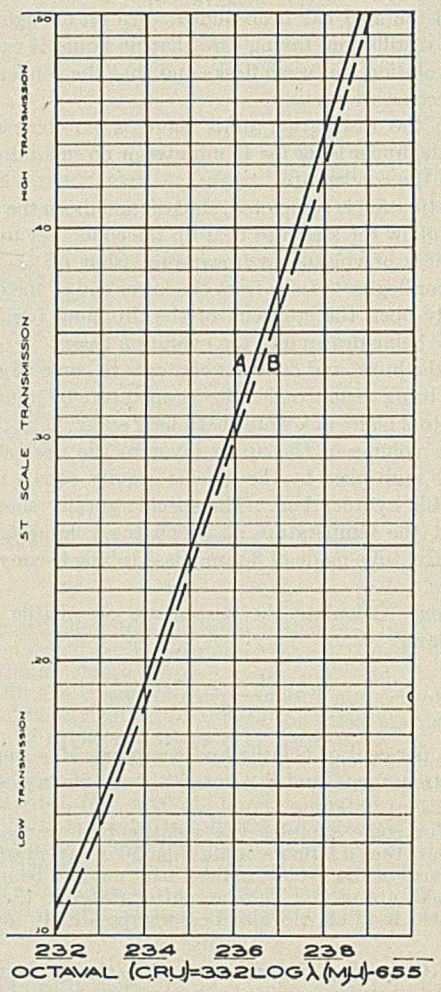

FIGURE 2. EFFECT OF ADDED COPPER ON BENZO FAST YELLOW 5GL

Magnifying cams
A. 30 mg. per liter of dye in water at pH 9.0, 27° C., measured in 5-cm. cell
B. Same as *A* but with 0.001 mg. per liter of Cu^{++} added

separating the two curves is readily divisible into ten parts, it is evident that 10^{-7} gram of copper per liter can be detected.

The colorimetric reaction with sodium diethyldithiocarbamate and copper as measured on the spectrophotometer gives a test in which 4×10^{-6} gram of copper per liter can be determined in a similar cell. Hence, on the basis of spectrophotometric measurement the Benzo Fast Yellow 5GL is about 40 times as sensitive as the sodium diethyldithiocarbamate.

The carbamate test is ordinarily considered to have a sensitivity based on visual colorimetry with a Lovibond colorimeter of about 10^{-5} gram, which closely approaches the spectrophotometric sensitivity. Visually the Yellow 5GL sensitivity would not so nearly approach the spectrophotometric sensitivity because a change of color, from a yellow to a redder yellow, is not so noticeable as the appearance of a color which is the case in the carbamate method. Hence, for visual work,

the sensitivity of the two methods of test would perhaps be equal.

The Yellow 5GL is also reactive to iron, chromium, and nickel, but to a smaller extent, detecting only about 5×10^{-5} gram per liter of iron.

It has been useful as a measure of the general purity of distilled water as regards presence of metallic ions, but no method has been worked out to make it a specific test for copper. No effort has been made to determine the optimum conditions or to determine whether other closely related dyes are better.

Direct Green B, which is also sensitive to copper, has been proposed (*3*), and has been found to have about the same sensitivity as the carbamate test spectrophotometrically. Hence the Yellow 5GL is also 40 times as sensitive as Direct Green B, based on spectrophotometric measurements.

The use of octaval (logarithm of wave length) for the abscissa of spectrophotometric curves (*2*) is somewhat unusual but is particularly convenient when magnifying cams are used as in Figure 2. Thus the visual range (375 to 750 mu) is divided into 100 logarithmic units and covers the range 200 to 300 c. r. u. This plotting range was used for the data of Figure 1. One fifth of this range, from 230 to 250 c. r. u., was magnified to full width and was the plotting range used for the data of Figure 2. For convenience in range-shifting and magnification changing, as is necessary in problems of this type, the use of a decimal system has been found most convenient.

The $\times$ 5 ordinate magnification need not be so flexible in the case of solutions, since their concentration can be changed to cause them to fall within the plotted range. Hence it is necessary to have the $\times$ 5 log log $1/T$ scale only in the plotting range 10 to 50 per cent transmission. This is the ordinate used in Figure 2. The desirability of the log log $1/T$ scale is generally recognized (*1*).

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Effect of Container on Soluble Silica Content of Water Samples

C. A. NOLL AND J. J. MAGUIRE, W. H. & L. D. Betz, Gillingham and Worth Sts., Philadelphia, Penna.

IN POWER plant operation, particularly with modern high-pressure boilers, the silica content of the raw water, feed water, boiler water, and steam has become of prime importance.

The silica content of a boiler water sample is of importance in limiting silica in the concentrated boiler water to a tolerable value, so as to prevent scale formation. Particularly at higher boiler pressures, careful control of the silica content of the boiler water and steam may be required for the limitation of siliceous turbine blade deposits. Silica plays an important role in the intercrystalline corrosion of boiler metal, and in evaluating the effect of this constituent under varying conditions it is important that the silica values obtained reflect the true conditions existing in the water sample.

Recently, methods have been developed for the controlled removal of silica from raw and boiler feed waters, and in the formulation of accurate recommendations for such silica removal it is necessary that the water analyses on which these recommendations are based be entirely representative of the silica content of the water. For the proper routine control of silica removal processes, it is obvious that the samples analyzed must be representative.

A recent article by Belyea and Moody covers in detail the sampling of steam and boiler water (*2*). This paper is concerned entirely with the storage of water samples after collection.

For the accurate determination of silica, glass containers should not be employed (*1*). Collins and Riffinburg (*3*) pointed out the large increase in silica that will occur in poor glass bottles over a period of 8 months; they concluded that samples of water in good bottles will not dissolve enough glass in a month to cause any detectable change in the ordinary mineral analysis and that no significant change will be caused in 6 months. They were primarily concerned with the effect of storage on natural or raw water and on distilled water samples, although they also tested dilute sodium carbonate solutions.

Data on resistance to chemical attack for four brands of chemical glassware have recently been presented (*7*).

Table I. Changes in Silica Content

Container	Temperature at Which Sample Added	Silica as SiO_2				
		Original sample	3rd day	5th day	7th day	14th day
	° C.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
Sample Typical of Raw or Feed Water						
Ordinary soda glass bottle	23	2.0	2.2	2.3	2.4	2.6
	95	2.0	2.4	2.6	2.8	3.0
Pyrex bottle	23	2.0	2.1	2.2	2.2	2.3
	95	2.0	2.2	2.3	2.4	2.4
Hard-rubber bottle	23	2.0	2.0	2.0	2.0	2.0
	95	2.0	2.0	2.0	2.0	2.0
Resin-lined can	23	2.0	2.0	2.0	2.0	2.0
	95	2.0	2.0	2.0	2.0	2.0
Sample Typical of Boiler Water						
Ordinary soda glass bottle	23	32.4	33.4	34.2	35.2	37.7
	95	32.4	33.9	35.1	36.2	38.6
Pyrex bottle	23	32.4	32.8	33.1	33.6	34.9
	95	32.4	33.4	33.8	34.3	35.7
Hard-rubber bottle	23	32.4	32.5	32.4	32.3	32.4
	95	32.4	32.4	32.4	32.4	32.5
Resin-lined can	23	32.4	32.1	32.4	32.6	32.1
	95	32.4	32.4	32.0	32.3	32.4
Sample Typical of Condensate						
Ordinary soda glass bottle	23	0.2	0.3	0.4	0.6	0.9
	95	0.2	0.4	0.5	0.8	1.0
Pyrex bottle	23	0.2	0.3	0.3	0.4	0.5
	95	0.2	0.4	0.4	0.5	0.6
Hard-rubber bottle	23	0.2	0.2	0.2	0.2	0.2
	95	0.2	0.2	0.2	0.2	0.2
Resin-lined can	23	0.2	0.2	0.2	0.2	0.2
	95	0.2	0.2	0.2	0.2	0.2

TABLE II. MINERAL ANALYSIS OF SAMPLES USED IN TABLE I

	Raw or Feed Water	Boiler Water	Condensate
Turbidity as SiO_2, p. p. m.	3.6	...	0.0
Color, units	0	200	0
Hardness as $CaCO_3$, p. p. m.	34	0	0
Sulfate as SO_4, p. p. m.	8	224	0.8
Chloride as Cl, p. p. m.	5.5	160	0.0
Total iron as Fe, p. p. m.	0.0	0.0	0.0
Phenolphthalein alkalinity as $CaCO_3$, p. p. m.	0	408	0
Methyl orange alkalinity as $CaCO_3$, p. p. m.	30	628	6
pH value	7.0	11.2	6.2
Silica as SiO_2, p. p. m.	2.0	32.4	0.2

While it has been definitely recognized that silica is picked up from glass bottles, the great majority of water samples are obtained in glass, on the assumption that the increase in silica content will not be of importance. This investigation was conducted partially to determine if such an assumption is justified in the case of samples obtained from the various points in a power plant's cycle.

To avoid the error introduced by glass bottles, tin and tin-lined containers have been suggested (*6*) but have not been found fully satisfactory (*5*, *6*). Schwartz (*5*) has suggested the use of hard-rubber bottles after a short period of aging, describing experience wherein tin-lined containers reacted with alkaline boiler waters to dissolve sufficient tin to interfere in the colorimetric determination of silica.

This study has been primarily directed to any change in the silica content of water samples over a 2-week period, which will cover the time usually elapsing between the collection and analysis of water samples. The samples of water were added to the containers both hot and cold to simulate conditions in practice. The glass containers used to obtain the data illustrated in the tables had, in each case, been "aged" by contact with water. Unless this precaution is taken with new bottles, a large increase in silica may result on first use of a container.

Table I illustrates the change in the silica content when four different types of containers are used with a sample typical of a raw water or feed water, both hot and cold (23° and 95° C.). Maximum increase of 1.0 p. p. m. of silica took place when the sample was added hot to the soda glass bottle. Although this increase was only 1.0 p. p. m. at the end of 14 days, it represents a 50 per cent increase over the original silica content of the water sample.

In similar tests on samples representative of boiler water, in 14 days the samples added hot to the soda glass and Pyrex bottles had increased 6.2 and 3.3 p. p. m. of silica as SiO_2, respectively.

Under similar conditions, using samples typical of condensed steam or condensate, the greatest pickup in silica was shown by the sample added hot to the soda glass bottle. This maximum increase is from 0.2 to 1.0 p. p. m., an increase of only 0.8 p. p. m. of silica as SiO_2, but a silica increase of 400 per cent compared with the original value. Where total solids are determined on a sample of condensed steam, storage of the condensed steam sample in glass may contribute to the sample a solids content several times in excess of the original value.

The silica values shown in Table I are the average of several tests. The original analysis of each of the three samples is shown by Table II. Silica was determined by the photoelectric method developed by Kahler (*4*). The accuracy of this method in the range of silica shown by Table I for raw or feed water and condensate is 0.1 p. p. m. of silica as SiO_2. With boiler water the accuracy is approximately 0.3 to 0.6 p. p. m. of silica as SiO_2. Any pickup of tin from the container will not affect silica determination by this procedure.

Within limits of analytical methods employed, no change was noted in the silica content of samples stored in hard-rubber bottles or in resin-lined cans.

Alkaline boiler water results in a greater increase in the silica content of the sample. The possibility of acidifying the boiler sample to decrease silica picked up from glass could be considered. However, such a procedure would alter the characteristics of the water sample, and it would be necessary to secure an additional sample, not acidified, to obtain a complete analysis. If containers which will not affect the silica content are employed, a complete mineral analysis can be made on the same sample.

In order to check on any change in the silica content of water samples shipped in ordinary tin-lined containers, several tests were made using 5-gallon tin-lined gasoline cans. Table III illustrates the results obtained with a boiler feed water and a boiler water. In each case, corrosion of the can was observed, with increase in the iron content of the sample. Corrosion of the can resulted in the formation of ferric hydroxide, and since this precipitate possesses the property of absorbing silica, a reduction of silica is shown by the tests in Table III. Table IV illustrates the original analysis of the feed water and boiler samples used in these tests. It is evident from these results that the use of tin-lined containers should be avoided, not only because tin interferes with some colorimetric silica determinations but also because removal of the protective tin coating permits corrosion of the iron and subsequent removal of silica from solution.

TABLE III. TEST ON ORDINARY TIN-LINED CONTAINERS

	Original Analysis	3rd Day	5th Day	7th Day
Sample Typical of Feed Water				
Total iron as Fe, p. p. m.	1.0	10.0	20.0	26.0
Silica as SiO_2, p. p. m.	21.6	21.3	18.6	18.2
Turbidity as SiO_2, p. p. m.	9.4	132	260	272
Sample Typical of Boiler Water				
Total iron as Fe, p. p. m.	0.1	5.0	8.0	16.0
Silica as SiO_2, p. p. m.	20.5	20.3	20.0	19.0
Turbidity as SiO_2, p. p. m.	13.8	66	164	200

TABLE IV. MINERAL ANALYSIS OF SAMPLES USED IN TABLE III

	Feed Water	Boiler
Turbidity as SiO_2, p. p. m.	9.4	13.8
Color, units	40	30
Hardness as $CaCO_3$, p. p. m.	46	0
Sulfate as SO_4, p. p. m.	56	448
Chloride as Cl, p. p. m.	5.5	276
Total iron as Fe, p. p. m.	1.0	0.1
Phenolphthalein alkalinity as $CaCO_3$, p. p. m.	0	304
Methyl orange alkalinity as $CaCO_3$, p. p. m.	38	436
pH value	6.9	10.7
Silica as SiO_2, p. p. m.	21.6	20.5

In order to obtain data on the effect of long storage periods with resin-lined cans several samples were placed in resin-lined containers, and were withdrawn for analysis after one month and after 13 months (Table V). With the exception of the resin-lined can which was filled with 0.02 *N* sulfuric acid, no change in iron content was noted after one month of storage. The can containing an alkaline boiler water showed an increase in the iron content from 0.2 to 2.0 p. p. m. at the end of 13 months and some drop in silica content. It would appear from these tests that resin-lined cans may safely be employed for storage of samples for a considerable length of time, provided no free mineral acid is present.

Some additional tests have been made on routine water sample shipments to the laboratory. In the case of two water samples, each was submitted in a 1-quart resin-lined can and in a 5-gallon unlined steel drum. In one water supply the resin-lined can showed a silica result of 8.6 p. p. m. as SiO_2 compared with a reduced silica content of the sample in the drum of 3.3 p. p. m. In

TABLE V. STORAGE TESTS WITH RESIN-LINED CANS

Type of Sample	Silica as SiO_2	Total Iron as Fe	Date of Analysis
	P. p. m.	*P. p. m.*	
Distilled water	0.0	0.0	5/3/40
	0.0	0.0	6/3/40
	0.0	0.1	6/3/41
Distilled water saturated with carbon dioxide	0.0	0.0	5/3/40
	0.0	0.0	6/3/40
	0.0	0.1	6/3/41
Sulfuric acid, 0.02 *N*	..	0.0	5/2/40
	..	1.0	6/3/40
	..	15.0	6/3/41
Alkaline boiler water added to can at 23° C.	29.7	0.2	5/3/40
	29.5	0.2	6/3/40
	28.7	2.0	6/3/41
Philadelphia tap water (Delaware supply) added to can at 95° C.	4.0	0.1	5/3/40
	4.1	0.1	6/3/40
	4.0	0.1	6/3/41

the other case, the resin-lined cans showed a silica result of 5.6 against 2.3 p. p. m. in the sample shipped in the drum. Considerable corrosion of the steel drums was evidenced, together with precipitation of iron. Samples were received in the laboratory 3 days after they had been taken and the analyses were completed on the fourth day after sampling.

In another case, a sample of water was forwarded to the laboratory in two containers, one ordinary soda glass and the other a resin-lined can. The sample secured in glass showed a silica content of 15.5 p. p. m. as SiO_2, whereas the sample in the resin-lined can showed silica as 7.2 p. p. m. Samples were secured January 17, 1941, and analyzed February 6.

The resin-lined can employed was a tin plate container, carrying two interior coats of organic protective coatings. The undercoat is a high baked cured modified alkyd resin varnish. The top coat is a baked vinyl chloride–vinyl acetate copolymer spirit varnish. This container is the standard beer package manufactured by the American Can Company.

Conclusions

In making recommendations for the removal of silica from water, designing feed water conditioning systems, setting silica limits for a boiler water, and determining the solids content of condensed steam samples, it is not safe to assume that the increase in silica from a glass container will be negligible. It is essential to secure water samples in containers that will not impart silica to the sample and to use containers that will not rust and so reduce the silica content of the water sample.

Hard-rubber bottles and resin-lined cans provide excellent containers for sampling and storage of water samples. In the handling of large numbers of water samples for silica determinations, the authors have found resin-lined cans economical and convenient.

Summary

Appreciable increase in the silica content of water samples may result from the use of glass bottles for sampling and for storage. This increase in silica is more marked with alkaline water, such as boiler water, than with raw water, feed water, and condensate. The increase in silica is also greater if the sample is placed in a bottle hot than if it is first cooled to room temperature. Silica pickup from Pyrex containers has been noted, although not to the extent experienced with ordinary soda glass.

The use of steel drums or tin-lined cans results in a corrosive action on the metal, precipitation of iron, and the lowering of the silica content of the water sample. The use of hard-rubber bottles or resin-lined cans prevents any change in the silica content of the water within limits of analytical error.

Acknowledgment

The authors wish to express their appreciation to W. H. & L. D. Betz, in whose laboratories this investigation was conducted. They are also indebted to the American Can Company for the resin-lined containers used in the various tests.

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Fluorescein As an Indicator in Bromometric Titrations

F. L. HAHN, Casilla 221, Quito, Ecuador

THE use of methyl orange or methyl red in bromometric titrations involves the inconvenience that the indicator may be destroyed by a local or temporary excess of free bromine before the equivalence point is reached.

Fluorescein, a highly sensitive reagent for bromate in the presence of bromide (*1*), permits one to observe the approach and the passing of the end point. The indicator solution may be prepared by dissolving 0.1 gram of fluorescein in 100 ml. of water containing some drops of sodium hydroxide. One drop of indicator is added to each 10 ml. of titrated solution.

In a bromometric titration of arsenious acid (strongly acidified with hydrochloric or sulfuric acid) the greenish yellow of the solution changes to a brownish yellow when the end point is approached. The change to a reddish brown indicates the end point. As the fluorescein reacts only slowly with bromine, it is necessary, near the end point, to wait some 15 seconds after each addition of reagent. Heating the solution to 40° to 50° C. will accelerate the reaction.

A permanganate solution (approximately 0.1 *N*) and a bromate solution (approximately 0.05 *N* plus 20 grams of potassium bromide per liter) were compared iodometrically. Then the arsenite solution was titrated with permanganate, using a little iodide as a catalyst, and with bromate solution. The results were:

1 ml. of $KMnO_4$ = 1.855 ml. of $KBrO_3$ (iodometrically)
= 1.853 ml. of $KBrO_3$ (with fluorescein)

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A Photoelectric Photometer for Rapid Grading of Naval Stores Products

ROBERT H. OSBORN, Hercules Experiment Station, Hercules Powder Company, Wilmington, Del.

A photoelectric color grader, especially suited to naval stores plant laboratories, is described. Its design is such that a single meter reading indicates the ratio of the transmissions of a sample for light beams of two colors. By proper choice of variables, any class in a wide range of transparent materials may be graded rapidly and without the necessity of avoiding dirt, haze, or surface imperfections in the samples.

A LARGE number of photoelectric instruments have been described in the literature in which transmission or reflection factors for light of two or more colors are measured (*1*, *9*, *10*, *11*). For certain types of colorimetric work, such as color grading, quantities involving ratios of such factors are required. These ratios must be calculated from the data furnished by instruments of the foregoing type.

In general, these instruments will also measure quantities proportional to the ratios of transmission or reflection factors of two different materials for light of the same color. Another instrument (*12*) measures quantities proportional to the differences between the transmission or reflection factors of materials for light of two different colors.

None of the photoelectric colorimeters investigated by the author has been suitable for the rapid routine color grading which is done in naval stores plants. Heretofore, the method of visual comparison with artificial standards has been used. Recognizing the limitations and inaccuracies inherent in such a procedure, means were sought whereby quantities proportional to the ratios of transmission factors of materials for light of two different colors could be obtained by means of single meter or dial readings from an instrument of the photoelectric type. Furthermore, the optical, mechanical, and electrical characteristics of the design which was finally chosen were so arranged that the readings were proportional to either the x, y, or z trichromatic coefficients (*6*) of the samples being graded, depending on the combination of characteristics chosen for that particular series of measurements.

The justification for this procedure is based on the observation made in this laboratory that the grades of samples having more or less uniform clarity and color characteristics can be based on one of their trichromatic coefficients. The choice of a coefficient for a particular type of sample depends on the position on the I. C. I. color mixture diagram (*6*) of the locus of points representing the complete range of colors of samples of that type. For example, Brice (*2*) has shown that the chromaticity differences for rosin colors are well represented by differences in x trichromatic coefficients. Accordingly, the official U. S. rosin standards have been spaced systematically on a scale of x trichromatic coefficients.

Theory of Instrument

Figure 1 is a schematic diagram showing the essential parts of a typical instrument designed for measuring the color of naval stores products. If a sample be placed in the space between the filter holder and the barrier layer photocell, using a filter having characteristics such that the response of the photocell is proportional to the sum of the X, Y, and Z tristimulus values of the sample, the indicating instrument (galvanometer or microammeter) may be set at some predetermined value by adjusting the iris diaphragm. Then, without changing this adjustment, a filter having characteristics such that the response of the photocell is proportional to the X tristimulus value alone is inserted in place of the first filter. The indicating instrument will then give a reading which will be proportional to the ratio of the transmission of the sample for the X beam to its transmission for the $X + Y + Z$ beam. This ratio, and hence the latter reading, will be proportional to the x trichromatic coefficient of the sample, as may be shown by the following analysis:

Let i_1 = photocell current output with the sample and the $X + Y + Z$ filter in position
i_2 = photocell output with the sample and the X filter in position
E = relative spectral energy of the lamp
s = relative spectral response of the photocell to a source having an equal energy spectrum
T_{X+Y+Z} = transmission of $X + Y + Z$ filter
T_X = transmission of X filter
T = transmission of sample
λ = wave length
k = a constant

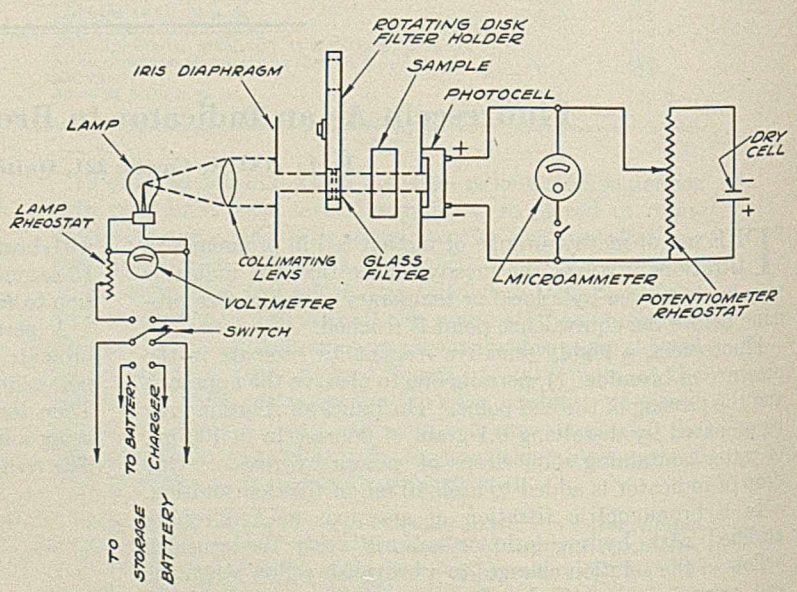

FIGURE 1. SCHEMATIC DIAGRAM OF PHOTOELECTRIC GRADER FOR TRANSPARENT AND TRANSLUCENT SAMPLES

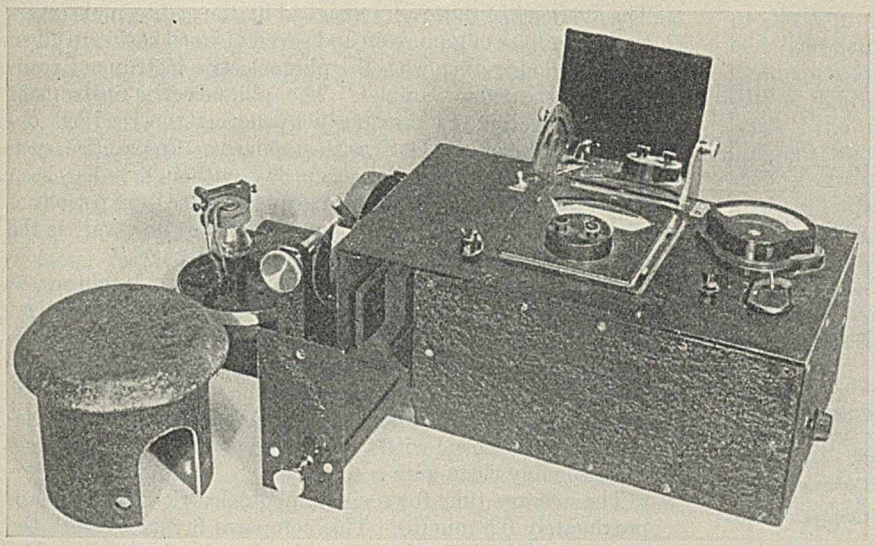

FIGURE 2. PHOTOELECTRIC COLOR GRADER

For low light intensities and low external resistance in the photocell circuit, the photocell current is known to be practically a linear function of illumination (*8*)—that is,

$$i_1 = k \int_0^\infty Es\, T_{X+Y+Z}\, T\, d\lambda \qquad (1)$$

$$i_2 = k \int_0^\infty Es\, T_X\, T\, d\lambda \qquad (2)$$

The integral in Equation 2 is equal to a constant times the X tristimulus value of the sample (*5*), while the integral of Equation 1 is equal to another constant times the sum of the X, Y, and Z tristimulus values of the sample. Dividing Equation 2 by Equation 1:

$$\frac{i_2}{i_1} = \frac{\int_0^\infty Es\, T_X\, T\, d\lambda}{\int_0^\infty Es\, T_{X+Y+Z}\, T\, d\lambda} = \frac{c_1 X}{c_2 (X+Y+Z)}$$

or

$$i_2 = \frac{i_1 c_1}{c_2} \frac{X}{X+Y+Z} = cx \qquad (3)$$

where

$c = \frac{i_1 c_1}{c_2}$ (i_1 is set at a constant value for each measurement)

and

$$x = \frac{X}{X+Y+Z} \quad \text{(see } 6\text{)}$$

A similar analysis applies to the measurement of y and z trichromatic coefficients.

By varying the constants of the circuit shown schematically in Figure 1, the scale of values can be expanded beyond a point which would be possible if the microammeter were connected directly to the photocell. In this circuit, a "bucking" potential is applied to the photocell by means of the voltage drop across a portion of a potentiometer circuit through which current from a 1.5-volt dry cell is flowing. In effect, a depressed zero is achieved by electrical means, and the scale may be magnified as much as desired within practicable limits.

Construction of Instrument

Figure 2 is a photograph of one of the instruments which was built in accordance with the foregoing principles. Three of these instruments have been in more or less continuous operation for more than a year, and have proved themselves to be well suited for the grading of naval stores products.

An 8-volt storage battery supplies current for a 50-candle power automobile spotlight lamp. A series rheostat controls the lamp voltage, which is maintained at 6 volts while the instrument is in operation. The lamp is situated at the focal point of a lens, from which a collimated beam emerges. After passing through an iris diaphragm, the aperture of which may be varied by means of a knob and worm and pinion gears, the narrowed beam is filtered. It is then transmitted by the sample and strikes the sensitive surface of a No. 732 Electrocell photocell mounted in a hermetically sealed case behind the sample compartment. The sample compartment is provided with a sliding sample drawer, so constructed that when the sample is properly placed in the drawer and pushed into the light beam, the compartment is tightly closed. A circular filter holder provided with a handle permits rapid changes from one filter to another. Space for eight filters has been allowed in anticipation of possible future requirements. The photocell current is indicated on a Rawson Type 507C microammeter, graduated with 100 divisions, and giving full-scale deflection at 30 microamperes. For the comfort of the operator an adjustable mirror is provided for reading the meter while the operator is in a sitting position.

A three-position selector switch permits the operator (1) to make an initial adjustment of the bucking voltage; (2) to make color measurements using the bucking voltage; and (3) to make measurements without the bucking voltage, or with the photocell connected directly to the meter. Once a day, the operator turns the selector switch to position 1. He then adjusts the rheostat on the right side-panel until the microammeter reads 100 or full scale. If measurements are to be made on pale and medium-colored samples, he then switches to position 2. The switch is turned to position 3 for the measurement of dark-colored samples. With the selector switch in this position, the color scale is a compressed version of the scale obtained with the selector switch in position 2.

In order to avoid the effect of variables such as aging of the lamp, dust on the filters, possible small changes in the spectral characteristic of the photocell, etc., calibrations are prepared each day with the aid of a set of permanent glass standards closely approximating in appearance the color series which is to be measured. Brice (*2*) has described the construction of a typical set of such standards for rosin.

It will sometimes be found that, in order to grade accurately very light or very dark samples, filters other than those giving the trichromatic coefficients must be used—for example, red and blue filters have been used in this laboratory for the grading of pale yellow samples, while deep red and neutral filters have been used for the grading of dark red samples. The range of sample colors must be studied carefully before a choice of filters is made.

By means of such filter combinations, it is possible to grade almost colorless liquids such as pine oil, turpentine, etc., pale liquid and solid resins, and dark resins such as Vinsol and Belro. The color bodies in the latter resins first must be diluted by dissolving the resins in a suitable organic solvent or mixture of solvents.

At present, no specific rules can be laid down for the design of the foregoing special filter combinations, since their selection in this laboratory has been based on cut-and-try procedures. However, further study on this problem is being planned.

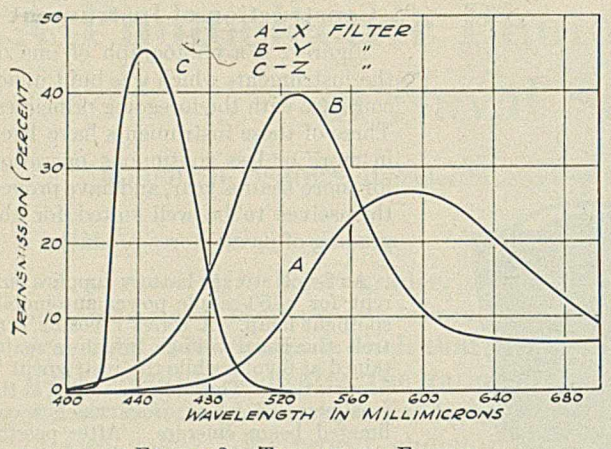

FIGURE 3. TRISTIMULUS FILTERS

A. *X* filter, 4.5-mm. Corning No. 330 + 3.0-mm. Corning No. 399
B. *Y* filter, 2.0-mm. Corning No. 450
C. *Z* filter, 1.0-mm. Corning No. 511 + 1.5-mm. Corning No. 038

Design of Filters

In Figure 3, *A*, *B*, and *C*, respectively, are the spectral transmission curves of the amber, green, and blue filters used in the instrument in conjunction with a lamp operated at a color temperature in the neighborhood of 2800° K. and an Electrocell barrier layer photocell to give first approximations to *X*, *Y*, and *Z* responses referred to Illuminant C (*6*). A Corning Aklo filter is being used in conjunction with the foregoing lamp-photocell combination to give a first approximation to the $X + Y + Z$ response. The spectral transmission curve of this filter is shown in Figure 4. For the purpose of grading, these approximations to the ideal filters have proved satisfactory. However, the need for an instrument which will evaluate the trichromatic coefficients more accurately has led to a consideration of the design of filters which will more closely approximate the ideals. The requirements for the spectral characteristics of source-filter-photocell combinations which will give *X*, *Y*, and *Z* tristimulus values have been listed by the National Bureau of Standards (*5*). Gage (*4*) has described a method by which glass filters may be selected with respect to kind and thickness to fit such requirements.

In order to evaluate x trichromatic coefficients accurately, the blue component of the *X* function must be taken into account in the filter design. Hunter (*7*) overcomes this difficulty in the measurement of *X* tristimulus values by adding a fraction of the reading obtained with his *Z* filter to that obtained with his *X* filter. In order to avoid this complication, a combination of glasses having the proper relative transmission in the blue as well as in the other parts of the spectrum is being sought. Calculations for this filter as well as for new *Y*, *Z*, and $X + Y + Z$ filters are now under way, and will be reported in a separate communication.

Operation of Instrument

The ultimate criterion for the success of an instrument designed to replace visual methods of grading must be its closeness of agreement with visual observations. Accordingly, a number of representative samples of both wood and gum rosins were graded independently by eighteen more or less experienced observers. Comparisons were made visually with the official U. S. rosin standards. The observers were asked to estimate to the nearest one-tenth grade. Although this was recognized as being a difficult task, results reported by the different observers were in surprisingly good agreement. The averages of the grades assigned by the eighteen observers to two samples of gum rosin and seven of wood rosin are given in Table I, together with the photoelectric instrument readings on the same samples. The photoelectric instrument had been calibrated previously by noting the readings obtained for the official U. S. rosin standards. In practice, such a calibration is made once each day, although it has been found that only very small changes take place over periods of several days. Progressive changes do occur, however, as the color temperature of the lamp changes with age.

In the visual grading of gum rosin the factor of brightness as well as that of chromaticity must be considered. However, the photoelectric instrument grades on the basis of chromaticity alone, so that if decreases in brightness due to dirt become large, grading errors will occur if the photoelectric method is used. No difficulty is encountered in the correlation of photoelectric with visual grading of either wood rosin or reasonably clean gum rosin.

The average time for a single photoelectric grading is approximately 0.5 minute. This compares favorably with the time required by the most experienced visual graders. The chief advantage of the photoelectric method is the elimination of discrepancies caused by eye fatigue, inaccurate grading by partially color-blind individuals, errors of judgment, and the like.

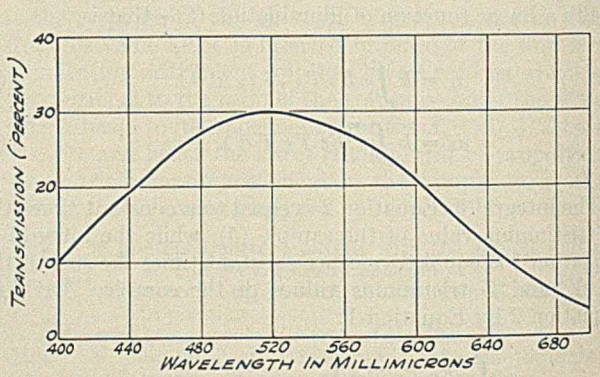

FIGURE 4. $X+Y+Z$ FILTER, 2.0-MM. CORNING NO. 398

Within limits, varying amounts of dirt or haze in gum rosins, smeared cover glasses, cracked samples, etc., introduce little or no error in the grades obtained with the instrument. Cut or poured cubes can be measured equally well. Of course, care must be taken that all samples of a given class are of the same thickness. In the case of rosins and resins, 0.875 inch is standard, while in the case of pale liquid products, 5 cm. is commonly used.

Other Uses of the Instrument

By employing "monochromatic" filters (*3*), the photoelectric grader has been used as a chemical colorimeter for the

TABLE I. COMPARISON OF VISUAL AND INSTRUMENT GRADING OF ROSIN

Sample	Instrument Grades[a]	Visual Grades
Gum rosin	I + 0.7	I + 0.5
Gum rosin	M + 0.6	M + 0.5
Wood rosin	G + 0.5	G + 0.5
Wood rosin	I + 0.0	I + 0.0
Wood rosin	M + 0.6	M + 0.6
Wood rosin	I + 0.9	I + 0.7
Wood rosin	K + 0.8	K + 0.7
Wood rosin	M + 0.1	M + 0.0
Wood rosin	H + 0.3	H + 0.3

[a] I + 0.7 means that the rosin is 0.7 grade lighter than I.

determination of small amounts of both organic and inorganic substances. In this respect, the methods employed do not, in general, differ from those described in the voluminous literature on the subject.

The tristimulus values X, Y, and Z of a sample may be measured by setting the selector switch to a position which connects the photocell directly to the meter; then, with one of the tristimulus filters in position, but with nothing else in the light beam, the iris diaphragm is adjusted until the meter reads 100 (full scale). The sample is then inserted in the beam, and the resultant meter reading is referred to a chart which gives the corresponding tristimulus value. The Y tristimulus value (brightness) is very often specified with the x and y trichromatic coefficients to describe completely the color of a transparent sample.

The instrument has also been used for the determination of haze. For this measurement, the brightness of the sample (Y tristimulus value) is compared to the known maximum brightness of a clear sample having the same chromaticity as the unknown.

Several of these instruments have been constructed in the company's shops. At the present time others are being manufactured for their use by a commercial instrument maker.

Summary

A photoelectric instrument suitable for the rapid routine color grading of transparent liquid or solid naval stores products is described. Essentially, the apparatus consists of a light source, colored glass filters, and a photocell. The design, however, is characterized by the fact that single readings obtained with the instrument are proportional to the ratio of the transmissions of a sample for light beams of two different colors. The electrical circuit is arranged so that the instrument scale may be expanded or contracted. In this manner, both light and dark colored samples may be graded. Within limits, the grades obtained with the instrument are independent of dirt, haze, or imperfections in the sample.

In addition to its use as a grader, the instrument has been used as a chemical colorimeter, to obtain tristimulus values of transparent samples, and to determine haze.

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A Simple Hydrogen Sulfide Generator

BRYANT W. POCOCK, L. SCHOLTEN, AND PAUL J. ERICKSON

Nash-Kelvinator Corporation, Lansing, Mich.

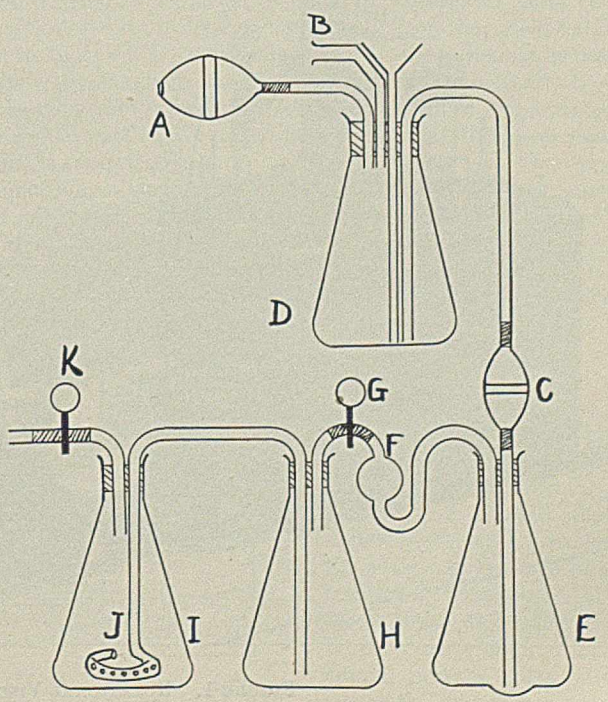
A HYDROGEN sulfide generator is a necessity in any chemical laboratory where the analysis of metals is to play an important role, particularly in these days of increasing demands for metal analysis and of correspondingly growing numbers of new control laboratories, which are springing up all over the United States.

The apparatus described is of a type which any chemist can probably construct from supplies already at hand. The parts are held together by clamps and support stands.

The most novel feature of the device is the delivery tube, J, which consists of a celluloid drinking straw purchased at a dime store and bent to form a circle at one end. The extreme end of the circle is crimped nearly together and the circle is bent to form a plane at right angles to the shaft. Small holes are bored into the top of the circle a few millimeters apart. The gas is delivered through these holes, thus increasing the area of contact between the gas and the liquid. (This is a modification of the Abson method for the recovery of asphalts from road mixes.)

The generating flask, E, is bumped outward somewhat at the bottom, to form a small interior concavity in which the acid will collect, to facilitate complete elimination of the acid by gas pressure. The reservoir, C, is a two-way rubber compression bulb, placed on a level with the bottom of the acid flask, D. Thus C will always hold enough acid to maintain a positive siphoning action.

H and F are traps, K and G are pinch clamps, and I is the precipitation flask. Ferrous sulfide sticks are placed above a layer of glass wool in E, and hydrochloric acid is poured into D through the funnel. To start the action initially, the finger is held at the safety tube, B, and acid is pumped into C and E by the rubber compression bulb, A.



High-Speed Rotational Viscometer of Wide Range

Confirmation of the Reiner Equation of Flow

HENRY GREEN
Interchemical Corporation, New York, N. Y.

IN A recent article by the writer on the tack of printing inks, (*5*) mention was made of the use of a high-speed rotational viscometer for measuring pseudoplastic materials and thixotropic plastics. Such an instrument is described in this paper, with data showing the application of the Reiner equation for determining yield value and plastic viscosity, a term employed here for the reciprocal of mobility.

The great importance of Reiner's work is not generally realized by industrial rheologists. Even Reiner has not published data tending to establish the validity of his own equation. This is regrettable, for it has caused this particular rheological contribution to remain practically unknown to industry since its initial publication in 1929.

In order to comprehend fully the advantages inherent in the rotational viscometer for measuring many types of industrial products, it is necessary to understand the nature of the rheological background immediately preceding Reiner's work.

The first important contribution to modern rheology was that of Bingham (*1*), who worked with a rather difficult medium, clay-water suspensions. Such materials have a tendency to separate, causing seepage and slippage. Bingham used a capillary-tube type of viscometer and produced flow curves by plotting force against rate of flow. So far as he could tell, he seemed to obtain straight-line relationships. The fact that the lower points of his curves fell off toward the origin was attributed to possible seepage and slippage, and it was also assumed that all curves for a given material intersected the force axis at the same point, regardless of the dimensions of the capillary used. With these ideas in mind Bingham felt justified in writing the equation of flow for plastics in capillary tubes as follows:

$$\text{Mobility} = \frac{8L\ V/t}{\pi R^4\ (F - f)} \qquad (1)$$

where R and L are the radius and length of the capillary, V/t is the volume of flow per second, F is the force causing the flow, and f is the intercept on the pressure axis. This is simply the well-known equation of liquid flow with the intercept, f, introduced. Obviously, it can fit only a linear flow curve.

Later, Bingham and Green (*2*) working with more tractable materials, pigments suspended in oil, showed that f was not independent of R and L. The lower points, however, still fell off toward the origin and this condition was still believed to be caused by seepage and slippage. Subsequent careful analysis showed that the pigment-vehicle ratio was exactly the same for the low points on the curve as for the high ones, proving that seepage could not be responsible for the condition at the lower end of the curve. This led to the micro-

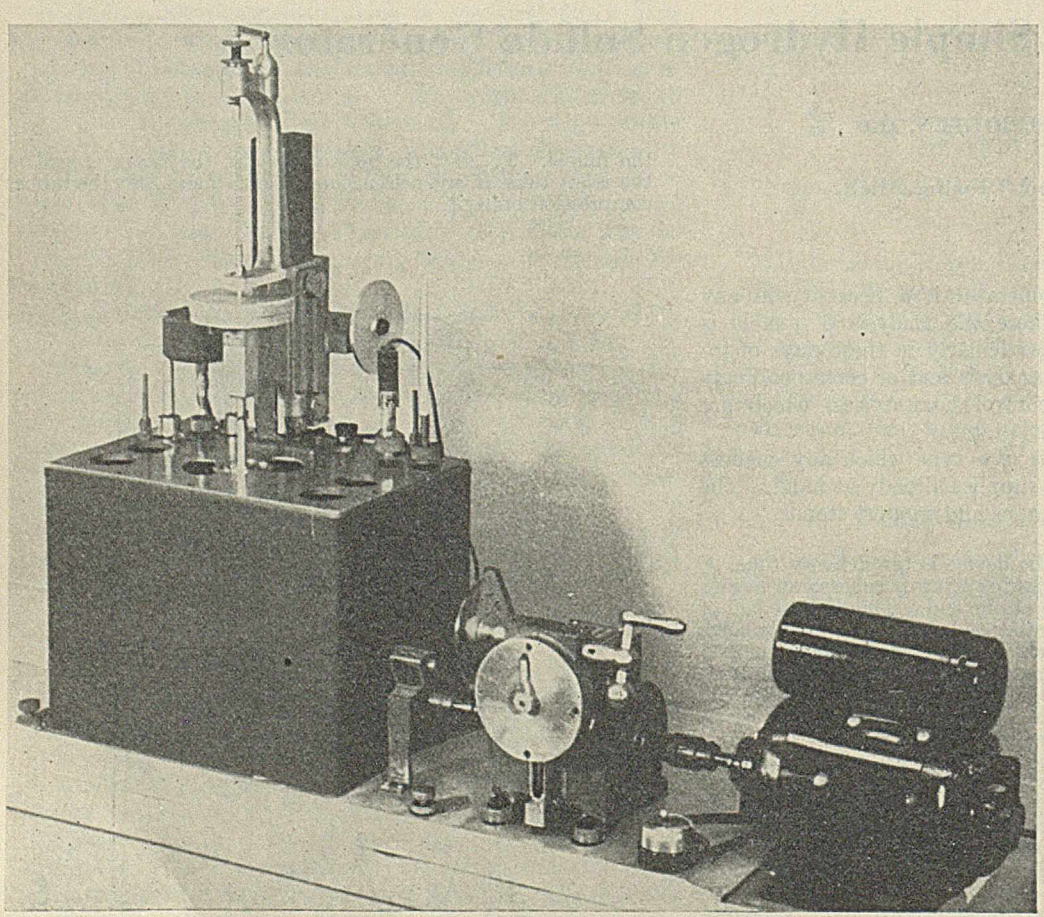


FIGURE 1. ROTATIONAL VISCOMETER

scopical examination of plastic flow in capillary tubes (*7*, *8*), which established the existence of plug flow and slippage.

Plug flow occurs whenever the force of flocculation is strong enough to hold the body of pigment together, a condition that exists at the lower end of the curve where the applied force is insufficient to cause telescopic shearing. As the force is raised, however, shearing commences, starting at the capillary wall and developing inward as the force is increased. This means that the model of flow is changing continuously until a state of complete laminar flow ensues; and it was believed that this state was attained at a finite distance from the origin.

Plug flow was also seen to be a contributory cause of slippage. In the case of pigment-oil suspensions the plug at the wall was always observed to be lubricated with a thin layer of the oil vehicle when examined microscopically. Since such a vehicle is a Newtonian liquid, it will flow under any pressure, no matter how small; hence the slightest applied force induced the lubricated plug to flow—i. e., to slip en masse. Obviously, if a small force causes slippage, larger forces cause more slippage, and the entire plastic flow curve becomes misleading by having imposed upon it a slippage flow curve (Figure 5).

Realizing that plug flow and slippage must modify the Bingham equation, Buckingham (*3*) in 1921 deduced the following equation as a substitute:

$$V/t = \frac{\pi R^4}{8LU}\left(F - \frac{4f}{3} + \frac{f^4}{3F^3}\right) + \frac{\pi R^3 e\phi F}{2L} \qquad (2)$$

where U, used throughout this paper as the reciprocal of mobility, is the plastic viscosity of the material, ϕ is the fluidity of the vehicle, and e is the thickness of the lubricating layers. The last term of Equation 2 gives the volume of flow per second caused entirely by slippage. [In the author's previous papers on tack (*5*, *6*) the symbol μ is used to designate plastic viscosity.]

Buckingham's equation, though resembling the experimentally determined flow curve, failed to coincide with it at its most important point—the place where the initial shearing of the plug occurs, which unfortunately, cannot be found by inspecting the experimental curve. It is necessary to know the location of this point in order to calculate yield value. The attempt to derive the yield value from the equation of the curve proved to be impracticable. Consequently, while Buckingham's equation is of great theoretical importance, it has little useful laboratory value.

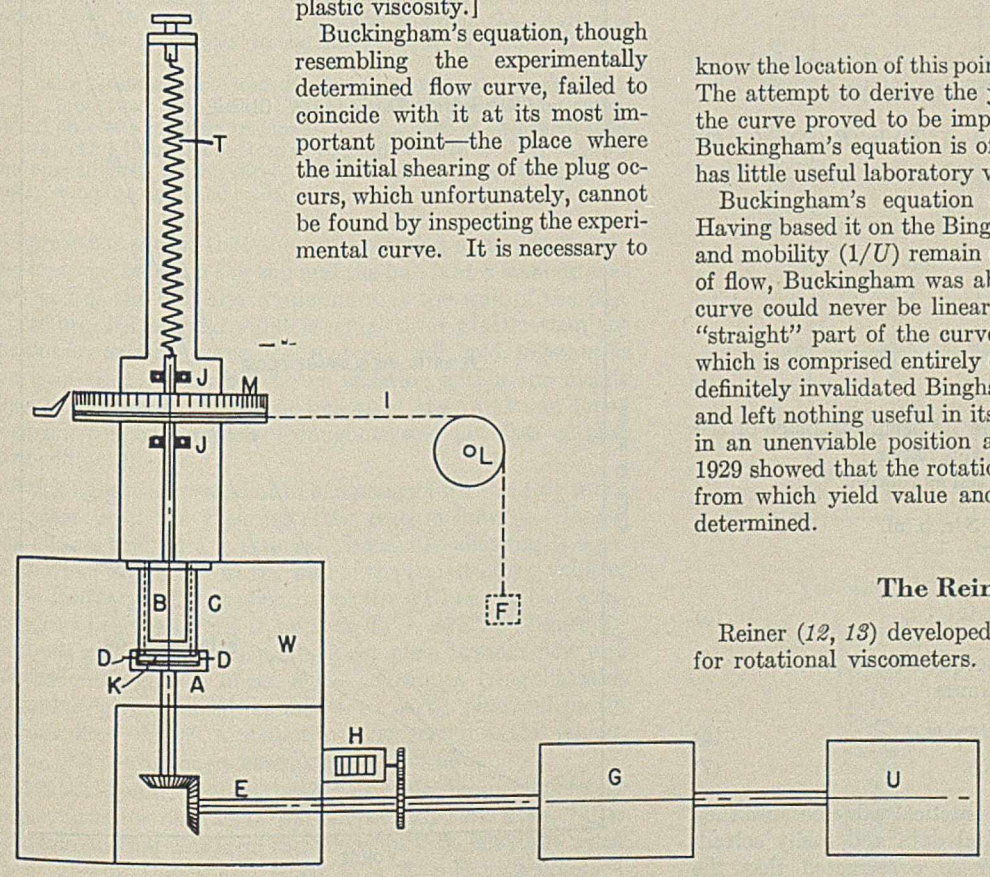


FIGURE 2. DIAGRAM OF VISCOMETER

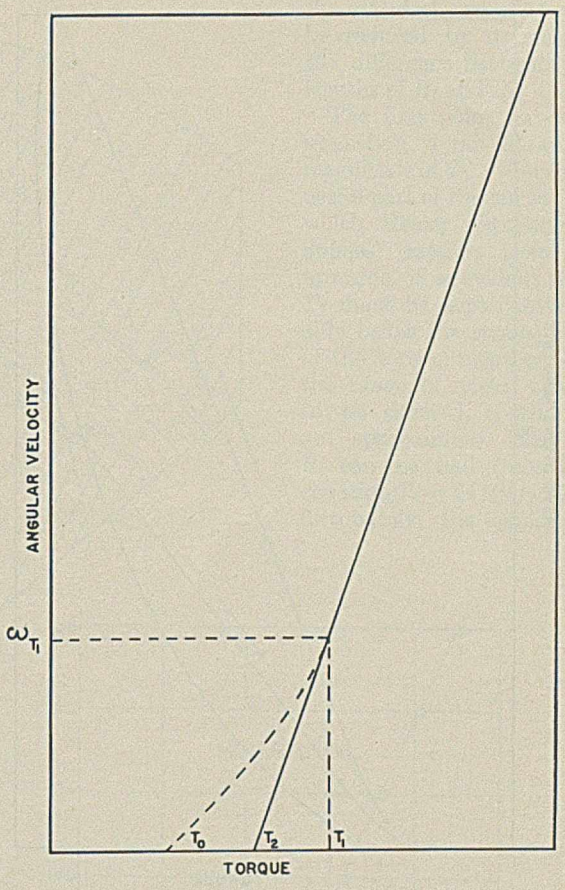


FIGURE 3

Buckingham's equation cannot be dismissed, however. Having based it on the Bingham assumption that yield value and mobility ($1/U$) remain constant during a change in rate of flow, Buckingham was able to show that the plastic flow curve could never be linear for capillary tubes and that no "straight" part of the curve exists except at the lower end, which is comprised entirely of slippage flow. This discovery definitely invalidated Bingham's equation for capillary tubes and left nothing useful in its place. Industrial rheology was in an unenviable position and remained so until Reiner in 1929 showed that the rotational viscometer gives flow curves from which yield value and plastic viscosity can easily be determined.

The Reiner Equation

Reiner (*12*, *13*) developed the theoretical equation of flow for rotational viscometers. He used the Bingham assumption of the constancy of f and U and showed that under these circumstances the plastic flow curve in a rotational viscometer becomes linear at a finite distance from the origin. The curved portion exists only where the flow is not com-

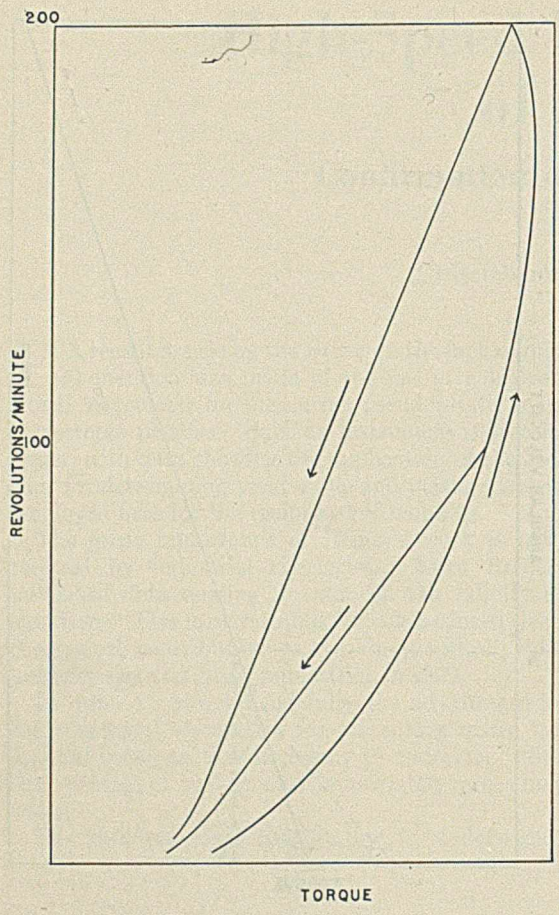


FIGURE 4

pletely laminar—i. e., in the transition period from total plug to complete laminar flow. The Reiner equation is

$$\Omega = (T/4\pi hU)(1/R_b^2 - 1/R_c^2) - (f/U) \ln (R_c/R_b) \qquad (3)$$

where

U = plastic viscosity
f = yield value
Ω = angular velocity
T = torque
R_b = radius of the bob
R_c = radius of the cup
h = height of the bob

(In the original Reiner equation R^4 occurs in place of the correct term, R^2, used throughout this paper.)

Reiner's equation can be rewritten as follows:

$$U = 9.55(T - T_2)\, S/\text{r. p. m.} \qquad (4)$$

and

$$f = T_2 C \qquad (5)$$

where T_2 = intercept on the torque axis
r. p. m. = revolutions per minute

$$S = (1/R_b^2 - 1/R_c^2)/4\pi h \qquad (6)$$

$$C = S/\ln (R_c/R_b) \qquad (7)$$

Equations 4 and 5 are of great practical value because they are applicable to the experimental data and easily solved, but they demand a viscometer so constructed that the necessary data can be obtained.

The Rotational Viscometer

The instrument described in this paper (Figure 1) is for the consistency range covered by such materials as oils, varnishes, paints, and printing inks. The object in designing the viscometer in the manner described here is (1) to obtain consistency curves, and (2) to eliminate certain detrimental features usually inherent in commercial rotational instruments. These faults are likely to be: either no means or very inadequate means for maintaining constant temperature control while the cup is rotating; no way of changing the speed of cup rotation quickly and noting immediately the new r. p. m. (the necessity for this is discussed in connection with thixotropy); insufficient strength in the torsion members (springs, wires, tapes), hence measurements at high speeds cannot be obtained with heavy materials without damaging these members; and no simple means for calibrating the torsion members without resorting to light and heavy standard oils, the viscosities of which are determined by capillary-tube methods. Light oils cannot be used for the heavy members. The serious mistake involved in using heavy oils for calibration will be shown in a subsequent paper by Ruth N. Weltmann.

The Viscometer

The essential parts of the viscometer are shown diagrammatically in Figure 2. They consist of a synchronous motor, U; a device, G, for quickly changing the speed of the shaft, E; a constant temperature bath, W; a rotatable cup, C, for holding the material being tested; a bob, B, suspended in the material; a torsion member T, from which B is suspended; and a scale, M, to record the degrees (arc) through which B is turned by the viscous or plastic drag imposed upon it.

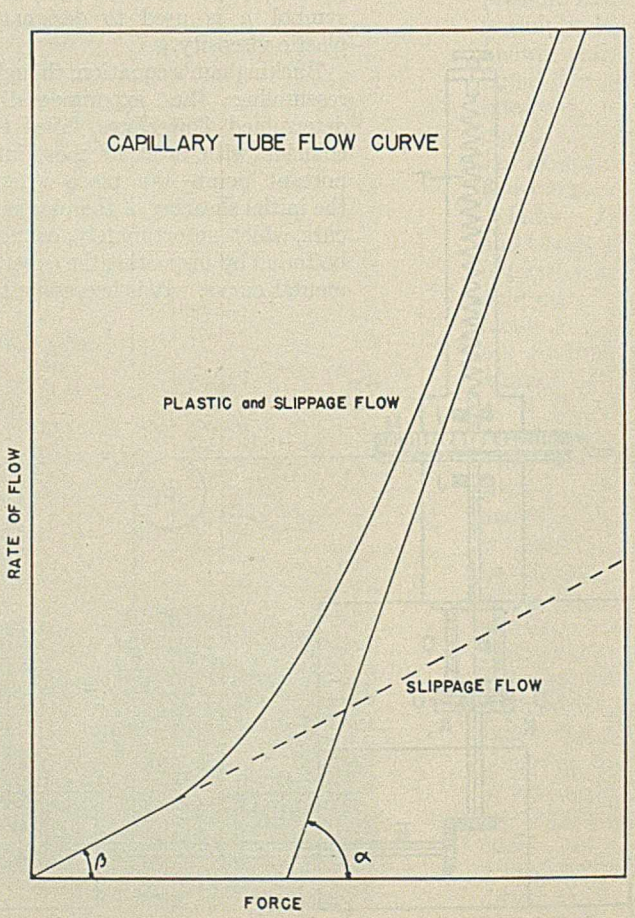


FIGURE 5

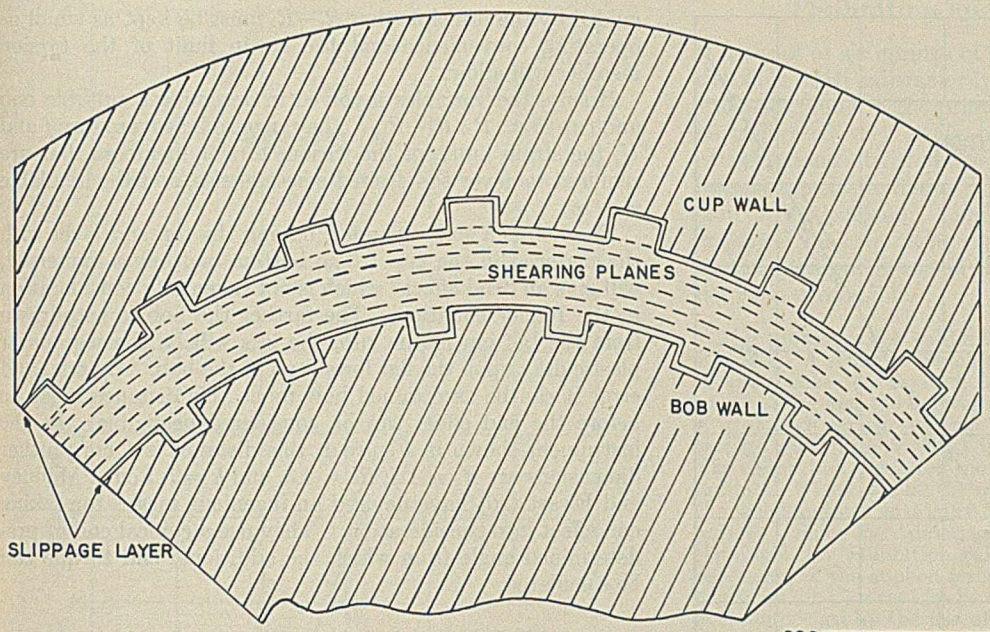


FIGURE 6. PLAN FOR REDUCING SLIPPAGE

For high-speed work on materials as heavy as lithographic inks, the viscometer must be substantially built. The motor, in the instrument shown in Figure 1, is 0.25 horsepower and can produce a maximum cup, C, speed of 400 r. p. m. The transmission, G, is made by the Briggs and Stratton Corporation and modified by changing somewhat the original speed-indicating dial, adding a fine-adjustment dial and a suitable handle. By turning the handle on the transmission, the cup speed can be continuously varied from 10 to 400 r. p. m., without stopping the rotation of the cup. This is essential in the measurement of thixotropic systems.

C has a removable bottom, K, for convenience in cleaning; this is an important time saver in plant control work. The cup is keyed onto the rotating platform, A, by means of two small pins, D, projecting from the bottom of the cup (Figure 2). By twisting the cup slightly in the direction of rotation, it is released and easily removed from the bath.

Reiner has shown that the force existing at any instant in the material between the cup and the bob is at a maximum at the wall of the bob and a minimum at the wall of the cup. Therefore, if the yield value is equal to or greater than the maximum existing force, the material will hold together as a whole—i. e., there will be no shearing within the plastic mass. If the yield value is less than the minimum force, shearing will be complete throughout and no mass or plug flow will occur.

Buckingham showed that in a capillary tube shearing is not complete until the shearing force reaches infinity. Reiner has shown that in a rotational viscometer shearing is complete when the torque at the wall of the cup attains a value of $T_1 = 2\pi R_c^2 hf$, and that shearing at the wall of the bob commences when the torque is equal to $T_0 = 2\pi R_b^2 hf$ (Figure 3). Torques greater than T_1 produce complete laminar flow and consequently give a linear curve. Torques lying between T_0 and T_1 give a mixed regime—i. e., partly plug and partly laminar flow—hence, a nonlinear curve ensues in this region, owing to a continuously changing model of flow.

It is the aspiration of all rheologists to produce a completely linear curve for plastics of the nonpseudoplastic type. It is now evident that this ideal can be attained theoretically when $T_0 = T_1$—in other words, when $R_b = R_c$. From a practical consideration this is impossible, but Reiner has shown that the extent of curvature can be reduced by decreasing the difference between the lengths of R_c and R_b.

The first point for consideration is the allowable magnitude of T_1. Since the useful part of the curve (for which Reiner Equation 3 applies) extends from T_1 upwards, it is evident that T_1 must be kept considerably below the strain limit of the torsion member. If the range of yield values to be covered is known, an approximate idea of R_c can be had from the equation $T_1 = 2\pi R_c^2 hf$. Unfortunately, the capillary-

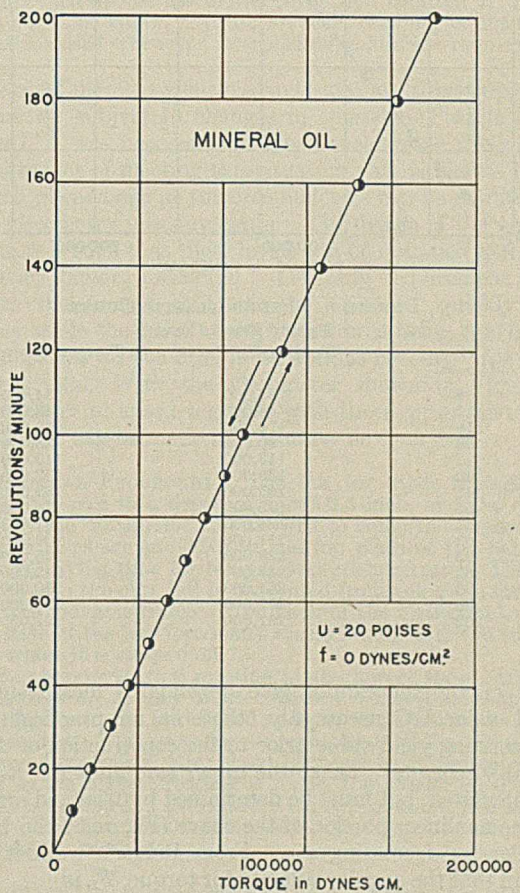


FIGURE 7. CURVE FOR NEWTONIAN LIQUID

Down Curve

Torque, T	R. p. m.	T/r. p. m.
181,500	200	907.5
161,980	180	899.9
143,960	160	899.7
125,980	140	899.9
107,840	120	898.7
89,860	100	898.6
80,880	90	898.7
71,890	80	898.6
62,900	70	898.6
53,920	60	898.7
44,930	50	898.6
35,950	40	898.7
26,960	30	898.7
17,970	20	898.5
8,990	10	899.0

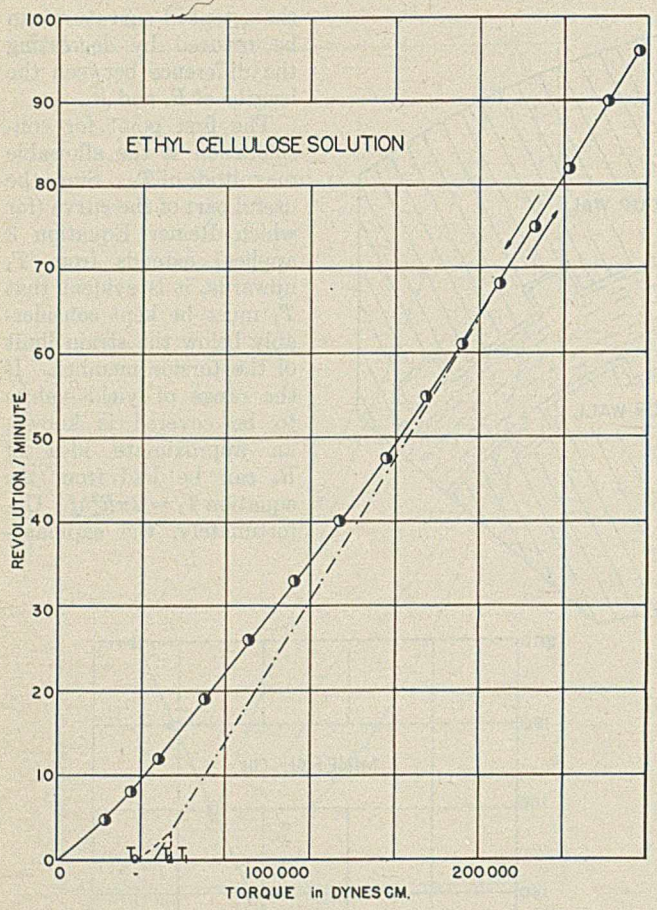


FIGURE 8. PSEUDOPLASTIC CURVE

R. p. m.	Up and Down Curve Torque, Up Curve	Torque, Down Curve
8	35,000	34,000
12	48,000	48,000
19	70,000	69,000
26	90,000	88,000
33	113,000	110,000
40	135,000	132,000
47	155,000	152,000
55	175,000	173,000
61	193,000	191,000
68	211,000	209,000
75	228,000	226,000
82	243,000	242,000
90	261,000	260,000
96	277,000	276,000
102	291,000	291,000

tube viscometer cannot give dependable measurements of yield value. Consequently, there is no practical way of determining yield value prior to the construction of the rotational viscometer; hence the upper safe limit for R_c cannot be calculated, but must be determined by trial and error.

The nonlinear portion of the curve (Figure 3) can be made smaller by decreasing ω_{T_1}. From Reiner's work it can be shown that the angular velocity for torque, T_1, is

$$\omega_{T_1} = \frac{f}{U}\left[\frac{R_c^2}{2R_b^2} - \ln\left(\frac{R_c}{R_b}\right) - 1/2\right] \qquad (8)$$

From this equation it is obvious that if f and U were known and a particular ω_{T_1} desired, satisfactory values for R_c and $R_c - R_b$ could be calculated. Since f and U are not known, except for values obtainable with capillary-tube viscometers, the investigator is again forced to resort to trial and error methods. Though ω_{T_1} is not directly dependent on h (see Equation 8) the ultimate selection of R_c and R_b will be influenced by U, the plastic viscosity. This factor, h, is a good starting point. Any h can be selected that the operator finds convenient, but the rest of the procedure is trial and error, guided by the principle that $R_c - R_b$ must be kept as small as operating convenience and the strain limit of the torsion member will allow.

Briefly, the variables involved in designing a suitable bob and cup are: R_c, $R_c - R_b$, h, the range to be covered by f and U, the strain limits of the various torsion members that are required to cover the desired consistencies, and the available r. p. m.

The bob is a solid cylinder, having the top end level with the material in the cup. The bottom end being immersed, will give an "end effect" which is not taken into consideration in the Reiner equation. The farther the bob is withdrawn from the bottom of the cup, the less will be the viscous or plastic drag upon the flat lower end of the bob. By trial and error it can be ascertained how much this distance must be before the end effect can be considered negligible. In the instrument shown in Figure 1, this distance is 1 cm.; other dimensions are $R_c = 1.5$, $R_b = 1.3$, and $h = 5.1$ cm. Mooney and Ewart (*10*) have devised an ingenious means for taking end effect into consideration. They use a conical end of predetermined angle from which the additional end torque can be calculated.

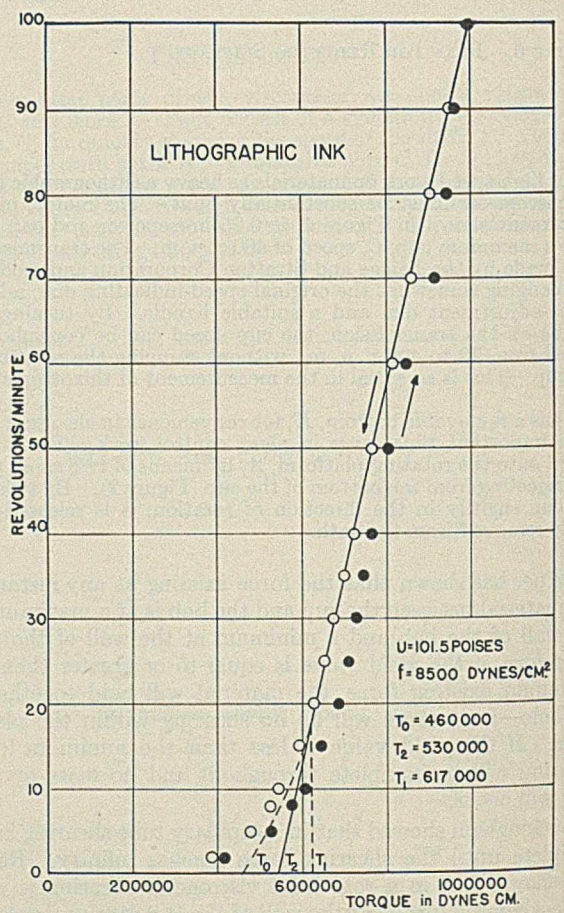


FIGURE 9. TYPICAL CURVE FOR THIXOTROPIC PLASTIC

Down Curve. T_2 = 320,000 Dynes per Cm.

Torque, T	R. p. m.	$(T - T_2)/r.\ p.\ m.$
1115×10^3	100	7.95×10^3
1040	90	8.00
945	80	7.81
875	70	7.93
788	60	7.80
725	50	8.10
640	40	8.00
600	35	8.00
558	30	7.93
518	25	7.92
468	20	7.40
420	15	6.67
355	10	3.50
335	8	1.88

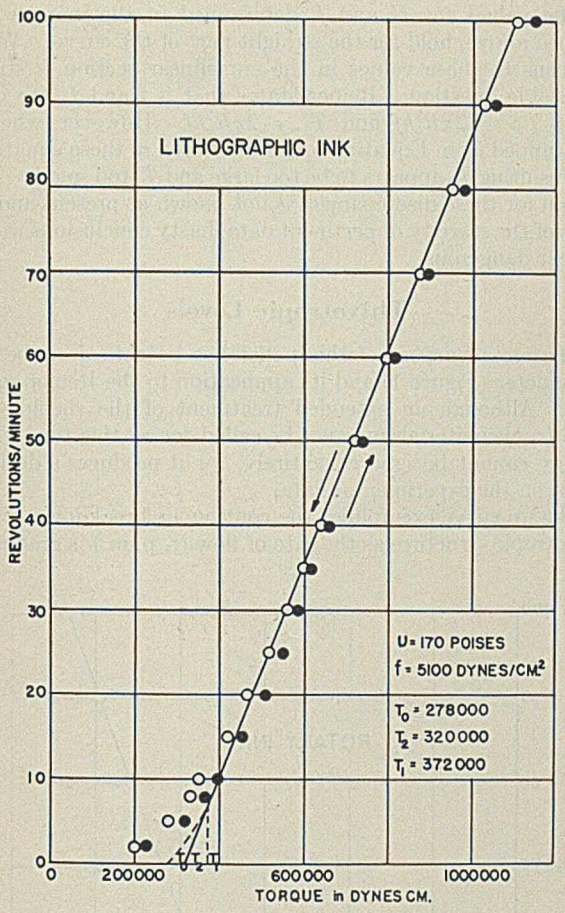


FIGURE 10. TYPICAL CURVE FOR THIXOTROPIC PLASTIC

Down Curve. T_2 = 530,000 Dynes per Cm.

Torque, T	$R.\ p.\ m.$	$(T - T_2)/r.\ p.\ m.$
990 × 10³	100	4.60 × 10³
958	90	4.76
900	80	4.63
860	70	4.71
810	60	4.67
760	50	4.60
720	40	4.75
700	35	4.86
665	30	4.50
650	25	4.80
620	20	4.50
585	15	3.67
538	10	0.80
518	8	..
470	5	..

The bob, B, is at the lower end of a vertical shaft which rotates on two sets of ball bearings, J, one set above and the other set below scale M. This plan gives great stability to the system, so that the bob once accurately centered with the cup remains that way indefinitely. The torsion medium is a helical spring, T. When in operation this spring supports the shaft and bob, thereby eliminating friction except the negligible amount existing in the ball bearings. The ball bearings simply function as a guide, keeping the shaft and bob rigidly centered. The bob, shaft, scale, and torsion spring are all attached to a single frame support which can be raised to bring the bob sufficiently above the top of the cup so that the cup can be removed when desired.

One of the principal faults of commercial rotational viscometers is their lack of adequate temperature control. Usually such instruments are made so that the surrounding bath must rotate with the cup making temperature control difficult. This difficulty has been completely overcome in the instrument described here. Because the cup is rotated by a shaft penetrating the bottom of a substantial bath, the necessity for an inadequately small rotating bath is eliminated, and thermostatic control can be maintained. In addition there is ample room for a stirrer, a cooling coil, and a thermometer, all of which are shown in Figure 1.

Calibration and Use of Viscometer

A series of six springs of different torsion constants is desirable in order satisfactorily to cover the entire range of consistencies found in the printing ink field. These springs can be calibrated very easily on the viscometer. Each spring can withstand a twist of one revolution without being strained beyond the elastic limit. The instrument is provided with a stop for this purpose. Liquids of known viscosity are usually employed for calibrating purposes, but this is not necessary on this instrument and in the case of the heavy springs it is not even permissible.

The procedure for calibration is shown diagrammatically in Figure 2. A string is attached to and wrapped around the scale M and thence over a wheel, L. Various weights, F, are attached to the string and the degrees of rotation of M are noted. When F is plotted against the scale reading, a linear curve (for helical springs and straight wires) intersecting the origin is obtained. The calibration value for the spring is the torque ($F \times g$ times radius of M) divided by the scale reading in degrees of arc. F is the weight shown in Figure 2 and g is the acceleration due to gravity. Since the calibration curve is linear and commences at the origin, the calibration value of the spring is a constant independent of the applied force. The scale on the variable-speed transmission, G, must also be calibrated in terms of r. p. m. This is accomplished by the use of the revolution counter, H, and a stop watch. The curve, r. p. m. *vs.* scale reading, is not linear and must be used whenever interpolated values are required.

Since most pigment vehicle suspensions are thixotropic and consequently subject to changes in consistency while being measured, it was necessary to give considerable thought to the best means of meeting this situation. It is shown below that such phenomena as thixotropic levels can be maintained during viscometry measurements. The design of the present instrument is such that these levels can be obtained and their consistency factors measured. The only requirement is to have an instrument that can be operated quickly and smoothly while the speed of cup rotation is being constantly changed except for the brief interruptions necessary for reading the scales. With the viscometer shown in Figure 1, thirty changes of speed together with the r. p. m. and scale (M) readings can be made in 3 minutes or even less.

OPERATIONAL PROCEDURE. The ink (or other material) is placed in the cup to a depth of about 0.5 inch, and the cup is keyed into the viscometer and allowed to come to temperature. Additional holes are provided in the top plate of the bath for extra cups, saving time for temperature maintenance. The bob is lowered into the cup, but is prevented from going too far by a stop on the movable frame at the back of the instrument. The introduction of the bob forces any excess ink up over the edge of the cup where it is scraped off.

The cup is now started rotating at the lowest speed, and the scale readings on M and G are recorded. The handle on G is turned slightly to the next speed and the two scale readings are again recorded. This procedure is repeated until the highest desirable speed is reached, after about 15 speeds have been recorded. As soon as the highest reading is made, the handle on G is set into reverse motion and a downward curve is obtained in a similar manner. This also should comprise about 15 points before the lowest speed is reached.

The up and down curves are now plotted, by plotting r. p. m. *vs.* torque (scale M reading times calibration value for the spring). If the material is an ordinary printing ink, it will be thixotropic and the up and down curves will not coincide. This condition is due to thixotropic breakdown. The two curves plotted together will make a loop which will be referred to as a "hysteresis loop". A large loop means considerable breakdown and, conversely, a small loop, small breakdown. No loop at all would indicate no detectable thixotropy as far as the viscometer is concerned. Materials that possess a yield value but give no hysteresis loop are considered by some investigators to be highly thixotropic. In this case complete thixotropic breakdown upon agitation is assumed to take

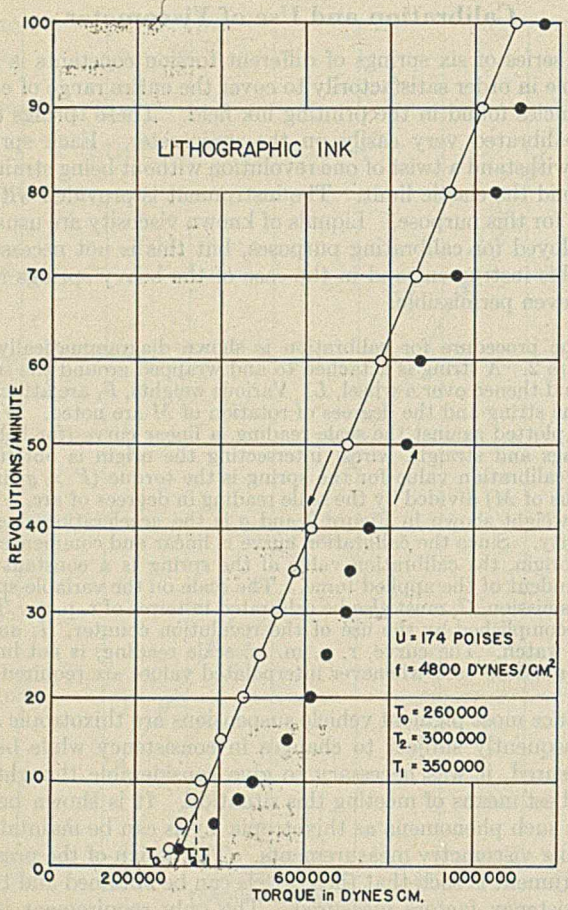


FIGURE 11. TYPICAL CURVE FOR THIXOTROPIC PLASTIC

Down Curve. T_2 = 300,000 Dynes per Cm.

Torque, T	$R.\ p.\ m.$	$(T - T_2)/r.\ p.\ m.$
1090 × 10³	100	7.90 × 10³
1018	90	7.98
942	80	8.03
868	70	8.11
780	60	8.00
702	50	8.04
622	40	8.04
585	35	8.14
538	30	7.93
485	25	7.40
458	20	7.90
408	15	7.20
360	10	7.00
340	8	5.00
318	5	3.60
288	2	..

place so rapidly that a loop cannot be recorded by the viscometer. If such were the truth, a material of this kind would show, after standing unagitated for awhile, a very marked change in consistency when suddenly touched or stirred with a spatula, but nothing to indicate a consistency change can be observed or felt. In addition, one would have to argue that the larger the hysteresis loop, the smaller the amount of thixotropy, which is contrary to common sense.

When the down curve is compared with the up curve, a marked difference will be noticed. The up curve is bow-shaped and lacks smoothness. The down curve is smooth and linear except at its extreme lower end. The linearity of the upper section of this curve is in conformity with Reiner's prediction and, therefore, indicates constant yield value and constant plastic viscosity in that region. After the experimental data obtained with the viscometer are plotted, a straight line is drawn through the maximum number of points on the down curve that will fall upon it. This line intersects the torque axis at T_2. From T_2 and the slope of this line, yield value and plastic viscosity are calculated by Equations 4 and 5.

The values for U and f, determined in the manner described above, hold for the straight part of the curve. What happens to these values in the curvilinear section is still a debatable question. Reiner states that if f and U are constant $T_0 = 2\pi R_b^2 hf$ and $T_1 = 2\pi R_c^2 hf$. However, when f, determined from Equation 5, is substituted in these equations the resulting T_0 appears to be too large and T_1 too small. The reason for these discrepancies is not known at present and, in view of the scarcity of pertinent data, hasty conclusions would appear dangerous.

Thixotropic Levels

The main purpose of this paper has been to describe the viscometer (Figure 1) and its application to the Reiner equation. Although an extended treatment of the rheology of thixotropic materials may not be called for at this time, thixotropy cannot be ignored entirely, for it produces a decided effect on the experimental data.

The up curve exemplifies the continuous breakdown of the thixotropic structure as the rate of flow (r. p. m.) is gradually

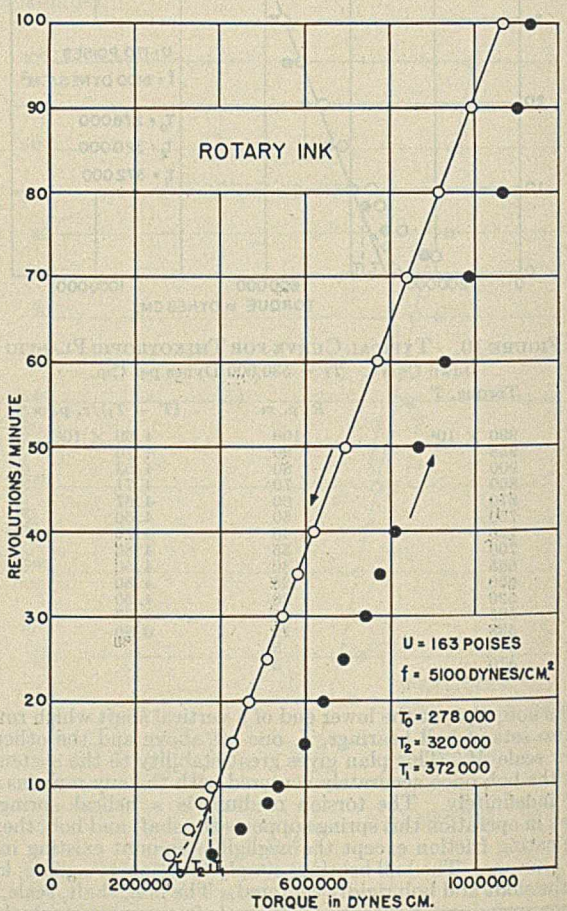


FIGURE 12. TYPICAL CURVE FOR THIXOTROPIC PLASTIC

Down Curve. T_2 = 320,000 Dynes per Cm.

Torque, T	$R.\ p.\ m.$	$(T - T_2)/r.\ p.\ m.$
1062 × 10³	100	7.42 × 10³
1990	90	7.44
905	80	7.31
838	70	7.40
770	60	7.50
688	50	7.36
615	40	7.38
580	35	7.43
545	30	7.50
502	25	7.28
460	20	7.00
420	15	6.67
378	10	5.80
358	8	4.75
325	5	1.00
280	2	..

increased. The down curve is maintained linear without any conscious effort on the part of the operator—i. e., there are no requirements other than continuous uninterrupted work. Obviously if the viscometer is stopped long enough, thixotropic buildup will become effective and linearity will cease. In order to obviate this possibility the viscometer has been designed to make quick and easy operation possible; hence the dozen or more measurements on the down curve can be accomplished in less than a minute.

When the above procedure is followed, linearity of the down curve results if pseudoplasticity is not involved, indicating that there exist at that time a constant yield value and plastic viscosity. The constancy of these factors shows that a temporary stability is maintained in the thixotropic structure; hence, a "thixotropic level" has been reached, the exact position of which is influenced by the pretreatment which the material has received. This includes handling and special treatments such as milling, etc., that might be given to the material prior to the test. Pretreatment covers the entire history of the material before commencing the down curve. The thixotropic breakdown received during the measurement of the up curve is one of the most important factors involved here. If the up curve is stopped at 200 r. p. m. the material will have received more breakdown than if 100 r. p. m. had been selected for the upper limit; therefore the curve will be shifted toward the ordinate. Consequently, for plant control purposes, the procedure for obtaining rheological data on thixotropic systems must be rigidly standardized (Figure 4).

The temporary maintenance of linearity is probably due to two factors. Normally a thixotropic substance breaks down more quickly than it builds up. On the down curve the speed of flow is being decreased, so that no further breakdown can be expected; also an appreciable buildup evidently takes more time than is employed for the completion of the down curve. Consequently the down curve can show no change in consistency, and linearity results.

The lack of coincidence of the up and down curves has been pointed out in the literature (*9*, *11*, *13*) at various times, but apparently nowhere have thixotropic levels been emphasized or discussed. This could be explained on the assumption that a suitable commercial viscometer had not been built for the purpose. These levels, however, are of great importance to investigators who are compelled to work with thixotropic systems, for they constitute something far more substantial than the usual one-point measurements made on unstable materials.

The hysteresis loop criterion for thixotropy must not be confused with the Goodeve (*4*) "coefficient of thixotropy". Goodeve's coefficient is the intercept which the curve makes on the force axis—a function of yield value. From the viewpoint presented in this paper the magnitude of yield value is not quantitatively related to the area of the hysteresis loop and, therefore, bears no quantitative relation to thixotropic breakdown and buildup.

The following questions are often asked: How far can the down curve (Figure 4) be shifted toward the ordinate by increasing the agitation—i. e., by raising the upper limit of the r. p. m.? Can all thixotropic materials be reduced to Newtonian liquids if sufficiently high rates of flow are used? It is doubtful if experimentation can give a conclusive answer to either question, for no matter how high the r. p. m. employed, it can always be argued that if higher r. p. m. had been available the results might have been different. There is, however, experimental evidence showing that the rate of shift toward the ordinate decreases as the r. p. m. is uniformly increased. This indicates that in the case of pigment suspensions, like heavy printing inks, an ultimate position for the curve might be attained without the yield values actually becoming zero. On the other hand, thixotropic materials unquestionably exist that can be reduced by agitation to a state where they give complete Newtonian flow.

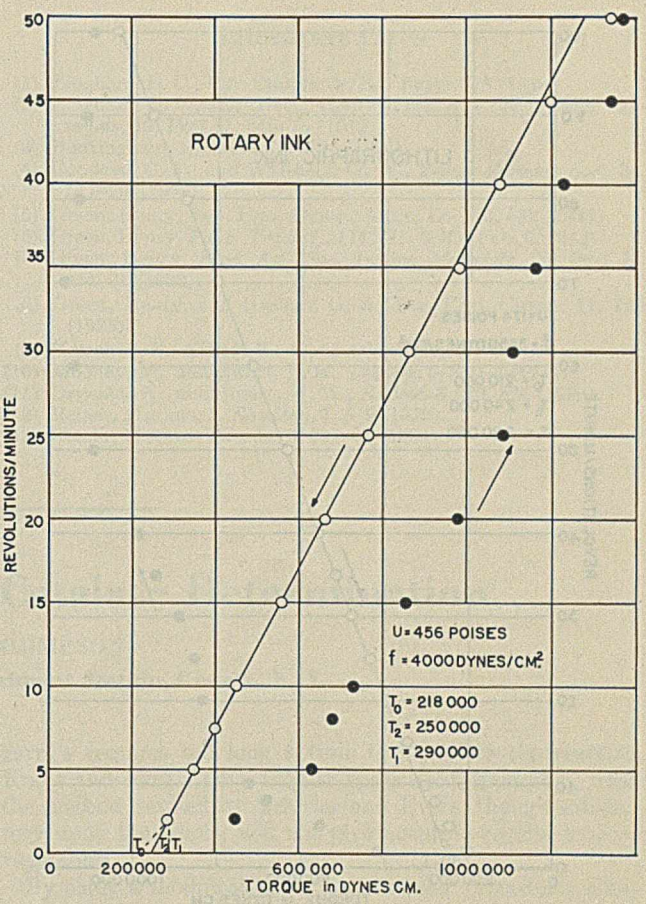


FIGURE 13. TYPICAL CURVE FOR THIXOTROPIC PLASTIC

Down Curve. T_2 = 250,000 Dynes per Cm.

Torque, T	$R.\ p.\ m.$	$(T - T_2)/r.\ p.\ m.$
1342 × 10³	50	21.8 × 10³
1200	45	21.1
1080	40	20.8
990	35	21.1
855	30	20.1
752	25	20.1
645	20	19.8
550	15	20.0
452	10	20.2
400	8	18.8
350	5	20.0
288	2	19.0

Slippage

One of the great virtues of the rotational viscometer is that it reduces slippage in most cases to a negligible amount. Exceptions will be found where syneresis occurs, but this, an abnormal condition, is not likely to be found in the field of materials covered by this article. Slippage arises from the viscous flow (Newtonian) of the lubricating layer of vehicle which always exists where the material contacts the wall of the viscometer. For any given material the thickness of this layer is the same, whether a capillary tube or rotational viscometer is employed. In the case of the capillary tube, the thickness of this layer often constitutes a substantial percentage of the radius; consequently, the flow curve contains a substantial proportion of slippage flow. This condition completely changes the shape and position of the curve, so that plastic viscosity calculated from its tangent in the customary manner might easily contain an error of 50 per cent or over. Angle α is too great by an amount equal to angle β. Unfortunately, β is very difficult to determine with sufficient

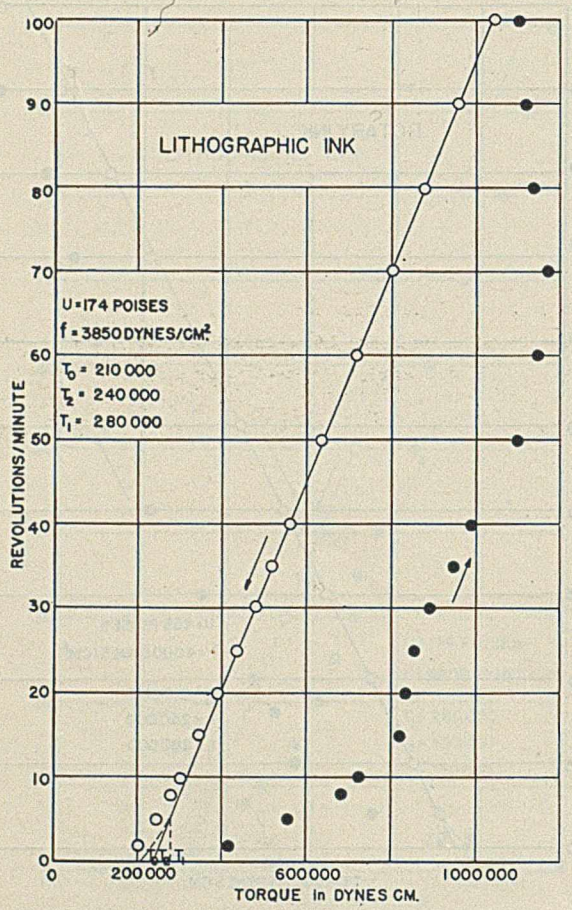


FIGURE 14. TYPICAL CURVE FOR THIXOTROPIC PLASTIC

Down Curve. T_2 = 240,000 Dynes per Cm.

Torque, T	$R.\ p.\ m.$	$(T - T_2)/r.\ p.\ m.$
1045 × 10³	100	8.05 × 10³
953	90	7.92
863	80	7.79
788	70	7.83
717	60	7.95
633	50	7.86
560	40	8.00
515	35	7.88
478	30	7.93
438	25	7.92
390	20	7.50
348	15	7.20
302	10	6.20
280	8	5.00
248	5	1.60
203	2	..

accuracy, and consequently corrections for slippage are not usually made (Figure 5).

In the rotational viscometer the slippage layer is relatively thin compared to the distance between the bob and cup, thus reducing slippage flow to an undetectable amount. This can be demonstrated experimentally. The capillary tube is smooth-walled and therefore ideal for permitting slippage. The wall of the bob and cup of the rotational viscometer, however, can be roughened, grooved, or altered, to reduce slippage. If the plan shown in Figure 6 is carried out with both the bob and cup walls grooved, slippage should be reduced considerably, if not eliminated altogether. If the width of the groove is equal to half the distance between the grooves, the area over which slippage can take place is reduced 33 per cent. Such a scheme has been carried out with printing inks and with similar pigment suspensions known to produce slippage when run in capillary tubes. The results were negative—i. e., no differences in yield values and plastic viscosities could be detected whether the material was run in a grooved or ungrooved viscometer. It is fairly safe to conclude, therefore, that if a reduction of at least 33 per cent of the slippage area does not produce measurable results, the entire slippage flow is negligible.

Pseudoplasticity

Certain types of materials, such as solutions of rubber, resins, and cellulose esters, give nonlinear curves, when sufficiently concentrated. Bingham has called these substances pseudoplastics and Ostwald refers to them as having "structural viscosity". Reiner has made an extensive study of the subject and states that the rheological characteristics of a pseudoplastic are a variable coefficient of viscosity and an absence of a real yield value.

From a practical viewpoint there is no convenient way of determining the controlling factors (constants) of the pseudoplastic curve. The initial viscosity at the beginning of the curve near the origin can be obtained approximately by taking a one-point measurement at the lowest r. p. m. This viscosity value is one of the constants of the equation. "Apparent viscosities" can also be calculated at any desirable r. p. m., if such calculations have a practical technical value. A pseudoplastic curve is shown in Figure 8.

Accuracy and Precision

In determining the accuracy of the viscometer, it is necessary to employ stable substances like Newtonian liquids, preferably using liquids of 20 poises or under. Such materials can be measured satisfactorily with a capillary-tube viscometer and so can be used for ascertaining the accuracy of any other type of viscometer.

One of the standard oils measured and sold by the National Bureau of Standards was obtained and its viscosity determined with the rotational viscometer. The torsion member was calibrated by the weight method described here. It was found that the Bureau of Standards' value could be checked with the rotational viscometer readily to within ±1.0 per cent. Measurements of plastic viscosity of thixotropic inks, using a definite r. p. m. for the upper limit, can normally be duplicated to within ±5.0 per cent. For practical routine work in industrial plants this degree of precision is satisfactory, especially where the viscosity range covered is as wide as in the oil, paint, and printing ink industries. In regard to checking yield values, the instrument shown in Figure 1 gives satisfactory results in the neighborhood of 1000 dynes per sq. cm. Yield values lower than 100 dynes per sq. cm. require for satisfactory precision a more delicately constructed instrument of greater sensitivity. Such a rotational instrument, built by the Research Laboratories of the Interchemical Corporation, can detect yield values as low as 5 dynes and differences in viscosities of as little as 0.001 poise.

To the rheologist who is accustomed to working with capillary-tube viscometers and materials of relatively low viscosity, the degree of precision given above will seem fairly low. However, in general, the technologist who makes viscosity measurements in an industrial plant almost invariably uses a one-point method. This will make impossible the calculation of yield value and plastic viscosity. The viscosity of a plastic determined by a one-point method is a variable, depending on the rate of shear and therefore of doubtful rheological value. To such an investigator a precision of ±5 per cent in plastic viscosity and ±20 per cent in yield value constitutes a very substantial improvement.

Experimental Data

The examples shown in Figures 9 to 14 were taken at random from about 5000 similar curves, and are entirely

typical. They certainly corroborate Reiner's prediction of linearity, and also prove the existence of definite thixotropic levels. The fact that the down curves are linear above T_1 means that U and f are constant above this point and can readily be determined from the simple linear equations, 4 and 5. These facts, in the opinion of the writer, justify the use of a properly constructed rotational viscometer and the application of the Reiner equation for industrial rheological measurements and calculations.

Acknowledgment

The author is indebted to Interchemical Corporation for permission to publish this work, to Ruth N. Weltmann who supervised the production of the laboratory data and gave valuable advice on the construction of the viscometer, and to Daniel Smith.

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Simplified Apparatus for Catalase Determination

ROBERT R. THOMPSON
New York State Agricultural Experiment Station, Geneva, N. Y.

A METHOD of simply and rapidly determining the extent of inactivation of the enzyme catalase, after the blanching process and before dehydration or freezing of vegetables, is presented.

Norgarrd (*2*), Knott (*1*), Pack (*3*), and Tressler and Evers (*4*) have described methods for catalase assay based on the amount of oxygen liberated by the action of the enzyme on hydrogen peroxide. While these methods are accurate, Norgarrd's requires too long a time to complete the reaction, Knott and Pack's both require specialized apparatus, while the method devised by Tressler and Evers, though satisfactory upon the whole, will not give accurate results with all vegetables.

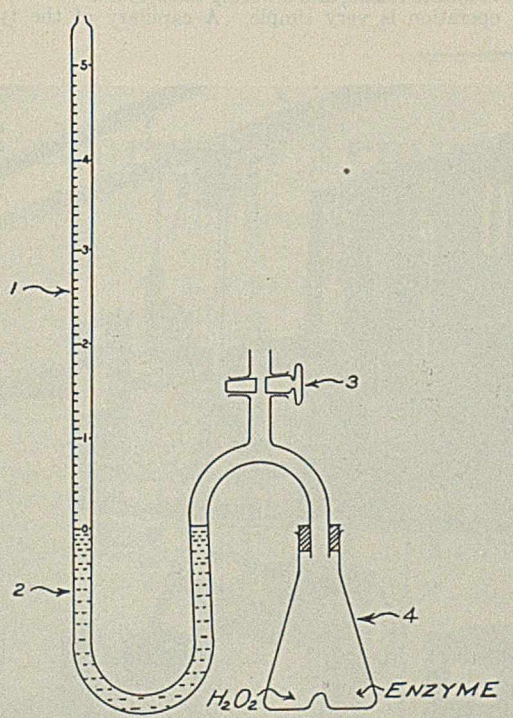

FIGURE 1. CATALASE APPARATUS

1. 5-cc. pipet graduated in 0.1 cc., fused to U-piece of tubing of same diameter
2. Water in tube, at 0 cc. level of pipet at start of reaction
3. Stopcock to adjust level of water after flask is attached
4. 50-cc. Erlenmeyer flask with divided bottom

By using a modification of the Tressler procedure, eliminating the fermentation tube and substituting the apparatus illustrated in Figure 1, the extent of inactivation can be determined accurately in 2 minutes, and the apparatus is simple to construct and inexpensive. Such a method should have value, especially in food-processing plants where it is necessary to make catalase determinations in a minimum period of time. The Canadian Government requires catalase tests run on all vegetables after blanching as a quality control measure for the dehydrated products.

PROCEDURE. An accurately weighed 1.0 gram sample is ground in a mortar with 0.6 gram of calcium carbonate and 1.0 gram of fine sand. Ten milliliters of water are added and the grinding is continued for about 2 minutes. One milliliter of this mixture is pipetted into one half of the special divided flask, and 2 ml. of hydrogen peroxide (Dioxygen) are placed in the other half. The flask is then attached to the manometer and the whole apparatus is suspended in a thermostatically controlled water bath at 20° C. When the apparatus reaches the bath temperature, the stopcock is closed (water level in U-tube set at 0 ml.) and the apparatus is shaken for 2 minutes. A reading of the pipet is then made to determine the amount of oxygen liberated. The catalase may be reported as milliliters of oxygen liberated by 0.1 gram in 2 minutes. For general use the calculations put forth by Tressler and Evers have been found adequate.

This method gives only relative values but is very useful for the estimation of a series of comparisons. It was designed for rapid factory laboratory use, but can be used where more quantitative values are desired.

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APPROVED by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 490.

Simplified Dropping Mercury Electrode for Polarographic Analysis

R. C. McREYNOLDS

University of Oklahoma Research Institute and Halliburton Oil Well Cementing Company, Norman, Okla.

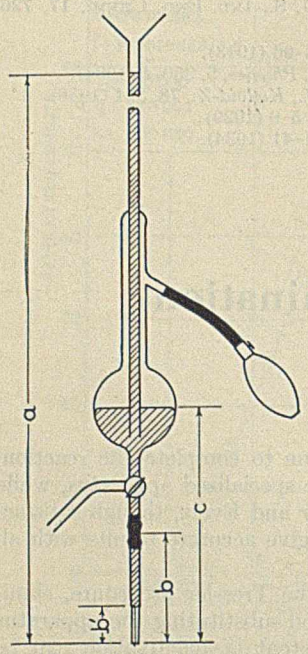

FIGURE 1. DROPPING MERCURY ELECTRODE

a. Adjustable mercury column, 24 to 70 cm.
b. Detachable capillary and tube, 11 cm.
b'. Actual capillary, 3 cm.
c. Minimum mercury level, 24 cm.

MANY different types of dropping mercury electrodes have been described since the simple mercury reservoir and capillary connected by rubber tubing were first used by Heyrovský (*1, 3, 4, 7–10*). All these, however, require the use of rubber tubing, which eventually causes contamination and plugging of the capillary, or are so complex that cleaning is difficult. Furthermore, the more elaborate ones require cumbersome mountings which make them difficult to use in connection with cells immersed in a constant-temperature bath. The most suitable arrangement should consist of a single piece of apparatus supported by one easily adjusted clamp and made entirely of glass. One such electrode, described by Mueller (*6*), operates on the Mariotte flask principle. This electrode was tried, but was found to have one disadvantage: In order to maintain the constant mercury pressure the apparatus must be evacuated to lower the mercury level to the end of a tube located below the mercury surface in the reservoir. This immersed end cannot be seen, and consequently a manometer must be employed to check against leaks and variations in pressure through room temperature and barometric changes.

The following apparatus is capable of supplying any desired mercury pressure in such a way as to allow accurate visual measurement and adjustment. It fulfills the requirements of simplicity of construction, is sturdy in spite of being made almost completely of glass and is suitable for simple and flexible mounting. It is easily cleaned and provides for reversing the direction of mercury flow through the capillary. This is often useful in removing contamination in the upper part of the capillary without dismantling the assembly. The apparatus is composed entirely of glassware to be found in any laboratory and exposes the mercury to only 0.6 cm. (0.25 inch) of neoprene tubing.

This apparatus, shown in Figure 1, is made of a 250-ml. distilling flask, a 2-mm. three-way T-stopcock, 40 cm. of 7-mm. tubing, and a rubber pressure bulb with a release valve of the type used on a baumanometer. Pulleys and counterweight (not shown) facilitate raising and lowering the system.

The operation is very simple. A capillary of the type de-

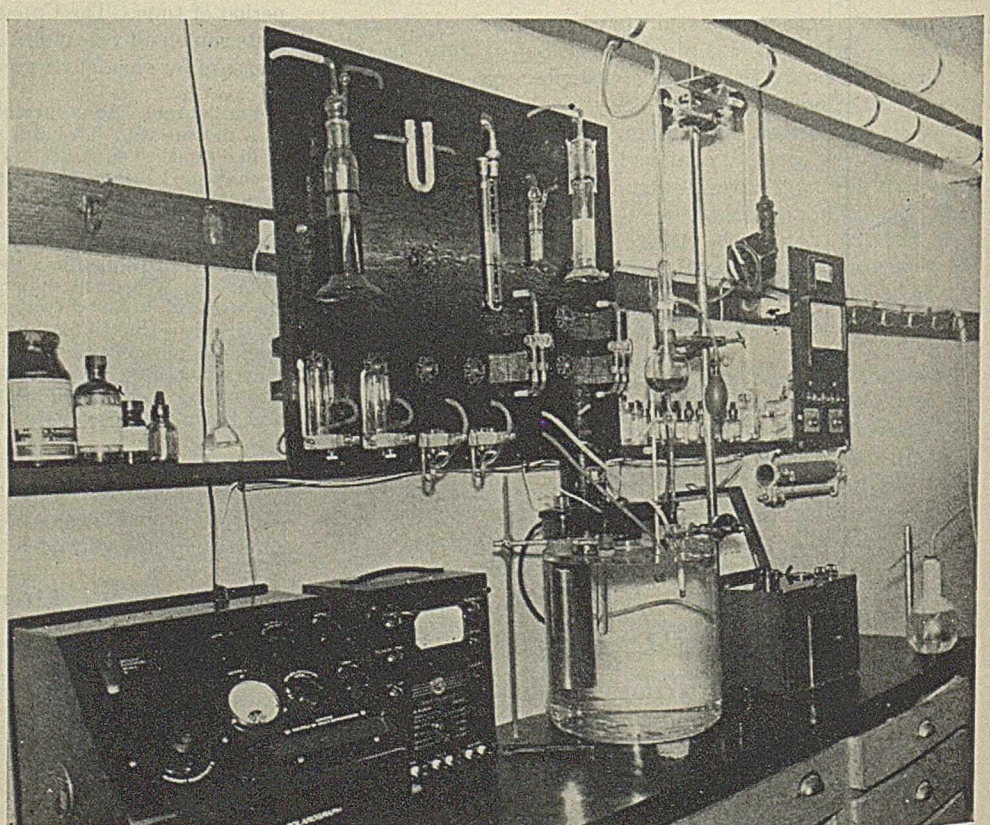

FIGURE 2. LABORATORY ARRANGEMENT FOR ROUTINE POLAROGRAPHIC ANALYSIS

Heyrovský XI polarograph, vacuum tube microammeter, constant-temperature bath, dropping electrode with counterbalance, vacuum tube potentiometer, and pH meter. Against the wall can be seen control board for degassing and part of equipment for bias current and damping condensers.

scribed by Maas (5) is attached to the lower end of the stopcock by means of a short length of neoprene tubing. The reservoir is half filled through the top funnel and the air space between the stopcock and the capillary is filled by turning the cock repeatedly. As the cock is opened, connecting the reservoir to the capillary, a few drops of mercury flow into the air space until the pressure is equalized. The cock is then turned to the side position, exposing the air space above the capillary to atmospheric pressure through the mercury drain arm. This process is repeated until the column is full and no air bubbles remain. The cock is left in the position connecting the capillary and the reservoir until it is necessary to drain the mercury from the reservoir.

With the ordinary capillary only one drop of mercury will flow, as long as no pressure is added, but the capillary must not be immersed in any solution except distilled water, for it will tend to be contaminated. The tip should not be immersed in mercury, as this will start the capillary flowing.

When the electrode is to be used, pressure is first applied through the rubber bulb until a few centimeters of mercury in excess of what is desired are obtained in the column. This is gradually reduced to the desired mark, usually 50 to 60 cm. by adjusting the release valve. The tip is now washed with distilled water and dried, and the entire asembly is lowered until the tip is suitably immersed in the electrolysis vessel. The 0.6 cm. (0.25 inch) of exposed neoprene tubing allows lateral movement and adjustment of the tip and prevents breakage.

At the conclusion of operation the assembly is raised, the tip is washed and dried, the mercury is dropped by opening the release valve, and the apparatus is left as it is. The tip may be protected from dust by a rubber policeman, or immersed in distilled water.

The apparatus is easily cleaned. This is important, for clogging of the capillary and erratic drop rate through partial contamination have caused much lost time in polarographic analysis. It has been found wise to remove all mercury from the reservoir and capillary every 40 days and thoroughly clean both it and the apparatus. If the capillary becomes clogged or the drop time becomes fast, slow, or erratic the capillary must be cleaned. Trouble near the tip may often be removed by placing the tip, with mercury flowing, in a solution of aqua regia and washing with distilled water (2). However, if the contamination is in the upper part of the capillary it may be removed by immersing the tip in mercury, attaching a vacuum line to the drain arm, and reversing the direction of flow by turning the stopcock. Should the capillary still remain clogged, it should be removed and cleaned thoroughly.

The fastest and most reliable way to assure absolute cleanliness is to attach a pump to the capillary and evacuate the latter while it is being heated on a hot plate. When the passage is cleaned, it is treated, still under vacuum, with concentrated nitric acid, with dichromate-sulfuric acid solution, with distilled water, and then dried for 1 to 2 hours.

This electrode, the polarograph, and auxilary equipment for routine analysis are shown in Figure 2.

Acknowledgment

The author wishes to express his indebtedness to J. Rud Nielsen for several helpful suggestions.

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A Laboratory Temperature and Humidity Cabinet

For Studying the Hygroscopic Properties of Tobacco

L. H. DAVIS, Philip Morris and Company, Ltd., Inc., Richmond, Va., AND
A. W. PETRE AND C. F. BAILEY, Mellon Institute of Industrial Research, Pittsburgh, Penna.

A laboratory cabinet is described which furnishes a circulating atmosphere of regulated temperature and humidity. Means of humidifying, dehumidifying, heating, and cooling are provided. Using this cabinet, the equilibrium moisture characteristics of five types of leaf tobacco important in cigaret manufacture have been studied over a range of atmospheric conditions.

A CIRCULATING atmosphere of regulated temperature and humidity is needed to study the equilibrium moisture characteristics of tobacco samples of various kinds. A laboratory cabinet to provide such an atmosphere can be built by installing readily available control instruments in a second-hand refrigerator of the side-icing type. Such cabinets have for some time been in satisfactory operation in the two laboratories reporting the present work. They are readily adjustable and are capable of covering a range of temperatures and relative humidities. The features provided are humidification, dehumidification, heating, and cooling.

Assembly of Instruments

Humidification operates continuously. Clay flower pots up to 25 cm. (10 inches) in diameter are used, filled with water, and when necessary are bound around the outside with cloth, fed by small wicks leading inside the pot.

Dehumidification is intermittent. Laboratory compressed air, controlled by a humidistat and a solenoid valve, is injected into the cabinet through the drain in the bottom. A strainer protects the solenoid and a needle valve regulates the pressure. Air is conducted by 1-cm. (0.375-inch) copper tubing extending about 20 cm. inside the cabinet. The humidistat controls relative humidity within ±1.5 per cent where the temperature is regulated to a range of 1° F. (0.55° C.).

Heating, which is intermittent, is controlled by a direct thermostat operating over a differential of 0.5° F. The heater is made of 16.75 meters (55 feet) of Chromel A, 20-gage wire wound on a slatted Transite cylinder 10.8 cm. in diameter and 14 cm. long. The wire coils are separated and held in place between turns of

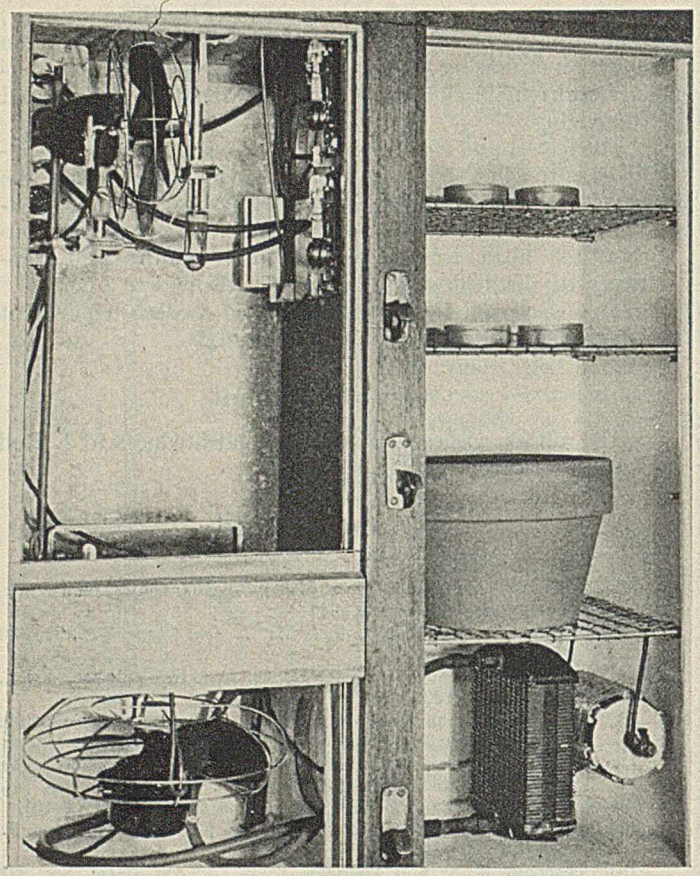

FIGURE 1. INSIDE VIEW OF CABINET

Upper left compartment. On right wall, humidistat and two thermostats, with attachments for outside adjustment; on back wall, panel with electric outlets for fans and control instruments. Thermometers are shown in operating position. Booster fan at bottom.

Right compartment. Sample shelves, unglazed clay pot for humidifying, cooler, and heater.

asbestos string wound about the individual slats. There is also some heat produced by the fans used to circulate air.

Cooling is intermittent. A direct thermostat and relay (or an inverse thermostat) actuates a 11.4-liter (3-gallon) per minute pump circulating water between an auto heater core inside the cabinet and 8 turns of coiled 1.25-cm. (0.5-inch) copper tubing in a 11.4-liter (3-gallon) insulated cooling reservoir, located outside. The circulating system is vented to an aspirator bottle on top of the cabinet, which acts as an injector.

To obtain wet- and dry-bulb readings, a hole 7 cm. in diameter, cut through the top of the ice compartment of the cabinet, is fitted with a wooden disk having a floor flange fastened on the bottom. A pipe from the flange supports a tube of water to wet the wet-bulb thermometer. The thermometers pass through holes 3.8 cm. apart, drilled through the disk and flange.

For adjustment of control instruments from outside the cabinet, a thrust or pull is transmitted to the instrument-setting levers by means of auto choke wires, in flexible cables, attached to rods passing through the box above the door. The rods are threaded, with a narrow groove cut through the threads, and to prevent torsion, a small fixed lug rides in the groove. Thrust or pull is caused by turning brass knobs with holes tapped through the center. Knobs and fixed lugs are held in place by a double yoke fastened to the outside of the cabinet. The flexible cables, wires, fixed lugs, and grooved rods (unthreaded) are the more recent type of dash control attachments obtainable at any large auto supply house. The yoke to hold the fixed lugs, the yoke in which the brass knobs ride, and the tapped brass knobs are added. Control instruments are mounted on a panel in the ice compartment and around the air passage.

The position of the instruments and working parts in the cabinet is shown in Figures 1 and 2. In Figure 1 the cooler and heater are displaced to the right of their operating positions, for purposes of photography. The electrical hookup is shown in Figure 3.

The cost of a cabinet of this type is approximately $290, distributed about as follows: small laboratory pump, $23; Minneapolis-Honeywell humidistat, $15; two Minneapolis-Honeywell bimetallic thermostats, $16; second-hand refrigerator, $10; two Taylor thermometers, $8; two fans, $15.25; cooling system, $12.25; outside instrument controls, $5.50; solenoid valve and air line fittings, $14.75; heater, $2.75; electrical fittings, $10.50; labor $159.50.

Operation of Cabinet

To attain an air velocity of 270 meters (900 feet) per minute past the wet-bulb thermometer (*2*), the thermometers are placed as close to the fan as possible. In addition, the mercury bulbs are located at points about the same radial distance from the center of the fan. These points are indicated by agreement of dry-bulb temperatures at the two positions. To obtain this agreement it may also be necessary to adjust the positions of the cooling and heating units. If anemometer readings are low, a second fan to promote circulation is advisable. The size of air ports between compartments in the cabinet affects air velocity.

As in sling psychrometer measurements, the wet-bulb wick should be wetted at intervals rather than continuously. The authors find it convenient to lower the wet bulb into a tube of water and raise it again to its fixed position for reading. With the thermometer positions in satisfactory adjustment and the control instrument settings adjusted to maintain a particular range, gravimetric determinations of water vapor can be made occasionally to check the relative humidity found by wet- and dry-bulb thermometry (*1*). For the gravimetric determinations, a tube passing from the cabinet through the thermometer

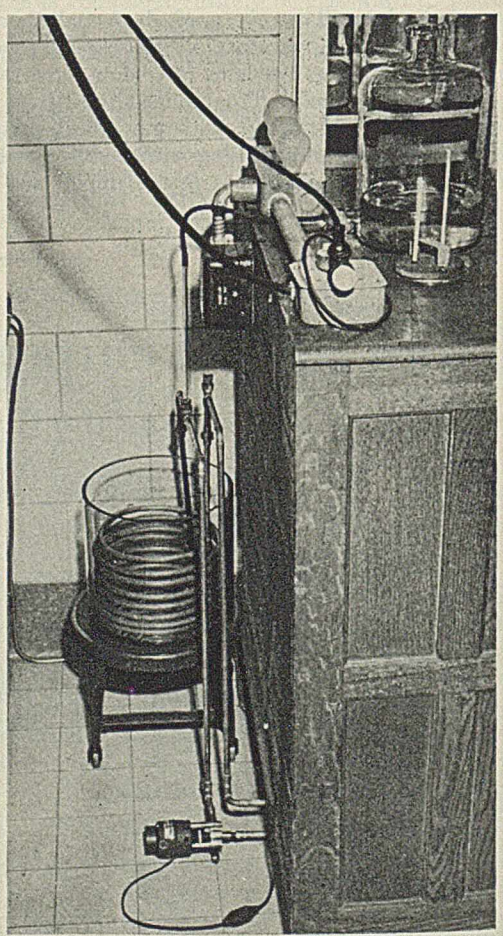

FIGURE 2. OUTSIDE ATTACHMENTS OF CABINET

Water-cooling system and pump, with aspirator bottle to keep system free of air; insulated bath removed to show coil. Compressed air line to cabinet against wall at left. On back top of cabinet, front panel with pilot light on lead to solenoid, connection to house current, and lead to pump. At rear of top, heater lamp bank and relay that controls pump.

well cover leads to a tared U-tube of anhydrous magnesium perchlorate thence to a guard tube containing the same reagent, and finally to an aspirator bottle. A 5-liter sample of air is drawn from the cabinet in 30 minutes, during which time a record of the thermometer readings is kept to obtain the mean observed relative humidity to be compared with that found by calculation from the weight of water vapor, as in Table I.

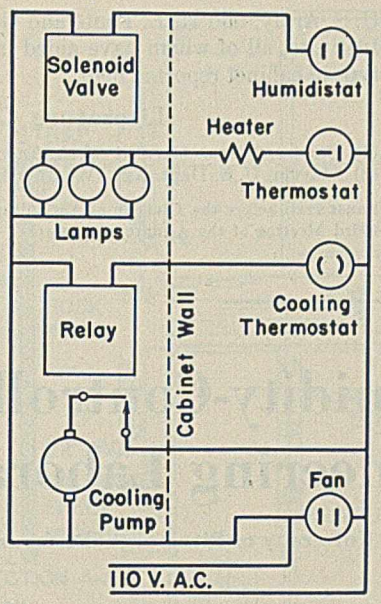

FIGURE 3. WIRING DIAGRAM

Without cooling continuously, temperatures can be maintained from room temperature to the upper limit of the thermostat range. Relative humidities range up to about 50 per cent above that of the room. For low humidity conditions the range is limited by the dew point of the compressed air, which may vary seasonally. The range of conditions studied is given in Table I. For the authors' purpose, lower temperature ranges could be obtained most conveniently by moving the cabinet to an unheated room in which compressed air is available.

The humidifying capacity chosen (size and number of clay pots of water) is only a little more than that necessary to maintain the desired humidity. In case of a sudden drop in outside humidity, the humidifying capacity chosen may prove insufficient. Air circulation, of course, accelerates exchange between outside and inside air and also raises the temperature several degrees, thus putting an additional load on the cooling and humidifying systems. Operating at high humidities, the inside cooling coil may condense moisture at the end of a cooling cycle and depress the humidity. (To attain very high humidities, a practicable device would be an atomizer operating on compressed air previously humidified by passing it through water contained in a vertical column of iron pipe of convenient diameter.) To overcome this depression, cooling water at a slightly higher temperature is obtained by putting the ice used in the external cooling reservoir into a bucket. Sufficient water is left in the reservoir to make contact with the bucket and cover two or three turns of the coil.

Moisture Equilibria of Leaf Tobaccos

In order to illustrate the kind of experimental work that can be done in this cabinet, the moisture-retaining properties of five types of leaf tobaccos commonly used in cigaret manufacture were studied: Turkish (Smyrna); Burley, U. S. type 31, grade C5F; Maryland, U. S. type 32, mixture of grades X2L and X2F; North Carolina flue-cured, U. S. type 12, mixture of grades C4L, C4F, and X2F; South Carolina flue-cured, U. S. type 13, mixture of grades C4L, C4F, and X2F.

The tobaccos were cut to shreds of about the width used for cigarets. Samples of approximately 6 grams each, contained in ointment tins, were exposed in the cabinet in duplicate until substantially constant weight was reached. This required about 6 hours, and was determined by capping the tins at intervals, withdrawing from the cabinet, and weighing. The moisture content of the samples was then determined by means of a Brabender semiautomatic moisture tester. The experiments were all made at the same temperature (80° F., 26.67° C.), while a 30 to 70 per cent range of relative humidity was covered.

The equilibrium moisture contents of the tobaccos at the several conditions studied are given in Table II. The significance of these data is emphasized in Figure 4, which shows that of the types studied, the flue-cured tobaccos are the most responsive to changes in humidity, being the most hygroscopic of all types at the higher humidities and the least hygroscopic of all types at the lower humidity. In sharp contrast is Maryland tobacco, whose moisture content is affected least of the five types by changes in humidity. The behavior of Burley and of Turkish lies between the two extremes.

TABLE I. RELATIVE HUMIDITY DETERMINED SIMULTANEOUSLY BY TWO METHODS

Wick	By Thermometers (A)	By Water Vapor Determination (B)		A − B
	%	*Grains/cu. ft.*	%	%
Silk	30.4	3.497	32.0	−1.6
	29.7	3.279	30.0	−0.3
	41.7	4.546	41.6	0.1
	40.8	4.590	42.0	−1.2
	51.2	5.596	51.2	0
	50.85	5.464	50.0	0.85
	58.4	6.259	57.2	1.2
	57.75	6.225	56.9	0.85
	68.25	7.485	68.5	−0.25
	69.5	7.676	70.2	−0.7
Cotton	38.9	4.293	39.3	−0.4
	51.7	5.753	52.6	−0.9
	58.6	6.478	59.25	−0.65

TABLE II. EQUILIBRIUM MOISTURE CONTENTS OF FIVE TYPES OF TOBACCO AT 80° F. AND RELATIVE HUMIDITY INDICATED[a]

	30%	40%	50%	60%	70%
	%	%	%	%	%
Turkish (Smyrna)	7.85	8.35	9.65	11.60	14.45
Burley, type 31	8.15	8.55	9.70	11.75	13.50
Maryland, type 32	8.50	9.10	10.35	11.60	13.10
North Carolina flue-cured, type 12	7.25	8.40	10.15	12.80	15.10
South Carolina flue-cured, type 13	7.50	8.75	10.45	13.25	15.10

[a] Each moisture percentage is the average of duplicate determinations.

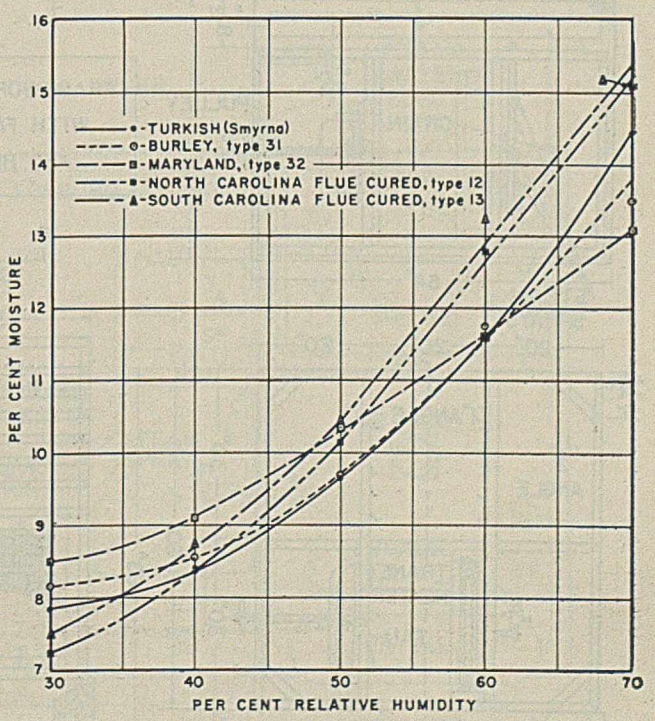

FIGURE 4. EQUILIBRIUM MOISTURE CONTENT OF CIGARET-TYPE TOBACCOS AT 80° F.

The success of this type of cabinet in dealing with tobacco problems involving moisture suggests that it can also be used in determining the moisture characteristics of a variety of other materials of plant and animal origin.

Acknowledgment

The authors wish to acknowledge the assistance and contributions of R. M. Cone of the Chemical Warfare Service, U. S. Army, and H. E. Foote and G. H. Alexander of Mellon Institute, all of whom have aided in the development of the type of cabinet reported here.

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PRESENTED before the Division of Agricultural and Food Chemistry at the 103rd Meeting of the AMERICAN CHEMICAL SOCIETY, Memphis, Tenn.

A Temperature- and Humidity-Controlled Dryer for a Chemical Engineering Laboratory

ROBERT M. SCHAFFNER[1] AND JAMES COULL, University of Pittsburgh, Pittsburgh, Penna.

DRYING is one of the important unit operations, and it is necessary that a chemical engineering laboratory provide suitable equipment for undergraduate experiments on drying and for carrying out research work. These two requirements present slightly different problems. Small commercially constructed dryers enable students to become familiar with the general operations and performance of the larger commercial units. However, unless the apparatus is constructed to special specifications, which increase the cost of the equipment, it is not entirely satisfactory for research work. On the other hand, small dryers which have been designed especially for research work (*2*) frequently have structural features quite different from commercial dryers.

The writers designed and constructed a humidity- and temperature-controlled dryer that meets most of the requirements for research and instructional purposes at a total cost of less than $700 for materials, heater, fan, and control instruments.

The details of the design were determined from the writers' experiences and from recently published papers on drying (*1–3*).

[1] Present address, Research Department, Standard Oil Company (Indiana), Whiting, Ind.

Design

The over-all size of the dryer is 5.5 feet long, 3 feet wide, and 5 feet high. The angle iron frame shown in Figure 1 was cut and welded and provisions for holding the trays, heater, fan, and pipe lines were made as shown. A 24 × 24 inch air heater consisting of horizontal steam pipes and vertical aluminum fins was purchased and attached to the frame as shown in section *A-A*. A 20-inch fan driven by a shaft and pulley was bought and attached to the frame, and a series of 1-inch angle iron pieces was bolted to the upper middle section of the frame to provide rests for the trays. The humidity supply line consisted of a manifold steam pipe with six outlets for sprays and was attached in front of heater. Upon completion of the framework, it was placed in position and bolted on a foundation of concrete 8 inches thick.

The walls of the dryer were constructed in small sections to enable any one of the panels to be removed without dismantling

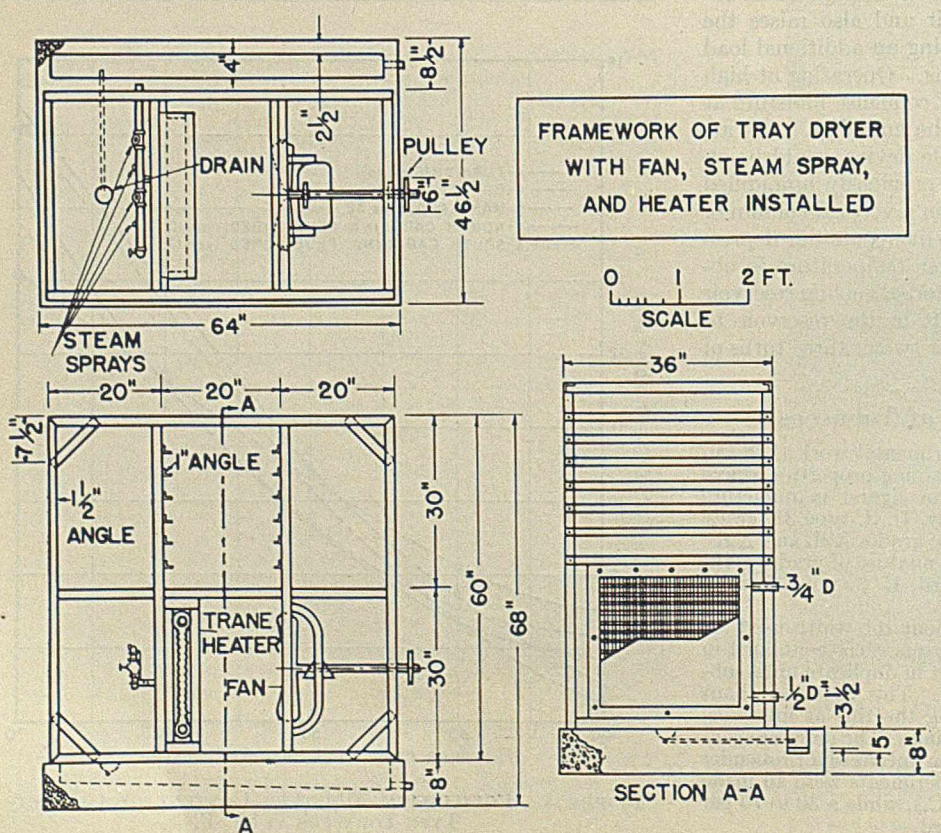

FIGURE 1

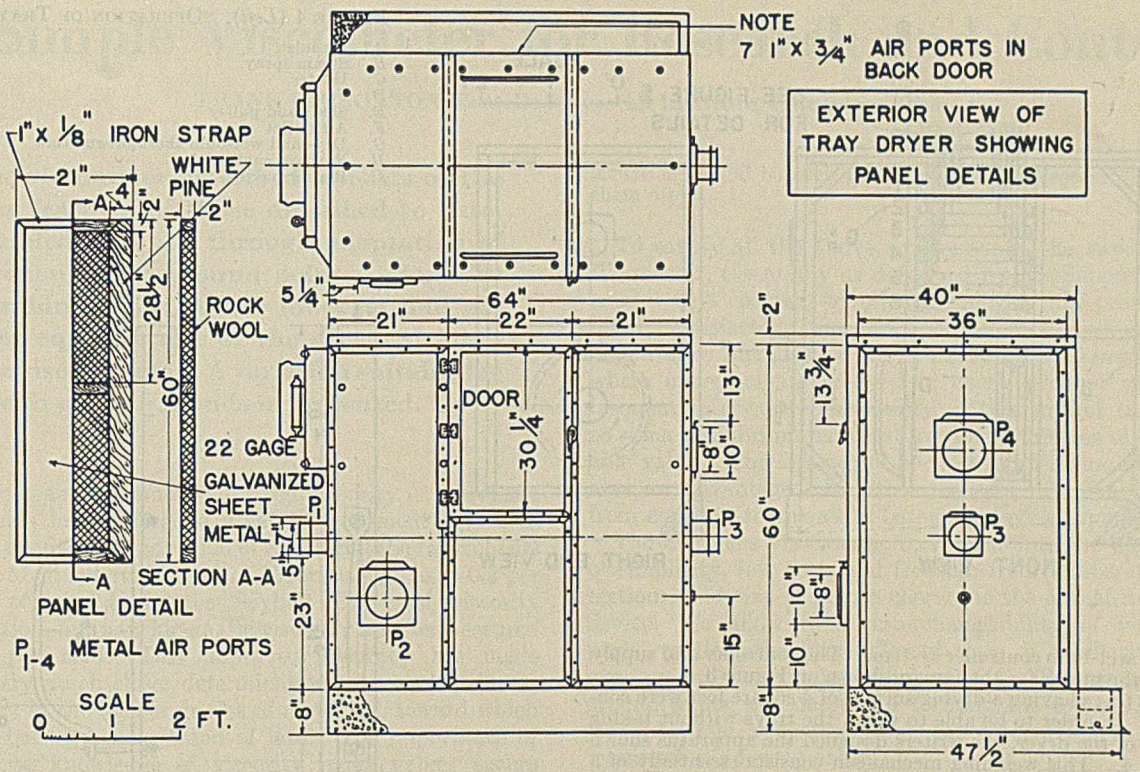

FIGURE 2

any of the others. The panels consisted essentially of white pine frames which surrounded the rockwool insulation. Each panel was then covered on all surfaces with galvanized sheet iron. All the overlapping edges of sheet metal were soldered together to prevent moisture from reaching the interior of the walls. Section *A-A*, Figure 2, illustrates the structural features of the panels. The ports, P_1 and P_3, for the air inlet and outlet and the observation ports, P_2 and P_4, were regular sheet metal air ducts with dampers. The top view of the roofing panels shows two slits which were used for inserting the weighing rods. Two door panels, one on each side of the tray compartment, were used on the dryer apparatus.

The automatic control apparatus was purchased and attached to the dryer as shown in Figure 3. Wet and dry-bulb vapor-type controllers open and close the steam lines to the sprays and heaters. When the dry-bulb temperature drops below the set condition, air opens a diaphragm valve attached to the heater steam line, and a similar setup is used for the steam

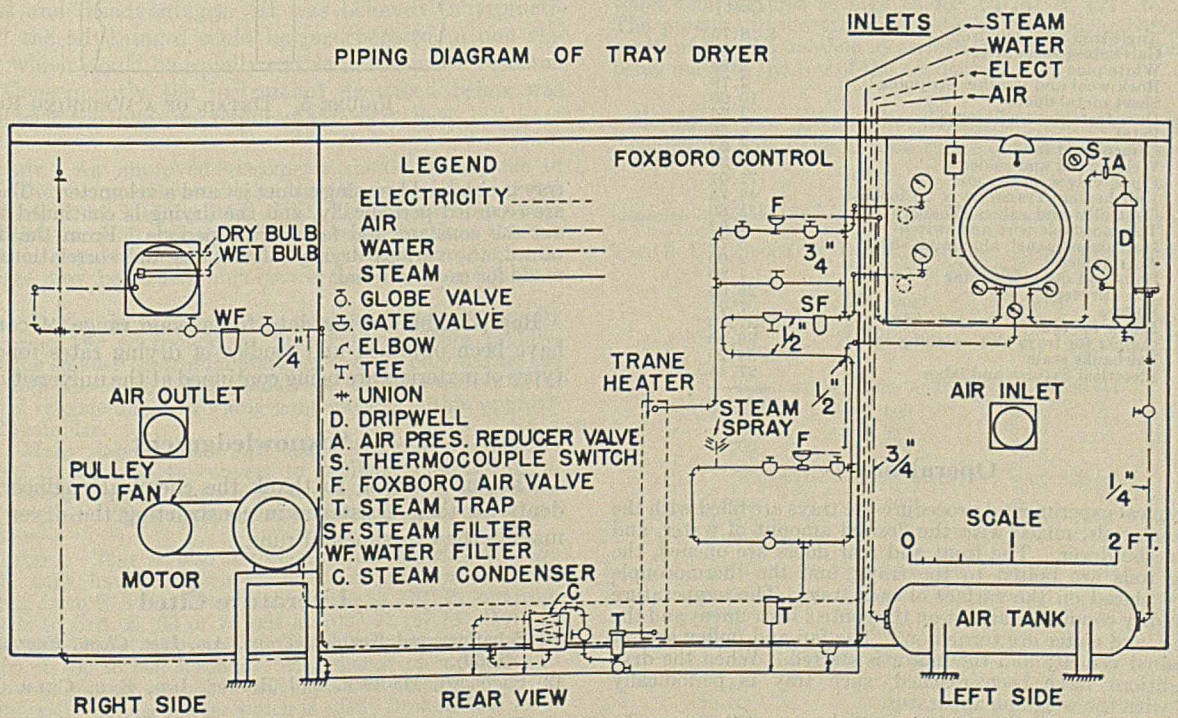

FIGURE 3

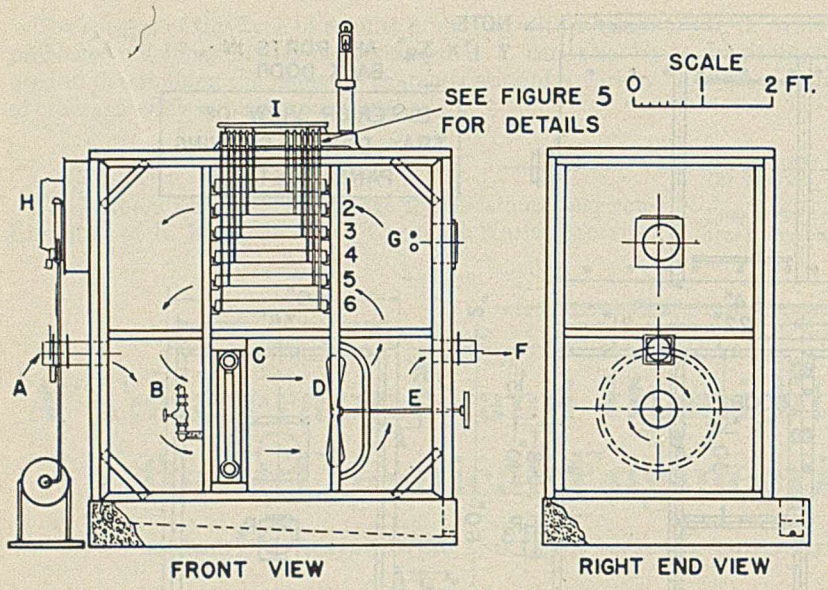

FIGURE 4 (*Left*). OPERATION OF TRAY DRYER

A. Air inlet
B. Steam spray
C. Heater
D. Fan
E. Shaft and pulley
F. Air outlet
G. Dry- and wet-bulb thermoregulators
H. Foxboro control
I. Platform scale

spray and wet-bulb controller system. The controller and supply lines and the motor for the fan are shown on Figure 3.

Copper trays having a drying surface of 4 square feet were constructed. In order to be able to weigh the trays without taking them out of the dryer, the writers designed the apparatus shown in Figure 4. This weighing mechanism consists essentially of a rectangular frame which is placed on a scale on the roof of the dryer, directly over the trays. To each tray, vertical rods (shown in detail in Figure 5) are bolted and extended up through the slots in the roof to the scale. The rods of a particular tray are hooked over the weighing frame when the weight of the tray is to be determined. By this method each tray can be individually weighed without disturbing the drying and without any loss of heat. Thermocouples were also placed on each tray and at various points in the dryer.

The itemized cost of the dryer for the price conditions prevailing in Pittsburgh during the fall of 1939 and spring of 1940 is as follows:

Unit	Cost
Angle iron and strip iron	$ 8.75
Galvanized sheet steel	11.85
White pine	2.88
Rock wool and weather stripping	2.79
Sheet metal ducts	10.00
Door fasteners and hinges	2.75
Paint	4.56
Cement and sand	3.25
Welding rod and solder	7.35
Pipes, valves, gages, etc.	72.01
1 air heater (Trane) 24 × 24 inches	49.75
Controller and valves (Foxboro)	325.80
Thermocouple wire and switch	2.62
Instrument panel, aluminum sheet	6.72
Thermometer	2.00
Bolts and other fastening	1.70
Fan (Breeze)	28.00
Pulleys	7.97
Motor for fan	37.00
Copper for trays and weighing rods	39.00
Fairbanks scale	34.20
Electrical fixtures and labor	27.45
	$688.40

Operation

In a typical experimental procedure the trays are filled with the testing materials, mixed with the desired amount of water, and placed in the dryer. The front and rear doors are opened, the weighing rods are bolted to the trays, and the thermocouple wires are placed on the surface of each tray. The temperature and humidity conditions are set on the control instrument and the steam, air, and water are turned on. The fan and pulley are set for a desired velocity and the motor is started. When the drying conditions have been reached, each tray is periodically weighed with the weighing apparatus.

The surface temperature of the materials on each tray may be determined with a potentiometer. The air velocity over each

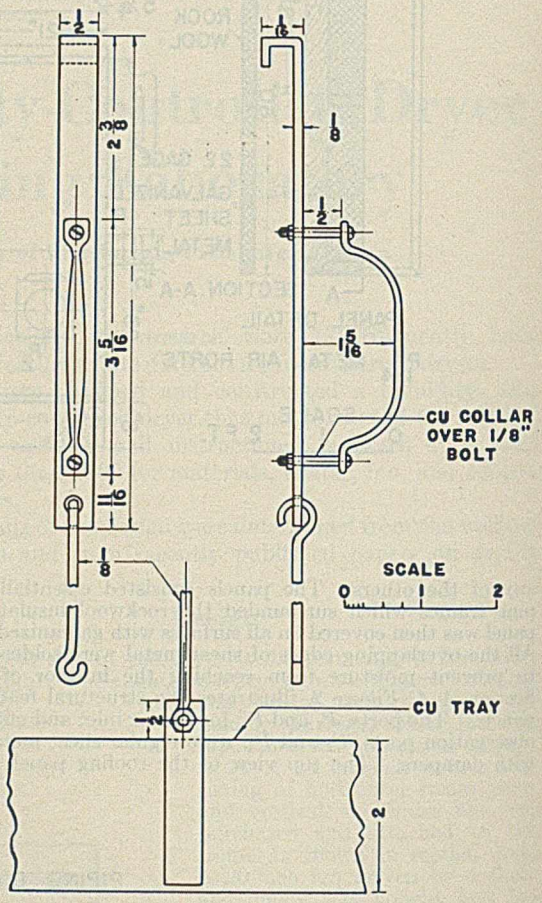

FIGURE 5. DETAIL OF A WEIGHING ROD

tray is obtained by using a duct jet and a velometer. These data are recorded periodically, and the drying is continued throughout the constant and falling rate periods. From the data obtained, the various drying calculations and correlations can be made for each material.

Reproducible drying data for a wide range of conditions have been obtained and studies of drying rates for various types of materials are being continued at the university.

Acknowledgment

The authors wish to thank the chemical engineering students for their assistance in constructing the dryer and for making the experimental runs.

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A Simple Viscometer for Research and Control

FRANK C. CROXTON, Battelle Memorial Institute, Columbus, Ohio

The viscometer described consists of the better features of those described to date, assembled into one through adaptation of interchangeable ground joints. Rapidity is combined with rather low cost and accuracy equal to any of the accepted kinematic viscometers. A variation suitable for use with opaque liquids is presented.

THE routine determination of the viscosity of petroleum products has undergone great improvement in recent years as a result of the adoption of capillary-tube instruments in A. S. T. M. standard methods. Errors as high as ±0.5 per cent are permissible in the Saybolt Universal viscosity determination, but now kinematic viscosity may be measured to ±0.2 per cent. This improved accuracy has made possible very much closer determinations of viscosity index, particularly in the lighter grades of motor oil, toward which there has been a strong trend of late. The importance of more precise knowledge of viscosity index values occurs particularly in meeting specifications in commercial production. Table I shows the effect on viscosity index (*2*) of small errors in viscosity at 210° F. (98.89° C.). The viscosity index error resulting from the permissible Saybolt Universal viscosity error amounts to several units in the S. A. E. 10 range. This becomes somewhat less in the heavier oils, as shown by the examples of S. A. E. 50 grade.

A number of capillary-tube viscometers have been described in the literature as contributions toward improved viscosity measurement, including the designs of Cannon and Fenske (*1*), FitzSimons (*3*), Ruh *et al.* (*4*), Ubbelohde (*5*), and Zeitfuchs (*6, 7*). All possess certain individual advantages and disadvantages. It was believed that practically all the advantages could be incorporated in one viscometer which would be equally usable in routine or research work. Consequently the instrument described below was designed with the following requirements as its basis.

ACCURACY. An improved viscometer should be capable of determinations as precise as obtainable with any of those recognized by A. S. T. M. Method D445-39T. It might suitably utilize the essential parts of one of the instruments described therein. It should be capable of still greater precision in research work, where time may be of less importance than in control laboratories.

SPEED. It should be possible to measure viscosities rapidly and to bring the equipment to proper temperature rapidly. Many of the smaller control laboratories operate only during the daytime and, therefore, it is of some value to them to be able to bring their viscometers to working temperatures within approximately 20 minutes.

COST. Many laboratories still using Saybolt viscometers would find it desirable to convert to capillary instruments in order to take advantage of their greater accuracy, if their price could be reduced. This, then, was considered to be an important requirement.

FLEXIBILITY. This is also associated with speed. A single laboratory may have occasion to determine the viscosities of oils ranging from S. A. E. 10 to bright stocks at 210° F. and from Diesel fuels to S. A. E. 60 or 70 oils at 100° F. (37.78° C.). It should be possible to make any of these measurements with an efflux time of 100 to 600 seconds. Any change of capillaries to meet this requirement should be accomplished quickly.

RUGGEDNESS. A viscometer which is easily broken is of little use in the long run and may become expensive. It is not believed that glass instruments per se are fragile, but their construction should be such that it will not be necessary to handle them often.

To satisfy all the above requirements, the vapor type of thermostat, essentially as described by FitzSimons (*3*), was used. This constant-temperature device has proved to be highly satisfactory, not only in research and inspection laboratories but also in the control rooms of process units where operators are enabled to check product quality at frequent intervals. The ability of this sort of thermostat to reach equilibrium temperature rapidly is often of considerable value. The absence of cyclical temperature changes is also an advantage. In these respects it differs radically from constant-temperature baths employing liquid media.

The Zeitfuchs viscometer (*6, 7*) combines the advantages of simplicity, low cost, and freedom from temperature corrections, and was therefore chosen as the actual measuring device. To allow rapid interchangeability of viscometer parts, particularly with different sizes of capillaries, these were mounted in the inner halves of 45/12 interchangeable ground joints, the outer half forming the top of the vapor jacket. Thus a change from one viscometer to another requires but a few seconds.

The construction of the instrument is shown in Figure 1. Each viscometer part, *A*, of whatever capillary bore, is constructed exactly according to the directions of Zeitfuchs and is sealed into the inner half of a 45/12 interchangeable ground joint, *B*, at such a point that the top of the overflow tip is about 2 cm. below the ground portion of the joint. The vapor thermostat consists of the jacket, *C*, with an outer half of a 45/12 joint at the top. Just above the enlarged portion at the bottom, a side arm joins the circulation tube, *D*, the lower end of which carries the liquid returning from condenser *E* to the main body of liquid, filling 0.5 to 0.7 of the enlarged portion of the jacket. The condenser is constructed preferably as shown, vapors being condensed in an annular space between cool surfaces. This is particularly important when operating at 100° F. with cooling water temperatures as high as 70° to 75° F. (21° to 24° C.). The pressure inside the thermostat is reduced and maintained constant by the method described by FitzSimons, connection being made to the top of the condenser.

Zeitfuchs has given the dimensions of six viscometers designed to cover the normal range of viscosities encountered

TABLE I. VISCOSITY INDEX ERRORS RESULTING FROM SMALL VISCOSITY ERRORS

True Viscosity at 210° F. *Cst.*	Measured Viscosity at 210° F. *Cst.*	Viscosity Error at 210° F. %	Viscosity Index
Kinematic viscosity at 100° F. = 20.550 cst.			
4.000	4.000	0.0	100.0
4.000	4.010	0.25	101.3
4.000	4.020	0.50	102.7
Kinematic viscosity at 100° F. = 26.820 cst.			
4.000	4.000	0.0	0.0
4.000	4.010	0.25	2.0
4.000	4.020	0.50	4.0
Kinematic viscosity at 100° F. = 249.31 cst.			
20.00	20.00	0.0	100.0
20.00	20.05	0.25	100.3
20.00	20.10	0.50	100.6
Kinematic viscosity at 100° F. = 551.07 cst.			
20.00	20.00	0.0	0.0
20.00	20.05	0.25	0.8
20.00	20.10	0.50	1.6

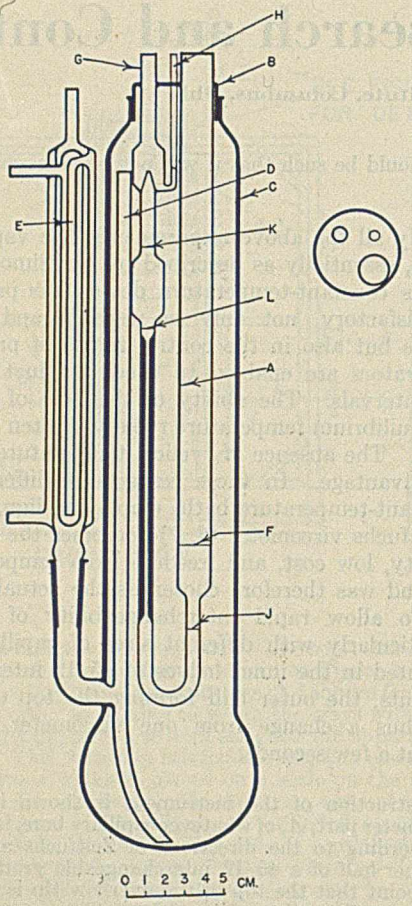

FIGURE 1. VISCOMETER

in petroleum products. Since viscometer constants somewhat different from these may be desired for special cases, the following equation is given for calculating capillary-bore radius, all other dimensions being held as described by Zeitfuchs:

$$\log r = \frac{\log C_1}{4} - 0.97169$$

where r = capillary bore radius in cm. and C_1 = viscometer constant when viscosity is in centistokes and time is in seconds. In general, the required capillary radius for any kinematic viscometer operating under the influence of gravity can be closely approximated by the following equation:

$$\log r = \frac{\log C_1 - \log\left(\frac{8V}{100\,\pi g}\right)}{4}$$

where V = volume in ml. between marks, g = gravitational constant in cm. per second per second, and other symbols are as in the preceding equation. The simplifying assumption that the average hydrostatic head is within a few per cent of the capillary length, is employed.

Viscometers with simple calibration constants, such as 0.1000 or 0.2500, have been advocated by some, but it is believed that in most applications little time is saved by this refinement. The Saybolt Universal units are still so firmly entrenched that it is usually necessary to convert from centistokes to S. U. seconds by use of a table. Furthermore, the kinetic energy correction often enters to a significant degree, thus requiring an added tabular reference. All conversions may be incorporated in one table, for each viscometer, giving the relation between efflux time and viscosity in S. U. seconds at the three commonly used temperatures.

To operate the viscometer, the appropriate liquid is added to the thermostat to a point about 1 to 2 cm. below the side arm. The most suitable liquids are methylene chloride at 100° F. (37.78° C.), acetone at 130° F. (54.44° C.), and tertiary amyl alcohol at 210° F. (98.89° C.). The proper viscometer is set in place, well lubricated with a material which is not too stiff at room temperature. An A.S.T.M. kinematic-viscosity thermometer hangs from the drain tube of the viscometer. The liquid is heated by means of an electric flask heater of approximately 250 watts at 100° and 130° F. or 350 watts at 210° F. For maximum flexibility a 550- to 660-watt heater, controlled by an autotransformer, may be used when alternating current is the source of power. In hazardous locations steam heat has been successfully employed.

Cool water is passed through the condenser. Pressure inside the thermostat is reduced by means of a water aspirator or other type of evacuating pump. The pressure will fall until air enters through the water column, the height of which determines the pressure and therefore the temperature inside the apparatus. The temperature is adjusted to the exact point desired by raising the water column to lower the temperature or by lowering the water column to raise the temperature. As described by Zeitfuchs, the liquid whose viscosity is required is poured into the large tube of the viscometer to mark F, and is raised by application of suction to G, with H closed, until the liquid level falls to J. The amount which has not overflowed through the tip is, then, the standard volume with which the viscometer is calibrated and with which viscosity determinations are made thereafter. Excess liquid is withdrawn through H. When the thermostat is installed, one of the viscometer parts is inserted and the orientation of the jacket adjusted so that the capillary will be truly vertical. Since in their manufacture the capillaries are placed parallel to the axis of the ground joint, all viscometer parts will be satisfactorily aligned when they are in place in the thermostat.

After filling the viscometer with the correct amount of liquid, viscosities are measured by merely noting the time required for the meniscus to fall from K to L. This, times the constant found in calibrating, less the kinetic energy correction, gives the kinematic viscosity of the liquid. Calibration is accomplished preferably by the use of water as a primary reference. Alternatively the viscosity standards of the A. P. I. or of the National Bureau of Standards may be used.

The average control and inspection laboratory would probably set up two vapor thermostats for each inspector giving his full time to viscosity measurements. One of these would operate at 210° F., the other at 100° F. A series of viscometer parts would be available, so that the viscosities of the various samples could be determined with an efflux time of 100 to 600 seconds, thus conserving the operator's time. If the viscosity at 210° F. of an S. A. E. 50 motor oil is required immediately after running an S. A. E. 10 oil, a quick change from a viscometer with a constant of approximately 0.025 to one with a constant of about 0.100 would provide efflux times of 150 to 200 seconds for each.

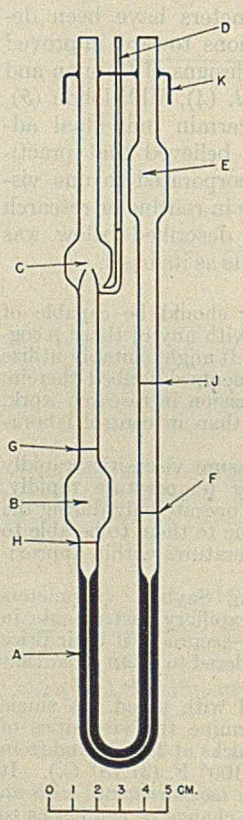

FIGURE 2. VISCOMETER FOR OPAQUE LIQUIDS

It is difficult to use any of the kinematic viscosity instruments, so far described, with opaque liquids such as residual oils and solvent extracts. For such applications, the instrument shown in Figure 2 was designed. It is a modification of the Zeitfuchs viscometer, possessing all its advantages, including convenience of proper filling.

In use, the viscometer is filled approximately to mark J. When the liquid has attained operating temperature, the level is depressed from J to F, the excess overflowing at C. To start a viscosity determination, the liquid level is depressed to a point a little below mark H. The efflux time is that elapsing during the passing of the meniscus between points H and G under the sole influence of gravity. Since the body of the liquid advances over the marks, there is no difficulty in the measurement of the efflux time even when its color is very dark. This instrument is suitable for use with residual oils, the less viscous solvent extracts, and similar materials; however, it is not designed for highly viscous materials of any type. Perhaps 2000 centistokes would represent the maximum practically measurable viscosity.

Acknowledgment

The author wishes to express his appreciation to R. Shutt for his continued interest during the course of this work.

Grateful acknowledgment is made to the Battelle Memorial Institute for permission to publish this material.

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Presented before the Division of Petroleum Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

An Electromagnetic Densitometer

A. R. RICHARDS, Trinidad Leaseholds, Ltd., Pointe-à-Pierre, Trinidad, B. W. I.

An apparatus is described in which the principle of balancing the attraction of a magnetic field against the upthrust on a submerged armature is used as a rapid method of measuring liquid densities. The precision of the determinations depends on the range of the instrument and is of the order of 1 part in 800 for densities between 0.62 and 0.82 gram per ml.

CONSTRUCTION of the densitometer described below was undertaken in order to facilitate density determinations on some two hundred 5-ml. samples every 8 hours. Ordinary hydrometers were unsuitable, since they require at least 20 ml. of sample, while pycnometer measurements would have been too slow.

The essential parts of the instrument consist of a small glass float held under the surface of the sample by an adjustable stop and a small coil surrounding the lower portion of the sample tube. If current passing through the coil is gradually increased, the resulting magnetic field will eventually exceed a critical value, such that the force on the armature will become sufficient to draw the float away from the stop. If suitable precautions are taken, the density of the sample may be determined accurately by measurement of the critical current.

Theory

The theoretical considerations affecting the design of the apparatus can be expressed in the following manner:

Let the pole strength induced in the armature be m and the magnetic potential at these poles be V_N and V_s. It follows that the potential energy, E, of the armature in the field is given by:

$$E = m(V_N - V_s) = \frac{m\Delta s\ (V_N - V_s)}{\Delta s}$$

where Δs is the distance between the poles.

Now $(V_N - V_s)/\Delta s = H$, the strength of the field, and $m\Delta s = M = vI$ where M, v, and I represent the magnetic moment, volume, and intensity of magnetization of the armature, respectively. Thus

$$E = vIH$$

The work done during a small displacement, ds, of the armature is given by the equation which follows:

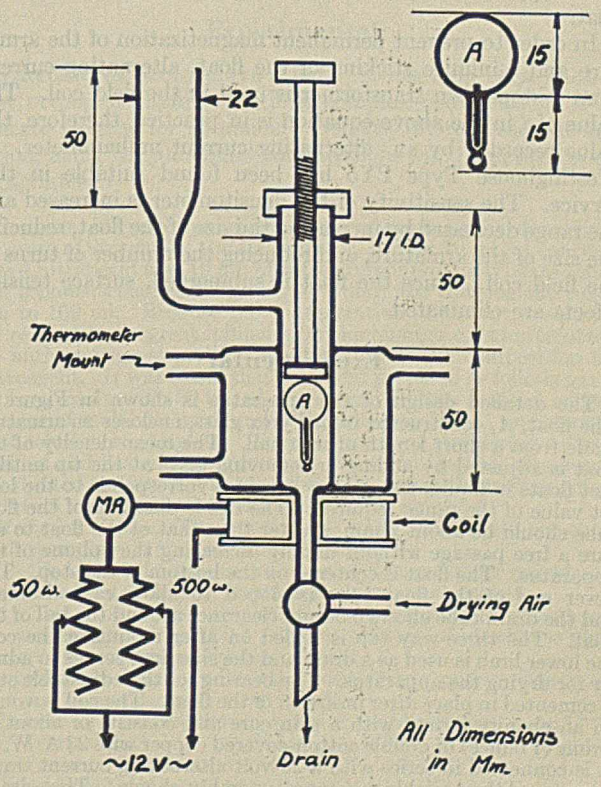


Figure 1. Diagram of Apparatus

$$Fds = vd(IH)$$

where F is the force acting on the armature along the direction of displacement. Then

$$F = \frac{vd(IH)}{ds}$$

The relation between I and H depends on the susceptibility, k, and the geometrical form of the armature. For small values of H, k may be regarded as constant and in general,

$$I = Hf(k)$$

and

$$F = \frac{vd(IH)}{ds} = \frac{vd(H^2f(k))}{ds} = AH\frac{dH}{ds}$$

Now $H = i\psi(s)$ where i is the current flowing in the coil producing the field, and $\psi(s)$ is a function determined by the configuration of the system. Therefore,

$$\frac{dH}{ds} = i\Psi'(s)$$

Hence

$$F = Bi^2\,\Psi(s)$$

Since the float always starts from the same position, the value of $\Psi(s)$ has a fixed value for any given position of the stop. Hence, $F = Ci^2$ where C is a constant.

If the volume of the float is V and the density of the liquid is ρ, the upthrust on the totally immersed float is ρV. When the current in the coil reaches the critical value the opposing force is $F + W$, where W is the weight of the float

$$\rho V = Ci^2 + W$$

or

$$\rho = Ri^2 + P$$

where R is constant, providing the geometrical arrangement of the apparatus is reproducible, and P is the density of the float.

In order to prevent permanent magnetization of the armature and minimize sticking of the float, alternating current from a step-down transformer is used in the field coil. The value of i in the above equation is in practice, therefore, the value recorded by an alternating current milliammeter. A Westinghouse Type PY5 has been found suitable in this service. The sensitivity of the densitometer is increased and the range decreased by increasing the size of the float, reducing the size of the armature, and reducing the number of turns in the field coil. Since the float is submerged, surface tension effects are eliminated.

Experimental

The detailed design of the apparatus is shown in Figure 1. The float, A, constructed from Pyrex glass, encloses an armature made from a short length of iron nail. The mean density of the float is adjusted by adding or removing glass at the tip until it just floats in liquid, the density of which corresponds to the lowest value of the range required. The inside diameter of the float tube should be about 2 mm. greater than that of the float to ensure a free passage without unduly increasing the volume of the apparatus. The float is centered on the bottom of the stop. The lower end of the float tube is sloped to allow easy drainage and the drain tube allows 0.5-mm. clearance around the tail of the float. The three-way tap is sealed on after mounting the coil; the lower limb is used as a drain and the side limb serves to admit air for drying the apparatus. The bearing for the adjustable stop is cemented in place after insertion of the float. The coil is wound on an ebonite former with a thin core and consists of about 28 grams (1 ounce) of double cotton-covered copper wire 23 A. W. G. It is connected in series with a 20-volt alternating current transformer and the variable resistance assembly shown. This circuit gives the most satisfactory control.

A water jacket completely surrounding the float chamber is used for maintaining a standard temperature during determinations. Drift due to rise in temperature of the coil is not noticeable with currents below 600 milliammeters and the insertion of a water jacket between the drain tube and the coil is not necessary. It is easy to maintain a temperature constant to within ±0.2° C. which produces an error of less than 0.0002 gram per ml. in the densities of gasoline fractions.

The instrument can be reset after cleaning by adjusting the position of the stop until the milliammeter reading for a liquid of known density agrees with the original calibration. This setting is checked by the use of a second liquid.

By analysis of the experimental figures given in Table I, it can be shown for this instrument that

$$d^{20}_{vac.} = 0.701\ i^2 + 0.621 \qquad (1)$$

Table I. Density Measurements

Current, Amperes	$d^{20}_{vac.}$ from Pycnometer	$d^{20}_{vac.}$ from Equation 1	Difference, Calcd. and Found
0.085	0.6255	0.626	+0.000 (5)
0.152	0.6370	0.637	+0.000
0.179	0.6429	0.643	+0.000 (1)
0.223	0.6563	0.656	−0.000 (3)
0.302	0.6842	0.684	−0.000 (2)
0.383	0.7230	0.723	−0.000
0.397	0.7309	0.732	+0.001 (1)
0.424	0.7445	0.746	+0.001 (5)
0.425	0.7458	0.747	+0.001 (2)
0.445	0.7598	0.759	−0.000 (8)
0.459	0.7673	0.768	+0.000 (7)
0.475	0.7795	0.778	−0.001 (5)
0.477	0.7811	0.780	−0.001 (1)
0.488	0.7874	0.788	+0.000 (6)
0.500	0.7962	0.797	+0.000 (8)
0.502	0.7974	0.798	+0.000 (6)
0.515	0.8082	0.807	−0.001 (2)
0.521	0.8146	0.813	−0.001 (6)

Although the range of measurement can be adjusted, it is not convenient to construct an instrument with a range of more than 0.2 gram per ml., since the precision is limited by the accuracy with which the milliammeter may be read, which is of the order of ±1 ma. over the 750-ma. range. Substituting the value of this uncertainty, δi, in the following equation

$$d^{20}_{vac.} \pm \delta d = 0.701\ (i \pm \delta i)^2 + 0.621$$

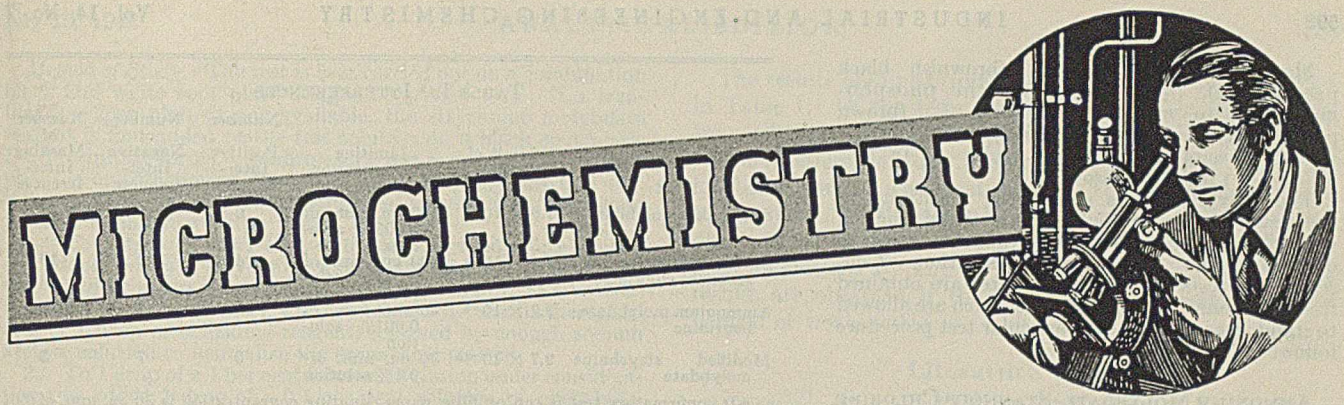
gives the maximum uncertainty in the density, δd, as ±0.0007 gram per ml. for currents not in excess of 500 ma. A similar error arises during calibration, so that the maximum error is not more than ±0.0014 gram per ml. If the instrument has been cleaned and reset but not recalibrated, a further additional error of not more than ±0.0007 gram per ml. must be included, making the greatest uncertainty under the least favorable conditions not more than ±0.0021 gram per ml. or 1.0 per cent of the useful range.

The difference between the observed and calculated densities shown in Table I exceeds in certain cases the estimated precision for given current values. This is due to absolute errors in the milliammeter, since it is stated by the makers that the values indicated may differ from the absolute values by 0.5 per cent of the full-scale readings of both the 250- and 750-ma. ranges. In view of the above, it is recommended that densities be read from an experimental curve determined for a given instrument and milliammeter and covering the entire range.

Since the sensitivity can be increased at the expense of the range, the ultimate precision is limited only by temperature control and the reproducibility of the initial system.

Acknowledgment

The apparatus was developed in the laboratories of Trinidad Leaseholds, Limited, to which company thanks are due for permission to publish this paper.



Detection of Orthophosphates by Means of Drop Reactions

PHILIP W. WEST AND THOMAS HOUTMAN

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.

MANY methods for detecting or determining orthophosphates are reported in the literature, but little has been published concerning their detection by means of drop reactions. In the work that has been reported, the studies of interferences have often been incomplete and there is little agreement between the results of various investigators. In order to evaluate the more promising reactions, comparative data concerning interferences and sensitivities were obtained. After an extensive survey of the literature, the strychnine molybdate (*2*), ammonium molybdate–stannous chloride (*3*), and ammonium molybdate–benzidine (*5*, *7*, *8*) tests were selected for study. A modified strychnine molybdate test devised by the authors was also included in the investigation.

Scope of Investigation

The following ions and compounds were studied, using 1 per cent solutions, in regard to the ion or compound in question:

Group I. Li^+, Na^+, K^+, Cu^{++}, Rb^+, Ag^+, Cs^+, Au^{+++}

Group II. Be^{++}, Mg^{++}, Ca^{++}, Zn^{++}, Sr^{++}, Cd^{++}, Ba^{++}, Hg^+, Hg^{++}

Group III. BO_2^-, $B_4O_7^{--}$, Al^{+++}, Ga^{+++}, Y^{+++}, In^{+++}, La^{+++}, Ce^{+++}, Tl^+

Group IV. CO_3^{--}, SiO_3^{--}, Ti^{+++}, Sn^{++}, Sn^{++++}, Pb^{++}, Zr^{++++}, Th^{++++}

Group V. NH_4^+, NO_2^-, NO_3^-, $H_2PO_2^-$, $P_4O_{13}^{------}$, $P_6O_{18}^{------}$, PO_3^-, HPO_4^{--}, $P_2O_7^{----}$, V^{+++}, VO_4^{---}, AsO_2^-, $HAsO_4^{--}$, Sb^{+++}, Bi^{+++}

Group VI. S^{--}, $S_2O_3^{--}$, SO_3^{--}, SO_4^{--}, Cr^{+++}, CrO_4^{--}, SeO_3^{--}, SeO_4^{--}, MoO_4^{--}, TeO_3^{--}, TeO_4^{--}, WO_4^{--}, UO_2^{++}, UO_4^{--}

Group VII. F^-, Cl^-, ClO_3^-, Mn^{++}, MnO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, ReO_4^-

Group VIII. Fe^{++}, Fe^{+++}, Co^{++}, Ni^{++}, Ru^{+++}, Rh^{+++}, Pd^{++}, OsO_5^{--}, Ir^{++++}, Pt^{++++}

Miscellaneous Substances. CN^-, $Fe(CN)_6^{---}$, $Fe(CN)_6^{----}$, CNS^-, acetate, oxalate, malonate, adipate, succinate, phthalate, tartrate, citrate, lactate, gluconate, *i*-inositol, *d*-sorbitol, mannitol, sucrose, dextrose, aniline, pyridine, resorcinol, and catechol

The solutions were made up and the results reported in the manner of West (*10*)—that is, interfering substances which gave a test similar to that given by orthophosphate were listed as "positive" interferences, those substances which inhibited the formation of true tests for phosphate were listed as "negative" interferences, and those substances which were so highly colored or gave such highly colored reaction products that test colors were hidden, were listed as "masking" interferences. The actual investigation of interferences was carried out with a ratio of HPO_4^{--} to interfering substance of 1 to 10. This ratio constituted a stringent test of the method and at the same time indicated what could be expected of it under reasonable working conditions. Where more favorable ratios exist there may be fewer interferences, but the use of the test in the presence of such questionable interferences would entail considerable risk. If ratios less favorable than 1 to 10 are encountered there may be a few more negative interferences than are reported in these studies. However, no additional positive interferences should be encountered unless the concentration of the test solution is increased beyond 1 per cent, which is the highest concentration to be recommended for use with drop reactions.

C.P. chemicals were used throughout the investigation.

Experimental

STRYCHNINE MOLYBDATE TEST. It has long been known that orthophosphate in various complex combinations is a delicate reagent for alkaloids. Denigès (*2*) reversed the reaction, using the alkaloidal combinations for the detection of phosphates.

Reagents. Denigès proposed a reagent made up by dissolving 0.5 gram of strychnine sulfate in water, adding 10 ml. of concentrated nitric acid and 10 ml. of nitro ammonium molybdate solution (Sonnenschein and Eggertz formula), and diluting the solution to 100 ml. Because the concentration of the nitric acid in the reagent has a great influence on the number of interferences, the authors suggest a slight modification in the composition of the reagent. It was found that a reagent prepared as follows gave the best results: To 30 ml. of concentrated nitric acid are added 2 grams of molybdic acid, and it is diluted to 75 ml., and stirred until solution is complete. Then 0.6 gram of strychnine sulfate is added and heated gently until all the strychnine has dissolved. It is diluted to 100 ml. and heated slightly below the boiling point for 3 to 5 minutes until a yellow solution is obtained.

Method of Study. The interference study was carried out on a black spot plate in the following manner:

1. To 1 drop of 1 per cent solution of element under consideration was added 1 drop of strychnine molybdate reagent.
2. To 1 drop of 1 per cent solution of element under consideration was added 1 drop of 0.1 per cent solution of phosphate plus 1 drop of strychnine molybdate reagent.

A yellow precipitate indicated a positive test, and variations in color due to interferences were noted.

Results of Investigation. Positive interferences: Au^{+++}, Be^{++} (very slight), VO_4^{---}, $HAsO_4^{--}$, WO_4^{--}, Pt^{++++} (slight). Negative interferences: V^{+++}, As^{+++}, Sb^{+++}, F^-, $C_2O_4^{--}$, CNS^-, (slight), $P_6O_{18}^{------}$, $P_4O_{13}^{------}$, $P_2O_7^{----}$, Ti^{+++}, Zr^{++++}, Sn^{++}.

Masking interferences: S^- (brownish black precipitate), $S_2O_3^{--}$ (reduces the phosphomolybdate to molybdenum blue), I^- (brown precipitate), MnO_4^- (color of ion), $Fe(CN)_6^{----}$ (brown precipitate), Ir^{++++} (color of Ir^{++++} colors test precipitate brown).

The polyphosphates reduce the sensitivity of the test probably through a competitive reaction with the reagent, but soon begin to revert to orthophosphate when put in solution. Consequently, tests for orthophosphates are obtained from solutions of polyphosphates which are allowed to stand, regardless of the particular test procedure followed.

Table I. Interferences

Test	Limit of Identification (Gram of P)	Limiting Concentration of HPO_4^{--}	Number of Positive Interferences	Number of Negative Interferences	Number of Masking Interferences
Strychnine molybdate	1.6×10^{-6}	100 cu. mm. of 0.005% solution	6	12	6
Ammonium molybdate–stannous chloride	1.6×10^{-6}	100 cu. mm. of 0.005% solution	4	2	10
Ammonium molybdate–benzidine	9.7×10^{-8}	30 cu. mm. of 0.001% solution	13	1	13
Modified strychnine molybdate	9.7×10^{-6}[a]	30 cu. mm. of[a] 0.1% solution	0	7	3

[a] If confirmatory test is run on filter paper, limiting concentration is 30 cu. mm. of 0.01 per cent solution in regard to HPO_4^{--}. This is equivalent to 9.7×10^{-7} gram of phophorus.

Ammonium Molybdate–Stannous Chloride Test. Denigès (*3*) proposed the ammonium molybdate–stannous chloride test for the detection of phosphates and arsenates. The heteropoly acid formed when ammonium molybdate is added to an acid solution of soluble phosphates or arsenates is readily reduced by stannous chloride. The molybdenum blue which is formed by this reduction is discussed by Denigès (*4*) in regard to stable and unstable forms. Chapman (*1*) showed that the silicomolybdate may also be formed when acidity is low. Once this complex silicomolybdate is formed it is stable, even after the acidity is increased. Interference, when as much as 700 parts per million of silica is present, is avoided if the acid is added first, followed by the molybdate reagent.

Reagents. Ammonium molybdate, 5 grams dissolved in 100 ml. water and poured into 35 ml. of nitric acid (sp. gr. = 1.2).

Stannous chloride, 0.96 gram of stannous chloride dihydrate dissolved in 50 ml. of 1 to 2 hydrochloric acid solution. This solution should be made up fresh.

Hydrochloric acid, approximately 4 *N*.

Method of Study. The test was carried out on a white spot plate.

1. To 1 drop of the 1 per cent solution of the element under consideration was added 1 drop of 4 *N* hydrochloric acid, plus 1 drop of ammonium molybdate solution, plus 1 drop of stannous chloride.

2. To 1 drop of 1 per cent solution of the substance under consideration was added 1 drop of 0.1 per cent solution of orthophosphate, plus one drop of 4 *N* hydrochloric acid plus 1 drop of ammonium molybdate solution, plus 1 drop of stannous chloride. A blue-green coloration was an indication of a positive test for phosphate.

Results of Investigation. Positive interferences: Be^{++} (very slight), Ti^{+++} (fades out quickly), $HAsO_4^{--}$, WO_4^{--}. Negative interferences: $C_2O_4^{--}$, lactate (slight).

Masking interferences: Au^{+++} (blue to black color), SeO_3^{--} (orange precipitate), SeO_4^{--} (orange precipitate), TeO_3^{--} (black precipitate, fades out quickly, so does not interfere with the test), TeO_4^{--} (same as TeO_3^{--}), S^- (black precipitate), $Fe(CN)_6^{---}$ (dark brown precipitate), $Fe(CN)_6^{----}$ (dark red color), CNS^- (red color), Pd^{++} (modifies test color to a very dark dirty green).

Ammonium Molybdate–Benzidine Test. Feigl proposed (*7*) the use of an acetic acid solution of benzidine hydrochloride as a means of confirming the presence of phosphorus in the yellow precipitates produced by ammonium molybdate. The precipitate, to which benzidine has been added, is held over an open ammonia bottle. If the precipitate is composed of ammonium phosphomolybdate, a blue color is developed. According to Feigl (*8*) a blue coloration will be obtained if 0.00066 mg. of phosphorus pentoxide is present. An even more sensitive test is obtained (*6*) if the ammonium molybdate solution is placed on "blue band" filter paper and dried in an air oven. If a drop of the test solution is added to freshly prepared molybdate paper, followed by a drop of benzidine and a drop of saturated sodium acetate solution, a blue fleck is formed if 0.05 microgram of phosphorus pentoxide is present. It has been claimed (*9*) that interferences with this test from silicates and borates are prevented if the ammonium molybdate solution contains 15 per cent tartaric acid. The use of tartaric acid, however, seems to be impractical, since it was found that it not only prevented reactions with silicates and borates, but also inhibited the reaction with phosphates. The molybdate paper–sodium acetate method was selected for study.

Reagents. "Blue band" filter paper is impregnated with 5 per cent ammonium molybdate solution and dried in an open air oven.

Benzidine, 0.05 gram of benzidine hydrochloride dissolved in 10 ml. of glacial acetic acid and diluted to 100 ml. with water.

Sodium acetate, saturated solution.

Method of Study. The test was run on the impregnated filter paper in the following manner:

1. To the impregnated molybdate paper was added 1 drop of 1 per cent solution of the ion being studied, plus 1 drop of benzidine solution, followed by 1 drop of the sodium acetate solution.

2. To the impregnated molybdate paper was added 1 drop of 1 per cent solution of the ion being studied, plus 1 drop of 0.1 per cent solution of orthophosphate. One drop of benzidine was then added, followed by 1 drop of sodium acetate solution. A blue fleck indicated a positive test for orthophosphate.

Results of Investigation. Positive interferences: Be^{++}, SiO_3^{--}, V^{+++} (color of ion), VO_4^{---}, $HAsO_4^{--}$ (this reaction is much slower than the phosphate test), $S_2O_3^{--}$, Cr^{+++} (color of ion), CrO_4^{--} (purple), SeO_3^{--} (slight), TeO_3^{--} (slight), BrO_3^- (slight), I^-, Fe^{++}, CN^-, $Fe(CN)_6^{---}$.

Negative interference: F^-.

Masking interferences: Cu^{++} (brown stain), Au^{+++} (brown to blue stain), Ti^{+++} (blue to black precipitate forms immediately upon addition to paper), Sn^{++} (same as titanium), NO_2^- (brown stain), Sb^{+++} (causes immediate formation of blue stain in the presence of phosphate), S^{--} (black stain), MnO_4^- (brown stain), Fe^{+++} (slight masking effect due to color of ion), $Fe(CN)_6^{----}$ (brown stain), catechol (brown stain), Ru^{+++} (masking is due to color of ion), Ir^{+++} (brown stain).

Modified Strychnine Molybdate Test. As a result of the investigation of known drop test procedures a modified strychnine molybdate test was developed which the authors believe superior to other tests for phosphate, particularly in regard to specificity (see Table I). The new test is identical to the Denigès strychnine molybdate procedure except that the precipitate formed with strychnine molybdate is treated with a reducing agent in order to establish the presence of phosphorus. Several reducing agents were tried, including stannous chloride, thiosulfate, 1-amino-2-naphthol-4-sulfonic acid, and benzidine. Benzidine proved to be the best of those tried.

Reagents. Strychnine molybdate, 2.0 grams of molybdic acid added to 20 ml. of concentrated nitric acid and diluted to 75 ml. with stirring until solution is complete. Strychnine sulfate (0.6 gram) is added and heated gently until all the strychnine has dissolved. It is diluted to 100 ml. and heated slightly below the boiling point for 3 to 5 minutes until a yellow solution is obtained.

Benzidine, 0.05 gram of benzidine hydrochloride dissolved in 10 ml. of glacial acetic acid and diluted to 100 ml. with water.

Sodium acetate, saturated solution.

Method of Study. The test is best carried out on a combination black and white spot plate designed by West (*11*). If a combination spot plate is not available, the strychnine molybdate reagent is first added to the test solution on a black spot plate. If a precipitate forms, a confirmatory test is run on a white spot plate. For detection of phosphate in quantities below 0.01 mg. it is suggested that the confirmatory test be carried out on a good grade of quantitative filter paper.

1. To 1 drop of 1 per cent solution of the ion being studied was added 1 drop of strychnine molybdate reagent. If a precipitate could be seen against the black background of the combination spot plate its identity was established by the further addition of 1 drop of benzidine reagent, followed by enough sodium acetate solution to neutralize the excess acid present.

2. To 1 drop of a 1 per cent solution of the ion under consideration was added 1 drop of a 0.1 per cent solution of phosphate, plus 1 drop of the strychnine molybdate reagent. If a precipitate could be seen against the black background of the combination spot plate its identity was established by the further addition of 1 drop of benzidine reagent, followed by enough of the sodium acetate solution to neutralize the excess acid. A blue-green color, after the addition of the sodium acetate solution, which could be seen against the white background of the combination spot plate, indicated a positive test for phosphate.

Results of Investigation. Positive interferences: None.

Negative interferences: As^{+++} (slight interference in a neutral solution), V^{+++} (no interference in a neutral solution), F^-, $C_2O_4^{--}$ (slight), $P_6O_{18}^{------}$, $P_4O_{13}^{------}$, $HAsO_4^{--}$ (slight).

Masking interferences: S^{--} (brown-black precipitate), MnO_4^-, $Fe(CN)_6^{----}$ (brown precipitate).

The results obtained from the interference study are listed in Table I. Of the tests studied not one was entirely free from all types of interference.

The interference study was run with solutions in which the ion being studied was most stable. This made it necessary to run some of the tests in rather strong acid solutions, others in basic solution. For detecting phosphates in unknown solutions by any of the four methods studied, best results are obtained if the original test solution is nearly neutral or weakly acid.

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Microestimation of Bromide as Pentabromorosaniline

WM. J. TURNER, Veterans' Administration Facility, Northport, N. Y., and University of California, Los Angeles, Calif.

GUARESCHI (*1*), in 1913, reported that bromine vapor caused paper impregnated with Schiff's reagent to turn violet. Since then there have been a number of unsuccessful attempts to apply this reaction to the quantitative determination of bromide (*2, 3, 5*). Although Wikoff, Bame, and Brandt (*4*) claim to have measured the bromide content of normal blood by its use, the present writer has been unable to duplicate their results.

There are described below the conditions under which bromide is quantitatively oxidized to bromine and substituted on rosaniline (reduction unnecessary) to give pentabromorosaniline, which can be separated completely from unreacted pigment by extraction into benzyl alcohol from 7 *N* sulfuric acid and determined photometrically.

Experimental

PREPARATION OF PENTABROMOROSANILINE. Two grams of bromine were added to 1 gram of rosaniline in dilute acetic acid. The purple precipitate was recovered in 92 per cent yield, based on the expected formation of pentabromorosaniline acetate. It was found to be impure, and was separated from chloroform-soluble material by Soxhlet extraction. It crystallized from methanol in dark green prisms with intense metallic luster. There was no sharp melting point. An analysis was conducted by E. R. Duncan, to whom the author is indebted for the following report:

$C_{22}H_{18}N_3Br_5O_2$:	Calculated,	C 34.87	Found, 34.91, 34.37
		H 2.42	3.03, 2.83

The salts of pentabromorosaniline are insoluble in water, but are soluble in polar organic liquids. They are strongly adsorbed even on glass. Triaminotriphenylcarbinol pigments are multiple indicators. The pentabromorosaniline may be separated from rosaniline by extraction from 7 *N* sulfuric acid by benzyl alcohol, at which strength of acid the rate of change of color with change of pH of pentabromorosaniline is minimal and its distribution coefficient between alcohol and acid is most favorable. At this concentration, the solubility of the yellow triacid form of rosaniline in benzyl alcohol is very low. The extinction curve of pentabromorosaniline in a benzyl alcohol extract from 7 *N* sulfuric acid is given in Figure 1. In benzyl alcohol, pentabromorosaniline follows Beer's law at 585 millimicrons. The molar extinction coefficient, $\bar{E}_{585} = 1.57 \times 10^5$, is calculated according to the formula:

$$E_\lambda = \frac{2.303}{d.c} (\log I_0/I)$$

OXIDATION OF BROMIDE TO BROMINE AND ADDITION OF BROMINE TO ROSANILINE. Of the many oxidizing solutions

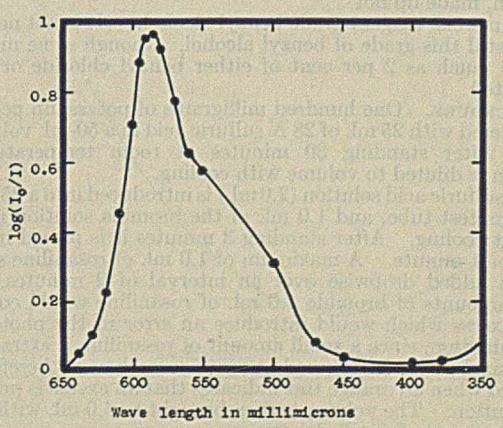

FIGURE 1. EXTINCTION OF PENTABROMOROSANILINE (DIACID FORM) IN ACID BENZYL ALCOHOL AT VARIOUS WAVE LENGTHS

TABLE I. SPECTROPHOTOMETRIC DETERMINATION OF BROMIDE IN POTASSIUM BROMIDE SOLUTION

Bromide		Transmission (Average of 2 Readings)	Bromine Observed	Error
Micrograms			*Micrograms*	%
4.00		87.60	4.05	+1.00
8.00		71.85	8.42	+5.25
16.00		51.90	15.60	−2.50
24.00		35.25	24.14	+0.58
32.00		25.55	31.24	−2.38
40.00		16.75	40.56	+1.40
	Chloride		Apparent Bromide Observed	
	Micrograms			
8.00	35.5	75.30	7.39	−7.6
16.00	35.5	54.10	14.69	−8.2
24.00	35.5	38.60	22.14	−7.8
32.00	35.5	27.50	29.62	−7.4
40.00	35.5	20.00	36.65	−8.4
24.00	10.65	37.50	22.78	−5.1
24.00	35.50	38.60	22.14	−7.8
24.00	177.50	37.65	22.69	−5.6
24.00	355.50	34.15	22.84	+3.5
	Normal Blood			
0.00	1–100	99.40[a]	1.73	..
4.00	1–100	83.35	5.15	+28.8
16.00	1–100	51.35	15.84	− 1.0
24.00	1–100	35.20	24.17	+ 0.7
32.00	1–100	26.30	30.61	− 4.3
40.00	1–100	18.95	37.84	− 5.4

[a] Same reading is obtained with a water blank.

which have been proposed for the liberation of bromine from bromide without the oxidation of chloride, the most satisfactory has been found to be persulfate. It was necessary, however, to transform the peroxydisulfuric acid ($H_2S_2O_8$) into peroxymonosulfuric acid (H_2SO_5) in order to obtain consistent and reliable results. The peroxymonosulfuric acid obtained by the method to be described below liberates bromine at a relatively slow rate, so that time must be allowed for the reaction to occur quantitatively. The solution is unstable and must be made daily from a suitable salt of peroxydisulfuric acid.

The addition of the liberated bromine to rosaniline occurs quantitatively, but at the dilutions employed it requires several minutes for completion. In contact with the oxidizing solution, the pigments are bleached quickly at room temperature, so that the reaction is best carried out as quickly as possible at 0° C.

Procedure and Analytical Results

REAGENTS. Powdered potassium persulfate ($K_2S_2O_8$), and 28 *N* sulfuric acid.

Solution of rosaniline base, 60 milligrams per liter of aqueous solution, made up hot.

Commercial reagent grade benzyl alcohol. (It is not necessary to redistill this grade of benzyl alcohol, although some may contain as much as 2 per cent of either benzyl chloride or benzyl benzoate.)

PROCEDURE. One hundred milligrams of potassium persulfate are covered with 25 ml. of 28 *N* sulfuric acid in a 50-ml. volumetric flask. After standing 30 minutes at room temperature the solution is diluted to volume with cooling.

The sulfuric acid solution (2.0 ml.) is introduced into a 25 mm. × 200 mm. test tube, and 1.0 ml. of the bromide solution is added without cooling. After standing 3 minutes it is placed in an ice bath for 1 minute. A maximum of 1.0 ml. of rosaniline solution is then added dropwise over an interval of 2 minutes. With small amounts of bromide 1.0 ml. of rosaniline would contain a large excess which would introduce an error in the photometric determination, since a small amount of rosaniline is extracted by the benzyl alcohol. The addition of rosaniline is therefore terminated when an orange tint indicates that an excess is present in the solution. The volume is then brought to 4.0 ml. with the required amount of distilled water.

Three minutes after the addition of the first drop of rosaniline, 10.0 ml. of benzyl alcohol are added and the tube is thoroughly shaken. The contents are poured into a centrifuge tube and spun for a few moments to clear and separate the phases. The red-purple supernatant alcohol phase is poured off and its transmission is measured in the photometer. In his determinations, the author has employed both the Beckman Model D spectrophotometer and the Coleman DM spectrophotometer with equally good results. A standardization is first carried out with known quantities of bromide. In the case of the determinations with the Coleman instrument, using a slit 5 millimicrons wide, at 585 millimicrons, square cuvettes 10.0 mm. deep, and with the temperature of the benzyl alcohol solution 26° C., he obtained the following formula in the standardization of the method against bromide:

$$\text{Micrograms of bromide} = 50.82\ (2\text{-log } T) + 1.13$$

For this equation, $\sigma_{(\text{est. } \gamma \text{ Br})} = 0.51$.

When measurements must be made with a visual color comparator it is best to work with bromide levels of 50 to 400 micrograms, and a rosaniline solution containing 450 mg. per liter. A color filter of yellow cellophane has been found satisfactory.

By the use of the Coleman DM spectrophotometer, results such as are given in Table I are readily obtainable.

One set of determinations made with a visual colorimeter on a sample of blood to which known amounts of bromide were added is given in Table II, using a rosaniline solution containing 450 mg. per liter.

The method is inapplicable in the presence of iodide, but is apparently not influenced by the presence of thiocyanate.

TABLE II. COLORIMETRIC DETERMINATION OF BROMIDE ADDED TO BLOOD

Bromide Added	Standard	Unknown	Bromide Found	Error
Micrograms			*Micrograms*	%
60	10	25.6	62.4	+4
80	20	40.3	79.4	−0.8
160	20	20.4	157	−2
240	20	13.2	242	+1
320	20	10.1	317	−1
400	20	8.6	372	−7

Standard: 160 micrograms of Br per milliliter.

Summary

A simple, rapid, inexpensive, and reliable method is described for the determination of bromide in solutions including biological fluids without preliminary separation from chloride. It is based on the reaction of bromine with rosaniline, and colorimetric or photometric determination of the color of the pentabromorosaniline extracted by benzyl alcohol from 7 *N* sulfuric acid solution.

Acknowledgment

The author wishes to express his appreciation to T. L. Jacobs and Charles D. Coryell for their assistance and suggestions, and for the use of their laboratories in this work.

He is indebted to Charles S. Roberts for his statistical analysis of the data in this paper.

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PUBLISHED with the permission of the Medical Director, Veterans' Administration, who assumes no responsibility for the views expressed herein.

CORRECTION: The photomicrograph on page 434 of the May issue represented cadmium iodide, and was furnished through the courtesy of Mary L. Willard.

Detection and Quantitative Determination of 4-Amino-2-methyl-1-naphthol

A Synthetic Vitamin K

AMEL R. MENOTTI

Chemical Laboratory, American Medical Association, Chicago, Ill.

THE hydrochloride of 4-amino-2-methyl-1-naphthol has been introduced to the medical profession as a water-soluble therapeutic agent which possesses vitamin K activity. Increased interest in this compound has necessitated the development of a chemical method for its detection and quantitative determination in preparations now on the market. The procedure described has been found suitable for the assay of preparations containing 4-amino-2-methyl-1-naphthol and yields consistent results with quantities as low as 0.02 mg. Hitherto, the assay of solutions and dry mixtures of 4-amino-2-methyl-1-naphthol hydrochloride has been dependent on the curative effect of the compound on vitamin K–depleted chicks (*4*). It is hoped that the proposed chemical method may supplant, in part, the more complicated biologic assay procedure.

Of possible chemical methods to be investigated, it was felt that a colorimetric method should take precedence over volumetric or gravimetric procedures because of the small quantities of material to be dealt with and the relative ease of colorimetric manipulation. Accordingly, a reagent was sought which would

Possess a high degree of sensitivity

Produce a color which would obey Beer's law of light absorption and be sufficiently stable to allow time for accurate color comparisons

Not be adversely affected by the presence of sodium bisulfite, since this compound is used to stabilize aqueous solutions of 4-amino-2-methyl-1-naphthol

Possess sufficient specificity to permit differentiation of the compound in question from its possible decomposition products

The latter characteristic is of importance because in the biologic method of assay such differentiation is not possible. One of the oxidation products of 4-amino-2-methyl-1-naphthol is 2-methyl-1,4-naphthoquinone (menadione), which possesses the same antihemorrhagic activity when measured on a molecular basis. Investigation of sodium pentacyanoammineferroate, $Na_3[Fe(CN)_5NH_3]$, as a possible reagent revealed that this compound possessed the desired characteristics.

Anger (*1*) described a colorimetric test for the detection of primary aromatic amines which required sodium pentacyanoaquoferriate, $Na_2[Fe(CN)_5H_2O]$, as the reagent. This test provides a basis for the procedure followed herein. In a discussion of Anger's test, Feigl (*2*) attributed the production of color to the substitution of the coordinately bound water molecule, in the pentacyanoaquoferriate complex, by a molecule of the aromatic amine according to the following reaction:

$$[Fe(CN)_5H_2O]^{--} + R{-}NH_2 \longrightarrow [Fe(CN)_5R{-}NH_2]^{--} + H_2O$$

During the course of this investigation, sodium pentacyanoaquoferriate as employed by Feigl (*2*) and sodium pentacyanoammineferriate were tested but were found to possess no advantage over the more readily prepared sodium pentacyanoammineferroate; consequently, the latter compound was chosen for the quantitative determination of 4-amino-2-methyl-1-naphthol. The procedure finally adopted depends on the interaction of sodium pentacyanoammineferroate in alkaline solution with 4-amino-2-methyl-1-naphthol to produce an intense blue color and the comparison of the intensity of this color with that produced by known quantities of the aminonaphthol.

The production of a blue color through the interaction of sodium pentacyanoammineferroate, $Na_3[Fe(CN)_5NH_3]$, and the aminonaphthol may be attributed to a reaction analogous to that which has just been shown—i. e., the replacement of the coordinately bound molecule of ammonia by a molecule of the aminonaphthol.

Curve *A* in Figure 1 represents an absorption spectrum typical of the colored solutions employed in the quantitative determination of 4-amino-2-methyl-1-naphthol. The solution employed to determine the curve shown was prepared by the addition of 1.0 mg. of 4-amino-2-methyl-1-naphthol to 1 ml. of the sodium pentacyanoammineferroate reagent solution. This mixture was allowed to stand for 15 minutes and was then diluted to a concentration corresponding to 0.004 mg. of aminonaphthol per ml. The solution exhibited but little absorption in the blue region of the spectrum.

Curve *B* illustrates the contribution to the total absorption made by the yellow colored reagent solution. The reagent exhibits no appreciable absorption above 5000 Å. For this reason, visual matching of the blue color of the solution is simplified, and more precise spectrophotometric measure-

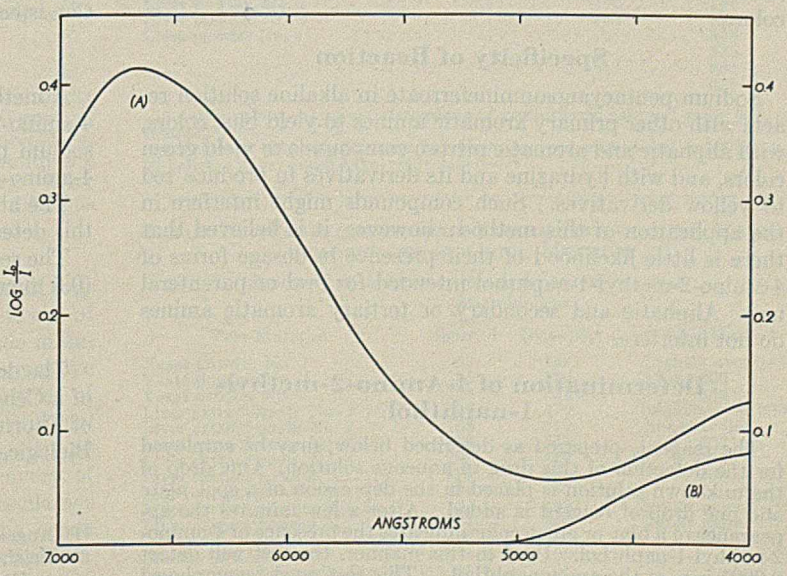

FIGURE 1. DETERMINATION OF 4-AMINO-2-METHYL-1-NAPHTHOL

A. Absorption of solution resulting from interaction of 4-amino-2-methyl-1-naphthol hydrochloride with sodium pentacyanoammineferroate

B. Absorption of sodium pentacyanoammineferroate reagent solution

ments of the absorption maximum at 6650 Å. would provide a highly accurate determination.

To test the applicability of Beer's law $\left(k = \frac{1}{c} \log \frac{I_0}{I}\right)$ to this solution, the values of $\log \frac{I_0}{I}$ were determined at 6500 Å. for various dilutions. It is obvious from the values of k (Table I) that the solution satisfies Beer's law within the limits of experimental error.

Accuracy of Method

The data reproduced in Table II were obtained by visual colorimetric assay of synthetic mixtures of known composition.

The greatest error occurred with the solutions of lowest aminonaphthol content because the concentration of the standard solution was maintained at 1.0 mg. per ml., while the synthetic mixtures varied in aminonaphthol content. The error is due to the difference in color caused by the presence of excess reagent in the solutions of low aminonaphthol content and may be eliminated by the use of a standard of appropriate strength.

The effect of bisulfite on the developed color was determined by adding known amounts of sodium bisulfite to solutions of equal aminonaphthol content, then adding the reagent and comparing the resulting colors. From the data obtained it was apparent that amounts of sodium bisulfite up to 5 mg. per milligram of 4-amino-2-methyl-1-naphthol had no effect on the color; quantities above this amount caused the color to develop more slowly and resulted in a reduction of the final color intensity.

Table I. Applicability of Beer's Law to Colored Solution Obtained by Interaction of Sodium Pentacyanoammineferroate with 4-Amino-2-methyl-1-naphthol

$\log \frac{I_0}{I}$	c, Concentration of Aminonaphthol *Mg./ml.*	k, $\frac{1}{c} \log \frac{I_0}{I}$
1.000	0.010	100
0.508	0.005	101
0.402	0.004	100
0.192	0.002	96
0.098	0.001	98

The presence of 2-methyl-1,4-naphthoquinone, an oxidation product of 4-amino-2-methyl-1-naphthol, was found to have no effect on the development and final intensity of the color.

Specificity of Reaction

Sodium pentacyanoammineferroate in alkaline solution reacts with other primary aromatic amines to yield blue colors, with aliphatic and aromatic nitroso compounds to yield green colors, and with hydrazine and its derivatives to produce red to yellow derivatives. Such compounds might interfere in the application of this method; however, it is believed that there is little likelihood of their presence in dosage forms of 4-amino-2-methyl-1-naphthol intended for oral or parenteral use. Aliphatic and secondary or tertiary aromatic amines do not interfere.

Determination of 4-Amino-2-methyl-1-naphthol

The reagent, prepared as described below, may be employed for the detection of this drug in aqueous solution. One drop of the unknown solution is placed in the depression of a spot plate and one drop of reagent is added. After a few minutes the appearance of a blue or green color indicates the presence of 4-amino-2-methyl-1-naphthol. Used in this manner, the test will detect 0.0005 mg. of the aminonaphthol. (This test must be employed with due regard to the interferences mentioned above.)

Reagents. Standard 4-amino-2-methyl-1-naphthol solution: 60.53 mg. of pure 4-amino-2-methyl-1-naphthol hydrochloride and 50.0 mg. of sodium bisulfite dissolved in 50.0 cc. of distilled water contained in a dark glass-stoppered bottle. Under conditions of normal usage this solution is stable for from 4 to 6 hours; when allowed to stand overnight it may decrease in strength as much as 10 to 15 per cent.

Sodium pentacyanoammineferroate solution: 250 mg. of sodium pentacyanoammineferroate and 500 mg. of anhydrous sodium carbonate dissolved in 25 cc. of distilled water. This solution is stable for about one week.

Table II. Analysis of Samples of Known Composition

4-Amino-2-methyl-1-naphthol Added *Mg.*	Quantity Found *Mg.*	Error *Mg.*
1.00	1.00	0.00
1.00	1.00	0.00
0.95	0.97	0.02
0.93	0.94	0.01
0.90	0.93	0.03
0.85	0.87	0.02
0.80	0.84	0.04

The crystalline reagent $Na_3[Fe(CN)_5NH_3]$ was first described by Hofmann (*3*). It may be prepared as follows:

Ten grams of sodium nitroprusside are ground to a fine powder and added to 30 ml. of concentrated ammonium hydroxide solution. The mixture is shaken to dissolve the salt, and the resulting solution is left overnight at from 0° to 10° C. The crystals which form are removed by filtration, washed several times with 95 per cent ethanol and once with absolute methanol, and dried over sulfuric acid in vacuum. (Additional crystalline material may be obtained in a finely divided state from the mother liquor by adding 95 per cent ethanol, filtering, and washing in the manner described. The material thus obtained is of lower purity than the crystalline substance which forms overnight, but it may be used effectively as a reagent.)

Procedure. For the assay of ampouled solutions, appropriate dilutions are made, so that the resulting solution contains approximately 1 mg. of 4-amino-2-methyl-1-naphthol per ml. Powdered mixtures which contain the drug may be extracted with distilled water containing 0.1 per cent of sodium bisulfite, added to inhibit decomposition of the drug. The extract should be diluted to contain about 1 mg. of 4-amino-2-methyl-1-naphthol per ml. of solution, and the final solution may be filtered if necessary.

The unknown solution (1 cc., calculated to contain about 1 mg. of 2-methyl-4-amino-1-naphthol) is transferred to a 50-ml. volumetric flask, 1.0 ml. of the standard aminonaphthol solution is placed in a second 50-ml. flask and, if necessary, the contents of the flasks are adjusted to approximately equal volumes with distilled water. Then 1.0 ml. of sodium pentacyanoammineferroate reagent is added to each flask, mixed, and set aside in the dark for 15 minutes. Finally, distilled water is added to the mark of each flask and mixed, and the solutions are compared in a colorimeter. If the solutions to be compared are found to vary more than 10 per cent in aminonaphthol content, it is best to carry out a second determination after adjusting the concentration of the standard to approximately that of the unknown. Consistently accurate results may be obtained in this manner.

Summary

A method developed for the quantitative determination of 4-amino-2-methyl-1-naphthol depends on the interaction of sodium pentacyanoammineferroate in alkaline solution with 4-amino-2-methyl-1-naphthol to produce a blue color.

The absorption spectrum of a typical solution obtained in this determination has been determined.

The reagent described will detect the presence of 0.0005 mg. (0.5 microgram) of 4-amino-2-methyl-1-naphthol.

Acknowledgment

The data for the absorption curves were obtained by means of a Cenco-Sheard spectrophotelometer through the courtesy of Thorfen R. Hogness, in the laboratories of Spectroscopic Biological Investigations, University of Chicago.

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Microbiologic Assay of Natural Pantothenic Acid in Yeast and Liver

Influence of Clarase Digestion

ELEANOR WILLERTON AND HOBART W. CROMWELL
Bacteriological Research Department, Abbott Laboratories, North Chicago, Ill.

MICROBIOLOGIC assays of natural pantothenic acid have often given much lower values than chick assays, because of the existence of part of the vitamin in combined form, in which it is unavailable to the test organism. That this combined form of pantothenic acid could be freed by enzyme digestion was noted in 1934 by Rohrmann, Burget, and Williams (*2*). Using yeast as the test organism, they obtained much higher assays with extracts from autolyzed tissue, especially liver, than from fresh tissue. Pennington, Snell, and Williams (*1*) advised autolysis of samples, wherever suitable, previous to microbiologic assay with *Lactobacillus casei*. Strong, Feeney, and Earle (*3*) also using *L. casei*, found that clarase digestion of yeast and animal tissues satisfactorily increased the pantothenic acid values obtained.

[Since the submission of this manuscript for publication a report by Waisman, Henderson, McIntire, and Elvehjem (*4*) has appeared, comparing the use of pepsin, clarase, and pancreatin in preparation of meats for such an assay. Pancreatin was found more effective than clarase in treatment of muscle tissue, and gave about the same results with softer tissue such as liver and kidney. Both were more effective than pepsin.]

Since accounts of the use of clarase have been rather lacking in detail, it seems worth while to record here experiences with this enzyme in digestion of yeast and liver preparations used in pharmaceutical manufacturing. These materials have consistently given the authors much lower values for pantothenic acid by the microbiological method than by the chick method. After adequate clarase digestion, however, the values obtained by the microbiologic method are higher, and compare favorably with those obtained by the chick method. In their assays the authors have followed the method outlined by Strong, Feeney, and Earle (*3*).

Test materials were digested at pH 5.0 and 37° C. under toluene. To 0.5 gram of the test sample were added 1.0 gram of the clarase powder and water to 10-cc. volume. If necessary, coarse particles, and particularly yeast cells, were broken up in a small glass colloid mill before incubation of the mixture. After digestion the toluene was removed, and appropriate dilutions of the mixture were made for testing.

Clarase is available as a dry powder in crude and concentrated forms, and from the standpoint of expense, it was of considerable interest to know whether or not the crude material would be satisfactory. In Table I are shown comparative results with the two forms. Only 10 per cent mixtures of the concentrated clarase are considered since, in the authors' experience, lower concentrations were inadequate with 48 hours' digestion time. In no instance was the recovery of pantothenic acid as great after digestion with crude clarase as with the concentrated enzyme, even though the crude material was used in as much as 20 per cent concentration. Possibly longer digestion would release more of the vitamin but, for control of manufacturing, 48 hours is about the limit of convenience, and some of the results suggest a possibility of loss of pantothenic potency with prolonged incubation.

In the light of this information, a number of different lots of yeast powder, yeast extract, and liver extract were tested, and one lot of Solvamin (Commercial Solvents Company). Assays were made without digestion, and after digestion of the samples with 10 per cent concentrated clarase for 48 hours at 37° C. Independently, assays on the same samples by the chick method were made by Mrs. F. Peirce Dann of the company's bioassay laboratories. Table II shows the results. The assays for pantothenic acid were much higher after digestion than before, and generally approximated the values reported by the animal method.

The clarase itself contains an appreciable amount of pantothenic acid which must be considered in evaluation of the results. Since the different lots contain varying amounts, a sample of each lot should be assayed after self-digestion when it is first used and occasionally thereafter.

The digestion of these materials, especially yeast, apparently produces, or releases, a substance into the digest that interferes with the metabolism of the test organism. The evidence of this is the progressively lower values obtained at

TABLE I. COMPARISON OF CRUDE AND CONCENTRATED CLARASE IN PANTOTHENIC ACID ASSAY[a]

(Clarase digestion, 48 hours)

Test Material	Crude 10%	Crude 15%	Crude 20%	Concentrated 10%
	Micrograms per gram			
Yeast powder	154	167	...	170
Yeast extract	346	...	...	358
Liver paste No. 1	324	323	...	470
Liver paste No. 2	...	178	...	213
Liver paste No. 3	...	...	470	565
Liver powder No. 1	...	...	130	198
Liver powder No. 2	...	...	388	548
Liver powder No. 3[b]	...	...	...	338
	...	...	...	335
	...	...	...	331
	...	...	...	327

[a] Assay values shown as micrograms of pantothenic acid per gram of test sample.
[b] Values of 338, 335, 331, and 327 were obtained after digestion 48 hours, 72 hours, 4 days, and 6 days, respectively.

TABLE II. PANTOTHENIC ACID VALUES OBTAINED BY MICROBIOLOGIC AND BY CHICK METHODS

(Expressed in micrograms per gram of test material)

Test Material	Microbiologic: Not digested	Microbiologic: Digested[a]	Chick Method
Yeast powder No. 1	55	137	Slightly over 165
Yeast powder No. 2	55	170	About 200
Yeast extract No. 1	223	321	360
Liver extract paste No. 1	357	370	Slightly over 300
Liver extract paste No. 2	165	213	Not over 300
Liver extract paste No. 3	456	565	600
Liver extract paste No. 4	288	448	450
Liver extract powder No. 1	219	338	360
Liver extract powder No. 2	204	357	...
Liver extract powder No. 3	124	198	300 or more
Liver extract powder No. 4	377	548	600 or more
Solvamin	426	1240	1200
Clarase (crude)	4.8	..	...
Clarase (concentrated), Lot 1	11.5	..	...
Clarase (concentrated), Lot 2	10.0	16.0	...
Clarase (concentrated), Lot 3	...	27.0	...

[a] Digested 48 hours with concentrated clarase 10%.

Table III. Calculations at Various Test Levels of Pantothenic Acid in a Yeast Powder after Clarase Digestion

Test Solution Added per Culture	Digestion with Concentrated Clarase 10%
Cc.	
0.5	188
0.75	173
1.0	177
1.5	153
2.0	133

the higher levels tested (Table III). More difficulty has been encountered with yeast than with liver preparations, perhaps because the lower potency does not permit sufficient dilution of the test sample beyond the range of activity of the inhibitor. With such a progressive decrease in values for pantothenic acid as the test level is increased, it is sometimes difficult to decide which, if any, of the figures are correct. Usually an average of calculations from the two or three lowest test levels has approached fairly closely to the potency obtained by the chick assay. It is probable, of course, that materials of lower potency would present a real difficulty because of the stronger dilutions required for testing.

The assays of the clarase itself also show the presence of an inhibiting substance, with some lots more than with others, but in none has this been enough to account for the effect in the digested samples of yeast or liver, which are tested in much weaker dilutions than the clarase alone.

Obviously, if this inhibition phenomenon could be overcome, less difficulty would be encountered in making calculations and the dependability of the method would be increased. The authors have not studied this problem except to try extraction of the digested material with hexane and with ether before testing. The interfering substance was not removed.

Summary and Conclusions

Digestion of 0.5-gram samples of yeast and of liver preparations with 1.0 gram of concentrated clarase in a total volume of 10 cc., for 48 hours at 37° C., has proved adequate for release of combined pantothenic acid. After such treatment the assay values by the microbiologic method compared favorably with those obtained by the chick method, although averaging somewhat lower.

Digestion with double this amount of crude clarase powder was inadequate.

Digestion of these materials with clarase apparently produces or releases a substance which interferes with the metabolism of the test organism, *L. casei*. This does not interfere seriously in testing materials of higher potency where test levels are out of range of the inhibiting factor. If this effect can be overcome, the dependability and usefulness of the method will be increased.

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Direct Determination of Sulfur

G. L. MACK and J. M. HAMILTON
New York State Agricultural Experiment Station, Geneva, N. Y.

An ammoniacal cuprous sulfate reagent is prepared by reducing a solution of cupric ammonium sulfate with hydroxylamine hydrochloride. The reaction of this reagent upon elemental sulfur in acetone solution to form colloidal cuprous sulfide has been made the basis of a turbidimetric method for the direct determination of sulfur.

The reagent was found to be capable of detecting 1 microgram of sulfur in 10 ml. of solution. The determination is fairly specific and accurate. The rapidity with which a large number of samples can be analyzed makes it especially useful for routine work. The method has been applied particularly to the analysis of sulfur in spray residues.

A RAPID method of analysis for sulfur in spray residues is much needed in the practical evaluation of commercial fungicides.

The usual procedure (*3*, *11*) has been to oxidize the elemental sulfur to sulfate, which is then precipitated and weighed as barium sulfate. The gravimetric method is so time-consuming that various volumetric (*6*, *8*, *13*, *14*) and photometric (*15*) procedures for the estimation of sulfate ion have been proposed. However, for work with spray residues, the oxidation itself requires a considerable amount of time, no matter whether the sulfur is first extracted from the plant material (*11*) or the whole sample is oxidized in an alkaline fusion (*1*). The same objection would apply to methods based upon preliminary reduction of sulfur to sulfide (*5*).

Thus a direct determination of sulfur in the solvent used for extraction from the plant material would be the most desirable procedure. A direct iodometric method has already been proposed by Fleck and Ward (*4*), and an alkalimetric method first suggested by Kühl (*7*) has been adapted to the analysis of spray residues by Small (*10*), but large errors inherent in these methods make them of little use for accurate work.

In 1929 Pierce (*9*) found that von Nagy Ilosva's reagent (*12*) could be used as an extremely sensitive test for carbon bisulfide in adulterated olive oil and noted that elemental sulfur also gave a test with the reagent.

After considerable experimentation the authors have modified the ammoniacal cuprous sulfate reagent so that it reacts quantitatively with elemental sulfur in solution to give cuprous sulfide which can be determined turbidimetrically.

Reagents

Stock Solution A. Cupric sulfate pentohydrate, 4.0 grams; ammonium hydroxide (28.3 per cent ammonia by weight), 48.0 ml.; distilled water to make 100 ml.

Stock Solution B. Hydroxylamine hydrochloride, 20.0 grams; distilled water to make 100 ml.

Reagent Solution. To 5 ml. of solution A add 5 ml. of solution B, then slowly add water to make 50 ml. and shake vigorously. The reagent is unstable and should be freshly prepared from the stock solutions each day. The rate of decomposition is increased by the action of light, of heat, and especially of oxygen. The reagent should thus be kept cool and out of direct sunlight, and the container should be closed with a Bunsen valve or a loosely fitting stopper, since nitrogen is slowly evolved from the solution. The complete decomposition of the reagent may take several days and is indicated by the sudden return of the blue color of ammoniacal cupric sulfate. The quality of the reagent solution may be tested by adding 1 ml. to 20 ml. of a 50 per cent solution of acetone in water. If no blue color appears on standing 3 minutes, the reagent is satisfactory for use. In practice the authors discard all solutions which have been made up more than 12 hours, since no trouble has been experienced with the stability of the reagent up to that time.

Table I. Precision of Results

Sulfur Taken	Average Deviation of 6 Determinations
Micrograms	*Microgram*
5	0.3
10	0.2
20	0.2
40	0.3
60	0.4

Preparation and Solution of Sample

A sufficient quantity of leaves or other plant material is taken to ensure a representative sample. The necessary number may vary from two or three hundred leaves from at least three trees for field samples to as few as five or ten leaves when a precision laboratory sprayer is employed. With large samples several hundred disks of known area are cut from the leaves and the sulfur is dissolved by stirring them for 2 minutes each in a series of beakers containing 250, 200, and 200 ml. of acetone. Further rinsing may be necessary with some samples, and in any case the final rinsing should be tested for sulfur by mixing 5 or 10 ml. of the acetone extract with an equal quantity of distilled water and adding 1 ml. of the cuprous sulfate reagent. The combined acetone extracts and washings are made up to a definite volume with more acetone and a convenient aliquot is taken for analysis.

Used acetone can be recovered by a single distillation, since extensive tests have shown that sulfur is not carried over with boiling acetone.

The acetone extracts and particularly the standard solutions of sulfur should be protected from direct sunlight. Investigation has shown that elemental sulfur undergoes a photochemical reaction when dissolved in organic liquids such as acetone, dioxane, and butyl carbitol. Ultraviolet light was found to be most efficient in producing this reaction, while the longer wave lengths had little effect. Thus, in a solution containing 200 micrograms of sulfur in 100 ml. of acetone, this reaction was 85 per cent complete in 20 minutes when exposed to radiation from a quartz-enclosed mercury vapor lamp 20 cm. above the center of the liquid and operating at 4.2 amperes and 120 volts. A similar solution required 11 days to reach the same stage of reaction when enclosed in Pyrex glass and exposed to indirect winter daylight.

The product of this photochemical reaction does not react with the cuprous sulfate reagent. The formation of combined sulfur can be prevented by wrapping the container in black paper and keeping it in a dark cabinet. A standard solution used periodically for the determination of calibration curves and repeatedly exposed for short periods of time to indirect daylight was found to have undergone no change in elemental sulfur content over a period of 4 months when the above precautions were observed.

Experimental Procedure

An aliquot containing not more than 75 micrograms of sulfur is pipetted directly into the photometer tube and diluted if necessary with pure acetone to a volume of 10 ml. Ten milliliters of distilled water are added and mixed by inverting the tube five times. The tube is carefully cleaned with a soft cloth and inserted in the photoelectric photometer and the instrument is adjusted to the maximum scale deflection. One milliliter of cuprous sulfate reagent is then added and the centents of the tube are thoroughly mixed by inverting five times. The tube is again wiped off and inserted in the photometer, and the scale deflection exactly 60 seconds after the addition of the reagent is recorded.

The galvanometer readings are related to micrograms of sulfur by means of a calibration curve. The experimental points on this curve are obtained by adding known increments of sulfur from a standard solution to a series of photometer tubes containing the blank acetone extracts. The sulfur in these solutions should be determined in exactly the same way as in the unknowns. A convenient concentration of sulfur for the standard solution is 400 to 500 mg. per liter, which may be diluted further if desired.

The sulfur for the standard solutions was recrystallized four times from thiophene-free benzene and dried in a desiccator.

An Evelyn photoelectric colorimeter was used in this work, but any good photometer could be used. For this determination a direct-reading type of photometer is to be preferred to the photoelectric null-point type or the neutral-wedge type, both of which must be manually adjusted to a drifting end point which is to be recorded at a definite time.

Interfering Materials

The light green color of the leaf pigments in the acetone extracts affects the galvanometer readings slightly, but this effect can be practically eliminated by using a filter having a 95 per cent light transmission between 5500 and 5850 Å. with a maximum transmission at 5650 Å.

A more serious source of interference is caused by the plant waxes and oil residues which affect the formation of the colloidal cuprous sulfide. Although correct results may be obtained by using a calibration curve obtained with a blank extract of the same materials, the reproducibility of the results is generally adversely affected.

In working with a laboratory sprayer glass plates coated with cellulose nitrate are sometimes used as a standard surface (*2*). A white turbidity is produced when water is added to the acetone extract, so that the final light transmission might be expected to be decreased. Actually, however, the formation of cuprous sulfide may be so inhibited that more light is transmitted than if the cellulose nitrate were absent.

Carbon disulfide, inorganic sulfides, and xanthates react with the reagent but sulfates, sulfites, thiosulfates, thiocyanates, organic sulfides and disulfides, and sulfones, mercaptans, and thiophenols do not. Carbon tetrachloride produces a red coloration with the reagent.

Table II. Recovery of Sulfur from Leaves and Glass Plates Sprayed with a Laboratory Sprayer

Type of Surface	Concn. of Sulfur	Weight of Spray Deposit	Calcd. Sulfur in Deposit	Sulfur Found
	Mg./g. spray solution	*Gram*	*Micrograms*	*Micrograms*
Glass	0.13	0.0403	5.2	5.9
Leaf	0.26	0.0411[a]	10.7	10.9
Glass	0.39	0.0414	16.1	15.8
Leaf	0.52	0.0403[a]	21.0	23.0
Glass	0.52	0.0403	21.0	22.8

[a] Deposit on leaves was not weighed. Weights given are averages of values determined on glass plates before and after leaves were sprayed.

Results

The reproducibility of results obtained by this method depends to a great extent upon careful technique. The formation of a colloidal precipitate is often affected by slight variations in the procedure. The precision attained in this laboratory is indicated in Table I. The deviation of a single determination should not exceed 1 microgram.

The accuracy of the method is shown in Table II. Apple leaves and glass microscope slides coated with cellulose nitrate were sprayed with known concentrations of sulfur. In a given time a nearly constant amount of spray is deposited on a given area of surface, so that the total amount of sulfur can be calculated. The agreement of the last two columns is satisfactory.

TABLE III. SOLUBILITY OF COMMERCIAL SULFUR PRODUCTS IN BUTYL CARBITOL AT 25.0° C.

Product	Equilibrium Concentration Approached from	Solubility of Sulfur G./l.
Recrystallized C. P. sulfur	Supersaturated soln.	2.18
	Unsaturated soln.	2.21
Mike sulfur	Supersaturated soln.	2.14
	Unsaturated soln.	2.26
Koppers flotation paste (dried at 90° C.)	Unsaturated soln.	2.34
Stauffer's paste (dried at 90° C.)	Unsaturated soln.	2.15
Stauffer's dry magnetic 70 paste	Unsaturated soln.	2.20

To determine whether commercial sulfur products contained appreciable quantities of interfering materials, the solubility of several of these products in the monobutyl ether of diethylene glycol was determined. This solvent, known commercially as butyl carbitol, may be substituted for acetone throughout the analytical procedure and the amount of sulfur in solution determined by this method. The results in Table III show that no appreciable interfering materials occur in the commercial fungicides tested and that the solubility of the sulfur in them is equivalent to that of recrystallized C. P. sulfur.

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A New Microtest for Iodide

DAVID HART AND ROBERT MEYROWITZ
Brooklyn College, Brooklyn, N. Y.

ALTHOUGH most chemical analyses depend upon the possibility of chemically converting the constituents to be detected into another characteristic form, the sensitivity of these chemical tests which depend upon a characteristic precipitate, gas, or colored or fluorescent solution is necessarily limited by the physical constants involved and the personal equation of the observer. However, by making use of catalyzed reactions, extremely small amounts of substances can be detected. Thus, in the detection of iodide, the use of catalyzed reactions has been very successful.

Feigl and Frankel (*4*) developed a method for detecting the presence of 0.05 microgram of iodide in a concentration of 1 part per million, based on the conversion of *o*-nitroaniline, its isomers, or other primary aromatic amines to form a diphenyl derivative with bromobenzene in the presence of cuprous iodide or a mixture of copper and potassium iodide. Using the catalytic effect of iodide upon the ceric-arsenite oxidation-reduction reaction, Kolthoff and Sandell (*6*) showed that 0.05 microgram of iodide can be detected in a concentration of 1 part in 500,000 (*3*). The authors have also presented a method (*5*) for detecting iodide by its catalytic effect upon the nitrite-arsenite oxidation-reduction reaction, whereby 0.2 microgram of iodide can be detected in a concentration of 1 part in 500,000.

Continuing their work on the detection of halides, the authors have developed a new, simple, and rapid microtest for iodide, which is based upon the catalytic effect of iodide on the nitrate-arsenite oxidation-reduction reaction and may be carried out in a small test tube or on a spot plate. A search of the literature revealed no mention of this effect, except where it was applied to the manufacture of arsenates by the oxidation of arsenious oxide with nitric acid. Smith and Miller (*8*), investigating the inhibitory effect of mercury on this reaction, showed that hydrochloric, hydrobromic, and hydriodic acids will act as catalysts. Shortly before this, Behse was granted a patent (*1*) for the manufacture of arsenic acid by means of nitric acid using hydrochloric acid as a catalyst. Later, Latimer (*7*) obtained a patent in which iodide was used as a catalyst. He also claimed that the other halogens, chloride, bromide, and fluoride, could be used as catalysts but that much greater concentrations of these were required.

Since both bromides and chlorides catalyze this reaction, conditions had to be obtained under which moderate amounts of these anions would not interfere in the detection of relatively small amounts of iodide. Using the procedure described below, the authors were able to detect 1.0 microgram of iodide in a concentration of 1 part in 50,000. The presence of 500 micrograms of either thiocyanate, bromide, chloride, or a mixture of these anions does not catalyze this reaction in this procedure. Other anions of the silver nitrate group which are likely to interfere—cyanides ferricyanides, ferrocyanides, and sulfides—are removed in the usual way (*2*) with cobalt nitrate.

Procedure for Detection of Iodide

To a small test tube (or a spot plate) containing 1 drop of the solution to be tested, add 1 drop of *M* sodium arsenite and 2 drops of water and mix thoroughly. Add 2 drops of concentrated nitric acid and allow to stand for 3 minutes after complete mixing. Next add 3 drops of 0.5 *M* silver nitrate, stir the mixture thoroughly, and add 1.5 *M* sodium carbonate dropwise. The formation of a red-brown precipitate of silver arsenate shows the presence of iodide. If the precipitate is yellow (due to silver arsenite), iodide is absent.

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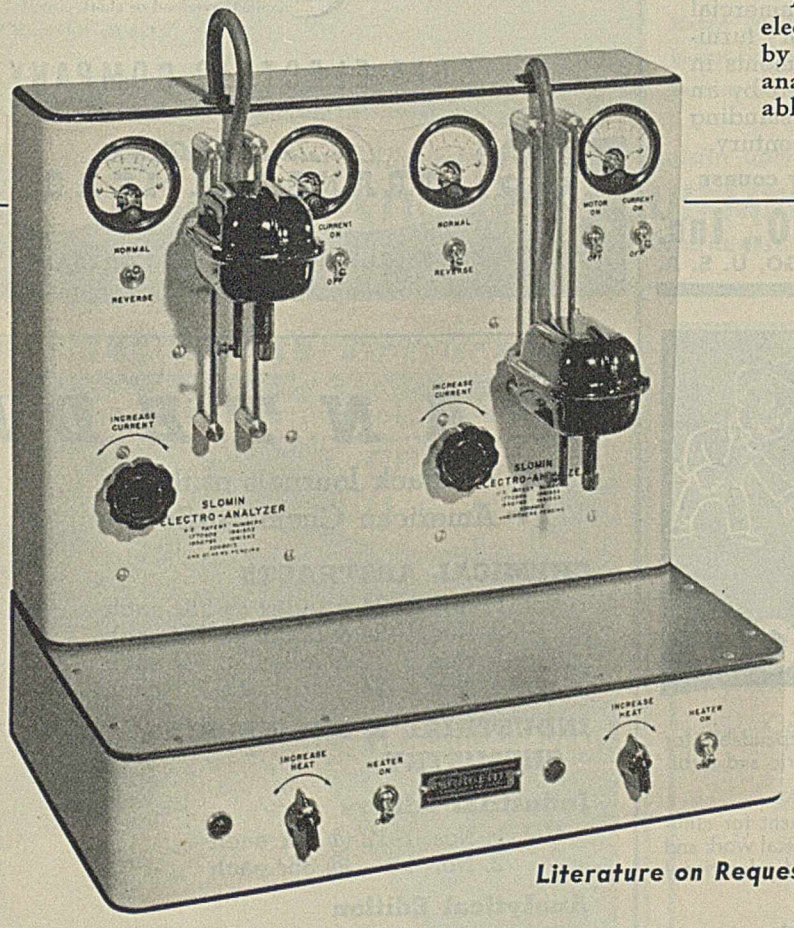

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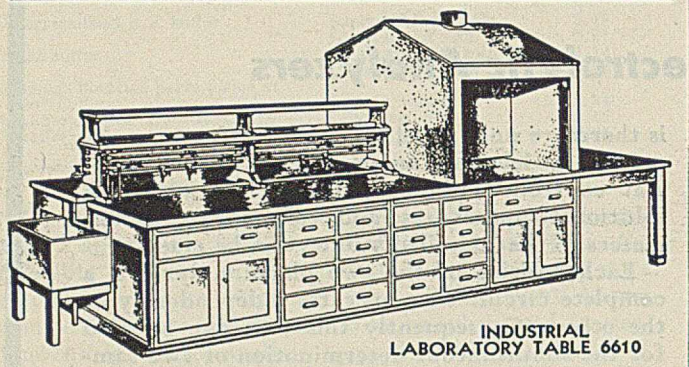

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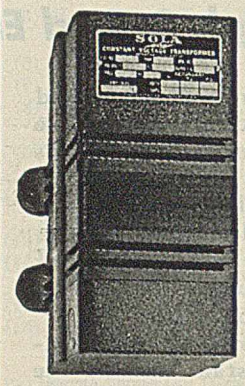

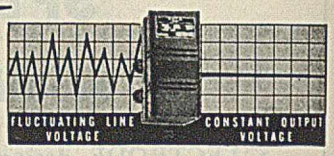

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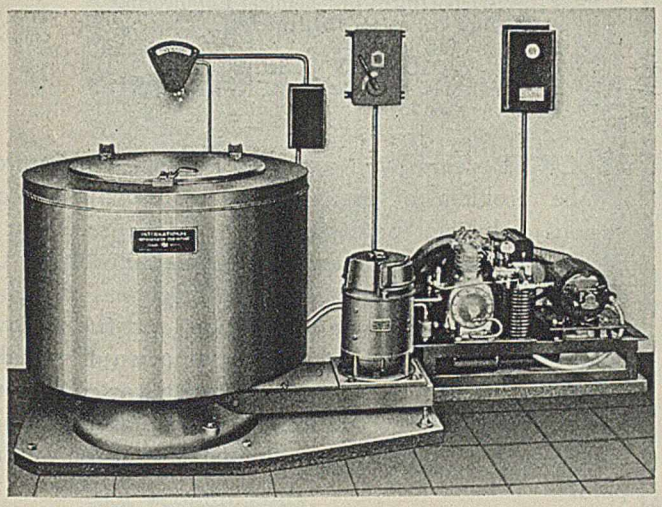

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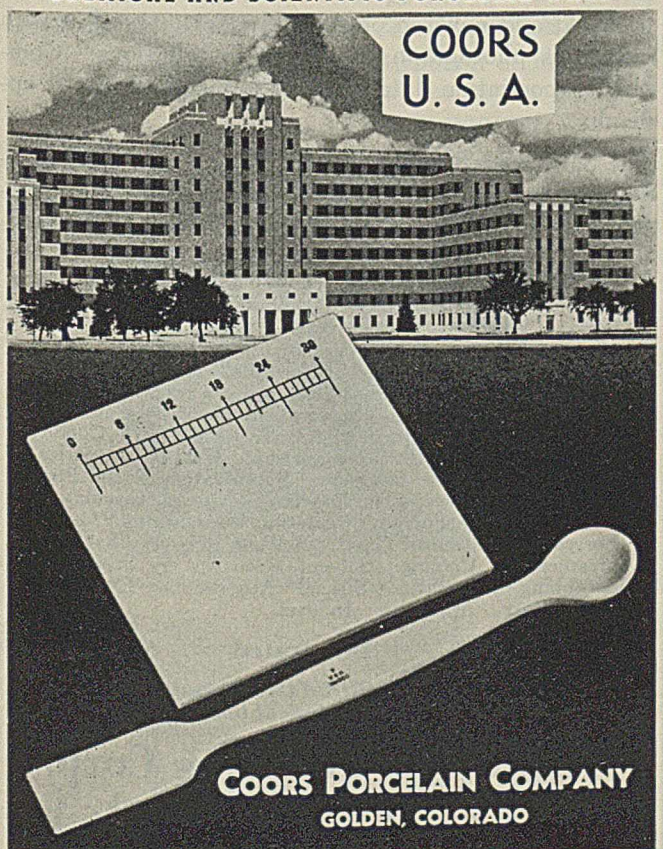

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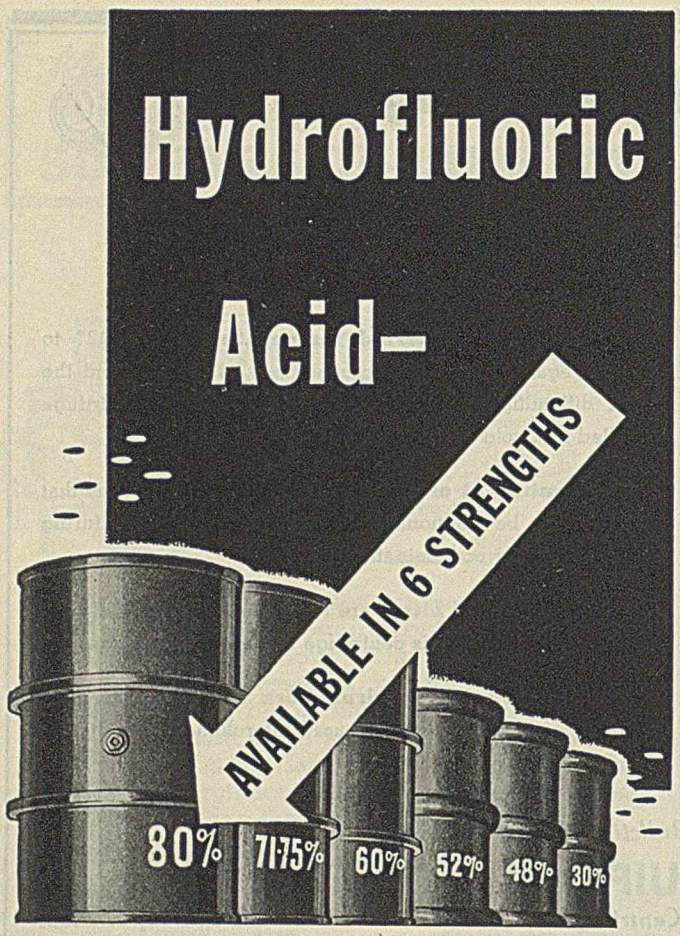

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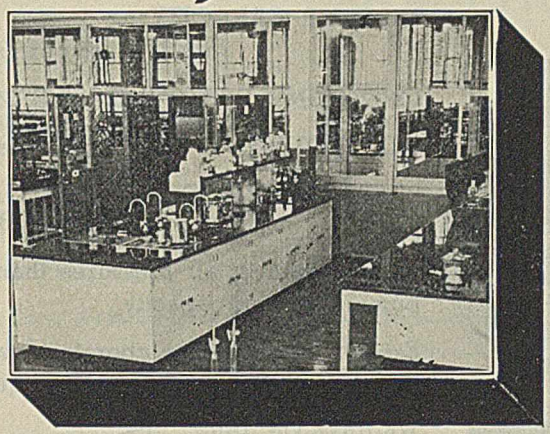

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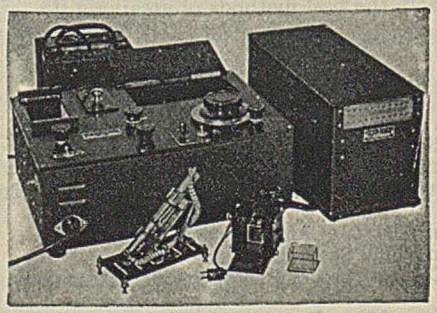

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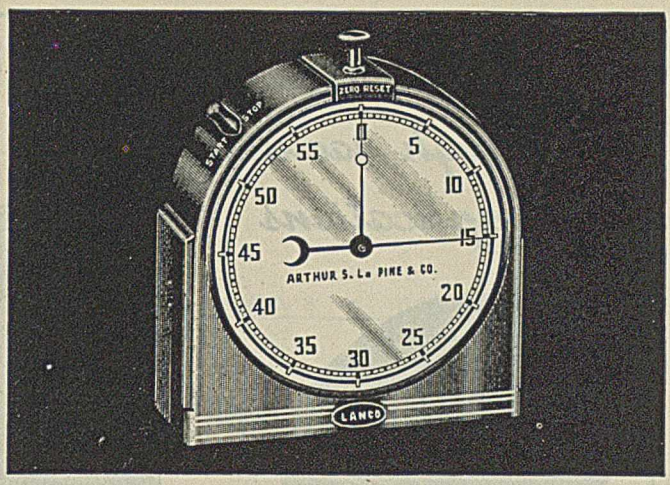

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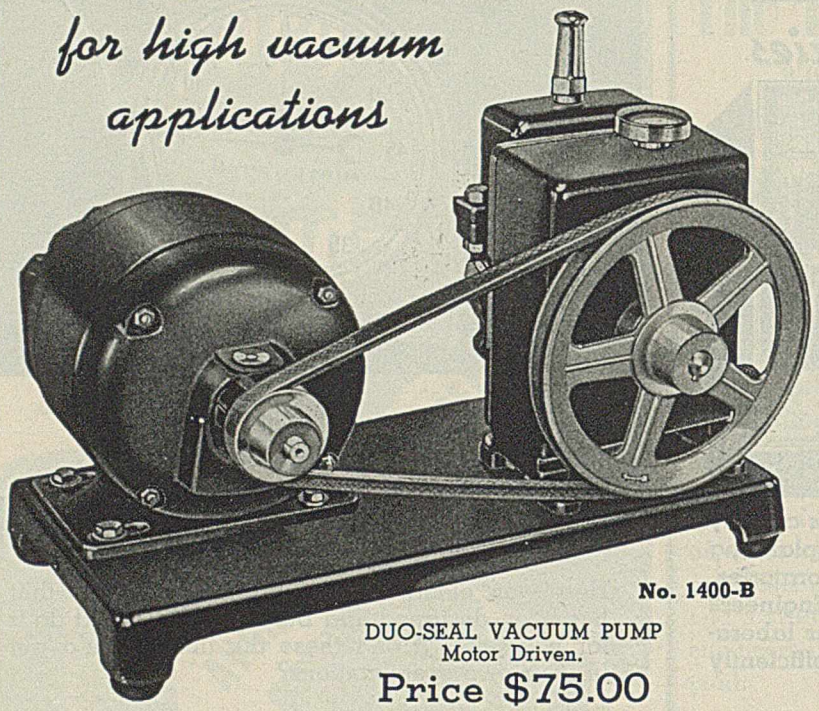

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