

# INDUSTRIAL and ENGINEERING CHEMISTRY

Vol. 31, Consecutive No. 35

Harrison E. Howe, Editor

ANALYTICAL EDITION

21,000 Copies of This Issue Printed

Issued September 15, 1939

Vol. 11, No. 9

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Publication Office: Easton, Penna.

Editorial Office: Room 706, Mills Building, Washington, D. C.

Telephone: National 0848. Cable: Jiechem (Washington)

Advertising Department: 332 West 42nd Street, New York, N. Y.

Telephone: Bryant 9-4430

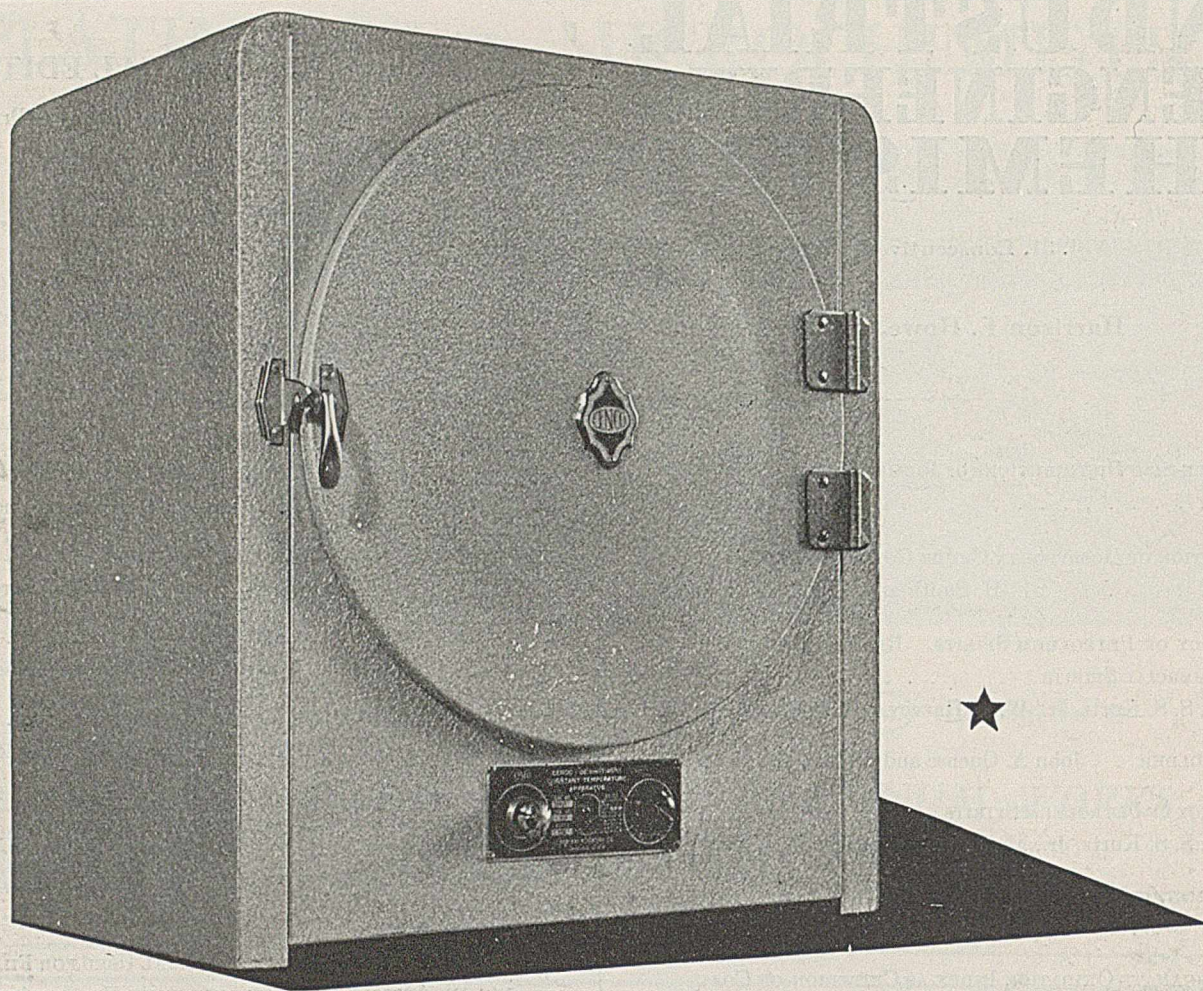
Published by the American Chemical Society, Publication Office, 20th & Northampton Sts., Easton, Penna. Entered as second-class matter at the Post Office at Easton, Penna., under the Act of March 3, 1879, as 48 times a year. Industrial Edition monthly on the 1st; Analytical Edition monthly on the 15th; News Edition on the 10th and 20th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

RATES FOR CURRENT NUMBERS: Annual subscription rates: INDUSTRIAL AND ENGINEERING CHEMISTRY complete \$6.00; (a) Industrial Edition \$3.00;

(b) Analytical Edition \$2.50; (c) News Edition \$1.50; (a) and (b) together, \$5.00. Foreign postage to countries not in the Pan American Union, \$2.40; (a) \$1.20; (b) \$0.60; (c) \$0.60. Canadian postage one third these rates. Single copies: (a) \$0.75; (b) \$0.50; (c) \$0.10. Special rates to members.

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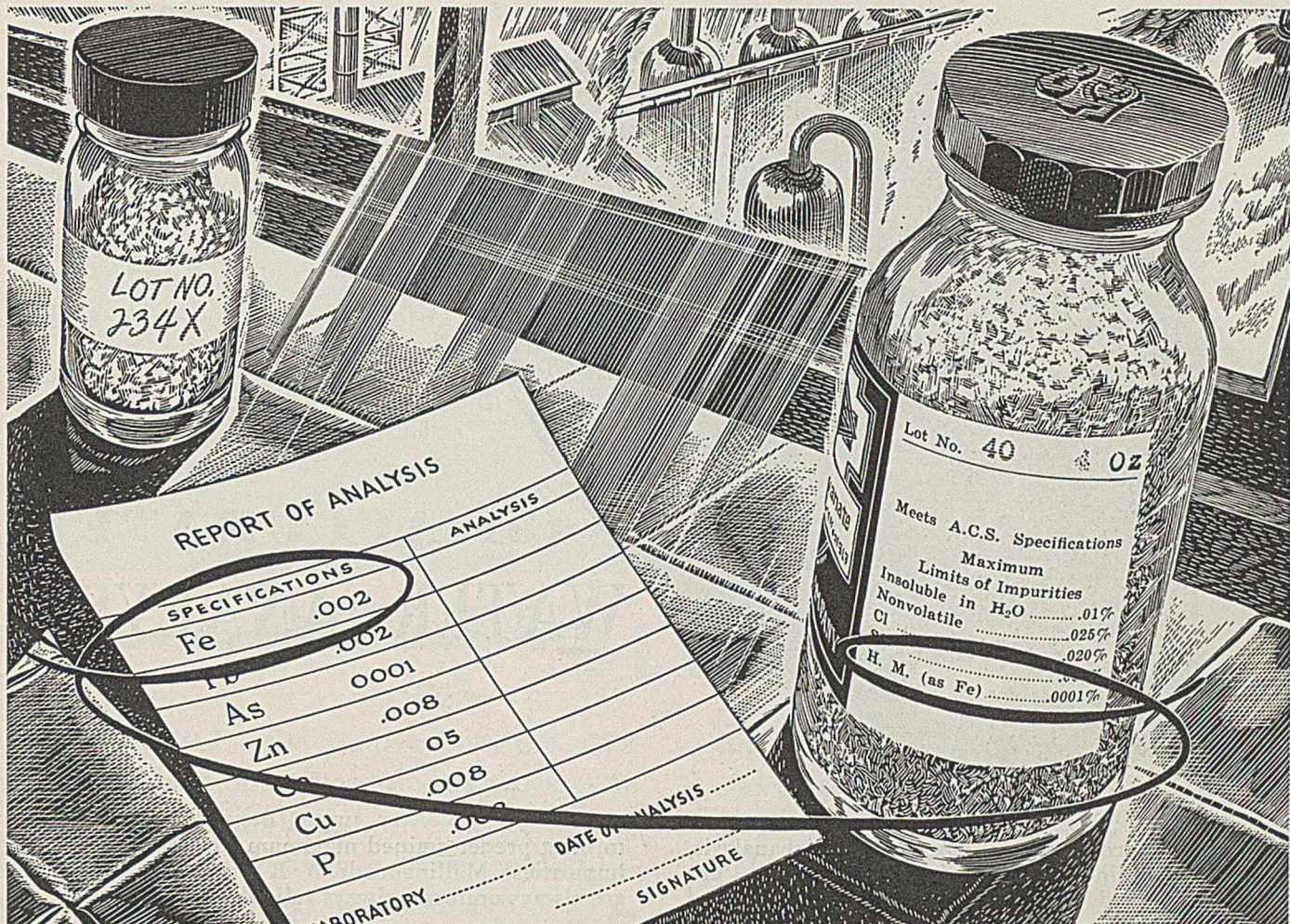
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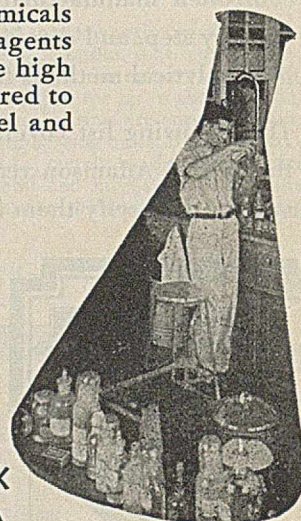
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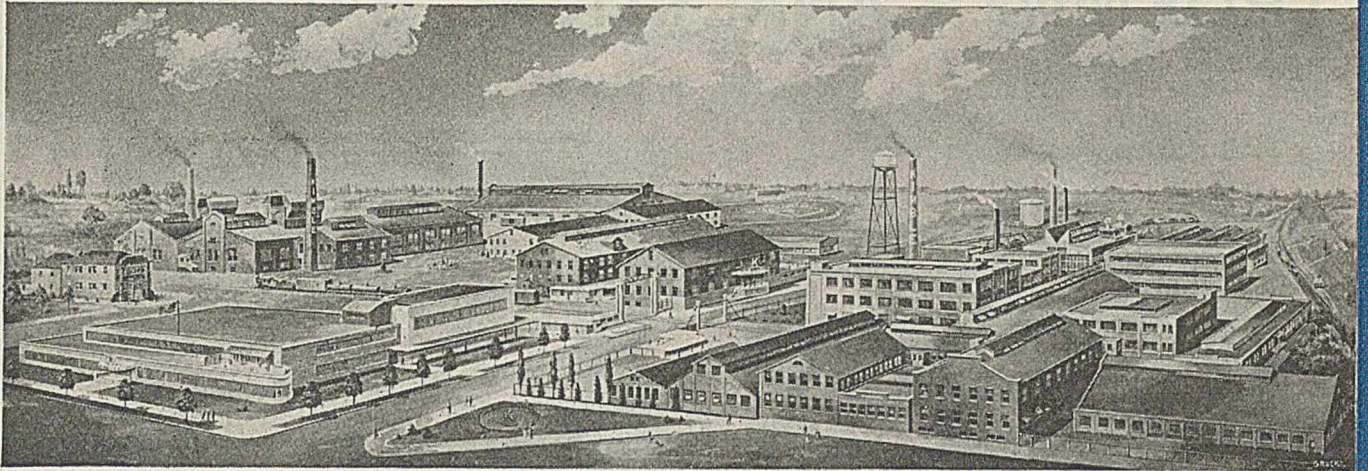
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


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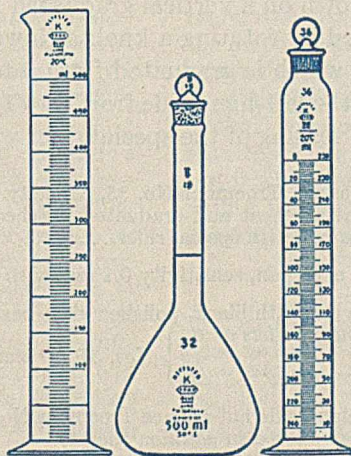
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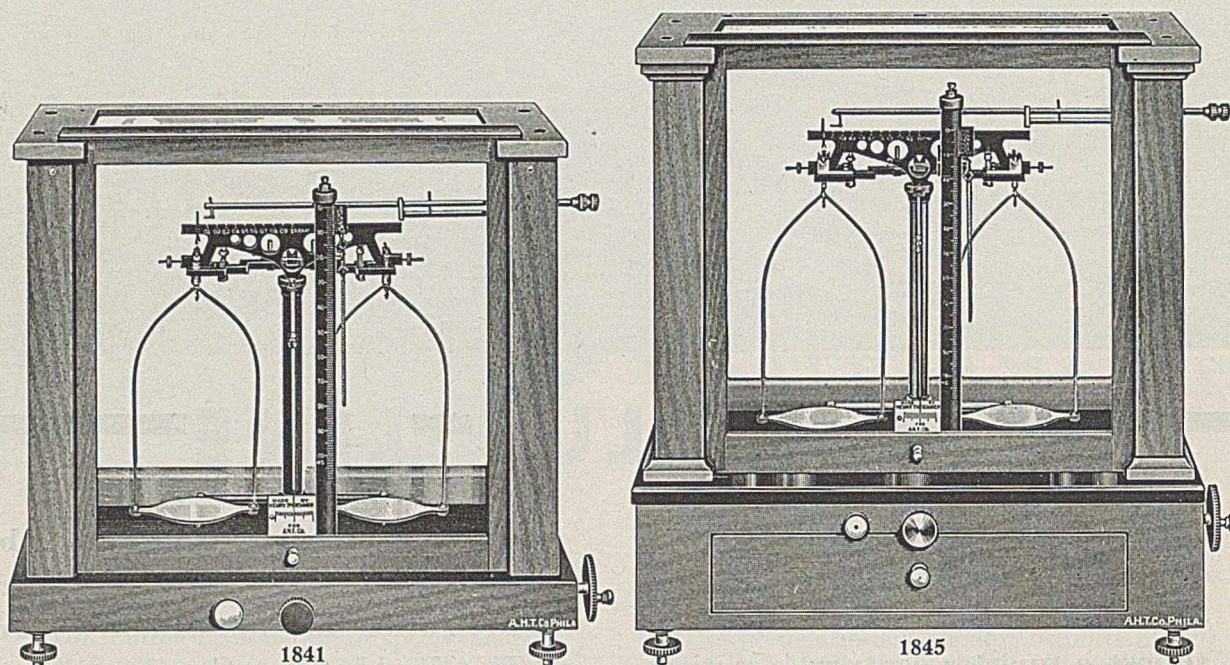
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# INDUSTRIAL and ENGINEERING CHEMISTRY

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Harrison E. Howe, Editor

## Particle-Size Distributions of Pigment Suspensions

### Determination with a Beaker-Type Centrifuge

S. W. MARTIN, National Lead Company, Titanium Division, Sayreville, N. J.

A method for the determination of the extent of disaggregation of pigments dispersed in aqueous and organic vehicles has been developed for particle sizes of 0.1 micron and above. The theoretical considerations of Romwalter and Vendl served as the basis for calculating the particle size distribution from a sedimentation curve obtained with a laboratory beaker-type centri-

fuge. Results are presented for a typical paint dispersion of a titanium dioxide pigment. To comply with industrial requirements, a rapid continuous method for the determination of size distributions from sieve through subsieve sizes is described for titanium dioxide pigment suspended in water. Illustrative data and additional possibilities for application are included.

THE particle size distributions obtainable under practical dispersion conditions are of fundamental importance in the application of finely divided materials for a wide variety of pigmentation purposes. Inherent in this are physico-chemical problems, the consideration of which necessitates quantitative methods designed for the determination of the completeness or extent of disaggregation of pigments suspended in aqueous or paint vehicles.

Although there exist considerable information and a voluminous literature on microscopic particle size measurements, these are subject to the following quoted limitations (8): "1. To obtain a satisfactory field for projection or photography, the mount should not be more than a few particles thick. This requires pressure on the cover glass or some other method of rubbing out the sample to a very thin layer and on such small amounts of material the procedure may result in a greater degree of deaggregation than it is possible to attain by the usual methods of commercial dispersion . . . . . In most cases, the particle size as observed microscopically will be at considerable variance with the effective particle sizes in an oil or rubber dispersion. . . . 2. In the case of nonuniform materials, difficulty is experienced in bringing both coarse and fine particles into focus at the same time. The lack of uniformity experienced in many pigments makes the method extremely laborious because of the necessity of measuring a large number of particles in order to obtain truly representative data." Then also (24), "Due to the optical fringes which appear on the particle images, it is dangerous to rely upon microscopic measurement in the range of 0.2 or 0.3 micron."

When this investigation was initiated, a literature survey showed that sedimentation methods offered interesting possibilities for eliminating the preceding objections, providing cognizance was taken of the colloidal principles involved in the preparation of stable suspensions. Thus, it was possible to avoid either the slow or rapid formation of flocculates (2). No difficulties were experienced with titanium dioxide as long as the dispersion technique and the medium were compatible with the wetting properties of the pigment. In the following, it will be assumed that aqueous suspensions were formed with a water-dispersing grade of titanium dioxide, whereas paint systems were made from oil-wetting pigments.

#### Sedimentation Methods

Since settling methods employing gravitational force have been well established, a procedure similar to that of Andreasen (3) was applied to a titanium dioxide dispersed with a high-speed mixer. The initial concentration of the suspension was 5 per cent.

The equivalent diameter was calculated from Stokes' law (Equation 1). A and B (Table I) denote the addition be-

TABLE I. GRAVITATIONAL SETTLING OF TITANIUM DIOXIDE SUSPENDED IN WATER

Settling Time Hours	Diameter Microns	Initial Pigment in Suspension	
		A %	B %
24	1.5	94	60
72	0.9	83	0.5
162	0.6	57	0.5



fore mixing of 0.1 and 1.0 per cent, respectively, of sodium silicate (pigment basis) whose alkali-silica ratio was 1 to 3.86.

It was observed that a dispersed titanium dioxide resisted settling while an excess of silicate produced rapid settling because of flocculation. However, because of the small sedimentation rate, differences in size distributions of good dispersions could not be measured with certainty. Another serious objection was the time interval of one week. To eliminate these, centrifugal force was substituted so as to increase the sedimentation velocities in accordance with a relationship derivable from Stokes' law.

$$V_g = \frac{d_1 - d_0}{18n} D^2 g \quad (1)$$

$$V_c = \frac{d_1 - d_0}{18n} D^2 W^2 X \quad (2)$$

$$V_c/V_g = \frac{W^2 X}{g} = R. C. F. \quad (3)$$

$V_g$  and  $V_c$  = the gravitational and centrifugal sedimentation velocities

$d_1$  and  $d_0$  = specific gravities of the pigment and suspension  
 $n$  = coefficient of viscosity of the medium  
 $D$  = the equivalent diameter of the particle of average weight  
 $W = 2\pi N/60$  where  $N$  is number of revolutions per minute  
 $X$  = distance in cm. of the particle from the axis of rotation  
 $R. C. F.$  = the relative centrifugal force

**CENTRIFUGAL SEDIMENTATION.** Centrifugal forces of varying magnitudes are experimentally available. Therefore, particle sizes amenable to centrifugalization have to be arbitrarily divided into (1) colloidal dimensions consisting of diameters from 0.1 micron to molecular dimensions, and (2) suspensoid sizes with a lower extreme at 0.1 micron and an upper limit with aggregate sizes of 30 microns.

The first group has been the subject of a large number of investigations by Svedberg (22), whose technique was employed by Nichols and Liebe (16) to determine the size distribution of lithopones dispersed in glycerol. A rutile titanium dioxide-glycerol suspension has also been studied with the same method to give the size distribution results of Kubelka and Srbek (13). A negligible quantity of material, less than 0.1 micron, was recorded. Table V contains the distribution values for a typical anatase type pigment. As a result, titanium dioxide pigment sizes could be given as primarily within the second category.

The individual particles or aggregates (2) referred to in this classification are sedimented conveniently with a beaker-type centrifuge, the application of which to monodispersed sols has been described by Hahn (11) and Schlesinger (20). Many materials, however, form polydispersed systems. Marshall (14) with a beaker-type centrifuge studied clays 2 microns and less in size. While the present investigation was being completed, Norton and Speil (17) published results on various clays also sedimented with a laboratory centrifuge. A range of 30 to 0.05 micron was covered, but the determinations required "two or three 8-hour days." In 1935, Romwalter and Vendl (19) presented the following theoretical basis for the calculation of a particle size distribution from a sedimentation curve obtained with a beaker-type centrifuge.

### Theoretical Considerations

If a polydispersed system is sedimented, after a time,  $t$ , the settled material can be divided into two parts: (1) a portion consisting of particles with diameters equal to or greater than  $D$ ; (2) the remainder, consisting of those particles which were sedimented even though their diameters were less than  $D$ . The theory for the evaluation of these two fractions from gravitational settling has been developed and confirmed by Odén (18). The validity of the application of Odén's

method to a sedimentation curve obtained with a beaker-type centrifuge has been established mathematically by Romwalter and Vendl:

$$\frac{1}{4.60 \log R/S} \frac{R^2 - S^2}{S^2} t \frac{dp}{dt} = \int_0^D F(D) dD \quad (4)$$

$p$  = mass of material sedimented after a time,  $t$   
 $R$  = distance from the axis of rotation to the bottom of the centrifuge tube  
 $S$  = distance from the axis of rotation to the meniscus of the suspension

$$D = \frac{6}{W} \sqrt{\frac{n \ln R/S}{2(d_1 - d_0)t}} \quad (5)$$

Since in any experimental work  $S$  and  $R$  are made constant, the left member of Equation 4 reduced to  $Ktdp/dt$ . This can be evaluated by applying Odén's method of tangential intercepts to the centrifugal sedimentation curve. Next, the amount of particles is obtained for a given diameter interval. The calculation is extended to include the entire range of sizes and, finally, the results are expressed as a particle size distribution.

### Size Distribution of a Titanium Dioxide-Glycerol Suspension

As a preliminary experiment, it was decided to examine a size distribution which overlapped the range in which microscopic size frequency measurements could be made with little difficulty. With this in view, a titanium dioxide pigment sample was suspended in a 91 per cent glycerol-water medium. The procedure was such that the suspension was formed with minimum work on the pigment. To ensure conditions of free settling of the particles, the final suspension contained 0.1 per cent of pigment.

**DETERMINATION OF THE SEDIMENTATION CURVE.** In the theoretical treatment previously outlined, one assumption was tacitly made that the centrifuge be free from vibrations. This requirement was satisfied in an International clinical centrifuge manufactured by the International Equipment Company. Although the centrifuge was in a constant-temperature room during sedimentation, the bowl temperature varied markedly, owing to the heat dissipated in the rheostat control. By removing the resistance from the immediate vicinity of the centrifuge and with the aid of the room controls it was possible to fix the temperature at  $22.5^\circ \pm 1^\circ \text{C}$ . The centrifuge speed was 1300 revolutions per minute. The centrifuge tubes were flat-bottomed vials with a diameter of 15 mm. and a height of 35 mm. To obtain a constant height, each tube was equipped with a scale, and by means of a magnifying glass 29 mm. of suspension were used for each sedimentation interval.

**SEDIMENTATION PROCEDURE.** A tube filled with suspension was placed in the centrifuge for  $t$  minutes, after which it was removed to a special holder so that with a capillary pipet, all of the suspension above 2 mm. from the bottom could be drawn off. The content of the pipet was washed into a 250-ml. beaker and slowly evaporated to dryness. To this, 10 ml. of concentrated sulfuric acid and 5 grams of ammonium sulfate were added. Boiling to dissolve the titanium dioxide produced discoloration, which was removed by the addition of a few drops of nitric acid. Dilution to 100 ml. in a volumetric flask followed. A portion was transferred to a Nessler tube, to which 5 ml. of 3 per cent hydrogen peroxide and sufficient distilled water for dilution to the 50-ml. mark were added. The yellow coloration produced was matched by mixing known amounts of a standard solution (1 ml. = 0.10 mg. of titanium dioxide) to a blank containing 5 ml. of hydrogen peroxide. A series of known dilutions were analyzed colorimetrically, and changes in titanium dioxide content could be measured with an accuracy of  $\pm 2$  per cent. Each tube was weighed before sedimentation and after removal of the suspension. With the initial concentration known and also the analyses, the percentage weight sedimented could be calculated. The results for all the values of  $t$  were collected in the form of a sedimentation curve.

**EVALUATION OF THE CONSTANTS OF STOKES' EQUATION.** The specific gravity ( $22.5^\circ \text{C}/22.5^\circ \text{C}$ ) of the glycerol-water



mixture was 1.2385, which according to Bosart and Snoddy (6) corresponded to a composition of 90.8 per cent glycerol. Interpolation of the tables of Sheely (21) gave 2.20 poises for the coefficient of viscosity. The specific gravity of titanium dioxide was taken as 3.90;  $\ln R/S = 0.362$ . Substitution of these values in Equation 5 gave:

$$D(\text{microns}) = 22.1/\sqrt{t} \quad (6)$$

$t = \text{minutes}$

Two completely independent determinations—i. e., preparation of suspension, centrifuging, colorimetric analysis, etc.—were performed. The agreement between the two sets of data is evident in Figure 1. Tangents were drawn at the indicated values of  $D$ . The successive differences in the tangential intercepts are incorporated in Table II.

The same suspension was placed in a counting chamber (30 microns in depth) and, with the aid of a microscope, the images of the particles were projected to a magnification of 8000 diameters. Table III contains the results of the microscopic count.

Tables II and III not only show data characteristic of each method but also permit the calculation and comparison of average weight diameters. Assigning the medium value for each class, the average particle size with respect to weight (microscopic)

$$\bar{D}_w = \Sigma nD^4/\Sigma nD^3$$

was 1.9 microns for the suspension under consideration. An average weight diameter for the distribution of Table II was calculated in accordance with a formula given by Gessner (10) and was equal to 1.6 microns. Considering the approximations made in the calculations, the above indicated fairly good agreement between the two methods of particle size analysis.

### Size Distributions of Titanium Dioxide Dispersed in a Paint Vehicle

Because of the increasing importance of particle size distribution considerations in paints, the technique was altered to permit sedimentation studies of pigment-paint vehicle systems. The laboratory beaker-type centrifuge has been utilized in accelerated tests for the settling of pigments in paints (23).

TABLE II. PARTICLE SIZE DISTRIBUTION OF TITANIUM DIOXIDE DISPERSED IN GLYCEROL

Diameter Microns	Per Cent by Weight
>3.0	5
3.0-2.0	9
2.0-1.0	66
<1.0	20

TABLE III. SIZE-FREQUENCY OF TITANIUM DIOXIDE DISPERSED IN GLYCEROL

Diameter Microns	Number of Particles $n$
<1.0	1000
1.0-2.0	260
2.0-3.0	40
>3.0	2

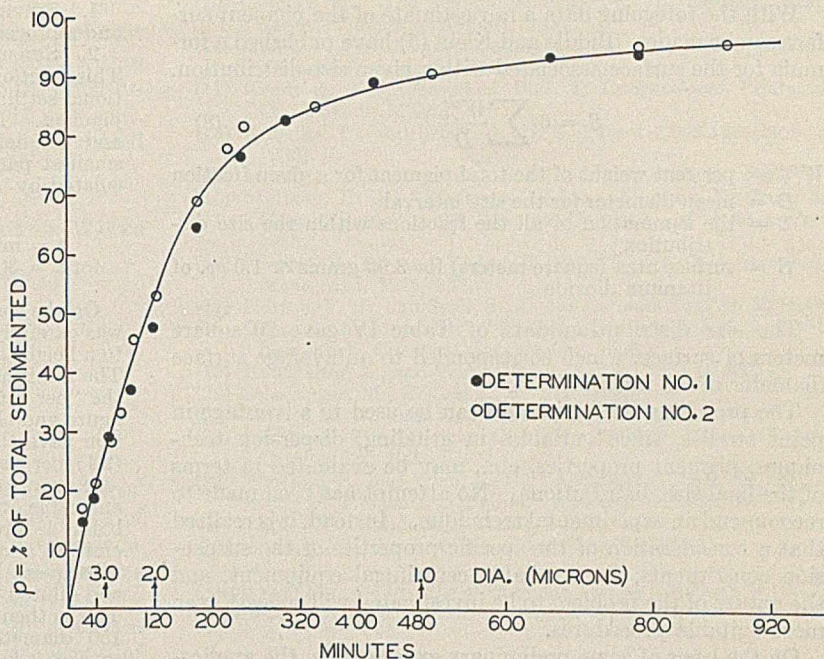


FIGURE 1. CENTRIFUGAL SEDIMENTATION OF TITANIUM DIOXIDE DISPERSED IN GLYCEROL

TABLE IV. PARTICLE SIZE DISTRIBUTION OF TITANIUM DIOXIDE DISPERSED IN A PAINT VEHICLE

Diameter Micron	Per Cent by Weight	Diameter Micron	Per Cent by Weight
>0.5	3	0.3-0.2	26
0.5-0.4	17	0.2-0.15	16
0.4-0.3	38		

**DISPERSION TECHNIQUE.** Two hundred grams of titanium dioxide were mixed with 108 grams of a special, prepared tung oil-linseed oil vehicle. (VM-1215 is well known to the paint trade and was developed by the Technical Service Laboratories of the Titanium Pigment Corporation, New York, N. Y.) This vehicle has excellent wetting properties and is recommended for titanium dioxide pigments in a wide variety of formulations. The paste was passed through a laboratory-size, three-roller mill whose setting was such that the rolls contacted with a minimum pressure. Three pastes were ground for the same pigment and each was diluted with mineral spirits to 5 per cent solids content.

**SEDIMENTATION PROCEDURE.** The final suspension was centrifuged at 1400 revolutions per minute in an International centrifuge (size 1). The speed was measured and controlled by means of an indicating hand tachometer to about  $\pm 10$  r. p. m. Wide mouthed, ground-glass-stoppered bottles 5.9 cm. (2.375 inches) in diameter and about 13.75 cm. (5.5 inches) high were employed, since they fitted snugly into the four centrifuge cups without any adjustments. After sedimentation, the suspension was poured into a beaker, stirred, and analyzed for titanium dioxide content. The gravimetric analyses for titanium dioxide were comparatively simple and rapid. A known weight of suspension in a tared crucible was taken and the volatile constituents were carefully evaporated until a charred residue remained. This was followed by calcination at 900° C. in an electric muffle. The ignited residue was weighed as titanium dioxide. Ash corrections were included.

The results of the sedimentations of three different suspensions of the same pigment were within  $\pm 5$  per cent of an average curve drawn through the values. The specific gravity (25° C.) of the final dilution of VM-1215 and mineral spirits was 0.85. An Ostwald viscometer (?) gave 0.015 poise for the viscosity of the mixture at 25° C. Since  $\ln R/S$  was 0.506, the result of numerical substitution in Equation 5 was

$$D(\text{micron}) = 1.87/\sqrt{t} \quad (7)$$

$t = \text{minutes}$

and the size distribution data are incorporated in Table IV.



With the foregoing data a fair estimate of the pigment surface can be made. Biddle and Klein (5) have published a formula for the surface associated with a given size distribution.

$$S = 6 \sum \frac{W\%}{\bar{D}} \quad (8)$$

$W\%$  = per cent weight of the total pigment for a given fraction

$\bar{D}$  = mean diameter for the size interval

$\Sigma$  = the summation of all the fractions within the size distribution

$S$  = surface area (square meters) for 3.90 grams or 1.0 cc. of titanium dioxide

The size distribution data of Table IV gave 20 square meters of surface, which corresponded to an average surface diameter of 0.3 micron.

The preceding determination can be used to advantage in paint studies, since variables in grinding, dispersion techniques, pigment properties, etc., may be evaluated in terms of the final size distributions. No attempt has been made to recommend an experimental technique. Instead, it is realized that a consideration of the specific properties of the suspension constituents, the available centrifugal equipment, and the nature of the problem to be investigated will suggest even more suitable procedures.

On the basis of some preliminary experiments, the application of the size distribution method is suggested for studying problems of compounding pigment in rubber. As an example, a titanium dioxide was incorporated into pale crepe rubber on a standard laboratory rubber mill. The pigment volume loadings could be varied from 10 to 15 per cent. After milling under constant conditions, the rubber mix was dissolved in toluene to produce a suspension of a given pigment content. This type of dispersion has been established by Gehman and Morris (9) with an ultramicroscopic technique. There remained the determination of the specific gravity and viscosity from which a centrifugal speed could be selected to give the required relative centrifugal force. A typical sedimentation curve was obtained and the particle size analysis made. Here again, it should be possible to evaluate the significance of milling variables by means of size distribution considerations.

In the manufacture and application of finished pigments, there arise size distribution problems, the solution of which by present methods involves an impractical expenditure of time and effort. It was felt that some importance could be attached to the development of simplified methods which were the result of a compromise between industrial requirements and those imposed by the fundamental principles of particle size measurements. Some final accuracy would have to be sacrificed. Nevertheless, it should be possible, for all practical purposes, to keep the precision losses within tolerable limits. The next section illustrates the feasibility of the aforementioned for an isolated case—namely, water dispersions of titanium dioxide.

### Determination of Particle Size Distributions of Titanium Dioxide Dispersed in Water

Experience with a variety of titanium dioxide-water suspensions (prepared by ball milling or high-speed agitation) has proved the existence of a range of aggregate sizes as well as varying particle size distributions. One extreme is determined by the retention on the 325-mesh sieve (44 microns). The other is in magnitude a few tenths of a micron. This wide range of sizes can be conveniently divided as follows:

1. Sieve fraction (44 microns and above)
2. Subsieve fraction
  - A. Gravitational sediment sizes (greater than 7 microns in diameter)
  - B. Centrifugal sedimentation sizes (less than 7 microns in diameter)

1. SIEVE FRACTION. Sieve measurements are well known and a procedure (1) can be recommended for this determination.

2. SUBSIEVE FRACTIONS. A. *Gravitational Sediment Sizes.* This fraction was measured by the sediment from the gravitational settling of a 5 per cent suspension containing 75 grams of pigment. The sedimentation was performed in a 2-liter beaker and the height was 12.5 cm. By means of Stokes' law, the smallest particle that could be completely settled out was calculated by

$$D(\text{microns}) = 36.4/\sqrt{t} \quad (9)$$

$t$  = minutes

for  $t$  = 30 minutes,  $D$  = 6.6 microns

On the completion of the sedimentation period, the suspension was carefully poured off from the sediment, which was reslurried to a height of 12.5 cm. and allowed to stand another 30 minutes. The resulting sediment was dried at 125° C. and weighed to give the "per cent of the total greater than 7 microns." With this figure and the "per cent retained by a 325-mesh sieve" subtraction gave the following: (1) per cent greater than 44 microns; (2A) per cent between 44 and 7 microns.

If a more detailed analysis of fraction 2A is desired, it is readily amenable to microscopic examination. Another suspension batch is prepared and procedure 2A is repeated. Drying is omitted and instead a fixed quantity of glycerol is added with subsequent homogenization of the mixture. A portion is taken and diluted to a pigment content of 1 mg. per ml. of suspension. This is then examined in a Fuchs cell (depth = 200 microns) at 150 diameters' magnification. A glass disk with calibrated squares is inserted in the eyepiece and with the aid of a mechanical counter, it is comparatively simple to isolate and count the aggregates of about 10, 20, and 30 and above microns. A sufficient number of fields are taken at random to give a total observed volume of 1 cu. mm. or more, depending on the accuracy desired.

B. *Centrifugal Sedimentation Sizes.* Included in this group was the material remaining in suspension after the completion of the gravitational settling. The centrifugal equipment was the same as that described under the heading "Size Distributions of Titanium Dioxide Dispersed in a Paint Vehicle." However, the procedure differed in that only three centrifugal sedimentations at 350 revolutions per minute—i. e., 5, 45, and 120 minutes—were required. After each, the suspensions were siphoned from the well-caked sediments, stirred, and tested for specific gravity with a Westphal balance. Temperature corrections were introduced through the specific gravity of the medium. The specific gravity difference permitted an interpolation from a calibration curve of the per cent of titanium dioxide in suspension. Next, centrifugal time was converted into equivalent diameters after the substitution of the following in Equation 5:

$$\begin{aligned} 1.13 \geq d_0 \geq 1.00 & & d_1 - d_0 = 2.8 \\ n = 0.010 \text{ poise} & & W = 36.6 & & \ln R/S = 0.506 \\ D(\text{microns}) = 6.36/\sqrt{t} & & & & (10) \\ t = \text{minutes} & & & & \end{aligned}$$

Thus for 5-, 45-, and 120-minute intervals, the equivalent diameters were 3.0, 1.0, and 0.5 micron, respectively, and the corresponding value of titanium dioxide contents gave the material less than the calculated size. Successive subtractions of these percentages yielded the per cent weight for more than 3, 3 to 1, 1 to 0.5, and less than 0.5 micron.

The less than 0.5 micron fraction for some titanium dioxide dispersions comprised the bulk of the pigment. It was of interest to extend the centrifugal sedimentation to the range of "individual particle" size. Additional sedimentation of 63 minutes at 1400 revolutions per minute left in suspension material which was assigned to the fraction less than 0.2 micron. A substantiation (at least in order of magnitude) was found in the fact that this material was on the border or below the limit of resolution of the microscope with an Apochromat HI 60 X objective (N. A. = 1.35). The theoretical resolving power for the system was 0.2 micron. Table V contains the complete size distribution of a well-dispersed titanium dioxide-water suspension.

The additional sedimentation at 1400 revolutions per minute was usually omitted, with the result that after standardization of the experimental procedure, four complete size distribution determinations could be readily made in a one-



man working day with a four-cup centrifuge. Once a complete set of size distribution data was available at 5 per cent titanium dioxide suspensions, it was observed that within narrow limits similar values were obtainable from the centrifugal sedimentation of dilutions to only 10 and 15 per cent. The viscosity also showed but little sensitivity to the increased pigment concentrations.

TABLE V. SIZE DISTRIBUTION OF TITANIUM DIOXIDE-WATER SUSPENSION

Diameter Microns	Per Cent by Weight
>44	0
44-7	Negligible
+3	2 ( $\pm 0.5$ )
3-1	5 ( $\pm 1$ )
1-0.5	18 ( $\pm 1$ )
0.5-0.2	74 ( $\pm 4$ )
<0.2	0.6

Since the preceding methods are dependent on Stokes' law, correct results can hardly be expected if the limits of validity of Stokes' law are exceeded. Critical radii considerations (15) are of especial importance. The calculations involved were performed and the sedimentation velocities used in this investigation satisfied the critical radii criteria.

Other materials, such as barium sulfate suspensions of varying degree of fineness, were submitted to size distribution tests. Ground ilmenite ores, in which sieve and especially gravitational settlings are the predominating fractions, have also come within the scope of the method. These particular materials have been singled out because of their importance to the titanium pigment industry.

There have appeared an ever-increasing number of surface active agents, many of which have been suggested as "wetting" or "dispersing" agents for pigments. As distinguished from the liquid-air interface, Bartell (4) has pointed out that there are "no reliable methods available for the measurement of the interfacial tensions at the solid interface. . . the methods as yet available are on the whole so difficult and time-consuming that they are not of general application." Therefore, the use of surface-active agents with pigments has been chiefly a matter of empiricism. If the action of these materials is viewed in terms of their efficacy in disaggregating pigments, it becomes possible to differentiate by the size distribution determinations between a wetting agent—i. e., one that lowers the surface tension of water without altering the aggregation—and a true dispersant for titanium dioxide. The latter not only increases the amount of fines at the expense of the coarser fractions but also imparts enhanced suspension stability or resistance to flocculation.

### Acknowledgment

The writer wishes to acknowledge the advice and keen interest of J. L. Turner, Director of Research, National Lead Company, Titanium Division.

### Literature Cited

- Am. Soc. Testing Materials, 1937 Supplement to Book of A. S. T. M. Standards, p. 104.
- Am. Soc. Testing Materials, Tentative Standards, p. 1614, 1938.
- Andreasen, A. H. M., *Angew. Chem.*, 20, 283 (1935).
- Bartell, F. E., *IND. ENG. CHEM.*, 31, 31 (1939).
- Biddle, S. B., and Klein, A., *Am. Society Testing Materials*, II, 36, 315 (1936).
- Bosart, L. W., and Snoddy, A. O., *IND. ENG. CHEM.*, 19, 506 (1927).
- Findlay, A., "Practical Physical Chemistry," p. 70, New York, Longmans, Green & Co., 1936.
- Gamble, D. L., and Barnett, C. E., *IND. ENG. CHEM.*, Anal. Ed., 9, 310 (1937).
- Gehman, S. D., and Morris, T. C., *Ibid.*, 4, 157 (1932).
- Gessner, H., "Die Schlämmanalyse," p. 213, Leipzig, Akademische Verlagsgesellschaft, 1931.
- Hahn, F. V., "Dispersoidanalyse," Vol. III, p. 336, Dresden, Theodor Steinkopff, 1928.
- Kendrick, A., *Information Bull.* 1, International Equipment Co., Boston, Mass.
- Kubelka, P., and Srbek, J., U. S. Patent 2,062,133 (Nov. 24, 1936).
- Marshall, C. E., *Proc. Roy. Soc. (London)*, A126, 427 (1930).
- Millikan, R. A., "Electrons, Protons, Photons, Neutrons and Cosmic Rays," p. 95, Chicago, University of Chicago Press, 1935.
- Nichols, J. B., and Liebe, H. C., *Third Colloid Symposium Monograph*, 1925, 268.
- Norton, F. H., and Speil, S., *J. Am. Ceramic Soc.*, 21, 89 (1938).
- Odén, S., in Alexander's "Colloid Chemistry," Vol. 1, p. 861, New York, Chemical Catalog Co., 1926.
- Romwalter, A., and Vendl, M., *Kolloid Z.*, 72, 1 (1935).
- Schlesinger, M., *Kolloid Z.*, 67, 135 (1934).
- Sheely, M. L., *IND. ENG. CHEM.*, 24, 1060 (1932).
- Svedberg, T., "Colloid Chemistry," New York, Chemical Catalog Co., 1928.
- Werthan, S., and Wien, R. H., "Accelerated Tests for the Settling of Pigments in Paints," Research Bulletin, New Jersey Zinc Co., Palmerton, Penna.
- Work, L. T., *Chem. & Met. Eng.*, 45, 249 (1938).

PRESENTED before the Division of Paint and Varnish Chemistry at the 97th Meeting of the American Chemical Society, Baltimore, Md.

## Estimation of Gossypol in Crude Cottonseed Oil

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THE method of Royce (1) for the estimation of gossypol in crude cottonseed oils uses the reagent pyridine in precipitating gossypol with aniline. Royce assumes that the precipitate is dianilinogossypol and from its weight calculates the corresponding quantity of gossypol. This assumption and procedure are invalid, for the precipitate which is weighed and calculated when pyridine is used is dianilinogossypol with two molecules of pyridine of crystallization which can be driven off by heating to constant weight 18 to 24 hours at 110° C., depending upon the amount of precipitate.

To demonstrate this, 0.2 gram of gossypol dissolved in peroxide-free ether was added dropwise to a hot mixture of petroleum ether (b. p. 60° to 68° C.), aniline, and pyridine, digested at 55° C., and allowed to stand. The precipitate was transferred to a Gooch crucible with a small amount of pyridine, washed with small amounts of petroleum ether, and dried 5 minutes at 100° C. and over phosphorus pentoxide at room temperature. The precipitate was found by analysis to be dianilinogossypol-dipyridine. Calculated for  $C_{42}H_{46}N_2O_6 \cdot 2C_5H_5N$ : N, 6.77; found, 6.68 and 6.66.

Dianilinogossypol was prepared from gossypol with aniline alone without the use of pyridine. It was recrystallized from boiling benzene and dried at 100° C. for 2 hours. Calculated for  $C_{42}H_{46}N_2O_6$ : N, 4.19; found, 4.11 and 4.10.

The dianilinogossypol-dipyridine was also prepared from crude cottonseed oil. This contained from 5.89 to 6.24 per cent of nitrogen, being low because of some loss of pyridine of crystallization in washing and drying the precipitate. Royce's method is not satisfactory, as some of the pyridine of crystallization in the precipitate is lost in washing and drying.

### Literature Cited

- Royce, H. D., *Oil and Soap*, 10, 183-5 (1933).

PUBLISHED with the approval of the Acting Director of the North Carolina Agricultural Experiment Station as No. 106 of the Journal Series.



# The Solvency of Petroleum Spirits

## Resin Solvency of Commercial Spirits

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PETROLEUM spirits are used in the paint and varnish industry both for dissolving natural or synthetic resins at approximately room temperature, and as a chilling and thinning material to add to mixtures of resin and drying oil after cooking at high temperatures.

The term "solvency" has been used in the industry to cover all manifestations of solvent power. Spirits with high solvency would be expected to dissolve resins or varnishes with ease and give dispersions of low viscosity and high stability. Such a broad and indefinite use of the term is likely to lead to lack of clarity in thinking, and to misunderstandings between laboratories. Therefore, for this work the following terms have been adopted: "Resin solvency" is used to describe the solvent power of spirits for resins when dissolved at room temperature without the addition of any third material; "varnish solvency," the solvent power of spirits for heated mixtures of drying oil and of resin; "dilution limit," the limit to which a varnish may be diluted without obtaining immediate precipitation (11, 25); and "dilution stability," the stability in storage of dispersions of varnish containing less than the limiting quantity of spirits as judged on the dilution limit basis (25).

Since this is at best a complex set of phenomena, it was decided to investigate first the most simple solvency relation—the solvency of spirits for resin at room temperature without the addition of any third material, or the "resin solvency."

The present paper is limited to the presentation of a practical means for evaluating the resin solvency of commercial petroleum spirits with a boiling range of 300° to 400° F. (149° to 204° C.). ["Petroleum spirits" is the approved A. S. T. M. term for this product. The term "mineral spirits" may include coal-tar distillates (A. S. T. M. D288-36T).]

### Fundamentals of Resin Dispersion

In evaluating the solvency of spirits for natural or synthetic resins which are completely soluble, it seems both logical and straightforward to judge the solvency by measuring the properties of these resin solutions themselves. This basis of judging solvency is very different from the kauri butanol test (3, 4, 5, 13, 18, 23, 30) which actually measures the amount of petroleum spirits that can be added, without causing precipitation, to a butyl alcohol solution of a resin that is essentially insoluble in petroleum spirits. Both the butyl alcohol and the insoluble resin are foreign to the problem at hand—namely, the relative ability of petroleum spirits to wet, solvate, and disperse the molecules of spirit-soluble resins.

The fundamental physics involved in the solution or dispersion of nitrocellulose molecules has been discussed in some detail by McBain (19). The fundamental point is that the molecules of the solvent must penetrate between the long chains of the nitrocellulose structure and have the ability to adhere more tenaciously to the molecular surface of the nitrocellulose chains than these chains can adhere to each other. Since soluble resins are now known to consist mainly of long-chain structures (10, 14, 27), this general picture should apply to all resins as well as to nitrocellulose. Furthermore, since different parts of the resin molecules usually consist of different type groups or linkages, a mixed solvent is usually able to wet and solvate the long chains more efficiently because each linkage or group in the chain can find in the solvent the

appropriate molecule of solvent (generally one of similar chemical type) to wet and solvate it. Therefore, in a perfect resin solvent the long chains become entirely separated from one another and the average or effective chain length is a minimum.

Staudinger has discussed the influence of chain length on viscosity and has shown that in both dilute (27) and concentrated solutions (27, 29), viscosity increases with length of chain for any given weight per cent concentration. It is, therefore, reasonable to believe that the relatively high viscosity observed when resins are dispersed in poor solvents is due to the tendency of the resin molecules to adhere to, or associate with, one another, thus increasing the effective chain length. That such association may be relatively stable in the case of molecules containing polar groups ( $-\text{COOH}$ ,  $-\text{OH}$ ,  $\text{C}=\text{O}$ ,  $-\text{NH}_2$ , etc.) dissolved in nonpolar solvents has been known for a long time. For example, it was reported years ago in the thorough text of Biltz (6) that the molecular weight of benzoic acid in benzene determined by either the freezing or boiling point method is nearly double the true value, showing clearly the existence in this case of association, even at the boiling point of benzene. Similar results have been obtained in this laboratory with long-chain organic acids such as oleic acid, stearic acid, and naphthenic acids in nonpolar solvents.

To sum up, a good solvent provides molecules capable of wetting and solvating all parts of the long-chain resin molecules, so that these long-chain molecules will have little tendency to associate with one another.

The fundamental studies of Staudinger (27, 28, 29), McBain (19, 20, 21), and Kraemer (14), therefore, provide strong support for the opinion of many workers (2, 9, 12, 22, 24, 26, 31, 32), that a "high solvency" solvent will give resin solutions of relatively low viscosity at any chosen concentration. In several recent publications (8, 23, 31) both viscosity and miscibility criteria of solvency are discussed. In the strictly practical papers of Ware and Teeters (32), and of Mantell and Skett (22), dependence upon viscosity data is advocated as a basis of judging solvency.

The barrier which now appears to prevent a clear understanding among various workers of the nature of "solvency" is the habit of using terms such as "solvent strength," "solvent power," or "solvency" (4, 12, 13, 18, 24, 30) as though they described a definite property like density or refractive index which should be the same independent of the manner in which it is determined. Actually "solvent power" is a meaningless term unless we specify what is being dissolved. There is no a priori reason for believing that "good solvency" as judged by the kauri butanol test will enable one to predict good solvency on the basis of a viscosity test with ester gum, dammar, Pliolite, or phenolic or alkyd type resins. Toby (31) says, "For each individual plant problem it is my thought that the viscosity of that specific gum employed should be tested with every projected solvent, as this will give us the most accurate and pertinent information for each specific need." The authors agree with this point of view, but feel that the problem can be simplified to a certain extent by studying the response of typical resins to a representative selection of technical solvents.

It was decided to confine this preliminary investigation to commercial petroleum spirits and to four types of spirit-



soluble resins, placing more emphasis upon variety of chemical types than on whether or not these resins are used commercially on a cold-cut basis. The resins actually used are as follows:

1. Straight phenolic and modified resins
  - A. Straight phenolic resins (also called "pure" or "concentrated" phenolic resins)
    - Super-Beckacite<sup>1</sup> 1001 (Reichhold Chemical Co.)
    - Amberol ST-137 (Resinous Products & Chemical Co.)
  - B. Modified Phenolic Resins
    - Beckacite 1100 (Reichhold Chemical Co.)
    - Amberol F-7 light (Resinous Products & Chemical Co.)
2. Ester gum
  - Ester gum 6 (American Cyanamid Co.)
  - Synthe Copal (Reichhold Chemical Co.)
3. Alkyd resin
  - Glyptal 2454 and 2464 (General Electric Co.)
4. Thermoplastic rubber
  - Pliolite (Goodyear Tire & Rubber Co.)

### Procedure

In planning the "resin solvency" portion of this general investigation of solvency, it was decided to choose a procedure which would make possible reproducible and precise viscosity measurements on resin solutions. Therefore, dissolving the resin by refluxing or otherwise heating the solvent and the resin was not seriously considered, because of the possibility of losing the light ends of the solvent, and the probability that it would be difficult to control with sufficient exactitude the effect of time and temperature of heating on the resin itself.

The procedure chosen, after some preliminary investigation, is as follows:

A clean dry 8-ounce (240-cc.) bottle is weighed to the nearest 0.05 gram using an accurate pan balance (Arthur H. Thomas Co., No. 1907, is suitable). Then 50 ± 0.05 grams of solvent are weighed into the bottle, making the final adjustment by adding solvent to the bottle on the balance by means of a pipet. Finally 50 ± 0.05 grams of freshly ground resin (grinder, A. H. Thomas No. 4265) are weighed on a glazed paper and added to the solvent in the bottle. The resin should be ground sufficiently fine to assure uniform dispersion of the material, but should not be ground to the consistency of a flour, because of difficulty in handling it in that state. The last of the resin usually adheres to the paper and must be brushed in with a camel's-hair brush. In case a concentration of more or less than 50 per cent is wanted, the appropriate weights of resin and solvent are taken, but the weight of the whole batch is kept at 100 grams.

As soon as the resin has been added, the bottle is tightly corked and then immediately placed in a shaking machine (A. H. Thomas No. 8916) with the bottle horizontal and lying lengthwise with the motion of the shaker. This shaker operates with a 7.5-cm. (3-inch) stroke, approximately 360 strokes per minute (180 ± 20 r. p. m. on drive pulley). Solution will usually take place overnight, 17 to 24 hours, but in a few cases, a longer time may be required. After solution is complete, the bottle should be centrifuged or allowed to stand until any lint or dirt in the resin solution has settled out.

The viscosity is measured at 77° F. (25° C.) using precision kinematic viscometers such as those designed by Fenske and co-workers (1, 33).

In order to obtain very reliable data for the present investigation, two bottles of solution were prepared in each case, and the viscosity of each mix was determined in a different viscometer. If the viscometers checked within 2 per cent, the average was accepted; if the check was not so good, the viscosities were re-checked.

The agreement of the data from sets of viscometers having capillary tubing of widely different diameter, and times of out-flow differing about tenfold, indicates that the deviation from Poiseuille's law is small or nonexistent for these dispersions. The data show that the viscosities are true viscosities at least for the limited range of shearing stress represented by the authors' viscometers.

<sup>1</sup> In the balance of this paper and in that following (17), the prefix "Super" before Beckacite 1001 has been omitted.

In the practical determination of resin solvency, it is desirable to adjust the concentration of the resin so that the viscosity in the standard blend will be in the range of 200 to 500 centistokes. The worst solvents, which are seldom below 30 resin solvency, will then not be over 1000 to 1700 centistokes, depending on the resin. In this range, mixing on the shaking machine is satisfactory, as are flow and drainage in viscometers of the Fenske or similar type. It is also recommended that concentrations be chosen at 5 per cent intervals—i. e., 40, 45, 50, 55, 60, 65, etc.

In the field of the straight phenolic and modified phenolic resins, Beckacite 1001 is very satisfactory from the point of view of uniformity, stability over long periods of time (Table IV), ease of dispersion, and reproducibility of viscosity measurements and is, therefore, recommended as the standard resin for this general field. Amberol ST-137 is similar to Beckacite 1001 and appears to be suitable for routine resin solvency work, but it has not yet been as thoroughly investigated as Beckacite 1001.

In the case of ester gum, either ester gum 6 or Synthe Copal may be used. These resins appear to be somewhat less uniform than the phenolic resins, and there is a pronounced tendency for change after grinding. The ester gum should, therefore, be ground on the same day that it is to be used and should be thoroughly mixed after grinding. These ester gums give almost identical viscosities.

Glyptal 2464, without added solvent, was very gummy and sticky and changed on exposure to air. Therefore, enough mixes were always planned to use up a whole can within a few hours of the time it was first opened. A wide-mouthed bottle must be used in preparing mixes with these resins. Reproducible results can be obtained with this resin, although more skill is required than with the other resins mentioned. Fifty to 60 per cent resin is about the right concentration for the alkyds thus far studied.

Pliolite resin is supplied in small hard pieces which are too tough to grind and, as received, are small enough to dissolve. This resin is uniform and is stable in storage for reasonable periods of time, probably because the condensation catalyst is thoroughly washed out in the process of manufacture (7, 16). Twenty per cent resin is sufficient in testing with Pliolite.

TABLE I. PHYSICAL PROPERTIES OF STANDARD BLEND (SOLVENT 1) AND CONSTITUENTS THEREOF

	Standard Blend	Diethylbenzene <sup>a</sup>	Decahydronaphthalene <sup>b</sup>	Isooctane <sup>c</sup>
A. P. I. gravity at 60° F.	40.5	31.0	27.6	71.4
A. S. T. M. distillation:				
Initial boiling point, ° F.	215	345	365	204
5%	232	347	368	206
10%	248	348	369	207
50%	353	350	372	208
90%	363	352	374	210
95%	367	353	376	210
End point	383	380	392	248
50% boiling point corrected for emergent stem:				
° F.	360	357	380	209
° C.	182	180	193	98
Density, d <sub>20/4</sub>	0.8185	0.8674	0.8867	0.6918
Refractive index, n <sub>D</sub> <sup>20</sup>	1.4566	1.4965	1.4780	1.3921
Refractivity intercept	1.0473	1.0628	1.0346	1.0461
Specific dispersion × 10 <sup>4</sup>	123	161	99	102

<sup>a</sup> Dow Chemical Co.

<sup>b</sup> Du Pont Co., technical grade.

<sup>c</sup> Isooctane, technical, reference fuel F, Standard Oil Co. of N. J.

### Standard Solvent

The choice of a standard solvent for this work presented some difficulty. In view of the fact that two widely used commercial petroleum spirits contained approximately equal proportions of aromatics, naphthenes, and paraffins, it seemed reasonable to use as a final standard a three-component blend of aromatic, naphthenic, and paraffinic compounds of technical purity. Diethylbenzene (Dow Chemical Company), decahydronaphthalene (Eastman No. P1905 or du Pont), and isooctane (reference fuel F, Standard Oil Company of New Jersey) are all available in a reasonably pure state.



The molecular volumes of these compounds are, respectively, 154.5, 155.5, and 165 cc.; therefore, blending equal parts by volume will give approximately equal parts on a mole per cent basis. This equal-volume blend was chosen as the reference standard and is designated throughout this paper as solvent 1. Its properties, and the properties of its constituents, are given in Table I. Solvent 1 is not intended for routine use, but merely as a standard liquid of constant solvency which can be used to calibrate selected samples of petroleum spirits which can then be used as working standards.

The value of 100 is assigned to solvent 1 merely as a basis for arriving at reproducible comparative values.

### Resin Solvency

The work of McBain and of Staudinger leads one to expect that a good solvent for a particular resin will separate the molecules of the resin from one another and produce a dispersion of minimum viscosity. In Figure 1, *A*, viscosity data for dispersions of a straight phenolic resin (Beckacite 1001) are plotted against the kauri butanol number of the solvents. Solvents 2 to 32, inclusive, are petroleum spirits; for most of these the properties are given in Table II. Solvent 1 is a standard blend of pure compounds, for which data are given in Table I. The left-hand scale in each case gives kinematic viscosity in centistokes; the right-hand scale gives viscosity in terms of Gardner-Holdt tubes (11), based on the absolute viscosity in poises specified for these tubes. Viscosities in poises were obtained by multiplying the kinematic viscosity

by the density of the resin solutions at 77° F. (25° C.). For the authors' solutions a good linear relation exists between kinematic and absolute viscosity; therefore, there is no inconsistency for these solutions in using both kinematic and absolute viscosity scales on the same graph. The density of the resin solutions for which the authors have thus far obtained density data fits the following approximate equation within about  $\pm 0.005$ :

$$\text{Density of resin solution at } 77^\circ \text{ F.} = \text{density of solvent at } 77^\circ \text{ F. (25}^\circ \text{ C.)} + 0.00288 \text{ weight per cent of resin} - 0.017$$

It is somewhat surprising that one equation will fit the data obtained for Pliolite, Beckacite 1001, Beckacite 1100, Amberol F-7, Glyptal 2464, and ester gum 6, and for solvents 1, 2, 4, 6, 7, 8, and 11.

The kauri butanol data shown were all carefully checked, standardization being against toluene and *n*-heptane (5).

In Figure 1, *A*, point 1 is standard blend 1. Spirit 2 is a commercial spirit, containing approximately equal quantities of paraffins, naphthenes, and aromatics, which was used as a working standard. Points 3 to 11, inclusive, are other commercial petroleum spirits of 300° to 400° F. boiling range. Solvents 2, 3, 5, 8, and 11 have kauri butanol values between 42 and 44, yet the viscosities of the solutions obtained with these solvents vary from 300 to 690 centistokes or from K<sup>+</sup> to U<sup>+</sup> on the Gardner-Holdt scale. These data show definitely that the kauri butanol test does not measure the ability of a spirit to wet, solvate, and disperse phenolic resins such as Beckacite 1001. Figure 1, *B*, *C*, and *D* show that the same statement can be made concerning dispersions of ester gum, alkyd, and modified rubber (Pliolite) resins.

It was desired to obtain an index for solvency based on viscosity, but one which would be approximately constant irrespective of the concentration of the solution and at least approximately independent of the temperature at which the viscosity data were obtained. Such an index was obtained rather simply in the following manner, starting with the data shown in Figure 1, *A*.

If the viscosity of each solution is divided into the viscosity of Beckacite 1001 in standard blend 1 and then multiplied by 100, the values obtained are shown in Table III. Viscosity ratios relative to working standard 2 are also given. A comparison of the data for Beckacite 1001, Beckacite 1100, and Amberol F-7 shows that these three resins of the straight phenolic and modified phenolic types (15, p. 162) all rate these spirit samples in practically the same order.

It was, therefore, decided to give this viscosity ratio, relative to pure compound standard 1, the name "resin solvency" (R. S.) and define it by the following equation:

$$\text{R. S.} = \frac{\text{kinematic viscosity of solution of X\% resin in standard spirit 1}}{\text{kinematic viscosity of solution of X\% resin in spirits under test}} \times 100$$

The resin solvency, being based on a standard blend of pure compounds, can be reproduced at any future time and is therefore suitable for permanent record. For comparison of several commercial spirits, ratios of the resin solvencies can be

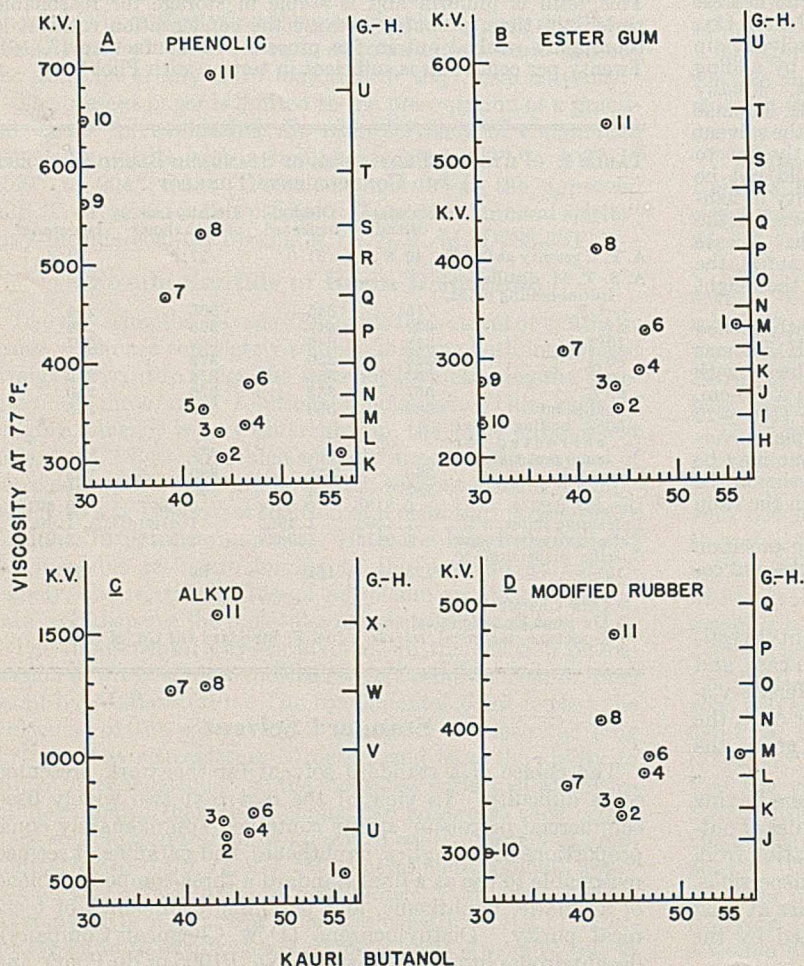


FIGURE 1. VISCOSITY OF RESIN SOLUTION vs. KAURI BUTANOL NUMBER OF SPIRITS



used—for example, relative resin solvencies (R. R. S.) based on spirit 2 are given in Table III for comparison with the actual resin solvency values.

Table III also gives the resin solvency, based on Figure 1, *B*, *C*, and *D*, for ester gum 6, Glyptal 2464, and Pliolite, respectively, and for Beckacite 1100 and Amberol F-7, for which graphs are not shown. It is clear that the resin solvencies of some solvents—e. g., 2, 3, and 4—are high with all these resins. Other solvents such as 8 and 11 are consistently low. Still other solvents are good for some resins and poor for others. For example, solvents 7, 9, and 10 are relatively good

solvents for Pliolite and ester gum 6, but are poor for the modified phenolic and alkyd resins.

The effect of concentration is shown in Figure 2, in which the resin solvencies based on pure compound blend 1 and relative resin solvencies based on spirit 2 are plotted for three concentrations of Beckacite 1001 and ester gum. In the case of both resins the relative resin solvency shows less change with concentration than the resin solvency. This means that the commercial petroleum spirit samples all have viscosity concentration curves of a similar type, whereas the viscosity concentration curve of the standard pure compound, blend 1, is

TABLE II. PHYSICAL PROPERTIES OF PETROLEUM SPIRITS USED FOR RESIN SOLVENCY DETERMINATIONS

Spirits	12	15	18	2	21	3	4	5	6	28	7	8
Resin solvency:												
Beckacite 1001	118	108	104	101	98	93	92	87	81	68	66	58
Ester gum 6	....	....	137	134	....	123	117	....	102	55	109	80
Glyptal 2464	....	....	....	77	75	71	75	....	68	....	41	41
Pliolite	....	....	117	115	113	111	105	113	100	....	107	93
Kauri butanol	44.6	44.1	43.0	44.0	43.3	43.7	46.4	42.1	46.9	66.4	38.5	42.2
Aniline point, ° F.	97.5	104.4	105.1	105.0	107.4	107.4	99.0	115	102	23.5	125	120
Density 20/4	0.7932	0.7940	0.7941	0.7927	0.7969	0.7958	0.8038	0.7928	0.8066	0.8641	0.7861	0.8024
Refractive index 20/d	1.4469	1.4472	1.4471	1.4472	1.4479	1.4479	1.4526	1.4452	1.4509	1.4882	1.4400	1.4447
Refractivity intercept	1.0503	1.0502	1.0499	1.0508	1.0497	1.0500	1.0507	1.0488	1.0476	1.0561	1.0469	1.0435
Specific dispersion × 10 <sup>4</sup>	121	123	120	120	124	120	125	116	119	145	112	106
Solvent viscosity, centistokes:												
77° F.	....	....	....	1.051	....	1.080	1.105	1.069	1.125	....	1.141	1.184
100° F.	....	....	....	0.896	....	0.924	0.941	0.913	0.941	....	0.968	1.000
Engler distillation:												
A. P. I. gravity at 60° F.	46.0	45.8	46.0	46.1	45.2	45.4	43.7	46.1	43.1	31.5	47.6	44.0
Initial boiling point, ° F.	295	303	303	304	307	306	308	300	311	357	300	305
5% 308	313	314	316	319	317	318	314	319	319	366	316	316
10% 311	317	318	319	322	321	321	317	322	322	372	320	319
50% 324	329	331	333	336	336	341	333	336	336	383	338	336
90% 341	348	352	358	357	357	369	362	361	402	402	364	367
95% 346	353	361	368	368	367	382	374	377	410	410	380	379
End point 377	378	383	390	391	394	396	392	395	417	417	414	392
						Cuts of 21				Cuts of 8		
Spirits	9	10	11	32	0-20	40-60	80-100	0-20	40-60	60-80	80-100	
Resin solvency:												
Beckacite 1001	55	48	45	30	157	102	51	73	56	50	32	
Ester gum 6	121	142	62	56	....	....	....	....	....	....	....	
Glyptal 2464	....	....	33	....	....	....	....	....	....	....	....	
Pliolite	....	127	79	....	....	....	....	....	....	....	....	
Kauri butanol	30.3	30.5	43.4	36.0	47	44.5	39	41.5	41.9	42.1	41.6	
Aniline point, ° F.	140.2	149.0	119	132	93.2	102.6	122.8	122.2	118.6	118.8	122.0	
Density 20/4	0.7730	0.7582	0.8065	0.8011	0.7920	0.7970	0.8005	0.7884	0.8003	0.8077	0.8184	
Refractive index 20/d	1.4336	1.4268	1.4467	1.4485	1.4457	1.4482	1.4492	1.4380	1.4442	1.4480	1.4543	
Refractivity intercept	1.0471	1.0477	1.0434	1.0479	1.0497	1.0497	1.0489	1.0438	1.0440	1.0441	1.0451	
Specific dispersion × 10 <sup>4</sup>	105	105	109	110	125.1	124.5	118.8	110.9	110.2	113.8	114.5	
Solvent viscosity, centistokes:												
77° F.	....	....	1.263	....	....	....	....	....	....	....	....	
100° F.	....	....	1.060	....	....	....	....	....	....	....	....	
Engler distillation:												
A. P. I. gravity at 60° F.	50.6	54.1	43.1	44.0	46.3	45.2	44.4	47.1	44.5	42.9	40.6	
Initial boiling point, ° F.	312	311	310	343	270	316	352	288	314	324	352	
5% 320	319	319	319	358	284	322	356	297	320	334	361	
10% 323	321	325	361	288	324	358	299	321	336	363		
50% 340	339	340	387	306	330	366	311	330	344	371		
90% 368	373	374	423	328	344	380	334	352	364	390		
95% 378	384	387	438	335	352	390	349	362	372	400		
End point 401	396	418	455	366	380	409	381	384	398	440		

TABLE III. RESIN SOLVENCIES AND RELATIVE RESIN SOLVENCIES

Spirits	Straight Phenolic, 55%		Modified Phenolic 50%				Alkyd, 50%				Rosin Ester, 65%		Modified Rubber, 20%	
	Beckacite 1001		Beckacite 1100		Amberol F-7		Glyptal 2464		Ester Gum 6		Pliolite			
	Standard blend	Working standard	Standard blend	Working standard	Standard blend	Working standard	Standard blend	Working standard	Standard blend	Working standard	Standard blend	Working standard	Standard blend	Working standard
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)
1	100	99	100	88	100	106	100	130	100	75	100	87	100	87
2	101	100	114	100	94	100	77	100	134	100	115	100	115	100
3	93	92	105	92	86	92	71	92	123	92	111	97	111	97
4	92	91	99	87	94	100	75	98	117	87	105	91	105	91
5	87	86	....	....	69	73	....	....	....	....	113	98	113	98
6	81	80	84	74	86	91	68	88	102	76	100	87	100	87
7	66	65	74	65	36	38	41	53	109	81	107	93	107	93
8	58	57	59	52	39	42	41	53	80	60	93	81	93	81
9	55	54	....	....	....	....	....	....	121	90	....	....	....	....
10	48	47	....	....	....	....	....	....	142	106	127	110	127	110
11	45	44	46	40	31	33	33	43	62	46	79	69	79	69
Kinematic <sup>a</sup> viscosity with standard 1	306	....	227	....	312	....	521	....	334	....	379	....	379	....

<sup>a</sup> Since different batches of the same grade of resin often differ somewhat, these viscosities are intended to show what authors obtained and are in no sense standard values.



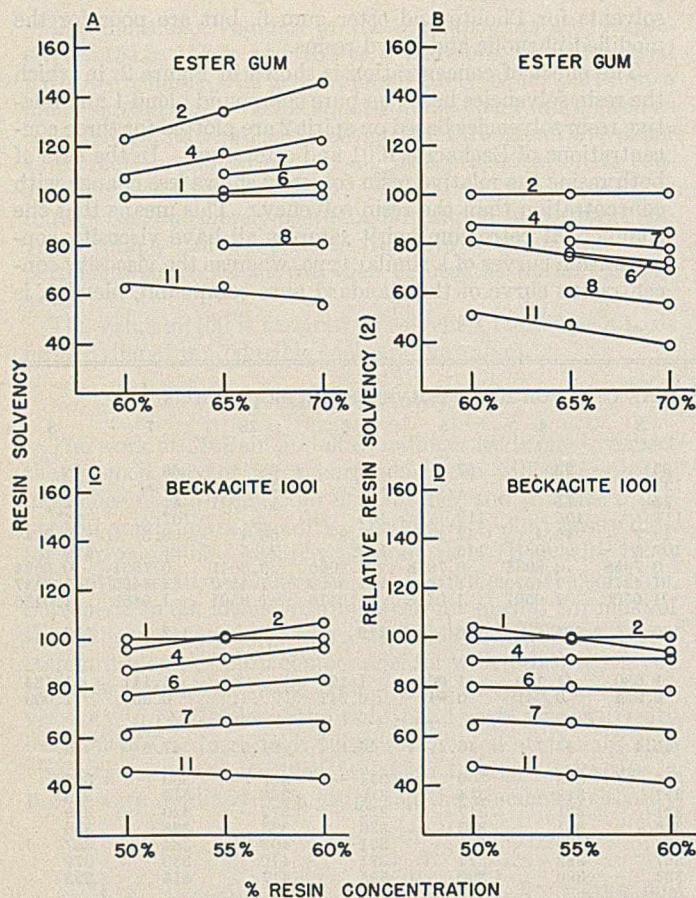


FIGURE 2. RESIN SOLVENCY AND RELATIVE RESIN SOLVENCY vs. RESIN CONCENTRATION

somewhat different. For the purpose of this work—namely, obtaining relative solvent power of various samples of commercial petroleum spirits—it is clear that the same order of solvency will be obtained irrespective of the concentration at which the comparisons are made. Data were obtained confirming this conclusion for Beckacite 1100, Amberol F-7, Glyptal 2454, and Glyptal 2464.

It is recommended that Beckacite 1001 be made up in 55 per cent concentration and ester gum 6 in 65 per cent concentration. For other resins, concentrations may be chosen on the basis suggested in the section on procedure.

The approximate constancy of the relative resin solvency at various concentrations makes it possible to construct a family of viscosity concentration curves such as those presented by Ware and Teeters (32). It is only necessary to have experimental data for the viscosity of the reference solvent at three concentrations and of the other solvents at one concentration. Curves drawn in this way based on the data for spirit 3 (resin solvency 93) with Beckacite 1001 in Table IV are shown in Figure 3. The viscosities of solvents 6, 7, and 11 are based on the relative resin solvency values in Table III. The seven experimental points on which this graph is based are shown as circles.

This graph is of interest since it shows clearly the difference between this work, in which viscosity ratios at one concentration (line X — Y) are compared, and the work of Ware and Teeters in which the concentrations at equal viscosity (line Y — Z) are compared. The order of solvency on either basis is the same.

The effect of temperature is shown in Table V, which contains data obtained at 77° F. (25° C.), 100° F. (37.8° C.), and 130° F. (54.4° C.). These data show that there is somewhat

TABLE IV. VISCOSITY vs. CONCENTRATION AND CONSTANCY OF VISCOSITY USING BECKACITE 1001<sup>a</sup>

Concentration % by Weight	Shipment of Resin	Date of Run	Kinematic Viscosity		
			Spirit 3	Spirit 4	Spirit 11
50	First	4-8-38	119	118	230
			119	120	230
		4-19-38	117	117	225
	Second	4-28-38	118	117	226
			122	123	236
			122	123	236
55	Second	4-28-38	336	330	699
			328	330	695
		5-24-38	327	335	707
	Fourth	10-6-38	332	335	691
			327	335	672
		2-2-39	329	335	672
60	Second	5-24-38	325	..	700
			321	..	..
			958	973	2161
			965	969	2172

<sup>a</sup> One shipment of Beckacite 1001 gave lower viscosities but the same relative resin solvencies and was also constant in storage. It is desired to emphasize the constancy of each sample in storage rather than the absolute agreement between three out of four shipments of this resin.

less viscosity difference at 100° F. (37.8° C.) and 130° F. (54.4° C.) than at 77° F. (25° C.)—i. e., the relative resin solvency of a poor solvent is somewhat better at the higher temperature.

The small influence of temperature on resin solvency is in line with data of Staudinger (27, p. 207) for polystyrol of approximately 120,000 molecular weight in tetralin. These data are reported in terms of specific viscosity, but by algebraic transposition it can be shown that for solvents of approximately the same viscosity-temperature slope the resin solvency must be independent of temperature if the specific viscosity is independent of temperature. (Specific viscosity = relative viscosity - 1. Relative viscosity = viscosity of solution ÷ viscosity of solvent.)

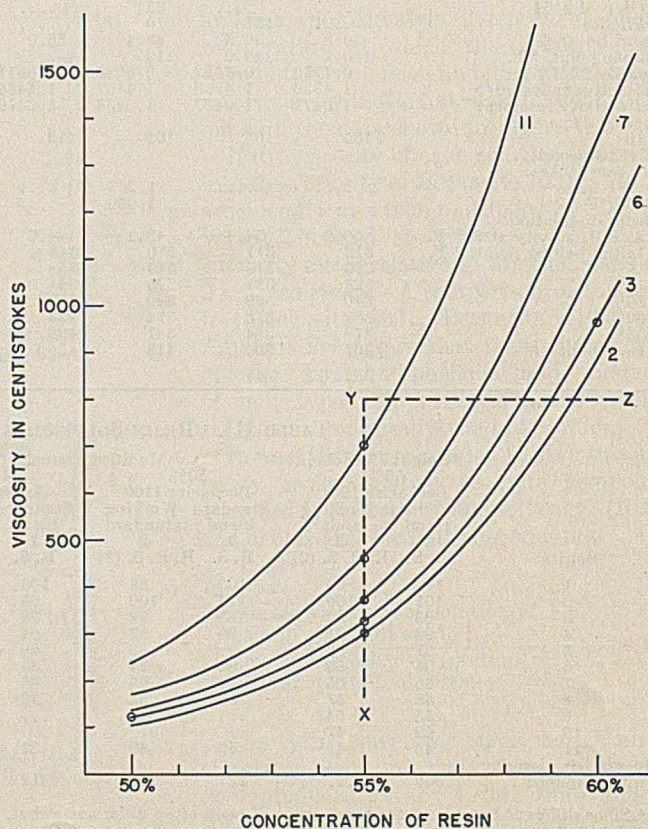


FIGURE 3. VISCOSITY IN CENTISTOKES vs. CONCENTRATION OF RESIN, PLOTTED FROM VISCOSITY RATIOS



TABLE V. EFFECT OF TEMPERATURE ON RESIN SOLVENCY OF SPIRITS

Temperature °F. °C.	Beckacite 1001, 55% Resin, 45% Solvent								Ester Gum 6, 65% Resin, 35% Solvent							
	Standard pure compound blend 1		Spirit 18		Spirit 8		Ratio of resin solvency <sup>a</sup>		Standard pure compound blend 1		Spirit 18		Spirit 8		Ratio of resin solvency <sup>a</sup>	
	K. V.	R. S.	K. V.	R. S.	K. V.	R. S.	8/18	7/15	K. V.	R. S.	K. V.	R. S.	K. V.	R. S.	8/18	7/15
77	25	319	307	104	737	43	41	61	301	220	136	475	63	46	50	
		319	307		736				300	218		477				
100	37.8	121	110	111	221	55	49	69	124.3	92.8	134	178	70	52	58	
		122	110		219				124.5	92.8		177				
130	54.4	47.3	40	119	69	69	58	77	50.8	38.7	131	64.6	78	60	66	
		...	40		69				50.8	38.7		64.9				
Change		...	...	+7	...	+12	+8	+8	...	...	-2	...	+7	+6	+7	
77-100° F.		...	...	+15	...	+26	+17	+16	...	...	-5	...	+15	+14	+14	
77-130° F.		...	...	...	...	...	...	...	...	...	...	...	...	...	...	

<sup>a</sup> Solvents 15 and 18 are of approximately balanced composition.

As a practical working temperature 77° F. (25° C.) was chosen, since it is slightly more selective and is fairly near room temperature in many laboratories during a considerable portion of the year. It would be possible, even though not particularly desirable, for a laboratory to determine resin solvency without a thermostat, provided the viscosities of both the standard and unknown were determined at the same time and the same temperature.

The data in Table V when plotted on the A. S. T. M. kinematic viscosity chart C (D341-37T) give good straight lines.

The data thus far presented show that the resin solvency for any spirit is little affected by the concentration of resin or by the temperature, but that there may be considerable difference in resin solvency determined with different classes of resins.

**Molecular Concentration of Solvent**

To determine the effect of boiling point on resin solvency, steam and fire distillations were made on two petroleum spirits of approximately balanced composition (3 and 21) and one petroleum spirit containing a large amount of naphthene (8).

Solutions containing equal weight per cent of resin were prepared with each series of cuts and with the original spirits. In Figure 4, A, the resin solvencies of the cuts relative to the original spirits in each series are plotted against the 50 per cent points of the A. S. T. M. distillations. All the points may be represented well by one curve, even though there is some scattering in the case of the four bottoms samples.

In Figure 4, B, curves are shown for cuts of petroleum spirits 8 and 21 made up with an equal number of moles of spirits per gram of resin. The molecular weights of these cuts of spirits were determined cryoscopically in benzene. Apparent molecular weights at three or more concentrations were obtained. The value used represents the extrapolated value corresponding to zero concentration. With the exception of the two bottoms, samples A and C, all the blends in each separate series had the same viscosity. Examination of the bottoms from spirit 21 revealed a slight difference in the per cent of aromatic hydrocarbon as compared with the other cuts of 21. Pure *p*-cymene was added to bottoms A to give it the same aromatic content as the other cuts of 21, and with this blend, point B was obtained, which is in line with the other points. The authors have not yet determined the reason for the deviation of point C from its line, but believe that it is connected with a slight difference in the composition of the bottoms and the overhead cuts. These data indicate strongly that as long as the composition in terms of hydrocarbon types is constant, blends made up on the basis of equal moles of solvent per gram of resin will all have the same viscosity even though the molecular weight of the solvent varies considerably.

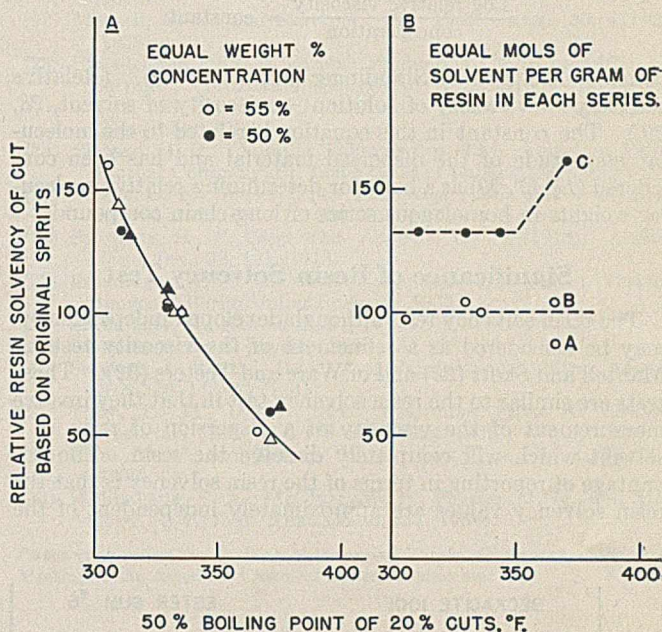


FIGURE 4. RESIN SOLVENCY OF CUTS RELATIVE TO ORIGINAL SPIRITS vs. 50 PER CENT BOILING POINT OF CUTS

The curves in Figure 4, A and B, show that, if blends are made from the cuts of any one spirit on the basis of equal moles of solvent of constant composition per gram of resin, the viscosities of solutions of phenolic resin will be approximately equal—i. e., the solvency on a molar basis is equal, at least over the range for which data have been obtained.

The gain in solvency with decrease in boiling point for any one type of spirit is, therefore, directly related to the gain in the number of molecules per unit volume or weight of the solvent.

Carrying this idea a step further it should follow that with any one type of solvent the number of grams of resin per gram mole of solvent should control the viscosity. To check this idea, Figure 5, in which log viscosity is plotted against grams of resin per gram mole of solvent ( $\times 100$ ), was prepared.

Data are presented for spirits 18 and 21 (which are almost identical with the working standard 2), for spirit 8 which is highly naphthenic, and for 20 per cent cuts of these spirits. It is clear that plotting viscosity against grams of resin per gram mole of solvent ( $\times 100$ ) puts all the data for any one spirit and resin on a single straight line.



TABLE VI. COMPARISON OF FOUR COMMERCIAL SPIRITS

Spirits	Composition Approximately Balanced				Composition Unbalanced			
	2		4		10		11	
50% A. S. T. M. boiling point, ° F.	333		341		339		340	
Approximate composition, volume %:	30		30		12		15	
Aromatics	25 to 30		30 to 35		10 to 15		70 to 75	
Naphthenes	40 to 45		35 to 40		73 to 78		10 to 15	
Paraffins								
	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)
Phenolic (Beckacite 1001)	101	100	92	91	48	47	45	44
Glycerol-resin (ester gum 6)	134	100	117	87	142	106	62	46
Alkyd (Glyptal 2464)	77	100	75	98	127	110	33	43
Modified rubber (Pliolite)	115	100	105	91			79	69

This would appear to be a valid modification of the well-known approximate relation

$$\frac{\text{Log relative viscosity}}{\text{concentration}} = \text{constant}$$

which is discussed by Staudinger (27, p. 59; 29). (Relative viscosity = viscosity of solution ÷ viscosity of solvent, 28, 29.) The constant in this equation is related to the molecular magnitude of the dispersed material and has been considered (14, 27, 29) as a basis for determining relative molecular weights in homologous series of long-chain compounds.

### Significance of Resin Solvency Test

The resin solvency test, although developed independently, may be considered as a refinement of the viscosity tests of Mantell and Skett (22) and of Ware and Teeters (32). These tests are similar to the resin solvency test in that they involve measurement of the viscosity of a dispersion of resin in a solvent which will completely dissolve the resin. The advantage of reporting in terms of the resin solvency is that the resin solvency values are approximately independent of the

concentration at which the test is made and of temperature. If the viscosity of solutions of a nonchanging resin in the working standard at several concentrations is known, it has been shown (Figure 3) that the viscosity at only one concentration need be determined on a new spirit in order to set up curves of the Ware and Teeters type.

Without discussing in detail the relation of the composition of spirits to their resin solvency, it is of interest to compare two commercial petroleum spirits having a balanced composition, with one rich in naphthenes, and another rich in paraffins. Table VI gives approximate composition data, resin solvency, and relative resin solvency data for such spirit samples.

Spirits 2 and 4, whose compositions are approximately balanced, show relatively little variation in resin solvency, although the higher boiling point of spirit 4 reduces all the resin solvenicities somewhat. Spirit 10, which is low in aromatics and naphthenes but rich in paraffins, is very satisfactory for ester gum and Pliolite but very poor for the phenolic type. Spirit 11, which is rich in naphthenes, has low resin solvency for all resins tried.

These data show, definitely, that conclusions concerning the relative solvency of aromatics, paraffins, and naphthenes based on the careful study of the kauri butanol test by Baldeschwieler, Morgan, and Troeller (3, 4) cannot be generalized to apply to a wide variety of materials (18). The data furthermore confirm the statement that one must always keep in mind what is to be solvated when considering "solvency."

The correlation of resin solvency values with the behavior of the solvent in actual manufacturing operations will require the cooperation of the consumer of spirits.

### Summary

There is no definite relation between the kauri butanol solvency of petroleum spirits and the viscosity of cold-cut solutions of resins dispersed in these spirits.

The resin solvency for cold-cut dispersions defined by the equation

$$\text{R. S.} = \frac{\text{kinematic viscosity of solution of X per cent resin in standard spirit 1}}{\text{kinematic viscosity of solution of X per cent resin in spirits under test}} \times 100$$

is approximately independent of the concentration at which the test is made and is approximately independent of the temperature of test.

The resins recommended for test purposes are: (1) Beckacite 1001 (Reichhold Chemical Co.), a straight phenolic resin, which can also represent the modified phenolic class as far as distinguishing between good and poor solvents is concerned; (2) ester gum 6 (American Cyanamid Co.) for the ester gum class of resins.

The relative solvent power of spirits depends upon the type of resin with which the resin solvency is determined.

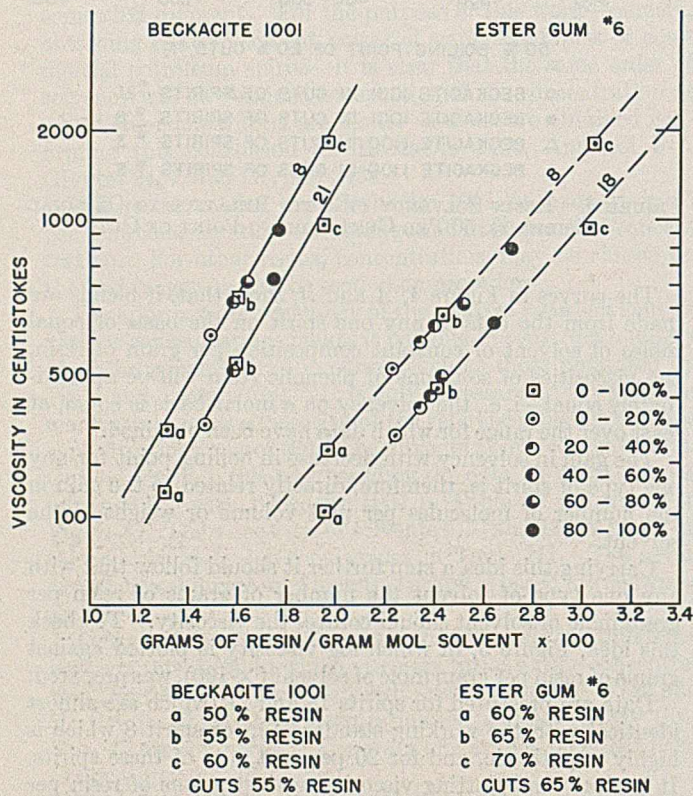


FIGURE 5. VISCOSITY IN CENTISTOKES vs. CONCENTRATION EXPRESSED ON A MOLAR BASIS



Spirits which contain approximately equal proportions of paraffins, naphthenes, and aromatics, however, have good solvency for any of the spirit-soluble resins.

Theoretical background based on the work of McBain, Kraemer, and Staudinger provides a reasonable explanation of the fact that relatively high viscosities are obtained when resins are dispersed in solvents which do not contain enough of the right type of molecule to solvate them completely.

The logarithm of the kinematic viscosity is proportional to the concentration expressed as grams of resin per gram mole of solvent. This is an extension of the generalization of Staudinger, and accounts for the lower viscosity of dispersions prepared with low-boiling cuts of spirits.

The entire study reported is confined to spirits or cuts lying within the boiling range of 300° to 400° F.

A means of standardizing the petroleum spirits used as a working standard is given. The ultimate standard is a mixture of equal volumes of diethylbenzene, decahydronaphthalene, and isoctane.

The resin solvency test is recommended as precise and quantitative, showing relative solvent power of spirits for resins on a cold-cut basis and in the absence of any third component.

### Literature Cited

- (1) Am. Soc. Testing Materials, Designation D445-38T.
- (2) Baker, F., *J. Chem. Soc.*, 103, 1653-75 (1913).
- (3) Baldeschwieler, E. L., Morgan, M. D., and Troeller, W. J., *IND. ENG. CHEM.*, Anal. Ed., 9, 540-3 (1937).
- (4) Baldeschwieler, E. L., Troeller, W. J., and Morgan, M. D., *Ibid.*, 7, 374 (1935).
- (5) Beard, L. C., Shipp, V. L., and Spelshouse, W. E., *Ibid.*, 5, 307 (1933).
- (6) Biltz, H., tr. by Jones, H. C., and King, S. H., "Practical Methods for Determining Molecular Weights," pp. 128, 194, Easton, Penna., Chemical Publishing Co., 1899.
- (7) Bruson, H. A., U. S. Patent 1,846,247, assigned to Goodyear Tire & Rubber Co. (1932).
- (8) Doolittle, A. K., *IND. ENG. CHEM.*, 30, 189-203 (1938).
- (9) Duclaux and Wollman, *Bull. soc. chim.*, (4) 27, 417 (1920).
- (10) Ellis, Carleton, *IND. ENG. CHEM.*, 28, 1130 (1936).
- (11) Gardner, H. A., "Examination of Paints, Varnishes, Lacquers, Colors," Washington, D. C., Institute of Paint & Varnish Research, 1935.
- (12) Joachim, B., *Applied Paint Varnish Chem.*, 2, 215 (American Paint Journal Co., St. Louis, Mo., 1937).
- (13) Kiehl, S. R., *Sci. Sec., Am. Paint Varnish Mfrs. Assoc.*, *Circ.* 319, 585-98 (1927).
- (14) Kraemer, E. O., *IND. ENG. CHEM.*, 30, 1200 (1938).
- (15) Krumbhaar, W., "Chemistry of Synthetic Surface Coatings," New York, Reinhold Publishing Corp., 1937.
- (16) Kurtz, S. S., Jr., U. S. Patent 2,052,411, assigned to Wingfoot Corp. (1936).
- (17) Kurtz, S. S., Jr., Lipkin, M. R., and Harvey, W. T., *IND. ENG. CHEM.*, Anal. Ed., 11, 484 (1939).
- (18) McArdle, E. H., *Chem. Met. Eng.*, 44, 598-601 (1937).
- (19) McBain, J. W., *J. Phys. Chem.*, 239-47 (1926).
- (20) McBain, J. W., Grant, E. M., and Smith, L. E., *Ibid.*, 38, 1217-31 (1934).
- (21) McBain, J. W., Haney, C. E., and Smith, L. E., *Ibid.*, 30, 312-52 (1926).
- (22) Mantell, C. L., and Skett, A., *IND. ENG. CHEM.*, 30, 417-22 (1938).
- (23) Philadelphia Paint & Varnish Production Club Committee on Solvents, "Proximate Analysis of Hydrocarbon Thinners," *Circ.* 568, *Sci. Sect., Natl. Paint, Varnish, Lacquer Assoc.* (November, 1938).
- (24) Pickard, G. H., "Volatile Thinners," p. 32-8, American Paint Journal Company, St. Louis (year of publication not given).
- (25) Picket, C. F., *Official Digest Federation Paint & Varnish Production Clubs*, No. 177, 300 (June, 1938).
- (26) Schwartz, H., *Z. Chem. Ind. Kolloide*, 12, 32 (1913); *J. Soc. Chem. Ind.*, 32, 191 (1913).
- (27) Staudinger, H., "Die hochmolekularen organischen Verbindungen," Berlin, Julius Springer, 1932.
- (28) Staudinger, H., *Kolloid Z.*, 51, 71 (1930).
- (29) Staudinger, H., *Z. physik. Chem.*, (A) 153, 410 (1931).
- (30) Stewart, J. R., *Sci. Sec., Am. Paint Varnish Mfrs. Assoc.*, *Circ.* 378, 143-53 (1931).
- (31) Toby, E. M., *Official Digest Federation Paint & Varnish Production Clubs*, No. 176, 261 (May, 1938).
- (32) Ware, V. W., and Teeters, W. O., *IND. ENG. CHEM.*, 31, 738 (1939).
- (33) Willihnganz, E. A., McCluer, W. B., Fenske, M. R., and McGrew, R. V., *Ibid.*, Anal. Ed., 6, 231 (1934).

PRESENTED before the Division of Paint and Varnish Chemistry at the 97th Meeting of the American Chemical Society, Baltimore, Md.

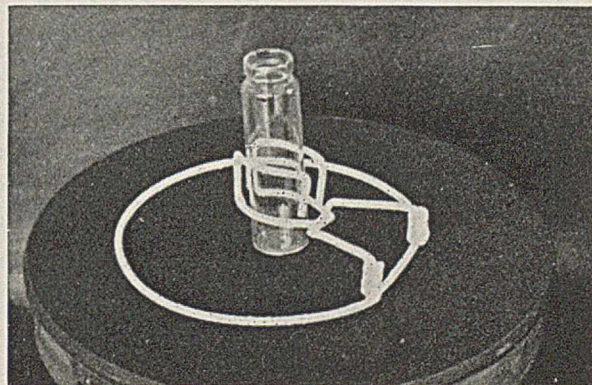
## Vial Holder

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THE vial holder depicted is of great convenience for heating test tubes or vials or filtering into them, as its large base prevents spilling.

The holder is constructed of two pieces of No. 13 W. & M. spring brass wire or No. 16 W. & M. copper-plated steel wire, one piece forming most of the ring, including the two spirals, and the other forming the jaws and the part of the ring connecting the two spirals. The ring may be 3 to 4 inches or more in diameter, the size of wire being increased with the larger diameters.

In filling or filtering into vials or test tubes, the holder frees both hands for manipulation. The jaws may be adjusted to allow any desired portion of a vial to project into a steam bath for heating. When heating on a hot plate, the vial can be raised from the plate to vary the intensity of heating. The holder serves as an individual test tube rack, facilitating the observation of exothermic and other reactions.



VIAL HOLDER



# The Solvency of Petroleum Spirits

## Graphic Determination of Resin Solvency from Boiling Point Density and Refractive Index

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THE experimental determination of resin solvency (3) is rather time-consuming and requires the attention of a skilled operator, if precise results are to be obtained. It has been found that the resin solvency of spirits and cuts of spirits boiling in the range 300° to 400° F. can be derived with considerable accuracy from the 50 per cent boiling point, the density ( $d_{20/4}$ ), and the refractive index ( $n_{20/D}$ ). The solvency thus derived is called the graphic resin solvency (G. R. S.).

Standard resins for each general class are chosen—for example, Beckacite 1001 (Reichhold Chemical Company) for the straight phenolic and modified phenolic classes (2), and ester gum 6 (American Cyanamid Co.) for the ester gum class. A graph is then prepared relating the density and refractive index to the resin solvency for a material of 50 per cent boiling point at 333° F.

If refractivity intercept (5, 7, 8) is plotted against density for a mixture of aromatic, naphthenic, and paraffinic hydro-

carbons, it has been shown (4) that the position of a point on such a graph is definitely related to the proportion of the components in the mixture. In the case of the present work, the solvent power or resin solvency of the spirits for chosen representative resins is needed, and not the composition in terms of hydrocarbon types. By determining the resin solvency of many samples of spirits of widely differing composition, but of known properties, it was found possible to construct Figure 1 which is intended for use with commercial spirits of approximately 300° to 400° F. boiling range. The derivation is a straight-forward empirical method based on properties of samples of commercial spirits and the viscosities of resin solution prepared with these spirits. This graph carries one directly from the density and refractive index to a "normal resin solvency" scale *A* for Beckacite 1001 and *B* for ester gum 6, which equals the resin solvency, provided the A. S. T. M. 50 per cent boiling point (1) of the spirits is 333° F.

The data necessary for the practical construction of this graph are given in Table I.

Points for two petroleum spirits, 2 and 4, of approximately balanced composition, one highly paraffinic petroleum spirit, 10, and one highly naphthenic petroleum spirit, 11, are plotted on the graph. One may say that, approximately at least, increasing resin solvency for Beckacite 1001 indicates an increasing per cent of aromatics, and that decreasing resin solvency for ester gum indicates an increase in the naphthene content.

It is clear that when the 50 per cent boiling point is 333° F. and the resin solvencies for Beckacite 1001 and for ester gum 6 are specified, the physical properties and approximate composition are also specified.

If the 50 per cent point differs from 333° F., two corrections must be applied to the "normal resin solvency" to obtain the graphic resin solvency. The first is a correction for the effect of variation in boiling point on the physical properties; the second is a correction for the change of molecular weight with change in boiling point which, in a mixture of any given weight per cent or volume per cent concentration, affects the number of moles of solvent per gram of resin.

Using the data for pure compounds tabulated by Ward and Kurtz (7), it was found that the effect of boiling point on the physical property graph would be taken care of by adding a

TABLE I. DATA FOR CONSTRUCTION OF RESIN SOLVENCY GRAPHS

	Phenolic Resins (Beckacite 1001)		Ester Gum Resins (Ester Gum 6)	
	$d_{20/4}$	$n - d/2$	$d_{20/4}$	$n - d/2$
Definitive points for line of 100 resin solvency	0.8300	1.0465	0.8300	1.0503
Interval of line spacing	0.7400	1.0553	0.7400	1.0388
	10 R. S. units = 0.00132 intercept unit		10 R. S. units = 0.00132 intercept unit	

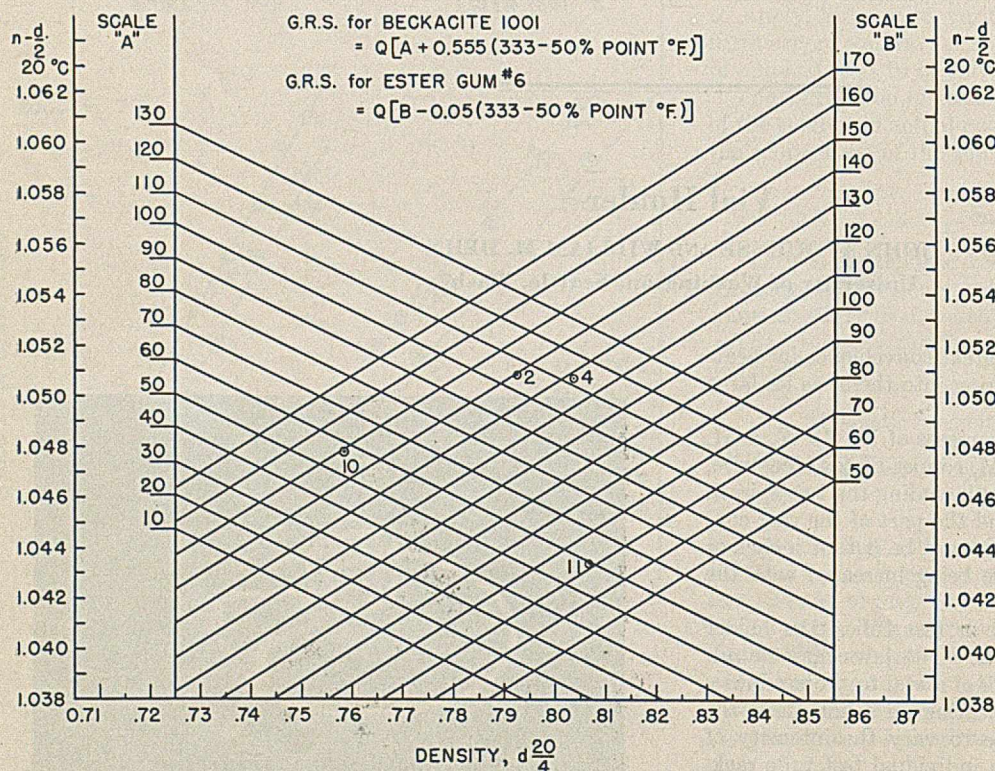


FIGURE 1. GRAPH FOR DETERMINING RESIN SOLVENCY FROM DENSITY, REFRACTIVE INDEX, AND 50 PER CENT BOILING POINT



TABLE II. Q FACTOR FOR EFFECT OF MOLECULAR WEIGHT IN CALCULATION OF GRAPHIC RESIN SOLVENCY FOR BECKACITE 1001 AND ESTER GUM 6

Boiling Point above 333° F.		Boiling Point below 333° F.	
° F.	Q	° F.	Q
333	1.00	333	1.00
334	0.99	332	1.02
335	0.97	331	1.03
340	0.90	330	1.05
345	0.83	325	1.13
350	0.77	320	1.22
355	0.71	315	1.31
360	0.65	310	1.41
365	0.60	305	1.52
370	0.55	300	1.64
375	0.50		
380	0.46		
385	0.42		
390	0.38		
395	0.34		
400	0.30		

correction, *a*, to the *A* scale of Figure 1, and subtracting a correction, *b*, from the *B* scale of Figure 1 where

$$a = 0.555 (333^\circ \text{ F.} - 50\% \text{ point } ^\circ \text{ F. at 760 mm.})$$

$$b = 0.05 (333^\circ \text{ F.} - 50\% \text{ point } ^\circ \text{ F. at 760 mm.})$$

The 50 per cent point is the volumetric 50 per cent boiling point as observed in the usual A. S. T. M. distillation (1). When determined at sea level, corrections for variation in barometric pressure may usually be neglected.

The correction for variation of molecular weight with boiling point was also worked out using three sets of data as follows: the A. S. T. M. 50 per cent boiling point, the linear relation between log kinematic viscosity and molecular concentration of solvent, and a curve relating 50 per cent boiling point to molecular weight for cuts of spirits (Figure 2). The molecular weights for the spirits curve in this graph were determined cryoscopically in benzene. For the authors' purpose the slope of the curve rather than the absolute value of the molecular weight is of importance. The agreement in regard to slope between the authors' data for cuts of spirits, and the average pure compound data, justifies extrapolating their data for spirits and cuts of spirits.

In regard to the 50 per cent boiling point, consideration was given to the system of Smith and Watson (6) which involves first calculating the volumetric average boiling point, and then correcting this value to another derived boiling point suitable for correlation with certain properties.

The volumetric average boiling points based on the 10, 30, 50, 70, and 90 per cent points for the spirits in Table II of (3) were consistently  $2^\circ \pm 1^\circ \text{ F.}$  higher than the observed A. S. T. M. 50 per cent boiling points.

The mean average boiling point of Smith and Watson, which they found to give a good correlation with molecular weight, leads to a correction of approximately  $-3^\circ \text{ F.}$  from the volumetric average boiling point. Therefore, in the case of spirit samples, the two corrections practically cancel—i. e., the observed 50 per cent point in the A. S. T. M. distillation is practically the same as the mean average boiling point. Therefore, the observed A. S. T. M. 50 per cent point was used without correction.

The authors' correction for effect of boiling point on molecular weight and consequently on viscosity of the dispersions takes the form of a multiplication factor designated as *Q*. The derivation of these *Q* factors is perhaps best illustrated by a definite example.

Consider a spirits of  $360^\circ \text{ F.}$  ( $182.2^\circ \text{ C.}$ ) 50 per cent boiling point (A. S. T. M.) which is to be referred to a standard 50 per cent boiling point of  $333^\circ \text{ F.}$  ( $167.2^\circ \text{ C.}$ ) A. S. T. M. Figure 2 shows that the molecular weights corresponding to these boiling points are 140.5 and 130, respectively. The

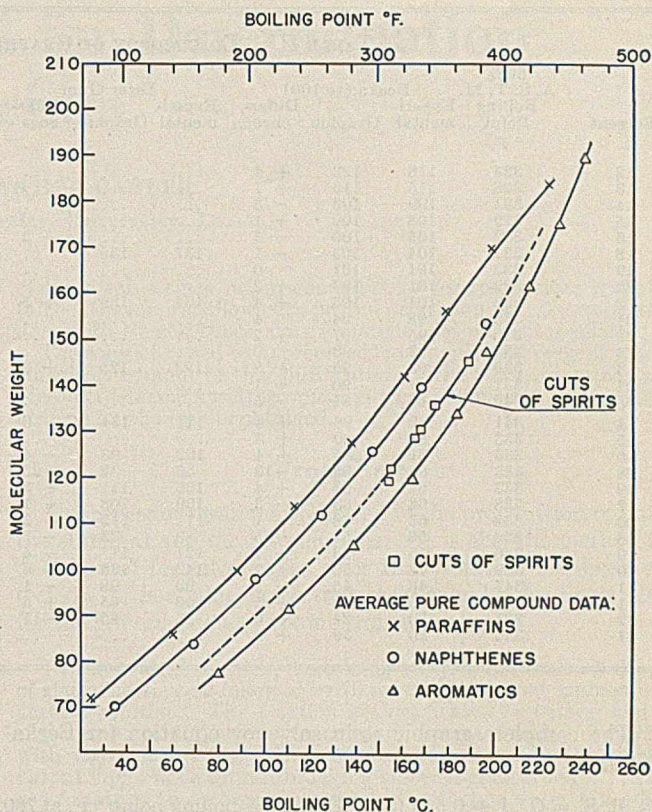


FIGURE 2. MOLECULAR WEIGHT vs. BOILING POINT

molecular concentration of solvent expressed as grams of resin divided by 100 times the gram moles of solvent is given by the following calculation:

Boiling Point of Solvent ° F.	55% Weight, Beckacite 1001	65% Weight, Ester Gum 6
333	$55 \div 100 \frac{45}{130} = 1.59$	$65 \div 100 \frac{35}{130} = 2.41$
360	$55 \div 100 \frac{45}{140.5} = 1.72$	$65 \div 100 \frac{35}{140.5} = 2.62$

The viscosities corresponding to these molar concentrations of solvent are obtained from Figure 5 (3) as follows:

Boiling Point of Solvent ° F.	55% Weight, Beckacite 1001 Centistokes	65% Weight, Ester Gum 6 Centistokes
333	325	269
360	500	422
Ratio of viscosities, Q	0.65	0.64

The viscosity of the solution made up with the high- or low-boiling solvent divided into the viscosity of the solution made up with the solvent having a 50 per cent point (A. S. T. M.) at  $333^\circ \text{ F.}$ , is the *Q* factor. As shown above, the *Q* factors calculated from the data of solutions of Beckacite 1001 and solutions of ester gum 6 check within about 1 per cent. This is so because the per cent change in grams of resin per gram mole of solvent for any given increment of viscosity is practically the same. It is not possible at present to generalize further, because there are indications that different scales of *Q* factors may be needed for resins of widely differing molecular complexity such as Pliolite.

Table II contains the *Q* factors calculated for this work. For intermediate boiling points, the factors may be obtained by interpolation.



TABLE III. COMPARISON OF GRAPHIC AND EXPERIMENTAL RESIN SOLVENCY

Solvent	50% A. S. T. M.			Beckacite 1001			Ester Gum			Solvent	50% A. S. T. M.			Beckacite 1001			Ester Gum				
	Boiling Point ° F.	Experimental	Graphic	Difference	Experimental	Graphic	Difference	Experimental	Graphic		Difference	Boiling Point ° F.	Experimental	Graphic	Difference	Experimental	Graphic	Difference			
12	324	118	122	+ 4	...	...	..														
13	323	115	116	+ 1	...	...	..														
14	331	109	106	- 3	...	...	..														
15	329	108	109	+ 1	...	...	..														
16	332	105	100	- 5	...	...	- 2														
18	331	104	103	- 1	137	135	..														
19	333	101	101	0	...	...	..														
20	332	101	103	+ 2	...	...	..														
2	333	101	105	+ 4	134	139	+ 5														
21	336	98	94	- 4	...	...	..														
22	330	95	97	+ 2	...	...	..														
23	336	93	93	0	...	...	..														
3	336	93	95	+ 2	123	125	+ 2														
24	331	91	90	- 1	...	...	..														
25	342	86	81	- 5	...	...	..														
4	341	92	96	+ 4	117	114	- 3														
5	333	87	90	+ 3	...	...	..														
6	336	81	85	+ 4	102	98	- 4														
28	333	68	55	-13	55	32	-23														
29	333	64	68	+ 4	106	111	+ 5														
7	338	66	63	- 3	109	108	- 1														
30	338	63	62	- 1	111	113	+ 2														
8	336	58	53	- 5	80	73	- 7														
9	340	55	53	- 2	121	117	- 4														
10	339	48	50	+ 2	142	136	- 6														
31	347	46	45	- 1	99	98	- 1														
11	340	45	50	+ 5	62	65	+ 3														
32	387	30	24	- 6	56	45	-11														
27	331	30	39	+ 9	...	...	..														
										21	0- 20%	306	157	166	+ 9	...	...	..			
											40- 60%	330	102	107	+ 5	...	...	..			
											80-100%	366	51	46	- 5	...	...	..			
										8	0- 20%	311	73	86	+13	...	...	..			
											40- 60%	330	56	64	+ 8	...	...	..			
											60- 80%	344	50	61	+11	...	...	..			
											80-100%	371	32	32	0	...	...	..			
										18	0- 20%	308	...	...	..	196	199	+ 3			
											20- 40%	321	...	...	..	160	157	- 3			
											40- 60%	326	...	...	..	143	147	+ 4			
											60- 80%	336	...	...	..	125	123	- 2			
											80-100%	361	...	...	..	82	78	- 4			
										8	0- 20%	306	...	...	..	117	135	+18			
											20- 40%	321	...	...	..	97	103	+ 6			
											40- 60%	331	...	...	..	85	86	+ 1			
											60- 80%	345	...	...	..	68	71	+ 3			
											80-100%	373	...	...	..	47	39	- 8			
																No. of Samples		No. of Samples			
											+ deviation					19		11			
											- deviation					14		14			
											No deviation					3		0			
											Av.						4.1		5.2		

The complete graphic resin solvency equation for Beckacite 1001 is

$$G. R. S. = Q [A + 0.555 (333^\circ F. - 50\% \text{ boiling point } ^\circ F. \text{ at } 760 \text{ mm.})]$$

For ester gum 6 it is

$$G. R. S. = Q [B - 0.05 (333^\circ F. - 50\% \text{ boiling point } ^\circ F. \text{ at } 760 \text{ mm.})]$$

In regard to the precision of data required, it is desirable that the density should be accurate within  $\pm 0.0005$  and the refractive index should be accurate within  $\pm 0.0002$ . A curve for correcting specific gravity 60/60 to d 20/4 for petroleum products has been published (7); therefore, densities of sufficient accuracy can be obtained by the careful use of large A. P. I. hydrometers and this curve. Pycnometer densities are, however, somewhat more reliable. Any modern Abbe refractometer should give refractive index measurements of sufficient accuracy.

For a more complete discussion of density and refractive index determination, one may refer to Ward, Kurtz, and Fulweiler (8).

As an example of the use of Figure 1, consider solvent 10 and the 0 to 20 per cent cut of spirit 18.

#### SOLVENT 10

50% A. S. T. M. boiling point, ° F.	= 339
Density (d 20/4)	= 0.7582
Refractive index (n 20/D)	= 1.4268
Refractivity intercept (n - d/2)	= 1.0477

The resin solvency for Beckacite 1001 is derived using the A scale of Figure 1. The A scale value corresponding to the given properties is 57. The a correction for 339° F. is  $a = 0.555 \times (333 - 339)$  or -3.3. Therefore, A corrected = 54. For 339° F. 50 per cent boiling point Q from Table II is 0.92. The graphic resin solvency =  $54 \times 0.92 = 50$ . The determined resin solvency was 48; therefore, the graphic resin solvency is in error by only +2 unit in this case.

#### 0 TO 20% CUT OF SOLVENT 18

50% A. S. T. M. boiling point, ° F.	= 308
Density (d 20/4)	= 0.7891
Refractive index (n 20/D)	= 1.4447
Refractivity intercept (n - d/2)	= 1.0502

The B scale value from Figure 1 corresponding to the above density and intercept is 138. The b correction for 308 is  $b =$

$0.05 (333 - 308) = -1.25$ . This correction must be subtracted; therefore, B corrected is 137. For 308 the Q factor (Table II) is 1.45. The graphic resin solvency =  $137 \times 1.45 = 199$ . The determined resin solvency with ester gum 6 is 196; therefore, the graphic resin solvency is in error by only +3 units.

Table III shows that in general the graphic resin solvency agrees with the experimental within  $\pm 5$  units. Since these graphs depend on the average properties of the compounds in natural spirits, they cannot be expected to apply to synthetic blends of pure compounds.

## Summary

Graphs have been developed so that the resin solvency of spirits for phenolic resins (Beckacite 1001, Reichhold Chemical Company) and ester gum resins (ester gum 6, American Cyanamid Company) can be determined from the A. S. T. M. 50 per cent boiling point, the density (d 20/4) and the refractive index (n 20/D).

Conversely, specifications of boiling point and resin solvency for ester gum 6 and Beckacite 1001, automatically specify the physical properties and approximate composition of the solvent.

These graphs give results agreeing with the experimental resin solvency within  $\pm 5$  units, which is considered satisfactory.

## Literature Cited

- (1) Am. Soc. Testing Materials, Designation D86-38.
- (2) Krumbhaar, W., "Chemistry of Synthetic Surface Coatings," p. 162, New York, Reinhold Publishing Corp., 1937.
- (3) Kurtz, S. S., Jr., Harvey, W. T., and Lipkin, M. R., *IND. ENG. CHEM., Anal. Ed.*, 11, 476 (1939).
- (4) Kurtz, S. S., Jr., and Headington, C. E., *Ibid.*, 9, 21 (1937).
- (5) Kurtz, S. S., Jr., and Ward, A. L., *J. Franklin Inst.*, 222, 563 (1936); 224, 583 (1937).
- (6) Smith, R. L., and Watson, K. M., *IND. ENG. CHEM.*, 29, 1408 (1937).
- (7) Ward, A. L., and Kurtz, S. S., Jr., *Ibid.*, *Anal. Ed.*, 10, 559 (1938).
- (8) Ward, A. L., Kurtz, S. S., Jr., and Fulweiler, W. H., "Science of Petroleum," Volume II, p. 1137, London, Oxford University Press, 1938.



# Colorimetric Method for Determination of Barium

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ALTHOUGH barium is commonly determined gravimetrically as the sulfate or chromate, the ignition of the sulfate and the careful drying of the chromate require considerable time. In the analysis of barium samples of relatively low concentration a colorimetric method should prove valuable as a time-saver. The tannic acid method recommended by Ammer and Schmitz (1) for colorimetrically determining barium is not very satisfactory, since the color obtained is transitory and lasts only from 3 to 5 minutes. Likewise, the method proposed by Friedrich and Rapoport (5), making use of sodium rhodizonate and gelatin, yields colored solutions that are not stable in the presence of light.

Solid barium chromate is sufficiently stable and uniform in composition to be used as a gravimetric method (2, 14) and when dissolved yields solutions that have been satisfactorily used as a basis for a volumetric method (13). It was therefore believed that the solution could well be used for colorimetrically estimating small amounts of barium.

The use of chromate solutions for colorimetrically determining small quantities of chromium is well known. The results are obtained rapidly and are recognized as accurate. The work of Horn (6) showed definitely that the maximum color sensitivity of chromate solutions lies between 0.004 and 0.008 *N*. Furthermore, Dehn (3) in his extensive studies on solutions of chromic acid, dichromates, and chromates states that below 0.01 per cent (calculated as  $H_2CrO_4$ ) "identical shades of yellow are obtained." Inasmuch as the more concentrated solutions are tinged with red it was decided to work with concentrations of barium that would yield chromate solutions comparable to those recommended by both Dehn and Horn.

With these considerations in mind the following work was undertaken and the results obtained were sufficiently accurate and reproducible to warrant using the method for the quantitative determination of barium.

Inasmuch as it is the authors' intention to use the method for work, in this laboratory, on relatively simple solutions, their primary aim was to determine whether or not consistently accurate results could be obtained by this method and if so, the optimum conditions. Since the method merely involves precipitating barium as the chromate, dissolving the precipitate, and using the resultant solution for colorimetric comparison, there was no reason to believe that any trouble would be encountered, inasmuch as each step had proved feasible in other procedures. The data obtained confirmed this belief.

## Apparatus

The work on the percentage absorption of the barium chromate solutions was carried out with a Lange, compensating type, photoelectric cell colorimeter. For consistent results it was found necessary to use as a light source the 6-volt bulb provided with the instrument in conjunction with two 6-volt storage batteries, connected in series and at full charge. Before taking readings the light was turned on and left burning for 30 minutes. No attempt to measure the constancy of voltage or current was made, since it is the consensus of opinion (8) that the photocell itself may be considered as a much more sensitive instrument for such measurements than an external voltmeter or ammeter. Schott's glass filters, which were also provided with the instrument, were used.

For the actual analyses a Klett colorimeter, provided with both 50- and 100-mm. cups, was used. The deeper cups proved to be

of little value since, when enough color for comparison was obtained, the more shallow cups proved deep enough. No work was done with Nessler tubes, since a matched set was not available.

The solutions used were prepared from analytical reagent grade chemicals without further purification. The traces of impurities present (detected spectroscopically) were insufficient to have any bearing on the results obtained.

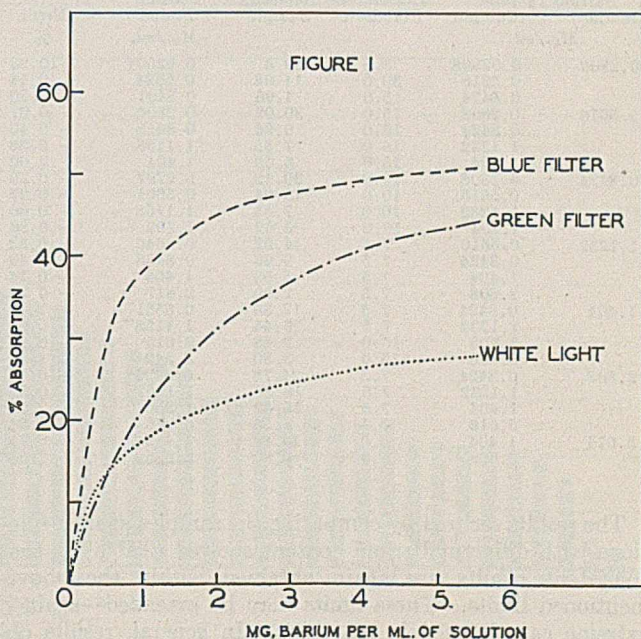
## Procedure

The procedure was that followed in the preparation of both the standard and sample solutions. It is also the method to be followed for all samples after their solution has been effected. It is analogous to that recommended by Scott (10) for the gravimetric and volumetric methods.

To the neutral solution, containing barium, are added 3 drops of glacial acetic acid followed by 10 ml. of 30 per cent ammonium acetate solution. The solution is then heated to boiling and a slight excess of 10 per cent ammonium chromate added dropwise with vigorous stirring. After 30 minutes' digestion the supernatant liquor is decanted through a sintered-glass crucible. The precipitate is then thoroughly washed with hot water (12), dissolved in 10 ml. of cold hydrochloric acid (1 to 1), and diluted to 100 ml. The resultant solution is used for colorimetric comparison.

## Data

The barium titer of the chloride solution used in the preparation of the standards and samples studied was determined gravimetrically both as the sulfate and chromate. From the absorption data obtained (Figure 1) it appears as though a blue filter should tend to greater accuracy in more dilute solutions while a green filter should increase the accuracy in the more concentrated solutions. Furthermore, the indications were that with white light the highest accuracy would be with solutions containing less than 1.5 mg. of barium per milliliter of solution. This range is slightly higher than





that indicated by Dehn and Horn. Unfortunately, no filters were available for use with the Klett, so that all the visual work had to be carried out with white light. It is intended, however, to determine the usefulness of the above-mentioned filters in conjunction with further work now being carried on.

TABLE I. DETERMINATION OF BARIUM

(Using standards containing the same amounts of barium)					
Barium Present Standard	Sample	Colorimeter Standard	Readings Sample <sup>a</sup>	Barium Found	Error
Mg./ml.				Mg./ml.	%
0.02808	0.02808	75.0	78.8 <sup>b</sup>	0.02683	-5.00
0.2808	0.2808	15.0	14.99	0.2810	+0.07
	0.2808	30.0	30.02	0.2806	-0.09
0.5616	0.5616	15.0	15.02	0.5608	-0.13
	0.5616	30.0	30.02	0.5612	-0.08
0.8424	0.8424	10.0	10.01	0.8416	-0.10
	0.8424	20.0	20.03 <sup>c</sup>	0.8412	-0.14
1.1232	1.1232	7.5	7.51	1.1217	-0.13
	1.1232	15.0	15.00	1.1232	0.00
1.404	1.404	7.5	7.50	1.404	0.00
	1.404	15.0	15.09	1.396	-0.57
2.808	2.808	7.5	7.51	2.804	-0.14
	2.808	15.0	15.06	2.797	-0.39
5.616	5.616	7.5	7.56	5.571	-0.80
	5.616	15.0	15.13	5.568	-0.85

<sup>a</sup> Average of at least two determinations, each being the average of five readings.

<sup>b</sup> Extremely difficult to match.

<sup>c</sup> Reddish tinge appears.

In Table I are shown the results obtained by comparing various solutions against standards made up simultaneously with the samples and having the same concentration of barium. The most consistent and reproducible results were obtained when solutions containing between 0.3 and 1.0 mg. of barium per milliliter were matched. The colorimeter readings were easily obtained and reproducible within this range. Although it is possible, with practice, to obtain favorable results with more concentrated solutions, measurements must be made through more shallow depths. Extreme care is necessary and the probable error in reading the instrument plays an important part in the determination. The color formed is too intense to permit ready matching at convenient heights of solution. Solutions containing less than 0.2 mg. of barium per milliliter of solution are insufficiently colored for use.

TABLE II. DETERMINATION OF BARIUM

(Using standards containing different amounts of barium)					
Barium Present Standard	Sample	Colorimeter Standard	Readings Sample	Barium Found	Error
Mg./ml.				Mg./ml.	%
0.2808	0.02808	3.5	39.3	0.02501	-10.93
	0.5616	30.0	14.98	0.5624	+0.14
	0.8424	15.0	4.96	0.8491	+0.80
0.5616	0.2808	15.0	30.02	0.2806	-0.07
	0.8424	15.0	9.96	0.8458	+0.40
	1.1232	15.0	7.55	1.1158	-0.66
	1.404	15.0	6.00	1.404	0.00
0.8424	0.2808	10.0	30.12	0.2797	-0.39
	0.5616	10.0	15.04	0.5601	-0.27
	1.1232	10.0	7.55	1.1158	-0.66
	1.404	10.0	6.02	1.399	-0.36
1.1232	0.5616	7.5	14.92	0.5646	+0.53
	0.8424	7.5	9.96	0.8458	+0.40
	1.404	7.5	5.99	1.406	+0.14
	2.808	7.5	2.99	2.817	+0.32
1.404	0.8424	7.5	12.30	0.8561	+1.62
	1.1232	7.5	9.44	1.1155	-0.69
	2.808	15.0	7.48	2.815	+0.25
2.808	5.616	15.0	3.80	5.542	-1.31
	0.8424	7.5	24.78	0.8499	+0.89
	1.1232	7.5	18.86	1.1167	-0.58
	1.404	7.5	15.42	1.366	-2.71
	5.616	7.5	3.56	5.916	+5.34
5.616	1.404	5.0	19.86	1.414	+0.71
	2.808	5.0	9.80	2.865	+2.03

The results secured by comparing the samples against solutions with different barium content showed (Table II) that consistent results are again obtained within the above-mentioned limits. These limits may be extended—again if extreme care is used in matching. In general, results ob-

tained by the use of standards similar in strength to the samples are slightly more consistent.

From these data it is evident that the colorimetric method is suitable, particularly within the concentration limits mentioned and preferably with the use of standards essentially similar in strength to the samples. Analysis of a fluorspar sample obtained from the National Bureau of Standards yielded 0.06, 0.06, and 0.09 per cent of barium oxide (average recommended by the bureau was 0.07 per cent). The fluorspar was put into solution by the recommended method (supplied on the certificate provided with the sample), the lead removed electrolytically, and the aforementioned procedure followed.

### Interfering Ions

Inasmuch as in future work one or more of the following cations may be present with the barium, it was thought advisable to investigate their effect upon the method. Barium chromate was precipitated in the presence (individually) of equivalent amounts of the chlorides of sodium, potassium, calcium, magnesium, and strontium. All but strontium had no effect upon the determination of barium. As was expected, strontium caused high results.

TABLE III. EFFECT OF STRONTIUM

(2 mg. of strontium per ml. of solution in a total volume of 100 ml. previous to precipitation)		
Barium Calcd.	Barium Found	Deviation
Mg./ml.	Mg./ml.	%
0.5578 <sup>a</sup>	0.7163	+28.42
0.5578 <sup>b</sup>	0.6140	+10.07
0.5578 <sup>c</sup>	0.5523	-0.29

<sup>a</sup> Single precipitation.

<sup>b</sup> Double precipitation with large excess of ammonium chromate.

<sup>c</sup> Double precipitation without addition of excess ammonium chromate.

The procedure recommended for the separation of barium and strontium as chromates by Skrabal and Neustadt (11) was found to yield a satisfactory separation with as high a ratio of strontium to barium in solution as 4 to 1. Their method consists in dissolving the initial impure chromate precipitate in nitric acid, neutralizing the resultant solution with ammonia water, boiling, and adding ammonium acetate drop by drop. This double precipitation without addition of further ammonium dichromate solution yielded final solutions singularly free from strontium. Although the method of Fresenius (4) is suitable in the presence of smaller amounts of strontium, it is not satisfactory when this ion is present in large excess. Precipitation as recommended by Robin (9) from a solution rich in ammonium chloride did not yield consistent results. Although the method of Kahan (7) seems suitable, no advantage over that of Skrabal and Neustadt was apparent, while the 3-hour wait she recommends seems a needless waste of time. The data summarized in Table III represent the average of at least four determinations for each method tried.

Varying the amount of acid used for effecting solution of the precipitate had no effect upon the color produced. Successive solutions were prepared containing equal amounts of barium chromate dissolved in 10 ml. of 1 to 1 nitric acid and in 10, 20, 30, and 40 ml. of 1 to 1 hydrochloric acid. No difference in color could be detected.

### Summary

Barium may be rapidly determined by precipitating as the chromate, dissolving in hydrochloric or nitric acid, and comparing the resultant solution with a colorimetric standard.

In analyzing a solid sample containing barium a sufficient weight of sample should be taken to yield a final solution (for



comparison) containing from 0.2 to 1 mg. of barium per milliliter of solution. The use of green and blue filters may extend these limits. For the lower concentrations, heights of 30 mm. in the colorimeter yield most consistent results, while for the higher concentrations heights of 15 and 20 mm. are recommended.

The presence of sodium, potassium, calcium, and magnesium ions in equivalent amounts does not affect the determination of barium.

The concentration of acid used to effect solution is not critical.

The presence of strontium ion leads to erroneously high results. Its effect may be obviated, as in the gravimetric method, by careful double precipitation.

Literature Cited

- (1) Ammer and Schmitz, *Wasser*, 8, Part II, 161 (1934).
- (2) Caron and Roquet, *Bull. soc. chim.*, 35, 1061 (1906).
- (3) Dehn, *J. Am. Chem. Soc.*, 36, 829 (1914).
- (4) Fresenius, *Z. anal. Chem.*, 29, 413 (1890).
- (5) Friedrich and Rapoport, *Mikrochemie*, 14, 41 (1933).
- (6) Horn, *Am. Chem. J.*, 35, 253 (1906).
- (7) Kahan, *Analyst*, 33, 12 (1908).
- (8) Müller, *IND. ENG. CHEM.*, Anal. Ed., 11, 1 (1939).
- (9) Robin, *Ann. chim. anal.*, 8, 445 (1903); *J. Chem. Soc.*, 86, ii, 149 (1904).
- (10) Scott, "Standard Methods of Chemical Analysis," Vol. I, 4th ed., p. 63a, New York, D. Van Nostrand Co., 1925.
- (11) Skrabal and Neustadt, *Z. anal. Chem.*, 44, 742 (1905).
- (12) Waddell, *Analyst*, 43, 287 (1918).
- (13) Waddell, *Can. Chem. J.*, 2, 136 (1918).
- (14) Waddell, *Mining Sci. Press*, 117, 495 (1918).

# Permanganate Oxidation Index as a Criterion of Coal Rank

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IN A previous paper (6) the senior author discussed the results of a study of the oxygen-absorbing properties of a series of coals ranging from the North Dakota lignites to the Pennsylvania anthracites in which the Heathcoat-Francis (3, 5) method employing a standard solution of potassium permanganate was used. It was shown that when these oxygen values, designated as permanganate numbers, were

plotted in bar graph form in descending series an excellent correlation was obtained with a series of coals arranged in a generally accepted ascending order of rank—i. e., high permanganate numbers corresponded with low-rank coal. In the words of Francis (2), "It appears to be a very promising method for determining the rank of a coal."

The present paper reports progress of this investigation

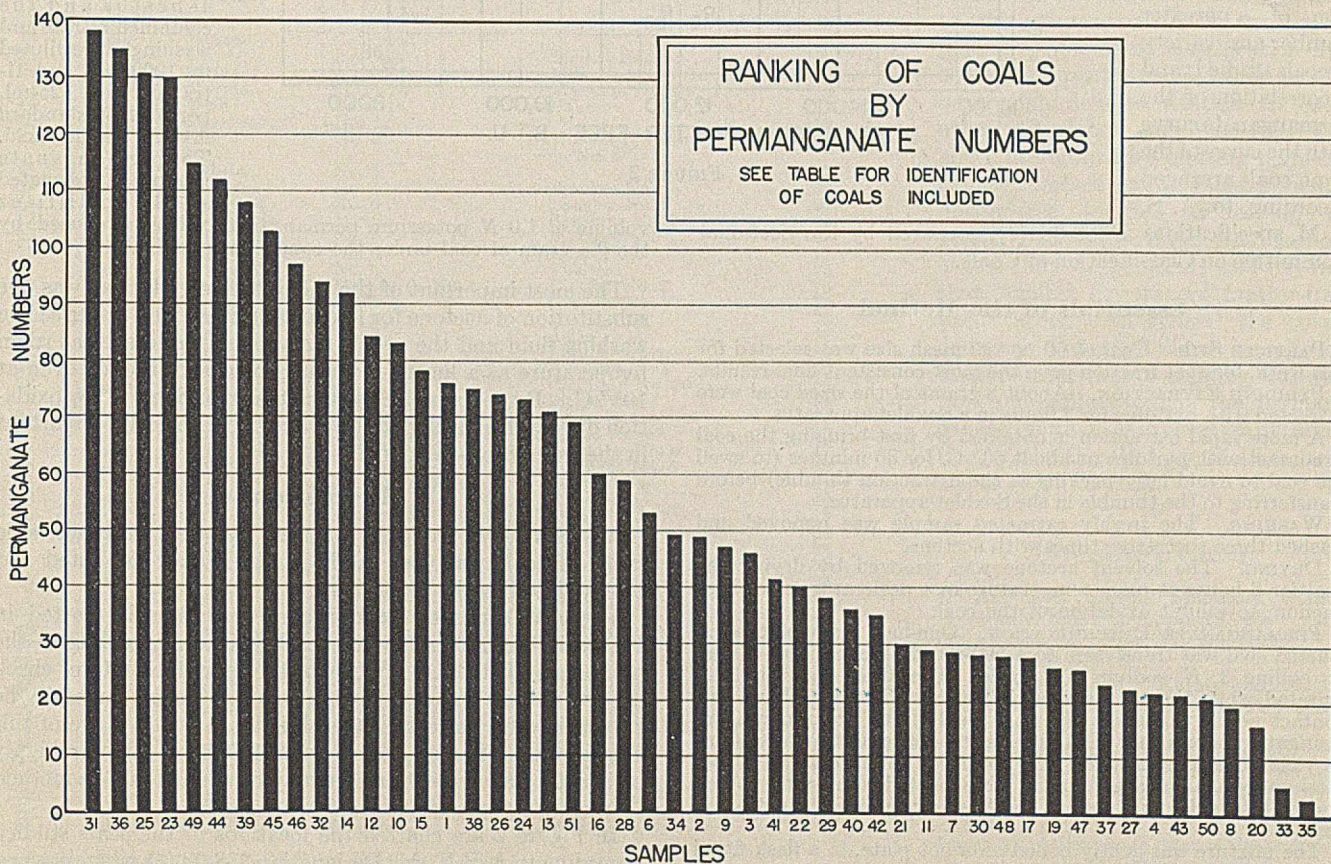


FIGURE 1



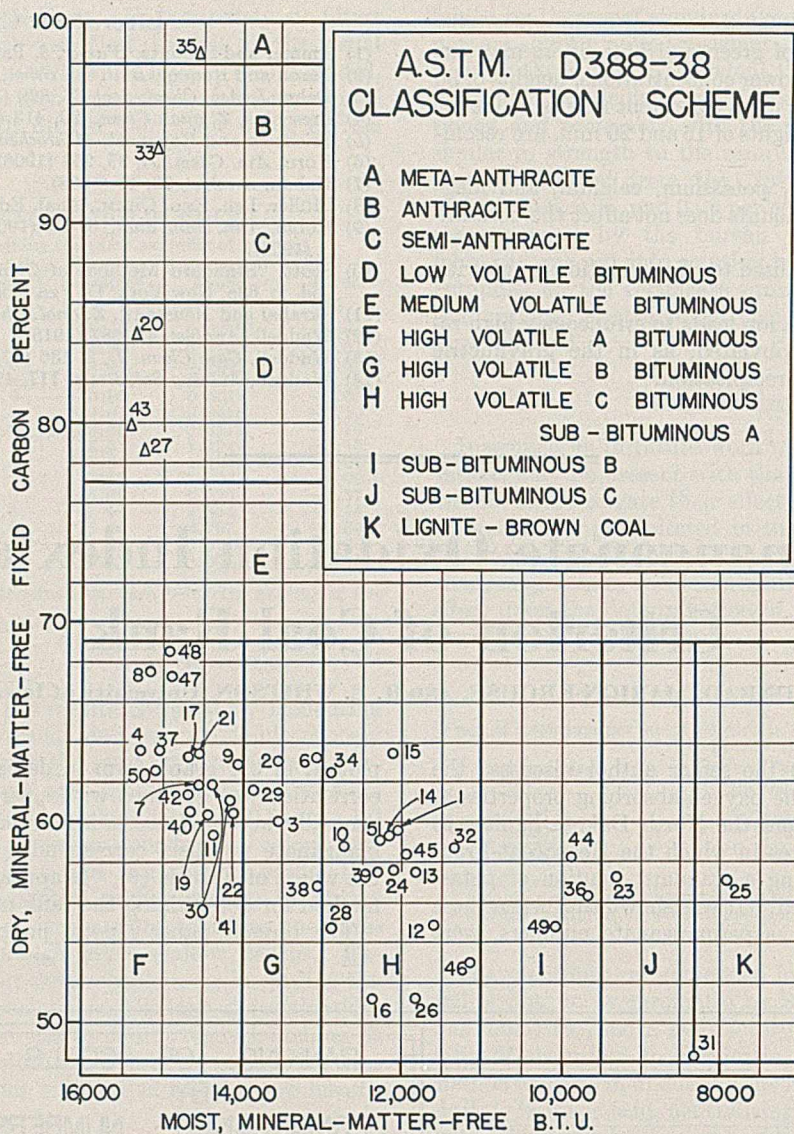


FIGURE 2

along three lines: an improvement of the method whereby greater accuracy and precision of the chemical work are obtained; the inclusion of a greater number and variety of coals studied; and a correlation of the permanganate curve with the curve of the same coals arranged according to A. S.

T. M. specifications D388-38 (1), prepared by the Sectional Committee on Classification of Coals.

### Essentials of the Method

**PARTICLE SIZE.** Coal of 60 X 100 mesh size was selected for this work, for that fraction gave the most consistent final results.

**PYRIDINE EXTRACTION.** About 8 grams of the sized coal were extracted with pyridine for 8 hours in a Soxhlet apparatus.

A more rapid extraction is obtained by first bringing the coal in contact with pyridine at about 60° C. for 30 minutes (to swell the coal to avoid later packing in the extraction thimble) before transferring to the thimble in the Soxhlet apparatus.

**WASHING.** The freshly extracted sample was removed and washed three successive times with acetone.

**DRYING.** The solvent acetone was removed by drying the coal for 6 hours at room temperature in a desiccator under high vacuum to inhibit oxidation of the coal.

**PERMANGANATE DETERMINATION.** One-half gram of the extracted coal was transferred to a 500-ml. flask containing 50 ml. of boiling 1 N sodium hydroxide. The flask was carefully agitated while the coal was being wetted. The length of this contact period influences the final results, but experimental investigation shows that 5 minutes is the optimum time necessary to yield consistent results. Two hundred milliliters of 1 N potassium permanganate solution were heated almost to boiling and transferred completely to the flask containing the extracted coal.

The mixture was gently boiled on a hot plate, in a flask fitted with a stirring device, and with a reflux condenser to prevent water loss. The reaction was permitted to proceed 1 hour from

the time of the permanganate addition.

The contents were then cooled with direct addition of about 200 grams of ice to check the reaction. The mixture was filtered through asbestos and the combined filtrate and washings were diluted to 1000 ml. and titrated into 25-ml. portions of standard 0.1 N oxalic acid. The permanganate number is calculated as the milliliter

volume of 1.0 N potassium permanganate solution reduced by the 0.5 gram of coal under the conditions specified.

The most important of the modifications adopted was the substitution of acetone for hydrochloric acid and water as the washing fluid and the use of the vacuum desiccator at room temperature as a means of drying instead of the air oven at 105° C. By so doing an appreciable error due to slow oxidation during this drying period is avoided, especially important in the case of low-rank coals.

### Discussion

A series of 49 samples covering the greatest practicable range of coals was used in the study. They are listed and briefly described in Table I.

The new series of permanganate numbers is plotted in Figure 1, the numerals under each bar corresponding to the numbers of Table I. A study of the reproducibility of check determinations showed that the mean deviation can easily be kept below 1.6 per cent. Considering the wide range of this constant in different coals—from 140 to 2—this is highly satisfactory agreement and we may conclude that the method is adequately precise.

In Figure 2 are charted the locations of the coals studied according to A. S. T. M. Designation 388-38 (1) wherein areas A, B, C, D, E, and F include those with dry, mineral-matter-



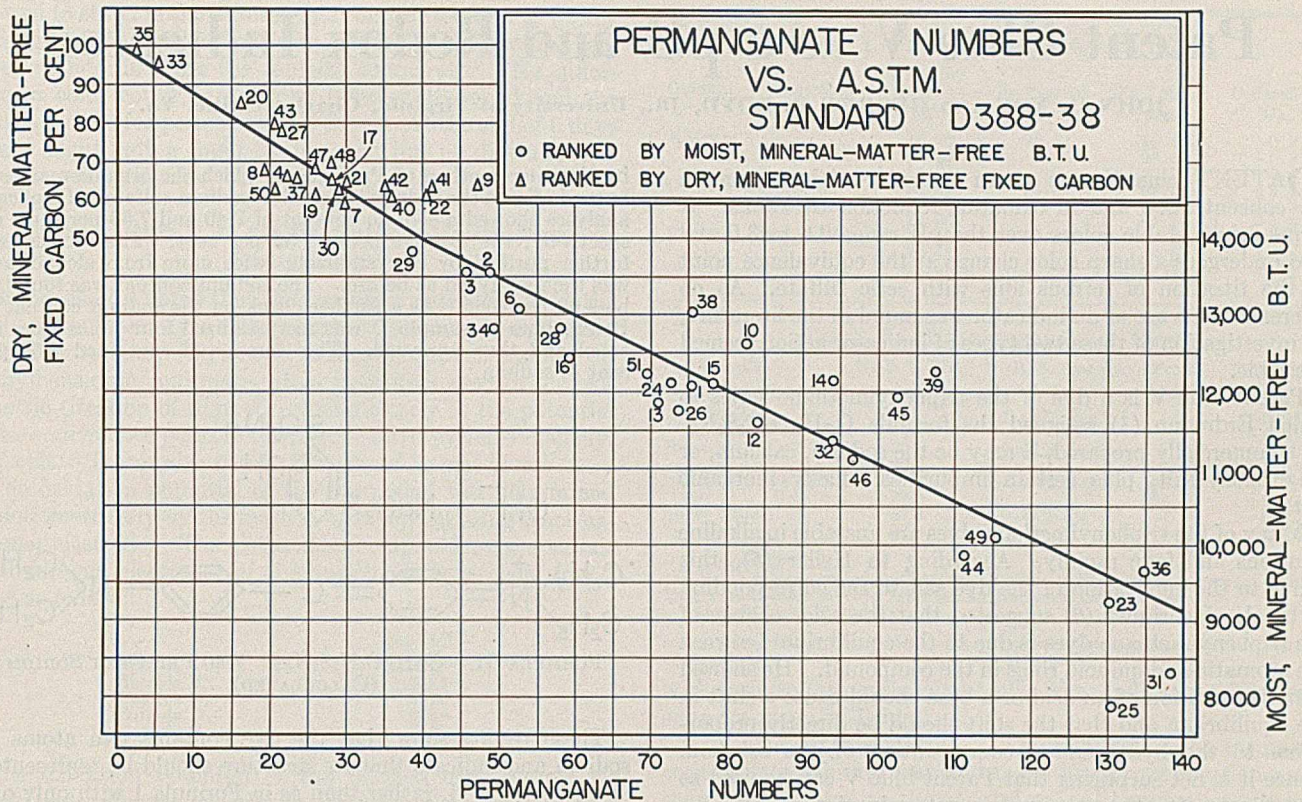


FIGURE 3

TABLE I. PERMANGANATE NUMBERS OF COALS

Sample No.	State	County	Seam <sup>a</sup>	Mine	Permanganate Number
31	Texas	Milam	Lignite	Sandow	138
36	Colo.	Jackson	Coalmont		135
25	N. D.	Divide	Noonan	Baukol-Noonan	130
23	Mont.	Blaine	Lignite	Milk River	130
49	Wyo.	Sheridan	Monarch	Monarch No. 45	115
44	Colo.	Weld	Laramie	Baum	112
39	Wyo.	Sweetwater	No. 1		108
45	Iowa	Polk	No. 3	Norwood-White No. 8	103
46	Iowa	Webster	No. 3		97
32	Iowa	Dallas	No. 3	Waukee No. 1	94
14	Ill.	Christian	No. 6	Langley No. 9	93
12	Iowa	Appanoose	Mystic	Sunshine No. 3	85
10	Ill.	Randolph	No. 6	Moffat No. 2	83
15	Ind.	Sullivan	No. 6	Friar Tuck	77
1	Ill.	Madison	No. 6	Thermal	75
38	Colo.	Gunnison	Mesaverde No. 1	Bulkley No. 2	75
26	Iowa	Monroe	No. 3	Graham No. 2	75
24	Ill.	Will	No. 2		73
13	Iowa	Mahaska	No. 3	Atlas	72
51	Ill.	Fulton	No. 6	Middle Grove	69
16	Ill.	Henry	No. 2	Atkinson	60
28	Ind.	Vigo	No. 5	Chieftain No. 20	59
6	Ill.	Franklin	No. 6	Ziegler No. 1	54
34	Ky.	Muhlenberg	Green River	Green River	49
2	Ill.	Saline	No. 5	Harco No. 47	49
9	Ky.	Perry	Hazard No. 7	Glomawr No. 5	47
3	Ky.	Hopkins	No. 6	Daylight No. 6	48
41	Va.	Lee	No. 10-Pardee	Bonny Blue	41
22	Ky.	Whitley	Jellico	Dixie Gem	40
29	Okla.	Okmulgee	Henryetta	Atlas No. 2	38
40	Va.	Lee	High Splint	Mayflower	36
42	Ky.	Harlan	Harlan	Crown	35
21	Ky.	Harlan	No. 5	Greatheart No. 31	30
11	Ky.	Union	No. 9		29
7	Ky.	Floyd	Elkhorn No. 1	Glo No. 1	29
30	Penna.	Butler	U. Kittanning		38
48	Ala.	Walker	Mary Lee	Gamma	28
17	Tenn.	Claiborne	Jellico	Eagan	28
19	Ky.	Perry	Hazard No. 4		29
47	Tenn.	Grundy	Sewanee	Palmer	26
37	Ky.	Pike	Alma		23
27	Penna.	Clearfield	L. Kittanning	Pennenee	23
4	W. Va.	Raleigh	Dorothy	Montcoal No. 1	22
43	Penna.	Tioga	Bloss	Morris Run No. 1	22
50	Ala.	Jefferson	Black Creek	Bradford	22
8	Va.	Russell	Red Ash	Candlewax	19
20	W. Va.	McDowell	Pocahontas No. 3	Upland No. 1	16
33	Penna.	Schuylkill	Skidmore	Brookside	5
35	Penna.	Schuylkill	Primrose	Mahanoy City	3

<sup>a</sup> Seam numbering follows authority of Keystone Manual (4).

free fixed carbon percentages above 69 per cent and G, H, I, J, and K those with moist mineral-matter-free thermal values less than 14,000 B. t. u. Acting on the assumption that if two independent systems of classification are both fundamentally sound they should bear some definite relation to each other, the authors combined Figures 1 and 2 in Figure 3 by plotting permanganate numbers against moist mineral-matter-free thermal values up to 14,000 B. t. u. (providing fixed carbon is less than 69 per cent) and beyond that, against dry mineral-matter-free fixed carbon. In general the curve describes a straight line; in spite of discrepancies it is a striking correlation and indicates that the permanganate number is a significant function of the chemical age of a coal and therefore of its rank.

Literature Cited

- (1) Am. Soc. Testing Materials, Standards, 1938 Suppl., pp. 157-62.
- (2) Francis, W., *Fuel*, 11, 171 (1932).
- (3) *Ibid.*, 12, 128 (1933).
- (4) Hale, S. A., ed., "Keystone Manual," New York, McGraw-Hill Publishing Co., 1938.
- (5) Heathcoat, F., *Fuel*, 12, 4 (1933).
- (6) Olin, H. L., and Waterman, W. W., *IND. ENG. CHEM.*, 28, 1024 (1936).



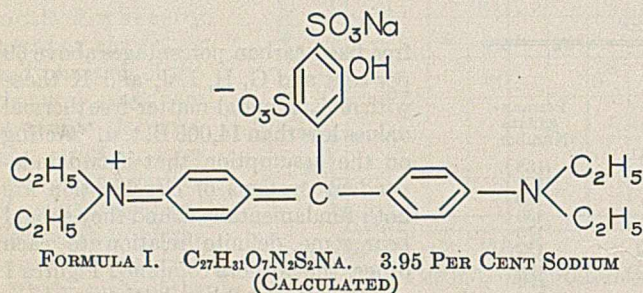
# Patent Blue V as a pH and Redox Indicator

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PATENT blue V acts as an indicator of hydrogen-ion concentration and in oxidation-reduction titrations. It forms bright stable colors over the pH range 0.8 to 3.0 and also undergoes a sharp color change at the equivalence point in the titration of ferrous ions with ceric sulfate. As no reference to its use as an indicator was found in the literature, an investigation of these two types of indicator action seemed desirable.

Patent blue V is a dye of the triphenylmethane series to which Erdmann (4) assigned the formula  $C_{27}H_{31}O_7N_2S_2Na$ . As commercially prepared, it may be the sodium, calcium, or magnesium salt, plus certain impurities, chiefly inorganic salts.

Many of the triphenylmethane dyes are unstable in alkaline solutions and fade rapidly. According to Heller (5), this is due to the enolization of the dye salt to the corresponding carbinol. Henriquez (6) suggested that the color change of the triphenylmethane dyes is due to the equilibrium between the aromatic and quinoid rings in the compound. He showed that the addition of an acid or a base should cause a shift in the equilibrium and that the shift should be directly proportional to the hydrogen-ion concentration of the solution. Hence it is not surprising that Patent blue V can be used as an indicator for the colorimetric determination of pH.



The triphenylmethane dyes have also been tested for use as indicators in oxidation-reduction reactions (1, 7). Like many of these indicators, Patent blue V changes from yellow to an orange-red color when it is oxidized with permanganate or ceric sulfate. Also like other dyes of the triphenylmethane series, Patent blue V is insensitive to dichromate and responds only to the stronger oxidizing agents.

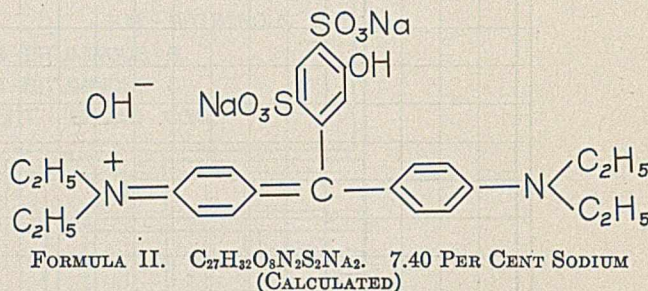
Knop (7) has investigated Patent blue A. This dye differs from Patent blue V in that it contains one  $CH_2C_6H_5$  group on each of the two nitrogen atoms in place of a  $C_2H_5$  group. Moreover, Knop's dye was the monocalcium salt. Its color transitions are similar to those of Patent blue V.

## Sources of Materials

Dyes from four different sources were used in these experiments. Sample A was obtained from E. I. du Pont de Nemours & Company, samples B and C from the General Dyestuffs Corporation, and sample D from Dr. K. Hollborn & Söhne (Leipzig). Sample E was made from sample A by extracting it with alcohol and recrystallizing twice from alcohol. Although sample A was used in the greater part of the authors' work, the others gave equally good results.

All the dye samples were tested qualitatively and no magnesium or calcium was found. However, all showed a positive test for sodium, and when sample A was analyzed quantitatively by precipitating the sodium as sodium uranyl zinc acetate, it was found to contain 14.3 per cent of sodium. Based upon Formula I,  $C_{27}H_{31}O_7N_2S_2Na$ , the compound should contain only 3.95 per cent of sodium. Sample E, the purified dye, was then analyzed

by the micromethod of Pregl (8) in which the organic matter is burned off and the sodium weighed as sodium sulfate. Duplicate analyses showed a sodium content of 7.40 and 7.63 per cent, respectively, the average being 7.52 per cent. The sample was further purified by recrystallizing twice more from alcohol and was then analyzed as before. The sodium content was found to be 7.62 per cent. As a further check on the sodium content of Patent blue V, sample D was recrystallized four times from alcohol and then analyzed. This compound contained 7.59 per cent of sodium.



These results show that the dye contains two atoms of sodium and indicate that its structure should be represented as in Formula II, rather than as in Formula I with only one atom of sodium.

Commercial Patent blue V is a dark blue or purple powder. It is highly soluble in water and alcohol, forming deep blue solutions. A 0.1 per cent aqueous solution was used in this investigation. If the volume of the solution being tested is 200 ml. or greater, a stronger solution—e. g., 0.5 per cent—of the dye may be used.

## Patent Blue V as a pH Indicator

To test the precision with which Patent blue V could be used as an indicator of pH, buffer solutions of various pH values were placed in the depressions of a spot plate and to each was added one drop of 0.1 per cent Patent blue V solution. The solutions thus formed were yellow at a pH of 0.8 and below, yellowish green to green at pH 1.2 to 2.0, took on a bluish tinge above 2.0, and finally became a pure blue at pH 3.0. The change in color is pronounced and the pH of a solution within the range of pH 0.8 to 3.0 can be determined to 0.1 pH unit by comparison with standards made up at intervals of 0.2 pH. The same dye sample must be used for both standards and unknowns, because solutions of the dye from different sources often exhibit slightly different colors at a given pH.

Buffer solutions of hydrochloric acid and sodium acetate were made from pH 0.75 through pH 3.2 according to the method of Britton (3). Check determinations were easily made upon these solutions throughout the range of pH 0.8 to 3.0. Buffers of these values were also obtained from the LaMotte Chemical Products Company and their pH values checked against the hydrochloric acid-sodium acetate solutions using Patent blue V. Color matching was made both by the spot plate method and with a roulette comparator (11) which required the use of 100 ml. of solution (in tubes 160 mm. to the mark). Check results were obtained by the two methods.

The colors formed by the indicator at the various pH values are very stable. Solutions throughout the effective range (pH 0.8 to 3.0) of the indicator were made up, using both the commercial product and the purified compound, and



allowed to stand in the diffused light of the laboratory. They were then compared at one-day intervals with freshly prepared standards using the roulette comparator. No difference in color could be detected between the aged and the fresh solutions for periods up to 5 days. At the end of 6 days a very slight fading could be detected, but no difficulty was encountered in making the match.

**Patent Blue V as an Oxidation-Reduction Indicator**

Brennecke (2) noted that the transition potentials of all the triphenylmethane dyes tested for use as oxidation-reduction indicators by Knop (7), as well as those of diphenylamine, diphenylbenzidine, and many other indicators used in the oxidimetric titration of iron, correspond closely to the potential at the equivalence point in the ferrous-ferric system—namely, 0.77 volt. This is also true in the case of Patent blue V.

The oxidation potential of the compound was determined potentiometrically by the method of Knop (7) using a normal calomel electrode. The potentials (compared to the standard hydrogen electrode) of the various samples were found to be as follows:

Sample	E <sub>0</sub> , Volt
Sample A	+0.75
Sample B	0.72
Sample C	0.72
Sample D	0.68
Sample E	0.78

The oxidation potential of the purified dye, sample E, corresponds almost exactly to that of the ferrous-ferric system.

Patent blue V cannot be used as a redox indicator in the titration of iron in solutions containing hydrochloric acid, on account of the dark brownish yellow color of the solution which obscures the orange color of the indicator. The yellow color is said to be due to the presence of complex anions such as FeCl<sub>4</sub><sup>-</sup>. In the Zimmermann-Reinhardt method, the yellow color is removed by the addition of phosphoric acid which forms slightly ionized, colorless ferriphosphate anions. In titrations with ceric sulfate, however, a phosphate "preventive solution" cannot be used because ceric phosphate is insoluble and precipitates out of the solution before the oxidant reacts with the ferrous ion.

Szebélledy (9) showed that ammonium fluoride can be used in place of phosphoric acid to bind the ferric ions into complexes and thus remove them from solution. But ceric fluoride is insoluble and precipitates out immediately when ceric sulfate is added to a solution containing ferrous ions and fluoride ions.

Certain organic acids with which the ferric ion forms complexes were investigated in the hope of finding a solution which would reduce the concentration of the ferric ion sufficiently to allow the use of Patent blue V in titrations with ceric sulfate in the presence of hydrochloric acid. Tartaric, citric, and succinic acids were tried, but in no case was a satisfactory "preventive solution" found.

If it is necessary to reduce the iron before titration, a reduction method not requiring hydrochloric acid must be used. The Jones zinc reductor and the Walden silver reductor (10) were used in the analyses reported in Table II.

The solutions titrated should be about 1 N with respect to sulfuric acid and enough indicator added to impart a distinct color to the solution. Usually from 3 to 5 drops of a 0.1 per cent solution are sufficient.

As a preliminary examination of the utility of Patent blue V as an indicator in oxidation-reduction titrations, aliquot samples of a standard ferrous ammonium sulfate solution were titrated with potassium permanganate; with ceric sulfate, using *o*-phenanthroline ferrous complex as indicator; and

TABLE I. TITRATION OF FERROUS IRON

Oxidant	Indicator	Oxidizing Solution Ml.	Fe Present Mg.	Fe Found Mg.	Difference Mg.
KMnO <sub>4</sub>	....	14.50	96.8	96.5	-0.3
		14.50		96.5	-0.3
		14.51		96.6	-0.2
Ce(SO <sub>4</sub> ) <sub>2</sub>	<i>o</i> -Phenanthroline	15.52	96.8	97.2	+0.4
		15.50		97.1	+0.3
		15.50		97.1	+0.3
Ce(SO <sub>4</sub> ) <sub>2</sub>	Patent blue V	15.49	96.8	97.0	+0.2
		15.48		96.9	+0.1
		15.48		96.9	+0.1

TABLE II. DETERMINATION OF IRON

Sample	N. B. S. No.	N. B. S. Average	Found	Difference
			%	%
Argillaceous limestone	1	1.63% Fe <sub>2</sub> O <sub>3</sub>	1.58	-0.05
Bauxite	1		1.62	-0.01
Sibley iron ore	39	5.66% Fe <sub>2</sub> O <sub>3</sub>	5.69 <sup>a</sup>	+0.03
	39		5.70 <sup>a</sup>	+0.04
Sheet brass	27B	68.23% Fe <sup>b</sup>	68.33 <sup>c</sup>	+0.10
	27B		68.30 <sup>c</sup>	+0.07
Sheet brass	37B	0.21% Fe	0.18	-0.03
	37B		0.19	-0.02

<sup>a</sup> Corrected for V.  
<sup>b</sup> Value recommended by National Bureau of Standards. Average value for permanganate method reported by Bureau is 68.34% Fe.  
<sup>c</sup> Corrected for V and Ti.

with ceric sulfate with Patent blue V as indicator. The results are given in Table I.

The indicator is reversible. In many titrations an excess of ceric sulfate solution was added to the ferrous solution and then back-titrated to the end point. Although the color of the oxidized form fades if allowed to stand for a short time, no error is introduced if the back-titration is made within 1 or 2 minutes after the excess oxidizing agent has been added.

Several standard samples from the National Bureau of Standards were analyzed for iron, using ceric sulfate with Patent blue V as indicator. Standard methods of analysis were used for each sample. The results are recorded in Table II.

**Summary**

An aqueous solution of Patent blue V may be used as an indicator for the colorimetric determination of pH over the interval 0.8 to 3.0. The colors range from yellow through green to blue and are stable for periods up to 5 days, after which a very slight fading may be detected.

Patent blue V can also be used as an oxidation-reduction indicator in certain volumetric methods. Although it cannot be used with dichromate or in the presence of hydrochloric acid, it can be used with permanganate or ceric sulfate if all hydrochloric acid is removed.

The oxidation-reduction potential of the indicator has been measured.

**Literature Cited**

- (1) Böttger, R. E., "Newer Methods of Volumetric Analysis," tr. by Oesper, R. E., p. 181, New York, D. Van Nostrand Co., 1938.
- (2) Brennecke, E., *Ibid.*, p. 182.
- (3) Britton, H. T. S., "Hydrogen Ions," p. 217, New York, D. Van Nostrand Co., 1932.
- (4) Erdmann, E., and Erdmann, H., *Liebigs Ann. Chem.*, 294, 376 (1897).
- (5) Heller, G., *Chem.-Ztg.*, 56, 902 (1932).
- (6) Henriquez, P. C., *Rec. trav. chim.*, 52, 991 (1933).
- (7) Knop, J., *Z. anal. Chem.*, 85, 253 (1931).
- (8) Roth, H., and Daw, E. B., "Quantitative Organic Microanalysis of Pregl," 3rd ed., p. 138, Philadelphia, P. Blakiston's Son & Co., 1937.
- (9) Szebélledy, L., *Z. anal. Chem.*, 81, 97 (1930).
- (10) Walden, G. H., Hammett, L. P., and Edmunds, S. M., *J. Am. Chem. Soc.*, 56, 350 (1934).
- (11) Yoe, J. H., and Crumpler, T. B., *IND. ENG. CHEM., Anal. Ed.*, 7, 281 (1935).



# Determination of Small Amounts of Copper in Spray Residues

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**D**URING the past few years it has been necessary for the author to make a large number of copper determinations on various surfaces sprayed with copper fungicides. The surfaces upon which the copper was deposited included the leaves and fruits of apples, cherries, and tomatoes, and certain synthetic surfaces, particularly Pyralin, which is at present being used in this laboratory for most of the studies on the deposition and retention of sprays.

A number of methods have been investigated, and two have been selected as the most satisfactory under the present conditions. Since an increasing number of workers in the fields of insecticides and fungicides are turning their attention to the copper compounds, and since few rapid methods for the determination of the small amounts of copper present upon plant surfaces have been described in the literature, the following two methods are presented briefly. These are modifications of well-known analytical procedures and have been used with complete success in this laboratory for some time.

## Method A

When copper is present in the sample in amounts greater than 2 mg., the most accurate and convenient method of determination is by direct weighing after electrodeposition on platinum electrodes. The determination of small quantities (under 50 mg.) is considerably more difficult, however, than the ordinary electrodeposition as followed in the case of copper ores or alloys. The procedure found satisfactory for leaf samples which have received one or more applications of copper sprays is as follows:

A sample of from 2 to 20 grams of the dried material is ashed at a temperature not exceeding 450° C. The ash is dissolved in nitric acid (1 to 1) and transferred to a 150-ml. beaker. To this solution are added 10 ml. of a saturated solution of ammonium nitrate and 1 gram of urea, and the volume is made up to about 100 ml. The electrolysis is then carried out in the usual manner, using a platinum gauze cathode and a rotating platinum loop anode. The current between the electrodes must be much lower than is usually recommended in the methods for the electrolytic deposition of copper described in the literature, and should not exceed 0.15 ampere. Currents in excess of this amount will cause the deposition of copper oxide. The time required for complete deposition is a function of the quantity present, but for the amounts normally present on leaf samples 15 minutes is usually sufficient.

Typical results on different types of leaf material are shown in Table I.

## Method B

When the total quantity of copper in the sample is less than 2 mg., it is usually not possible to weigh the metal directly with sufficient accuracy. Samples of fruits and small areas of synthetic surfaces sprayed in the laboratory usually bear less than 1 mg., and hence require a method of analysis sensitive to smaller amounts.

After thorough trials of several methods, including the chromotropic reagent method of Ansbacher, Remington, and Culp (1), the xanthate method (7), and the thiocyanate method of Elvehjem and Lindow (4), the method of Callan and Henderson (2) as modified by Cockburn and Herd (3) was selected as most adaptable to the present use.

The method as finally adopted in this laboratory is as follows:

The solution containing the copper is freed from organic matter, if the latter is present, by digestion with sulfuric and nitric acids. For routine analysis of fruits, it has been customary to wash the surfaces thoroughly in hot 10 per cent nitric acid solution, making the washings to volume and digesting an aliquot portion. The laboratory sprayed plates are washed in 50 per cent nitric acid and the wash solution is concentrated, made to volume, and used without digestion.

The solution, free from organic matter, is neutralized with concentrated ammonium hydroxide, and about 10 ml. are added in excess. This mixture is then boiled for a few minutes, allowed to stand for 30 minutes, filtered through a fast filter paper, and washed. The entire filtrate, or an aliquot of it, is transferred to a Nessler tube, 25 ml. of concentrated ammonium hydroxide are added, and it is made to a volume of 100 ml. The tube is then placed in a photoelectric colorimeter of the type described by Frear and Haley (5) or Samuel and Shockey (6), the light intensity is adjusted to the maximum, 1 ml. of a 1 per cent solution of sodium diethyl dithiocarbamate is added, the solution is stirred, and a second reading is taken. By calibrating the instrument with known amounts of copper, the reading in microamperes may be converted directly into milligrams of copper. A typical calibration curve is shown in Figure 1.

## Accuracy of Method B

For the greatest accuracy, a sample should be selected which contains between 0.05 and 0.15 mg. of copper. Numerous recovery tests have been run with apple wash solutions containing no copper, to which have been added known amounts of copper as copper sulfate. A typical set of re-

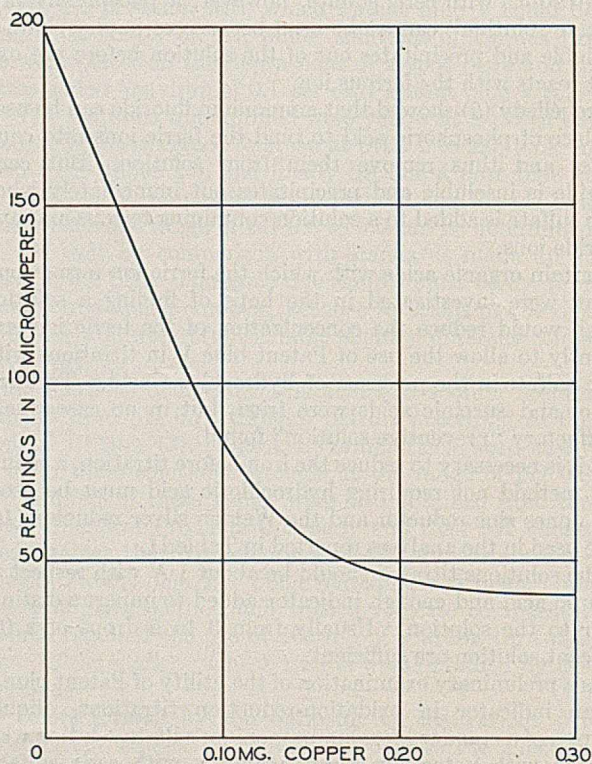


FIGURE 1. TYPICAL CALIBRATION CURVE



TABLE I. COPPER PRESENT IN APPLE AND CHERRY LEAVES AS DETERMINED BY ELECTROLYTIC METHOD

Type of Leaf	Treatment	Copper Present	
		A	B
		Mg./sq. m.	
Apple	1 application of $\text{Cu}_3(\text{PO}_4)_2$	27.92	27.57
	1 application of Cupro-K	23.08	23.43
	2 applications of copper arsenate	65.31	64.48
Cherry	1 application of $\text{Cu}_3(\text{PO}_4)_2$	101.55	99.94
	2 applications of basic copper sulfate	26.82	25.21

TABLE II. RECOVERY OF ADDED COPPER SULFATE TO APPLE WASH SOLUTIONS

Copper Added	Copper Recovered	
	Mg.	%
0.050	0.050	100
0.075	0.076	101
0.100	0.098	98
0.150	0.142	95

sults is shown in Table II. Each figure is the average of duplicate determinations. Replicate determinations usually agree within 2 microamperes (about 0.003 mg.).

If a photoelectric colorimeter is not available, the unknown solutions may be compared with standards in a colorimeter. In this case the color should be developed in both standards and unknowns at the same time, since the ability of the colored solution to transmit light decreases slightly on standing.

When using solutions in which no organic matter is present, such as the washings from the plates sprayed in the laboratory, the procedure may be simplified for the sake of rapidity by the elimination of the filtration, if the standardization is carried out under the same conditions.

### Summary

Two methods are presented for the rapid determination of copper on surfaces sprayed with insecticide or fungicide mixtures containing this element. The first method, for quantities greater than 2 mg., is a modification of the usual procedure of weighing the metal directly after electrodeposition. The second method, for smaller quantities of copper, is based on the photoelectric measurement of the color produced by sodium diethyl dithiocarbamate.

### Literature Cited

- (1) Ansbacher, Remington, and Culp, *IND. ENG. CHEM., Anal. Ed.*, 3, 314 (1931).
- (2) Callan and Henderson, *Analyst*, 54, 650 (1929).
- (3) Cockburn and Herd, *Ibid.*, 63, 482 (1938).
- (4) Elvehjem and Lindow, *J. Biol. Chem.*, 81, 435 (1939).
- (5) Frear and Haley, *Penna. Agr. Expt. Sta., Bull.* 304 (1934).
- (6) Samuel and Shockey, *J. Assoc. Official Agr. Chem.*, 17, 141 (1934).
- (7) Scott, "Standard Methods of Chemical Analysis," Vol. 1, p. 197, New York, D. Van Nostrand Co., 1922.

AUTHORIZED for publication as paper No. 899 in the journal series of the Pennsylvania Agricultural Experiment Station.

## Determining Riboflavin A Fluorometric and Biological Method

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THE establishment of riboflavin as a dietary essential has been the incentive for numerous investigations involving its biological and physico-chemical properties. Its fluorescence in ultraviolet light has suggested the possibility of utilizing this characteristic as a basis for its quantitative determination; under proper conditions as little as one part in 100,000,000 may be detected by this means. A preliminary outline of a quantitative method applicable to solutions of lactoflavin (riboflavin derived from milk) was published in 1936 (3). Since that time the method has been further perfected and applied to various materials, and also used to determine quantitatively small amounts of riboflavin required for certain precision studies involving the water-soluble vitamins (1, 4).

In order that the usefulness of any physical or chemical method for determining known vitamin entities may be fully appraised, it is necessary to correlate the results obtained with the biological response from experimental animals. The results from the fluorometric method presented in this paper have been correlated with a biological method based upon the principles of simplification and standardization previously proposed (1, 4).

Application of the fluorometric principle for the quantitative determination of riboflavin must be predicated upon the examination of appropriate solutions in which extraneous matter does not significantly interfere with the degree of

fluorescence or its observation. Potentially, each riboflavin bearing material presents a different problem in respect to the treatments required to extract the active material, and to obtain a solution suitable for examination. Obviously solutions of pure material present no such problems; likewise, many impure riboflavin concentrates, especially those obtained from whey or whey derivatives following a preliminary adsorption, frequently require no preliminary treatment other than proper dilution. Adsorbates and miscellaneous products require complete elution or extraction if reliable quantitative results are to be referred to the original carrier. The general procedure followed in the present study involves the use of an 80 per cent acetone-water mixture. Lactoflavin or natural riboflavin as derived from milk was used for the development and study of the methods hereinafter presented.

### Extraction and Preparation of Riboflavin Solutions for Fluorometric Examination

PURE OR COMPARATIVELY PURE SOLUTIONS OF RIBOFLAVIN. Such solutions of unknown concentration are diluted to match the fluorescent color of standard riboflavin solutions of known concentration.

ELUTION OF RIBOFLAVIN FROM CLAY ADSORBATES AND SIMILAR RESIDUES. A 2-gram sample is shaken with 400 ml. of an 80 per cent acetone-water (by volume) mixture in the dark at room temperature for 30 to 45 minutes, the eluate is filtered off, and the residue is washed with 10 to 15 ml. of the acetone mixture.



TABLE I. GROWTH RATE OF WHITE RATS

[From varying amounts of lactoflavin (natural riboflavin) predetermined by fluorometric method]

Period Weeks	Negative Controls (No Riboflavin)		2 $\gamma$ per Day		5 $\gamma$ per Day		10 $\gamma$ per Day		15 $\gamma$ per Day	
	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams
1	2.53 $\pm$ 0.26	2.53	2.66 $\pm$ 0.37	2.66	8.20 $\pm$ 0.71	8.20	11.97 $\pm$ 0.62	11.97	14.98 $\pm$ 0.31	14.98
2	4.60 $\pm$ 0.69	2.30	4.72 $\pm$ 0.98	2.36	15.00 $\pm$ 0.95	7.50	21.90 $\pm$ 0.94	10.95	27.42 $\pm$ 0.55	13.71
3	7.61 $\pm$ 0.87	2.54	6.96 $\pm$ 1.22	2.32	20.55 $\pm$ 1.63	6.85	31.26 $\pm$ 1.64	10.42	37.69 $\pm$ 0.65	12.56
4	8.92 $\pm$ 0.89	2.23	7.84 $\pm$ 1.60	1.96	26.80 $\pm$ 2.27	6.70	39.59 $\pm$ 1.86	9.89	48.54 $\pm$ 0.95	12.13
5	10.09 $\pm$ 0.90	2.02	9.20 $\pm$ 2.00	1.84	31.75 $\pm$ 2.21	6.35	48.66 $\pm$ 2.26	9.73	59.95 $\pm$ 1.40	11.99
6	10.62 $\pm$ 0.91	1.77	10.92 $\pm$ 2.20	1.82	36.60 $\pm$ 2.41	6.10	55.88 $\pm$ 2.22	9.31	73.19 $\pm$ 1.80	12.19
7	11.22 $\pm$ 1.13	1.60	12.74 $\pm$ 2.67	1.82	39.20 $\pm$ 2.09	5.60	63.78 $\pm$ 2.32	9.11	.....	.....
8	12.50 $\pm$ 1.19	1.56	13.76 $\pm$ 2.83	1.72	43.20 $\pm$ 2.14	5.40	71.00 $\pm$ 2.35	8.82	.....	.....

A repetition of such elutions and washings is carried out until the final eluate shows no or at least only a slight yellow fluorescence when examined in "black light" as hereinafter described.

Following the last acetone treatment, the residue is transferred to a beaker, 25 to 30 ml. of water are added, and the suspension is boiled for 3 to 5 minutes; the suspension is then cooled and 112 ml. of pure acetone are added. This mixture is then transferred to the original elution flask, agitated for 15 to 20 minutes, and filtered, and the residue is washed with 80 per cent acetone. All eluates and washings are combined and made up to a convenient volume for preparing a series of graduated dilutions.

**PREPARATION OF SOLUTIONS FROM FLUID OR SEMIFLUID LACTOFLAVIN CONCENTRATES.** Riboflavin concentrates in fluid, semifluid, or paste form should be thoroughly mixed to assure a uniform sample. A 2-ml. or 2-gram sample is diluted 1 to 1000 with warm water or a 50 to 80 per cent acetone-water mixture. If no appreciable sediment or suspended matter is apparent, further dilutions may be made for final examination. If, however, the initial dilution shows any significant amount of sediment, flocculated, or suspended material, the original sample should be subjected to the 80 per cent acetone treatment as applied to the adsorbates.

**EXTRACTION OF LACTOFLAVIN FROM DRY WHEY AND SIMILAR WHEY PRODUCTS OR DERIVATIVES.** A 10-gram sample is eluted with 80 to 85-ml. quantities of 80 per cent acetone acidified to 0.25 *N* with sulfuric acid. This mixture is refluxed for 20 to 30 minutes, the extract is decanted or filtered, and the residue is subjected to a second or third similar treatment. Following the final extraction and filtration, the residue is washed with neutral 80 per cent acetone. The filtrates and washings are combined and made neutral to litmus with sodium hydroxide, and an aliquot sample is further diluted for final examination.

**EXTRACTION OF RIBOFLAVIN FROM MISCELLANEOUS PRODUCTS.** Various products have been subjected to the 80 per cent acetone extraction as applied to dry whey, but in all instances the refluxing periods were extended to 2 to 4 hours.

Dry yeast is heated in a drying oven at 100° C. for 5 days; the acetone in the combined extracts and washings is evaporated, and the remaining aqueous solution is neutralized and filtered prior to dilution for final examination.

Alfalfa meal, wheat bran, liver meal, and ground raw peanuts are dried to constant weight at 100° C.; neutral 80 per cent acetone is employed. The acetone from the combined extracts is evaporated and the remaining aqueous solution is washed from 3 to 10 times with petroleum ether for the removal of interfering fluorescent material, prior to diluting for final examination.

Corn meal and soybean meal are extracted in the same way as dry yeast, with the exception that the final dilutions of the soybean meal extract are made with neutral 80 per cent acetone instead of water.

### Fluorometric Examination of Riboflavin Solutions in Black Light

**PREPARATION OF STANDARD RIBOFLAVIN SOLUTIONS.** Standard solutions of riboflavin are prepared from pure crystalline material by dissolving approximately 10-mg. quantities, weighed on microbalances to within  $\pm$ 20 micrograms, in 20 per cent alcohol. Such a stock solution containing 100 micrograms per ml. is used for preparing substandards with concentrations varying from 0.5 to 0.01 microgram per ml. The following concentrations are included in the series: 0.5, 0.3, 0.25, 0.2, 0.18, 0.16, 0.14, 0.12, 0.10, and thence to 0.01 microgram per ml. by 0.01-microgram intervals. The series of substandards is maintained in appropriate nonfluorescing vials of 8- to 10-ml. capacity, closed with rubber stoppers carefully cleaned by boiling 3 times with 95 per cent alcohol and finally rinsed with distilled water. If desired,

the solutions may be made up with distilled water containing 5 ml. of 40 per cent formalin per liter in lieu of 20 per cent alcohol.

**EXAMINATION IN "BLACK LIGHT."** A graduated series of dilutions of the unknown solution neutral to litmus is matched for intensity of the fluorescent color against the standard tubes of known riboflavin content. A Fluoray lamp is used as the source of "black light" (3). The observations are made in a totally darkened room or compartment against a nonreflecting and nonfluorescing black background.

The beam of ultraviolet radiation is projected directly on the tubes without intervening screen other than the standard heat-resisting red-purple filter No. 587 (manufactured by the Corning Glass Works, Corning, N. Y.), provided with the lamp and an integral part thereof. In examining certain riboflavin-bearing solutions, observations of the fluorescence may be made through filter screen No. 351 (Corning Glass Works) to eliminate the interference of blue fluorescing substances. This screen removes the blue-green radiations down to 4920 Å. It is not necessary to use this screen when examining pure riboflavin solutions or dilute solutions of riboflavin concentrates obtained as the eluate from many riboflavin adsorbates, particularly those derived from whey concentrates; likewise, its use is not recommended when suspended or colloidal material produces a gray or opalescent color in the ultraviolet rays.

At least three dilutions of the unknown sample should be made to match the intensity of the yellow fluorescence of the standard solution tubes within the range of 0.02 to 0.1 microgram per ml. (The readings at the three concentrations should check in accordance with the known dilution of the unknown. For example, if dilution *A* of the unknown matches the intensity of the fluorescent color of the standard tube containing 0.08 microgram per ml., dilution *B* of the unknown prepared by diluting *A* with an equal volume of distilled water should check the standard tube containing 0.04 microgram per ml., etc.) For greater precision a fourth dilution of the unknown may be made, using the three concentrations within the range mentioned and the fourth concentration to match one of the standard dilutions within the 0.1- to 0.2-microgram range. The average calculated riboflavin content as determined by the multiple readings is the reportable value.

**PRECAUTIONS.** All standard solutions should be stored in total darkness and all unnecessary exposure to the ultraviolet radiation avoided. At least one reserve set of standard solution tubes should always be kept shielded from all light. At frequent intervals the standard dilutions in current use should be compared with the reserve set. If there is distinguishable fading of the fluorescent color, particularly at the lower concentrations, or if there is a bluish haze in the standards employed for assay purposes, such manifestations are evidence of gradual destruction of the riboflavin. The tubes should be immediately replaced by new standards in which no such deterioration has taken place.

### Biological Method for Determining Riboflavin

The biological method for determining riboflavin, as used for determining the correlation of the animal response with the riboflavin content of various materials as determined by the fluorometric method, follows.

White rats 22 to 25 days old weighing 40 to 50 grams are placed in individual metal cages with screened bottoms and supplied a basal ration of the following composition: min-free casein (Labco, distributed by the Borden Co., Life Products Department, 350 Madison Ave., New York, N. Y.), 20 parts; sucrose, 69 parts; hydrogenated vegetable oil (Crisco), 3 parts; salt mixture No. 40 (2), 4 parts; powdered agar-agar, 2 parts;



TABLE II. GROWTH RATE OF WHITE RATS

[From varying amounts of lactoflavin (natural riboflavin) predetermined by fluorometric method and carried by fuller's earth adsorbates]

Period Weeks	Sample B1454, 19.7 Mg. = 5 $\gamma$ per Day		Sample B1454, 59 Mg. = 15 $\gamma$ per Day		Sample B1458, 51.5 Mg. = 15 $\gamma$ per Day		Sample B1459, 16.6 Mg. = 5 $\gamma$ per Day	
	Cu-mula-tive Grams	Weekly av. Grams	Cu-mula-tive Grams	Weekly av. Grams	Cu-mula-tive Grams	Weekly av. Grams	Cu-mula-tive Grams	Weekly av. Grams
1	6.97	6.97	12.97	12.97	14.47	14.47	7.97	7.97
2	13.46	6.73	28.46	14.23	24.96	12.48	15.71	7.85
3	17.14	7.05	33.39	11.13	34.39	11.46	22.14	7.38
4	24.58	6.14	44.58	11.14	43.58	10.89	26.83	6.71
5	27.66	5.53	52.16	10.44	57.66	11.53	32.16	6.44
6	32.66	5.44	65.13	10.86	70.63	11.77	35.63	5.94

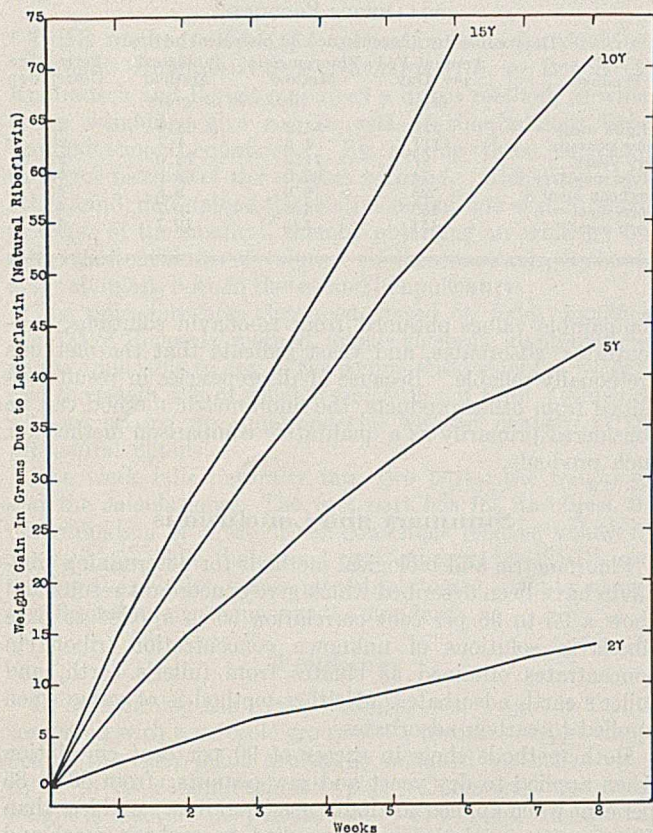


FIGURE 1. GROWTH RATE OF WHITE RATS

Varying amounts of lactoflavin (natural riboflavin) per day as predetermined by the fluorometric method

and cod liver oil, 2 parts. The animals are maintained on this unsupplemented diet for 1 to 2 weeks, during which constant or declining weight is established. Only an insignificant gain in weight takes place during this period. At this point the following supplements are provided per rat per day: 12.5 micrograms of pure vitamin B<sub>1</sub> (Merek or equivalent) and 100 mg. of autoclaved rice polish concentrate (Labco). The rice polish concentrate available in desiccated form is dissolved in water at a 7.5 per cent concentration, the pH adjusted to 8.5, and the alkaline solution autoclaved 5 hours at 120° C. These supplements are fed together in aqueous solution, the requisite amount being carried in 2.5 to 3.5 ml. supplied in small glass caster cups.

Growth is stimulated for a short period following introduction of the riboflavin-free water-soluble factors provided by this supplement. Constant weight or a rate of gain in weight not exceeding about 1 to 2 grams per week is again established after a period of about 2 to 3 weeks. At this point the animals are considered in proper condition for receiving the unknown material for the riboflavin assay. Graduated amounts of the assay sample are supplied to different groups of animals each day in addition to the primary supplements. Growth is immediately

resumed and soon becomes established at a rate commensurate with the amount of riboflavin supplied.

Negative control groups receiving the basal ration and the primary riboflavin-free supplement should be maintained throughout the assay period. Growth response due to riboflavin is computed as the difference between that shown by the negative controls and that induced by the sample through a period of not less than 4 weeks and not exceeding 8 weeks. This method for determining growth response due to variable amounts of lactoflavin was employed in determining the values shown in Figures 1 and 2 and Tables I, II, and III.

### Correlation of Results from Fluorometric and Biological Methods

The following data correlating the riboflavin determinations as made by the fluorometric method with the results obtained from the biological method involve numerous comparisons extending over a period of about 2 years. An equal number of male and female animals are represented in each comparison. All quantities of riboflavin indicated as being fed in known amounts were computed from the results obtained by the fluorometric method. Tables I and II and Figure 1 show the results obtained from riboflavin provided in pure form and as carried by fuller's earth adsorbates.

The data from the variable amounts of pure riboflavin show a substantially uniform and constant rate of growth for a period of 6 to 8 weeks commensurate with the amount provided. However, the different rates of growth are not maintained at exactly the same mathematical ratio at which the riboflavin was fed. The ratio between the average rate of growth per week from the 2- and 5-microgram levels is 1 to 3.08 instead of the theoretical 1 to 2.5; from the 2- and 10-microgram feedings it is 1 to 4.89 or very close to the theoretical 1 to 5 ratio; from the 2- and 15-microgram levels it is 1 to 6.04 instead of 1 to 7.5; from the 5 to 15 levels the ratio is 1 to 1.86; and from the 10 to 15 levels it is 1 to 1.85.

From these comparisons it might be concluded that the most reliable range of growth rate lies between 6 and 10 grams per week for not less than 4 weeks and not more than 8 weeks. Such a rate of growth conforms fairly well to the calculated gain per week attributable to each microgram of riboflavin per day, as it is to be noted that the average rate of growth per week from the 2 micrograms per day feeding is 2.06 grams, or the equivalent of 1.03 grams per microgram. On the basis of this computation the theoretical rate of growth at the 5-microgram level should be 5.15 grams per week, whereas the data show an average of 6.58 grams; the theoretical rate at the 10 micrograms per day level should be 10.30 grams per week; the actual average is 10.16 grams. These results substantiate the general conception that 2 to 3 micrograms of lactoflavin per day are necessary to induce a 3-gram gain per week, this amount being equivalent to 1 Bourquin-Sherman unit of vitamin G or B<sub>2</sub>.

The growth response obtained from experimentally and commercially produced fuller's earth adsorbates (Table II) fed at predetermined levels calculated to carry 5 and 15 micrograms of riboflavin as determined by the fluorometric method, is substantially the same as that obtained from the same amount of riboflavin fed in pure solution, the correlation being from 92 to 98.6 per cent. While this correlation in biological response based in turn upon the values obtained by the fluorometric method is considered remarkably close, and serves to show that the riboflavin carried by such adsorbates is fully available to the animal, or substantially so, such deductions are not applicable to all riboflavin adsorbates.

Various carbons are known to be highly efficient adsorbents for riboflavin, but removal of the riboflavin from such



adsorbates is not easily accomplished by ordinary means. In order to determine comparative differences in the retention properties of fuller's earth and carbon adsorbates, riboflavin solutions of known concentration were adsorbed on these materials, and the adsorbates were thoroughly washed and subjected to the 80 per cent acetone elution treatment, and likewise tested by the biological method. The fuller's earth adsorbate permitted a growth response calculated to be the equivalent of 96 per cent of that resulting from the same amount of riboflavin fed in pure solution. The carbon adsorbate eluted with 80 per cent acetone yielded only a trace of riboflavin. When subjected to the biological test in quantities known to contain from 5 to 50 micrograms (16.7 to 166.7 mg. of carbon) no growth resulted, indicating conclusively that the animal was unable to utilize the riboflavin adsorbed on these particular carbons. The results from the 166.7-mg. quantities carrying 50 micrograms of riboflavin indicated not only that the animal was unable to release the riboflavin, but also that the carbon actually adsorbed from the intestinal tract the water-soluble supplements supplied with the basal ration (Figure 2).

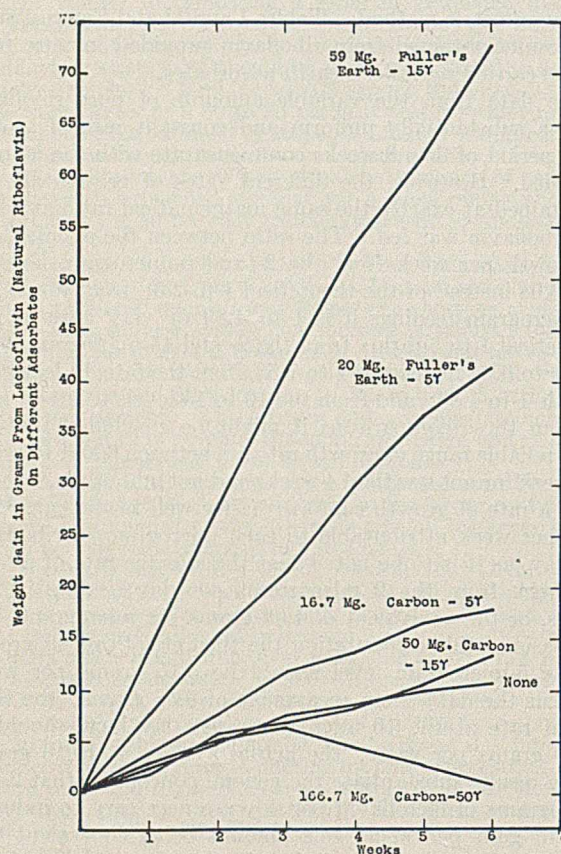


FIGURE 2. GROWTH RATE OF WHITE RATS

Varying amounts of lactoflavin (natural riboflavin) per day as carried on fuller's earth and carbon adsorbates

The correlation of the results from the fluorometric and biological method as applied to miscellaneous products was ascertained by first determining the riboflavin content fluorometrically. The milligrams of substance required to furnish given amounts of riboflavin were calculated; these calculated quantities were fed to the test animals daily to determine how the growth response compared with that obtained from solutions of known riboflavin content and of proved biological potency. By using the growth per week attributable to 1 microgram of riboflavin per rat per day as

shown by the basic data (Table I) it was possible to interpret the growth response from the test products in terms of the amount of riboflavin contained in each. A comparison of the results from the two methods is shown in Table III, from which it will be noted that while the values from yeast and peanuts are closely comparable, those from alfalfa meal and liver meal are less satisfactory; the results from the soybean meal and corn meal are at variance by more than 50 per cent.

It would appear from these results that the fluorometric and biological methods cannot be employed interchangeably for all miscellaneous products with assurance that the same interpretation of riboflavin content will result. However,

TABLE III. CORRELATION OF RIBOFLAVIN CONTENT OF MISCELLANEOUS PRODUCTS

Product	(Determined by fluorometric and biological methods)			Percentage Correlation
	Amount Fed per Day	Fluorometric Method	Biological Method	
	Mg.	$\gamma$ riboflavin per gram		
Alfalfa meal	227	33.2	28.4	85
Raw peanuts	1111	4.5	4.7	95
Dry yeast	87	71.2	73.0	97
Liver meal	54	85.0	68.0	80
Soybean meal	526	19.0	8.5	45
Corn meal	455	4.5	10.7	42
Corn meal	1351	4.5	10.7	42

comparable values obtained from riboflavin solutions, concentrates, adsorbates, and yeast indicate that the methods are equally reliable. Because of discrepancies in results obtained from other products, the fluorometric method can be considered primarily as a qualitative comparison method for such products.

### Summary and Conclusions

Fluorometric and biological methods for determining riboflavin have been described which give concordant results and show a 95 to 96 per cent correlation when applied to pure riboflavin solutions of unknown concentration, riboflavin concentrates obtained as eluates from fuller's earth, and fuller's earth adsorbates. Neither method is of value when applied to carbon adsorbates.

Both methods show in excess of 90 per cent correlation when applied to dry yeast and raw peanuts; from 80 to 85 per cent when applied to alfalfa meal and liver; and less than 50 per cent correlation when applied to soybean meal and corn meal.

One microgram of lactoflavin (natural riboflavin derived from milk) per rat per day causes a growth response of substantially 1 gram per week for a period of 6 to 8 weeks through a 2- to 10-microgram per day feeding range.

The fluorometric and biological methods may be used interchangeably for certain types of riboflavin solutions and adsorbates with equal reliability. The fluorometric method applied to such types of riboflavin-carrying materials gives consistent check results within 10 per cent variation from independent determinations and different operators; more experienced operators readily obtain check results within 3 to 5 per cent variation.

### Literature Cited

- (1) Bender, R. C., and Supplee, G. C., *J. Am. Chem. Soc.*, 59, 1178 (1937).
- (2) Steenbock, H., and Nelson, E. M., *J. Biol. Chem.*, 56, 355 (1923).
- (3) Supplee, G. C., Ansbacher, S., Flanigan, G. E., and Hanford, Z. M., *J. Dairy Sci.*, 19, 215 (1936).
- (4) Supplee, G. C., Bender, R. C., and Babcock, L. C., *IND. ENG. CHEM., Anal. Ed.*, 10, 636 (1938).



# Calibration of Weights

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A rigorous modification of Richards' method is described, including standardization in terms of a standard reference mass. Its advantages are mechanical simplicity, ease of checking for arithmetical errors, and wide applicability. A mathematical discussion of the validity of Richards' method is given.

THE methods of weight calibration thus far described follow Kohlrausch (6, 8), Richards (10), or Benoit (2). Kohlrausch and Benoit employed a direct method, in which group weighings give rise to sets of simultaneous linear "computational equations." By solving these equations, the error in each of the weights is found. Richards, on the other hand, determined the relative magnitude of each weight in terms of the smallest, thereby obtaining an arbitrary but self-consistent series of values. Of these methods, Richards' is the simplest, both in theory and in application.

The procedure here described, based on Fales' modification (4) of Richards' method, avoids algebraic manipulations, and is applicable to any of the common sequences of weights, and to certain sets of weights which do not form a sequence, without setting up equations and without changes in the procedural details.

The work falls naturally into two parts: the weighings, and the calculations. The first part has for its object the determination of a set of self-consistent relative values for the weights, while the second part concerns itself with converting the relative values into absolute c. g. s. units, using a certificated reference mass as the standard.

## Weighings

In determining the relative values, each weight in turn is compared with a suitable group of its predecessors, as shown below, the rider being arbitrarily assigned a relative value equal to its denominational value. Commonly the 5-mg. weight is used, but as pointed out by Hurley (5) this may be a source of error. Since interpolative weighings depend on the sensitivity, which in turn depends on the assumed weight of the rider, there are two unknowns—the 5-mg. weight and the rider. The difficulty may be avoided by either of two devices. The first is to make the rider itself the basis of the relative system, thereby producing a system with only one unknown. The other way, practical but not rigorous, is to retain the two unknowns, but first to "prove the rider" as described by Fales (4, section 83). In the latter method, care is taken that the rider agrees closely with the 5-mg. weight. If the agreement is not within the probable error of a weighing, a different rider should be chosen. In general, it is urgent that the rider be very close to its denominational value in order to avoid an inconvenient correction which depends upon the location of the rider.

By means of the weighings, the relative values are all determined—that is, the 5-mg. weight is known in terms of the rider; the 10 in terms of the 5 and the rider; the 20 in terms of the 10, 5, and rider; and so on, to the largest weight of the set. In order to convert this self-consistent set of values into the standard c. g. s. values, the magnitude of the "relative unit" must be found in terms of the c. g. s. system. To this end it is necessary and sufficient to know the value of some

large weight in terms of both systems. The standard reference mass is convenient for this, its c. g. s. value being already known, and its relative value being easily found by comparison with the others. The quotient of the two values is a multiplying factor for changing relative into absolute. The large number of significant figures involved in such a computation makes it worth while to consider an indirect method for carrying out the work.

## Calculations

Let us consider some of the mathematical properties of the proportion

$$\frac{a}{r} = \frac{A}{R} \quad (1)$$

Upon applying "alternation" and "division," we have

$$\frac{a - A}{r - R} = \frac{A}{R} \quad (2)$$

Or, if we had multiplied by the arbitrary factor  $1/n$ , prior to these operations

$$\frac{a - A/n}{r - R/n} = \frac{A}{R} \quad (3)$$

Whence

$$a = \frac{A}{R} (r - R/n) + \frac{A}{n} \quad (4)$$

The proof of these derived forms may be had by multiplying out and canceling, thus arriving immediately at the original proportion, Equation 1.

Richards stated that his method depended on "the properties of small numbers in the presence of large ones," and a number of attempts have been made to explain this or to disprove it. For example, it has been discussed by Eaton (3), and further developed by Hurley (5). From a practical point of view these authors conclude Richards' method to be correct, but they fail to point out the mathematical basis of the method.

Referring to the foregoing equations, let  $A$  and  $a$  refer to the absolute c. g. s. values;  $R$  and  $r$  to the arbitrary relative values. The capitals refer to the certified standard of mass, while the lower-case letters refer to each particular weight of the set, in turn.  $A/R$  is seen to be the conversion ratio already mentioned. Values  $r$  are the observed data, the relative values. The ratio  $A/R$  is not applied directly to the values  $r$ , but to a derived quantity,  $r - R/n$ , in which  $n$  is so chosen as to make the whole quantity extremely small. The latter condition is fulfilled if  $n$  is taken as the ratio of the nominal value of the standard to each nominal weight in turn. Values  $n$  are then whole numbers or simple fractions (Table I).

With  $n$  chosen in this manner, quantities  $r - R/n$  become the corrections to the "relative aliquots," and they are of the same order as the final corrections. These values multiplied by the conversion ratio,  $A/R$ , give the corrections to the "absolute aliquots," where the term "aliquot" means the  $n$ th submultiple of the value of the standard weight in either system. This mathematical trick for simplifying the arithmetic depends on the properties of equal ratios; hence it is no approximation, but is rigorous.

Richards followed the same procedure as given here, up to the formation of the corrections to the aliquots, which he left in that form, calling them the final corrections. Using the same nomenclature as above, but letting  $w$  represent the final adjusted values and  $W$  the assumed standard value of



TABLE I. BEGINNING OF TABULAR COMPUTATION

(Ratio $A/R = 49,998.00/49,601.75 = 1.008$ )							
1	1a	2	3	4	5	6	7
Denomi- nation, Grams	Sub- multi- ple $n$	Relative Values $r$	Relative Aliquots $R/n$	Relative Differ- ences $r - R/n$	Absolute Differ- ences $(r - R/n) \times A/R = a - A/n$	Absolute Aliquots $A/n$	Absolute C. G. S. Values $(a - A/n) + A/n = a$
100	1/2	99,211.53					
50, standard	1	49,601.75	49,601.75	****	****	49,998.00	49,998.00
50	1	49,606.02					
20	5/2	19,842.35					
10	5	9,920.95					
10	5	9,920.83					
5	10	4,960.64					
...	.....	.....					
...	.....	.....					
...	.....	.....					
<i>Mg.</i>							
10	5,000	10.07					
10	5,000	10.06					
5	10,000	4.92					
5, rider	10,000	5.00					

the reference weight (Richards assumed  $W = 10.00000$  grams), we have

$$w = r \frac{W}{R} = r \frac{1}{R/W} = r \frac{1}{1 - \left(\frac{W-R}{W}\right)} \quad (5)$$

a rigorous equation, which Richards approximated as follows:

$$w = r \frac{1}{1 - \left(\frac{W-R}{W}\right)} \doteq r \left[1 + \left(\frac{W-R}{W}\right)\right] = r + \frac{W-R}{W/r} \quad (6)$$

$$w \doteq r + \frac{W-R}{W/r} \doteq r + \frac{W-R}{n} = \frac{W}{n} + \left(r - \frac{R}{n}\right) \quad (7)$$

The first approximation comes from discarding all terms except the first two, in the infinite binomial series. The second approximation involves the substitution of the coefficient  $n$  (equal to  $R/r = W/w$ ) for the quantity  $W/r$ . Comparison of this with Equation 4 shows the true equation to be

$$w = \frac{W}{n} + \frac{W}{R} \left(r - \frac{R}{n}\right) \quad (8)$$

Hence there is a third approximation, in that  $W/R$  is taken to be unity, which is all right in most cases, but not in all (in

Table II, see the corrections to the 100-gram, 50-gram, and 20-gram weights). Therefore Richards' system depends not only upon "the properties of small numbers in the presence of large ones" in the sense intended (7), but also upon the relative magnitude of the units in the  $w$  system and in the  $r$  system.

PROCEDURE. Following Richards, the tabular form of computation is used, all computations being done directly in the table, without recourse to scratch paper, except in the case of the division  $A/R$ . Orderliness and convenience are the great advantages of the arrangement, which makes for rapid, systematic prosecution of the work. The arrangement's simplicity makes for ease of checking, a point that is too often insufficiently emphasized. The author's experience is that workers of all types are far more prone to mistakes in the computations than in the observations. In the tabular arrangement, mistakes may be located almost at a

glance—for example, a skilled computer required slightly less than 5 minutes, actual timing, for checking all the computations of Table III.

Referring to Table I, let it be assumed that the relative values have been obtained, including that of the standard weight. They are listed in descending order, to the nearest 0.01 mg. (actual precision may be from 0.03 to 0.08 mg.), in column 2. Thus far the absolute value is known for only one weight—the standard, in this case assumed to be a 50-gram weight. This value appears in the appropriate place in column 7. The relative and absolute values of the standard weight are also placed in columns 3 and 6, respectively, under the headings of "aliquots."

When these figures have been entered, the aliquot columns are next filled in by writing the successive fractional parts or aliquots of the standard weight in each line, according to the denominations in column 1. The factor  $n$  is given in column 1a, and is the ratio of the denominational value of the standard to each denominational value in turn. In arriving at the aliquot corresponding, for example, to the 20-gram weight, the value of the standard is divided by 5/2. For the 10-gram weight, the divisor is 5, and so on down the line. All the lesser aliquots are simply obtained from those for 50, 20, and 10, by merely shifting the decimal point to the left.

It will be found in practice that the relative aliquots differ very little from the relative values of the weights to which

TABLE II. CONTINUATION OF COMPUTATION

(Ratio $A/R = 1.008$ )						
1	2	3	4	5	6	7
Denomi- nation, Grams	Relative Values $r$	Relative Aliquots $R/n$	Relative Differ- ences $r - R/n$	Absolute Differ- ences $(r - R/n) \times A/R$	Absolute Aliquots $A/n$	Absolute C. G. S. Values $a$
100	99,211.53	99,203.50	8.03	8.09	99,996.00	100,004.09
50, standard	49,601.75	49,601.75	****	****	49,998.00	49,998.00
50	49,606.02	49,601.75	4.27	4.30	49,998.00	50,002.30
20	19,842.35	19,840.70	1.65		19,999.20	
10	9,920.95	9,920.35	0.60		9,999.60	
10	9,920.83	9,920.35			9,999.60	
5	4,960.64	4,960.18			4,999.80	
...	.....	.....			.....	
...	.....	.....			.....	
...	.....	.....			.....	
<i>Mg.</i>						
10	10.07	9.92			10.00	
10	10.06	9.92			10.00	
5	4.92	4.96			5.00	
5, rider	5.00	4.96			5.00	



TABLE III. COMPLETE COMPUTATIONS FOR A 1-2-3-5 SEQUENCE

(Ratio  $A/R = 100,000.20/99,567.22 = 1.004$ )

1	2	3	4	5	6	7	8	9
Denomi- nation Grams	Relative Values	Relative Aliquots	Rela- tive Differ- ences	Absol- ute Differ- ences	Absolute Aliquots	Absolute Values	Rounded Values	Correc- tions in 0.1 Mg.
100, standard	99,567.22	99,567.22	****	****	100,000.20	100,000.20	Standard	Value
50	49,782.14	49,783.61	-1.47	-1.48	50,000.10	49,998.62	49,998.6	-14
30	29,870.71	29,870.16	0.55	0.55	30,000.07	30,000.62	30,000.6	6
20	19,913.49	19,913.44	0.05	0.05	20,000.04	20,000.09	20,000.1	1
10	9,957.02	9,956.72	0.30	0.30	10,000.02	10,000.32	10,000.3	3
5	4,978.52	4,978.36	0.16	0.16	5,000.01	5,000.17	5,000.2	2
3	2,987.09	2,987.02	0.07	0.07	3,000.01	3,000.08	3,000.1	1
2	1,991.34	1,991.34	0.00	0.00	2,000.00	2,000.00	2,000.0	0
1	995.72	995.67	0.05	0.05	1,000.00	1,000.05	1,000.1	1
<i>Mg.</i>								
500	497.86	497.84	0.02	0.02	500.00	500.02	500.0	0
300	298.68	298.70	-0.02	-0.02	300.00	299.98	300.0	0
200	198.94	199.13	-0.19	-0.19	200.00	199.81	199.8	-2
100	99.60	99.57	0.03	0.03	100.00	100.03	100.0	0
50	49.75	49.78	-0.03	-0.03	50.00	49.97	50.0	0
30	29.88	29.87	0.01	0.01	30.00	30.01	30.0	0
20	19.87	19.91	-0.04	-0.04	20.00	19.96	20.0	0
10	9.93	9.96	-0.03	-0.03	10.00	9.97	10.0	0
5	4.99	4.98	0.01	0.01	5.00	5.01	5.0	0
5, rider	5.00	4.98	0.02	0.02	5.00	5.02	5.0	0

they correspond. This fortunate circumstance is an important feature of the method, since the next operation is to subtract algebraically the aliquots from the relative values. The differences are placed in column 4. The progress of the work so far is shown in Table II, in which the aliquot columns

terms of a 100-gram Bureau of Standards certified weight as a primary reference standard. It was found convenient to conduct the standardization in groups of five, using a 50-gram auxiliary weight to make up the total of 100 grams. There is no reason for not calibrating ten at a time except the possibility of confusion attendant upon the use of so many outwardly identical objects at once. The actual computation is shown in Table IV. One of the 10-gram weights was assumed to weigh exactly 10,000 arbitrary relative units, and the weights of the others were found by intercomparison. The computation for the absolute value of the 50-gram weight was carried through in each case, in order to compare the several values thereby found. This served as a partial check upon the group calibrations.

This method is at least as precise as any of the methods now in use. If greater precision is desired, it must be sought by the use of multiple weighings, as, for example, in the method of Benoit (1, 2, 9) in which the method of least squares may be used for adjusting the residues. For the set of weights first described, thirty-one weighings were necessary, using Borda's substitution weighing. This may seem disadvantageous when it is considered that by suitable grouping of the weights the number of weighings may be reduced to twenty-two, but in such a case it is necessary to set up and solve a set of simultaneous equations, different for each sequence of weights.

TABLE IV. COMPARISON OF SECONDARY STANDARDS IN GROUPS OF FIVE

(Ratio  $A/R = 100,000.30/99,999.26 = 1.00001$ )

1	2	3	4	5	6	7
Denomination and Description Grams	Relative Values	Relative Aliquots	Relative Differ- ences	Absolute Differ- ences	Absolute Aliquots	Absolute C. G. S. Values
100, N. B. S. test	99,999.26	99,999.26	****	****	100,000.30	100,000.30
50, auxiliary	49,999.94	49,999.63	0.31	0.31	50,000.15	50,000.46
10, No. 6	10,000.00	9,999.93	0.07	0.07	10,000.03	10,000.10
10, No. 7	9,999.87	9,999.93	-0.06	-0.06	10,000.03	9,999.97
10, No. 8	9,999.62	9,999.93	-0.31	-0.31	10,000.03	9,999.72
10, No. 9	10,000.18	9,999.93	0.25	0.25	10,000.03	10,000.28
10, No. 10	9,999.99	9,999.93	0.06	0.06	10,000.03	10,000.09

have been filled in, and the first few subtractions written in column 4. These differences never contain more than three significant figures, and usually not more than two. They are all of the order of milligrams or less.

When the subtractions have all been performed, the next step is changing the differences to absolute values, through the ratio  $A/R$ . These results, the "absolute differences," are to be written in column 5. Upon adding these algebraically to the absolute aliquots in column 6, the absolute values are obtained; these are written in column 7. The computation is best completed columnwise, each column being worked upon in turn, thereby grouping all subtraction operations, all divisions, all additions, etc. To illustrate the versatility of the method, complete computations are given in Table III for a set of weights of the 1-2-3-5 sequence. Columns 8 and 9 of Table III give, respectively, the values rounded off to the precision limits and the list of corrections.

The method has been in use for three years with quantitative analysis classes, with a high degree of success. It has been found useful not only for calibration of weights in sets, but also for the calibration of certain secondary standards of mass. These are of 10 grams each, and were calibrated in

For accuracy and simplicity, without algebraic complication, the present method is far in the lead. Its advantages may be summed up as simple theory, logical arrangement, directness of the computation, ease of checking for errors, and applicability to all sequences without change. For an extended list of additional references, see (11).

Literature Cited

- (1) Anon., Natl. Bur. Standards, *Circ.* 3, (1918).
- (2) Benoit, "Etalonnage des Series de Poids. Travaux et Mémoires du Bureau International des Poids et Mesures," Vol. 13, 1907.
- (3) Eaton, *J. Am. Chem. Soc.*, 54, 3261 (1932).
- (4) Fales, "Inorganic Quantitative Analysis," 1st ed., New York, Century Co., 1925.
- (5) Hurley, *IND. ENG. CHEM., Anal. Ed.*, 9, 239 (1937).
- (6) Kohlrausch, "Lehrbuch der praktischen Physik," 9th ed., Teubner, 1901.
- (7) Nernst and Schoenflies, "Mathematische Behandlung der Naturwissenschaften," p. 303, Munich, Wolf, 1895.
- (8) Ostwald, "Manual of Physical Chemical Measurements," New York, Macmillan Co., 1894.
- (9) Pienkowsky, Natl. Bur. Standards, *Sci. Paper* 527 (1925).
- (10) Richards, *J. Am. Chem. Soc.*, 22, 144 (1900).
- (11) Thornton, *J. Chem. Education*, 14, 270 (1937).



# Hydrogen Peroxide in the Colorimetric Determination of Iron by Thiocyanate

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IN DETERMINING iron colorimetrically by the thiocyanate process it is customary to oxidize the iron by permanganate. Van Urk (9) used permanganate followed by peroxide or persulfate. The authors have preferred to use peroxide alone, as its use avoids the introduction of the highly reactive manganese ion and of sulfates. That sulfates are undesirable is indicated by the work of Hedenström and Kunau (8), who studied the effect of salt concentration on the discharge of the red iron-thiocyanate color. Calculation from their data shows that the salt-thiocyanate ratio for effective color discharge is four times as great for chlorides as for sulfates. One would naturally assume, then, that sulfates are four times as effective as chlorides in preventing the development of the red color and so to be avoided whenever possible.

It is known (4) that powerful oxidizing agents produce yellow substances from thiocyanate, particularly at higher temperatures, although Sharma (7) says that pure ammonium thiocyanate, from which traces of iron have been removed, does not give a color with peroxide, hydrochloric acid, or chlorine. Sharma also further states, as do Patten and Smith (5), that traces of iron are present in thiocyanates. Evidently the ordinary thiocyanate reagent contains traces of iron and is customarily used with this impurity present, as noted by Winsor (10).

To ascertain the effect of hydrogen peroxide in producing colored substances in sodium thiocyanate solutions to which no iron had been added, a normal sodium thiocyanate solution was made 0.18 *M* with hydrogen peroxide and allowed to stand overnight. A yellow precipitate and a red solution were present next morning. To find out how much hydrogen peroxide can be used safely, other experiments were made in which peroxide was mixed with thiocyanate with and without hydrochloric acid. The data are collected in Table I.

effect. The figures indicate that a solution about 0.0024 *M* with peroxide is of satisfactory strength.

Practically, to get the right amount of peroxide it is not necessary to standardize the peroxide solution. Instead, to three tubes, containing the same quantities of acid, iron, and thiocyanate, definite varying amounts of peroxide are added—say, 10, 20, and 30 drops, respectively. If the 10- and 20-drop tubes give the same color and the 30-drop tube is slightly yellowish, the limits are thereby set as 10 to 20 drops. Further, if a solution of peroxide is standardized two or three times at intervals of some days or weeks further standardization is unnecessary, as the subsequent strength of the solution can be read from the straight-line graph expressing the ratio of moles per day.

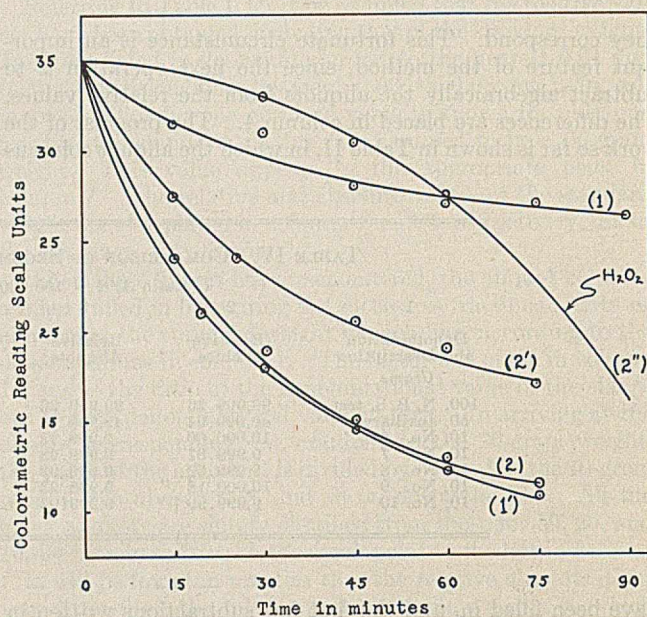


FIGURE 1. RATE OF FADING OF FERRIC THIOCYANATE  
Fe, p. p. m. Fe/CNS 1/9280. HCl/CNS 0.01/0.16 *N*  
1, March 6, cloudy, dark  
1', 2'. July 1, bright  
2, 2". March 16, mostly bright

Acid alone with ordinary analytical grade of thiocyanate will produce colored substances but not, as the authors found, if kept below 0.1 *N* when the thiocyanate is as high as 0.4 *N*.

The use of permanganate for oxidizing iron necessitates a reading at the moment the permanganate fades, in order to avoid negative error. With hydrogen peroxide the iron thiocyanate color lasts for some time. To study the fading of the red color, experiments were made both with and without hydrogen peroxide, no permanganate being used. The colorimetric reading was plotted against time and zero time was set at 35 scale units. The results are shown in Figure 1.

It is evident that without peroxide (curves 1, 1', 2, 2'), the fading is rapid, while with 0.0028 *M* peroxide (curve 2'') the color is stable for at least 5 minutes. Curve 1 was made on a cloudy day in March, curve 2 on a bright day in March, and 1' and 2' on a bright day in July, all exposed to north

TABLE I. COLOR PRODUCED IN THIOCYANATE SOLUTIONS

(Varying amounts of hydrogen peroxide and hydrochloric acid)

Tube No.	CNS, <i>N</i>	0.68 Per Cent $H_2O_2$ , <i>M</i>		HCl, <i>N</i>	Remarks
1	0.4	0.25	0.001	0	No color
2	0.4	0.25	0.001	0.01	Slight yellow color on mixing
3	0.4	0.74	0.003	0	No color
4	0.4	0.74	0.003	0.01	Slight yellow color on mixing
5	0.4	0.74	0.003	0.10	Slight yellow color on mixing
6	0.3	0.2	0.0008	0.01	
7	0.3	0.4	0.0016	0.01	
8	0.3	0.6	0.0024	0.01	Very slight color in all tubes
9	0.3	0.8	0.0032	0.01	
10	0.3	0.2	0.0008	0.1	
11	0.3	0.8	0.0032	0.1	
12	0.2	0.2	0.0008	0.01	No color
13	0.2	1.0	0.004	0.01	Very slight color
14	0.2	1.0	0.004	0.1	Very slight color

It is evident that color develops with lower concentrations of peroxide and thiocyanate when the solution is acid. A solution develops no color when it is 0.2 *N* in thiocyanate, 0.01 *N* in acid, and 0.0008 *M* in peroxide. Increasing thiocyanate one and one-half times, peroxide ten times, or acid ten times, produces a very slight yellowish color, but this color is too slight to be of analytical importance and the authors frequently exceeded these amounts without noticeable



light. The much faster fading in bright light is in conformity with the findings of other workers (1, 2, 6, 8). In other experiments carried out in tall Nessler tubes of 50-ml. capacity the amount of hydrogen peroxide was increased and the time during which the red color was permanent was greatly lengthened. The results are given in Table II.

TABLE II. TIME OF FADING OF FERRIC THIOCYANATE WITH HYDROGEN PEROXIDE PRESENT

Iron P. p. m.	NaCNS, N	H <sub>2</sub> O <sub>2</sub> , M	HCl, N	Time of Fading
0.1	0.2	0.0032	0.01	No fading in 15 minutes
0.1	0.02	0.0037	0.01	No fading in 2.5 hours

Further studies are being made by one of the authors on the rate of ferric thiocyanate fading under definite light conditions.

The fading is believed by the authors to be due to the reduction of the iron and oxidation of the thiocyanate. If that is true, it should be possible to restore full color to a faded iron determination by adding peroxide. To test this hypothesis a solution 0.0028 M in peroxide, the same as used in making curve 2, Figure 1, was allowed to stand several hours. After 4 hours the fading had progressed from 35 scale units to 4. The addition of a second amount of peroxide, equal to the first, restored the original color.

During the past 12 years many hundreds of colorimetric iron determinations have been made in this laboratory using peroxide alone as the oxidant; the results are the same

whether peroxide or permanganate is used, but, because of the fading of the ferric thiocyanate as soon as the permanganate is exhausted, precautions must be taken, when using this procedure, or the results will be low.

### Summary

Hydrogen peroxide is a more satisfactory oxidant for iron than permanganate in the thiocyanate determination of iron. The red color can be made stable for several minutes, depending on the amount of peroxide used, and the faded color may be restored if necessary by the addition of more peroxide. Too much peroxide may cause a yellowish interfering color due to oxidation products of thiocyanate.

### Literature Cited

- (1) Baudisch, O., and Welo, L., *J. Biol. Chem.*, 61, 261 (1924).
- (2) Bhattacharyya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, 6, 143, 197 (1929).
- (3) Hedenström, A., and Kunau, E., *Z. anal. Chem.*, 91, 17-25 (1932).
- (4) Offord, H. R., *IND. ENG. CHEM., Anal. Ed.*, 7, 93 (1935).
- (5) Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Can.* (3), 22, III, 221 (1928).
- (6) Pulsifer, H. B., *J. Am. Chem. Soc.*, 26, 967 (1904).
- (7) Sharma, B. S., *J. Chem. Soc.*, 1930, 308.
- (8) Sharma, B. S., *J. Soc. Chem. Ind.*, 48, 336 (1929).
- (9) Urk, H. W. van, *Pharm. Weekblad*, 63, 1101-7 (1926).
- (10) Winsor, H. H., *IND. ENG. CHEM., Anal. Ed.*, 9, 445 (1937).

FROM theses presented by Majel M. MacMasters and Chester L. French for the M.S. degree.

## New Light Sources for Colorimetry

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THE application of a colorimetric method of analysis requires that the system under consideration follow Beer's law, which is theoretically valid only for monochromatic light. However, in practice, it is customary to use continuous or band emission light sources and filter combinations which produce incident illumination of varying degrees of monochromation. In addition to the possibility of major deviations from Beer's law there are other difficulties inherent in such procedures. When permanent standards, differing from the unknown, are used the difference in hue between unknown and standard is greater the broader the spectrum of the incident illumination. In addition, the practical difficulty of determining small changes of transmission in a restricted spectral region in the presence of strong accompanying transmission in other regions (background) becomes greater as the width of the spectrum of the incident light increases.

Although approximations to monochromatic light have been obtained by the use of appropriate filters or combinations of filters, the necessary approximation can often be secured in this way only by the use of exceedingly intense sources (which in the case of tungsten filament lamps generate large amounts of heat) or by the sacrifice of intensity of illumination and therefore of speed and precision.

The lamps described herein were developed in order to secure very high intensity sources of illumination which were relatively cool and whose emission was concentrated in some

restricted spectral region. These permitted the use of thick filters and the attainment of near monochromation without too great a loss of intensity. These lamps were used with the standard Klett-Beaver visual colorimeter, but can be adapted readily to other instruments such as the photoelectric colorimeter, etc.

For the colorimetric determination of sodium chlorophyllins (unpublished work) in aqueous solution use was made of a neon source. The lamp was a spiral of 6-mm. tubing 45 mm. long and 35 mm. in external diameter. With this was used a Corning signal red filter (No. 243) and the standard was a copper sulfate solution (1). The precision attainable (in the determination of concentrations) in this way was approximately 5 parts per thousand for nine readings made in 2 minutes.

For the colorimetric determination of  $\alpha$ -naphthylamine (unpublished work) a green fluorescent lamp was used in conjunction with a Corning Sextant green (No. 401) filter with a pentammino cobaltic chloride solution (1) as the standard. This lamp was in the shape of a doubled "U" and was 11 cm. long and 30 mm. in external diameter. The precision attainable in this case was the same as that given above.

Both these lamps, when in use, were inserted in the place ordinarily occupied by the 25-watt tungsten lamp in the Klett-Beaver colorimeter. Similar lamps, as well as a blue fluorescent lamp, can be obtained in a variety of designs from Claude Neon Lights, Inc., Long Island City, N. Y.

### Literature Cited

- (1) Kasline, C. T., and Mellon, M. G., *IND. ENG. CHEM., Anal. Ed.*, 8, 463 (1936).



# Cell and Dropping Electrode for Polarographic Analysis

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IT HAS been common practice in polarographic analysis with the dropping mercury electrode (2) to employ a stationary pool of mercury on the bottom of the cell as the second electrode (usually anode). When this procedure is used, and the current-voltage curves are obtained by means of a polarograph, the observed decomposition voltages and half-wave voltages are in terms of the total applied e. m. f., and hence they depend on the potential of the quiet electrode. Since the potential of the quiet electrode is a variable quantity, depending on the nature and concentration of the foreign salts present in the solution, the values of the half-wave applied e. m. f. are not entirely characteristic of the reducible or oxidizable substances present. The half-wave potentials on a current-voltage curve are only characteristic of the particular electroreducible or electrooxidizable substances present when the values are referred to an external reference electrode of constant known potential. In order to obtain the characteristic half-wave potentials which are required in qualitative polarographic analysis, it is necessary to measure the potential of the quiet electrode against the external reference electrode either at the beginning or the end of the electrolysis and to subtract this value from the half-wave values of the total applied e. m. f. (2).

These extra operations can be eliminated and the characteristic half-wave potentials obtained directly by dispensing with the stationary pool of mercury and employing the reference electrode itself (usually a saturated calomel electrode) as the second electrode of the cell (1, 2, 5). This technique has the further practical advantage of eliminating the extra mercury for the quiet electrode.

The authors have found that the H-cell shown in the diagram is very convenient for practical work. The solution to be analyzed is placed in the left half of the cell and the reference electrode in the right half. Electrolytic connection between the two halves of the cell is made through a sintered-glass diaphragm fused into the middle of the cross arm. To prevent streaming of one solution into the other through the diaphragm, the reference electrode side of the cross arm is filled with a plug of agar containing the same electrolyte used in the reference electrode. When not in use, the left half of the cell is filled with water to prevent the agar plug from drying out and cracking.

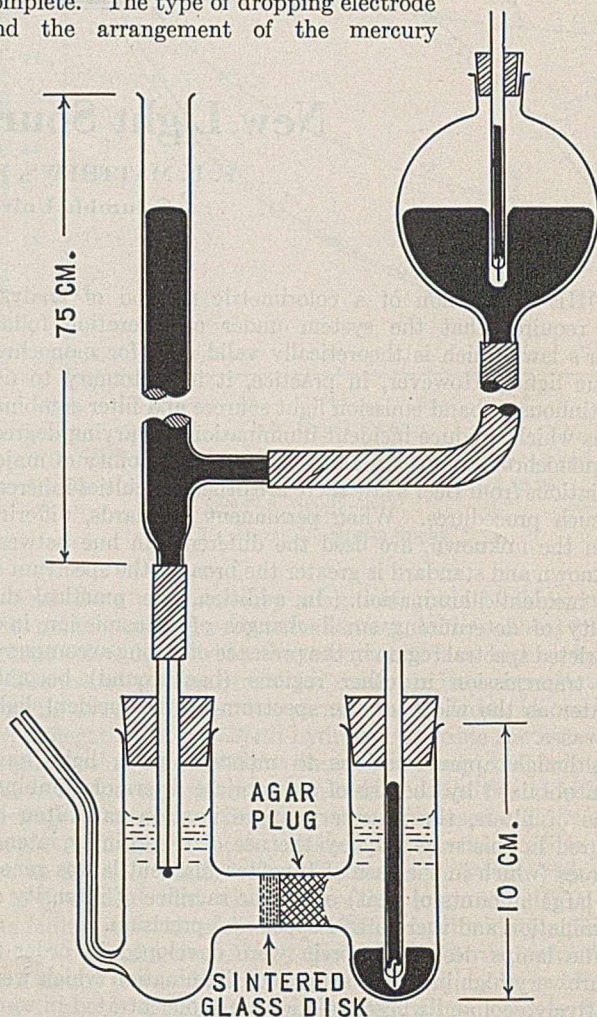
For most practical work a saturated calomel electrode is very convenient as reference electrode, but any other reversible electrode may be used. The area of the reference electrode should be at least 1 sq. cm., or larger, so that it will not become polarized and will retain a constant potential during the electrolysis (2, 6). The reference electrode needs to be renewed only at infrequent intervals.

The authors have also used a silver-silver chloride reference electrode, which in certain respects is handier than a calomel electrode. It remains depolarized during an electrolysis and its potential is as constant and reproducible as that of a calomel electrode. The silver-silver chloride electrode can be prepared either by cementing a piece of silver foil, to which a copper lead wire has been soldered, into the end of a glass tube, or by silver-plating a platinum plate electrode. Its area should be at least 1 sq. cm. or greater. If the silver electrode is to be used as anode in a chloride solution no further treatment is necessary, but if it is to be used as cathode it should be given a coating of silver chloride by polarizing it anodically in a dilute solution of hydrochloric acid.

If the presence of chloride ions interferes in the solution to

be analyzed, a mercury-mercurous sulfate electrode, in saturated potassium sulfate, can be used as the reference electrode (1). The potential of a saturated mercury-mercurous sulfate reference electrode is about +0.6 volt with respect to the normal hydrogen electrode, which is considerably more positive than the potential at which appreciable anodic dissolution of mercury from the dropping electrode takes place (about +0.4 volt *vs.* N. H. E., 2, 7). At the start of the electrolysis when the applied e. m. f. is zero and the dropping electrode is simply short-circuited with a mercury-mercurous sulfate reference electrode, a negative (2) current usually results. This initial negative current will be large when the solution to be analyzed contains halide or other ions which depolarize the dropping electrode (7). In such cases the applied e. m. f. should be increased by a few tenths of a volt to balance out the initial negative current, before connecting the cell to the circuit and recording the current-voltage curve.

The capillary side tube in the left half of the cell is for the introduction of hydrogen or nitrogen to remove air from the solution before electrolysis. During this operation, which requires 10 or 15 minutes, the rubber stopper which carries the dropping electrode is loosened to allow the gas to escape, and is resealed when the removal of air is complete. The type of dropping electrode and the arrangement of the mercury





reservoir shown in the diagram is more convenient than the classical arrangement (2). The dropping electrode proper consists of an 8-cm. length of commercial capillary tubing with a uniform internal diameter of 0.05 mm. (obtainable as "marine barometer tubing" from the Corning Glass Works, Corning, N. Y.). The use of commercial capillary tubing for the dropping electrode has been recommended by Maas (4) and Siebert and Lange (8). The influence on the diffusion current of the geometrical characteristics of the capillary has been discussed in detail by Lingane and Kolthoff (3).

The capillary is connected by a short length of rubber pressure tubing to a vertical tube filled with mercury, which is connected by rubber pressure tubing to the mercury reservoir. The vertical "stand-tube" facilitates the measurement and accurate setting of the pressure on the dropping electrode.

Literature Cited

- (1) Hohn, H., "Chemische Analysen mit dem Polarographen," Berlin, Julius Springer, 1937.
- (2) Kolthoff, I. M., and Lingane, J. J. (detailed review of the fundamental principles of the polarographic method), *Chem. Rev.*, 24, 1-94 (1939).
- (3) Lingane, J. J., and Kolthoff, I. M., *J. Am. Chem. Soc.*, 61, 825 (1939).
- (4) Maas, J., Dissertation, Amsterdam, 1937; *Collection Czechoslov. Chem. Commun.*, 10, 42 (1938).
- (5) Maassen, G., *Angew. Chem.*, 50, 375(1937); "Physikalische Methoden in chemischen Laboratorium," Berlin, Verlag Chemie, 1937.
- (6) Majer, V., *Collection Czechoslov. Chem. Commun.*, 7, 146, 215 (1935); 9, 360 (1937).
- (7) Revenda, J., *Ibid.*, 6, 453 (1934).
- (8) Siebert, H., and Lange, T., *Chem. Fabrik*, 11, 141 (1938).

# Silicotungstic Acid Determination of Nicotine

## Errors Involved and a New Technique for Steam-Distillation of Nicotine

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THE estimation of nicotine in tobacco and proprietary nicotine preparations by the official method of the Association of Official Agricultural Chemists (1) is a time-consuming and cumbersome procedure, calling for the steam-distillation of 1000 to 1500 ml. of liquid with subsequent aliquoting and precipitation of the nicotine with silicotungstic acid. In view of these facts, the writers have developed a new technique which has proved very convenient. In the course of the work a number of errors inherent in the precipitation of nicotine with silicotungstic acid were encountered. They are of such magnitude and importance in any procedure using silicotungstic acid as the precipitant that it becomes essential to discuss them. Spies (2, 3) has already called attention to the variation in solubility of nicotine silicotungstate with changes in acid concentration of the precipitating medium. Errors from this source are insignificant for any but microdeterminations.

by varying the amounts of wash solutions. However, under any given set of conditions, the error introduced by retention of the silicotungstic acid reagent by filter paper will be fairly constant. Since only relative amounts of nicotine are considered in the experiments reported below, it was thought not essential to correct for such error. When a highly refined determination of the absolute amount of nicotine present in a given material is desired, it becomes essential to estimate and correct for this error.

### Retention of Reagent by Filter Paper

Experience in this laboratory and elsewhere indicates that an error is introduced in the official method of the A. O. A. C. (1) on account of the retention of silicotungstic acid by filter paper. Experiments designed to determine the magnitude of such error were carried out.

### Effect of Temperature on Solubility of Precipitate

Low results may also be obtained in the determination of nicotine, because the solubility of nicotine silicotungstate varies directly with temperature. To show this fact, aliquots of a nicotine hydrochloride solution containing approximately 10 mg. of nicotine were all subjected to the following treatment:

Mixtures containing 100 ml. of water, 3 ml. of hydrochloric acid (1 to 4), and varying amounts of silicotungstic acid reagent (12 per cent) were passed through several makes and grades of filter papers. Each paper was washed with a definite amount of hydrochloric acid (1 to 2000) and burned, and the residue was ignited in a platinum crucible according to the method of the A. O. A. C. (1).

The details of the treatments and the weights of the residues are presented in Table I. Without varying the quantity of wash liquid, and for a given filter paper, the residue obtained varies directly with the quantity of reagent used. Considerable variation is obtained with different papers and also

Three milliliters of hydrochloric acid (1 to 4) were added to each aliquot and the mixtures were diluted to 100 ml. The nicotine was precipitated with 12 per cent silicotungstic acid solution and allowed to stand at room temperature for about 1 hour until all the precipitates had settled and appeared to be crystalline. Duplicate samples were subjected to the following treatments, after which the precipitates were filtered and washed with hydrochloric acid (1 to 2000); the determination of nicotine

TABLE I. RETENTION OF SILICOTUNGSTIC ACID BY FILTER PAPER

Experiment No.	Filter Paper	Composition of Solution Filtered				Weight of Residue				Av. Mg.
		1 + 4 HCl Ml.	H <sub>2</sub> O Ml.	Silico- tungstic acid Ml.	Wash Liquid Ml.	1 Mg.	2 Mg.	3 Mg.		
1)	C. S. and S., No. 589, 9-cm., white ribbon	3	100	1	100	0.8	0.8	...	0.8	
2)		3	100	3	100	1.0	1.0	...	1.0	
3)		3	100	5	100	1.5	1.8	...	1.7	
4	Munktell, 9-cm., No. 00	3	100	3	100	1.2	1.0	0.6	0.9	
5	C. S. and S., No. 589, 9-cm., white ribbon		100	3	100	1.6	1.0	0.8	1.1	
6	C. S. and S., No. 589, 9-cm., blue ribbon	3	100	3	100	0.5	0.8	0.7	0.7	
7)	C. S. and S., No. 589, 9-cm., white ribbon	3	100	3	100	0.8	1.0	0.9	0.9	
8)		3	100	3	300	0.6	0.6	0.6	0.6	
9)		3	100	3	500	0.6	0.4	0.5	0.5	



was completed as in the official method (1). (1) Samples stood for 8 hours at 0° C. (2) Samples stood for 8 hours at room temperature (about 25° C.). (3) Samples stood for 20 hours at room temperature (about 25° C.). (4) Samples were placed in constant-temperature bath at 35° C. for 8 hours. (5) Samples were placed on steam bath, 80° to 90° C. for 3 hours and filtered hot.

The data in Table II demonstrate that for best results one should allow the nicotine silicotungstate precipitate to stand overnight at 0° to 10° C. before filtering. Better crystallization is effected if the mixture is placed on the steam bath for a short time before holding at the lower temperature.

TABLE II. SOLUBILITY OF NICOTINE SILICOTUNGSTATE

Experiment No.	Nicotine Taken Mg.	Volume of Solution Ml.	Temperature ° C.	Reagent Ml.	Nicotine Found		
					1 Mg.	2 Mg.	Av. Mg.
1	10	100	0	1	9.87	9.88	9.875
2	10	100	Room	1	9.75	9.83	9.790
3	10	100	Room	1	9.80	9.80	9.800
4	10	100	35	1	9.62	9.53	9.575
5	10	100	80-90	1	8.11	8.22	8.165

### New Technique for Determination of Nicotine

As previously pointed out, dissatisfaction with the apparatus and technique employed in the official method (1) led to the development of a more satisfactory apparatus with corresponding improvements in technique. The apparatus described below, illustrated in Figure 1, is not only time-saving but seems to give more consistent results than does its more cumbersome parent.

**APPARATUS.** The apparatus is a simple steam-distillation outfit which can be constructed, for the most part, from materials at hand in the average chemical laboratory. It consists of a 500-ml. Pyrex Florence flask, A, used to generate steam, which is passed through the delivery tube, B, under the surface of the liquid in distilling flask, C. The steam generator has a three-hole rubber stopper. One hole carries the steam outlet tube, another a glass stopcock which serves to relieve excess pressure, and through the third passes about 90 cm. (3 feet) of 6-mm. tubing for a pressure gage.

The 50-ml., round-bottomed, Pyrex distilling flask, C, is connected through a two-hole rubber stopper and by means of a safety trap, D, with a small vertical water condenser, E. The delivery tube, F, is adjusted in such a way that it dips beneath the surface of the liquid in the 200-ml. Pyrex beaker, used to receive the distillate. Rubber connections are used as shown in Figure 1. Changes in steam pressure can be obtained by adjusting the stopcock opening or by controlling the flame of the Bunsen burner. A small microburner is used to keep the liquid in the distilling flask as low as desired. The entire outfit is assembled on a single ring stand. It can be moved around as desired and does not occupy more than 3.6 sq. meters (2 feet square) of horizontal space.

**PROCEDURE.** It is desirable to use for analysis a sample that contains from 5 to 10 mg. of nicotine, but as little as 2 mg. or less can be determined by this method. Tobacco dusts and other dry preparations of nicotine are usually weighed directly into the distilling flask. In the case of liquid preparations, such as nicotine sulfate solutions of high nicotine content, it is more convenient to weigh the sample in a weighing bottle, transfer it to a suitable volumetric flask, dilute to volume, and pipet a 5-ml. aliquot into the distilling flask. The sample is covered with 2 to 3 ml. of water, and 2 drops of phenolphthalein indicator solution are then added. Sodium hydroxide solution (about 40 per cent) is introduced in slight excess as determined by the indicator. The flask is immediately attached to the outfit and steam is passed into it. A steam pressure of 456 to 608 kg. per sq. meter (1.5 to 2 feet of water) is maintained throughout the run. The beaker used to receive the distillate contains 3 ml. of hydrochloric acid (1 to 4) and about 5 ml. of water. As soon as the distillation proceeds at a smooth rate, the microburner should be used to reduce the volume of liquid in the flask. Distillation is continued for 30 minutes, at the end of which time the liquid in the distilling flask should be reduced almost to dryness and the volume of distillate should preferably not exceed 100 ml. When the distillation is complete, the condenser and delivery tube are washed out and the volume of distillate is adjusted to about 100 ml.

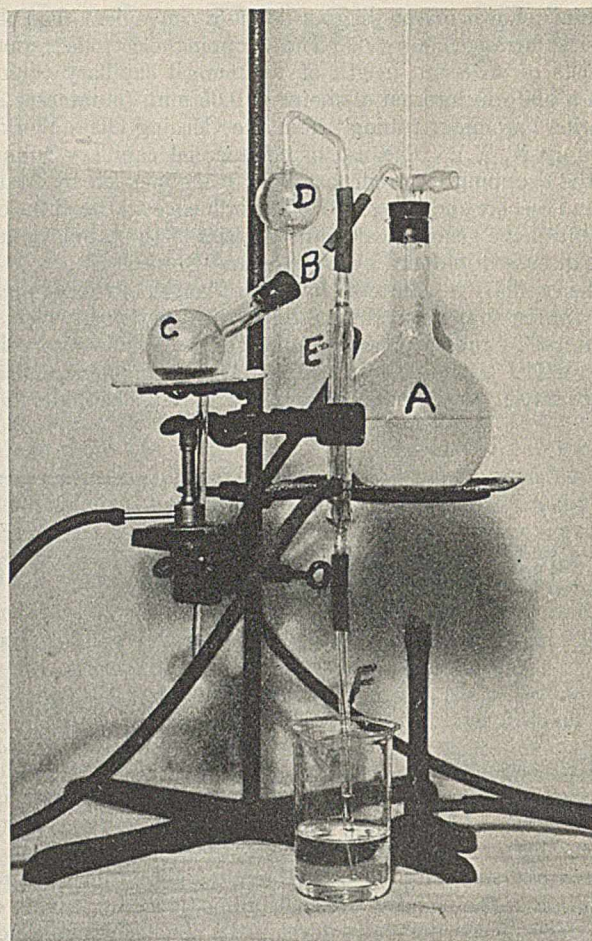


FIGURE 1. APPARATUS

To precipitate the nicotine, 1 ml. of silicotungstic acid (12 per cent solution) is used for every 10 mg. of nicotine or less. After precipitation the covered samples are heated on the steam bath for 15 minutes, cooled slowly to room temperature, and maintained at 0° to 10° C. overnight. The samples are filtered through C. S. and S., No. 589, white ribbon filter paper, and washed with 100 to 200 ml. of hydrochloric acid (1 to 2000). Further determination of the nicotine is made according to the procedures of the A. O. A. C. (1).

TABLE III. ANALYSIS OF LIQUID NICOTINE

Method	No. of Determinations	Stock Solution Ml.	Nicotine Present Mg.	Nicotine Found			% Av.
				High Mg.	Low Mg.	Av. Mg.	
Direct precipitation	3	5	5.80	5.78	5.77	5.78	99.67
	5	10	11.60	11.65	11.54	11.60	100.00
	5	25	29.00	29.10	29.00	29.04	100.14
New method of distillation	2	5	5.80	5.83	5.83	5.83	100.52
	2	10	11.60	11.63	11.58	11.61	100.08

### Tests of the Procedure

A large number of preliminary experiments were made to determine the length of time necessary for complete distillation of nicotine. No difficulty was experienced in obtaining complete recovery of the nicotine from tobacco powders and proprietary preparations, using a distillation period of 20 minutes. As a safety measure in routine work, it is better to continue the distillation for 30 minutes. Accordingly, 30 minutes has been given as the distillation time in the procedure described above. To analyze a sample of tobacco un-



TABLE IV. DETERMINATION OF NICOTINE IN A COMMERCIAL NICOTINE SULFATE SOLUTION

Method of Analysis	Weight of Sample Grams	Aliquot		Alkali Used	Nicotine in Aliquot Mg.	Nicotine Found %	
		For analysis	For precipitation				
A. O. A. C. (1)	1.0896 2.0203	...	25/500	NaOH	21.87	40.14	
		...	10/500	NaOH	16.23	40.17	
				NaOH	16.20	40.09	
					Av.	40.13	
Proposed method	1.0438	5/250	...	NaOH	8.47	40.57	
				NaOH	8.47	40.57	
				NaOH	8.46	40.53	
				Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	8.47	40.57	
					8.44	40.43	
	Av.	40.53					
Aliquot diluted and precipitated directly	1.0438	5/250	...	...	8.54	40.91	
					8.54	40.91	
					8.53	40.86	
					8.56	41.00	
	Av.	40.92					
Diluted aliquot filtered through 9-cm., C. S. and S., No. 589, white ribbon filter paper before precipitating nicotine	1.0438	5/250	...	...	8.36	40.05	
					8.37	40.09	
						Av.	40.07

TABLE V. ANALYSES OF COMMERCIAL TOBACCO POWDERS

Sample	No. of Determinations	Method of Analysis	Weight of Sample Grams	Aliquot for Precipitation	Average Nicotine Obtained Mg.	Nicotine Found		
						High %	Low %	Av. %
	2	A. O. A. C.	5.0	200/500	9.84	0.51	0.47	0.49
	2	Proposed method	0.3		1.52	0.52	0.50	0.51
2	2	A. O. A. C.	3.0	200/500	14.29	1.19	1.19	1.19
	2	Proposed method	0.3		3.45	1.15	1.15	1.15
3	2	A. O. A. C.	2.0	200/500	16.20	2.07	1.98	2.03
	2	Proposed method	0.3		5.89	1.97	1.95	1.96
4	2	A. O. A. C.	2.0	100/500	8.21	2.07	2.03	2.05
	2	Proposed method	0.3		6.05	2.02	2.02	2.02

usually rich in nicotine, it would probably be necessary to modify the procedure by decreasing the size of the sample taken for analysis or by increasing the length of time of distillation.

To show that complete recovery of nicotine is obtained by the method described, 1.160 grams of Merck's c. p. nicotine were acidified with a little dilute hydrochloric acid and made to a volume of 1 liter. Aliquots of this stock solution were used for trial determinations, diluting 5-, 10-, and 25-ml. portions to 100 ml., adding 3 ml. of hydrochloric acid (1 to 4), and determining the nicotine with silicotungstic acid solution as previously described. Another series of aliquots was steam-distilled according to the new procedure. The results of these determinations, given in Table III, show that complete recovery of the nicotine was obtained. The high results are probably due to retention of some reagent in the filter paper and some adsorption on the precipitate itself.

In Table IV are recorded the results of several methods of determining nicotine in a sample of commercial nicotine sulfate solution, guaranteed to contain 40 per cent of nicotine. In the first series, the method of the A. O. A. C. was used (1). In the second series, where the new distillation procedure was used, the amount of sodium hydroxide solution was varied from a bare excess to 6 drops in excess. Solid barium hydroxide [Ba(OH)<sub>2</sub>·8H<sub>2</sub>O] was used as the alkali in some cases and was added in amounts varying from 0.2 to 0.5 gram. Two series were run in which aliquots of the diluted sample were analyzed without previous distillation.

The new method of distillation gives slightly higher results than the method of the A. O. A. C. (1) and indicates more complete recovery of nicotine. The high values obtained in the case of direct precipitation indicate the presence of nonvolatile impurities in the material. The low results from the filtered samples indicate that the filter paper retains some nicotine. The authors have obtained other evidence that filter paper adsorbs nicotine under certain conditions.

Four finely ground and air-dried samples of commercial tobacco powder were analyzed by the two methods and the results recorded in Table V. In every case except the first, where the percentage of nicotine was very low, lower but more consistent results were obtained by the new method—just the opposite of what occurred in the analysis of nicotine sulfate solutions. However, the samples used in the A. O. A. C. method contained larger amounts of nicotine than those used in the new method. Table III shows that for direct precipitation, the aliquots containing larger amounts of nicotine gave higher results. These differences can be explained on the assumption that adsorption or occlusion of silicotungstic acid takes place to a much greater extent where large amounts of nicotine are being precipitated.

A series of experiments, using the new apparatus, was carried out to show the effect of using varying amounts of different alkalies—sodium hydroxide and barium hydroxide. The barium hydroxide was weighed to the nearest 10 mg. and the sodium hydroxide was introduced as drops of a strong sodium hydroxide solution, whose strength was previously determined by titration. The tobacco powder employed in these analyses was sample 2 used in the comparison of the two methods of distillation. Table VI shows that excessively large amounts of sodium hydroxide give abnormally high results. This is not true of barium hydroxide and can be explained on the ground that barium hydroxide reaches a limit of solubility and hence much less alkali can be present in solution. It seems probable that the higher results obtained with large excesses of sodium hydroxide are due to something besides nicotine. Whatever may be the cause, for more consistent results the sodium hy-

TABLE VI. EFFECT OF TYPE AND AMOUNT OF ALKALI USED FOR NICOTINE IN TOBACCO POWDERS

Alkali	(Weight of sample, 0.3 gram. Distillation time, 20 minutes)	
	Weight of Alkali Grams	Nicotine Found %
NaOH	0.025	1.12
	0.12	1.13
	0.60	1.15
	1.20	1.24
	2.30	1.24
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	0.05	1.10
	0.10	1.14
	0.30	1.15
	0.50	1.14
	1.00	1.15
	2.00	1.14



dioxide should be limited to a slight excess over that necessary to produce an alkaline reaction or the use of solid barium hydroxide should be adopted.

### Acknowledgment

The authors are indebted to G. E. R. Hervey for the photograph of the apparatus described in this paper.

# Thallos Carbonate as an Acidimetric Standard

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HAC and Kámen (2) have suggested the use of thallos carbonate as an acidimetric standard, and Berry (1) has recommended it for standardizations of acids and potassium iodate.

Without knowledge of these two papers, a thorough investigation of thallos carbonate was started with the purpose of establishing its suitability for standardizing acids, and is reported fully elsewhere (3). Some of the observations made command interest in this connection.

With regard to preparation of the salt, the effect of thallos carbonate on glass appears to have escaped notice. It was found that only platinum vessels in recrystallizations will give pure thallos carbonate.

Hac and Kámen have chosen the extraordinary way of providing the absence of copper, lead, and bismuth in the thallos nitrate used for the preparation, but testing the carbonate itself for only sodium and nitric acid. In the case of sodium the sensitivity of the test was not established. Neither they nor Berry gives tests for purity applicable to an unknown sample of the carbonate. Having spectroscopically ascertained the sufficient purity of a sample, tests with and without the addition of the impurity show that the following tests will prove the absence of (<0.01 per cent present) magnesium, calcium, barium, aluminum, iron, manganese, lead, silver, mercury, potassium, sodium, chloride, nitrate, and sulfate.

If 0.5 gram of the substance gives a perfectly clear solution in 5 ml. of hot water, the absence of magnesium, calcium, barium, aluminum, iron, manganese, and lead is indicated.

If 0.5 gram of the substance dissolved in 5 ml. of 2N sulfuric acid gives neither precipitate nor coloration with hydrogen sulfide the absence of silver and mercury is indicated.

Five grams dissolved in 100 ml. of water are added to 5 ml. of bromine covered with a layer of water, and 25 ml. of 25 per cent ammonia are then slowly added to the mixture. The precipitate of thallic hydroxide is filtered off and washed once with water. The combined filtrates are evaporated to dryness in a platinum crucible and the ammonium salts driven off. The crucible is weighed and the residue extracted with 10 ml. of hot water. The washed and dried crucible is re-weighed. Loss in weight not exceeding 0.5 mg. shows absence of potassium and sodium.

If 0.5 gram in 5 ml. of 2N nitric acid gives no opalescence with silver nitrate, the absence of chloride is shown.

When 0.5 gram is boiled with 1 ml. of water, cooled, and mixed with an excess of a 1 per cent solution of diphenylamine in concentrated sulfuric acid, no coloration shows absence of nitrate.

To show absence of sulfate, 0.5 gram is dissolved in 3 ml. of 2N of hydrochloric acid and cooled. The solution is decanted and evaporated to a very small volume (approximately 0.5 ml.). After cooling, the liquid is decanted and one drop of a 5 per cent solution of barium nitrate is added. If no turbidity occurs on standing for 12 hours, no sulfate is present.

It was confirmed that thallos carbonate is stable up to at least 150° C. and nonhygroscopic up to 80 per cent relative humidity and that it does not absorb carbon dioxide from air.

Bromocresol purple was found to be a most suitable indicator, particularly as it gives a perfectly sharp end point in boiling solution.

### Literature Cited

- (1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 4th ed., pp. 60-1 (1935).
- (2) Spies, J. R., *IND. ENG. CHEM., Anal. Ed.*, 9, 46-7 (1937).
- (3) Spies, J. R., *J. Am. Chem. Soc.*, 58, 2386-8 (1936).

APPROVED by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 329.

To give a practical proof of the suitability of thallos carbonate, the normality of hydrochloric acid was established by gravimetric determinations of the chloride, and by standardizations against sodium carbonate. This acid was then used to determine the strength of the different samples of thallos carbonate. The results were:

Gravimetric. *N* HCl: 0.10066, 0.10070, 0.10075, 0.10071, 0.10073; mean, 0.10071 ± 0.014 per cent  
Standardization against Sodium Carbonate. *N* HCl: 0.10076, 0.10069, 0.10068, 0.10077; mean, 0.10073 ± 0.024 per cent  
*N* HCl used as Standard. *N* = 0.10072 (±0.02 per cent)

TABLE I. STRENGTH OF THALLOUS CARBONATE

Sample	%	Mean %
Recrystallized in glass vessels. (After taking each sample the bulk was recrystallized.)		
1	99.89, 99.91	99.90
2	99.78, 99.75	99.76
3	100.05, 100.02	100.04
4	99.88, 99.87	99.88
5	99.96, 99.96	99.96
6	100.08, 100.08	100.08
7	100.03, 100.04	100.03
Recrystallized in alkali-resistant glass		
1	99.84, 99.85	99.84
2	100.05, 100.06	100.06
3	99.87, 100.06	99.96
Recrystallized in platinum vessels		
1	99.89, 99.91	99.90
2	100.02, 100.01	
	100.02, 100.03	
	99.99, 100.05	
	100.02, 100.03	100.02
	99.99	
3	100.01, 100.00	100.00
	100.01	100.00

A comparison between the figures for gravimetric determinations and standardizations against sodium carbonate and thallos carbonate shows that the individual determinations are in closer agreement with each other (standard deviation 0.017 per cent), whereas greater discrepancies are found among the determinations made gravimetrically (standard deviation 0.03 per cent) or with sodium carbonate (standard deviation 0.04 per cent).

Avoiding glass in the final recrystallizations, thallos carbonate can be readily prepared in a pure state and is then excellently suited as an acidimetric standard.

### Summary

Tests to determine the purity of thallos carbonate as a primary standard in acidimetry have been described.

The results obtained by standardizing hydrochloric acid in various ways agree very closely with those obtained using thallos carbonate recrystallized in platinum.

### Literature Cited

- (1) Berry, *Analyst*, 64, 27 (1939).
- (2) Hac and Kámen, *Chem. Listy*, 26, 6 (1932); *Collection Czechoslov. Chem. Commun.*, 4, 145 (1932).
- (3) Jensen and Nilssen, *Arkiv. Mat. Naturvidenskap*, 42, No. 6 (1939).



# A Device to Prevent Bumping and Promote Boiling

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NUMEROUS devices have been advocated to prevent bumping in distillation, but with possibly one exception (1) none has proved completely dependable.

Most of them function fairly well at the start of a distillation, and as long as boiling is not interrupted. However, temporary removal of the source of heat, the addition of more liquid to the distillation flask, or an increase in pressure, in the case of vacuum distillation, often renders the devices ineffective.

The need for a convenient and dependable device to ensure smooth ebullition is particularly acute in fractional distillation at reduced pressure, where bumping may cause flooding and otherwise seriously disturb the operation of the column.

The "boiling tube," glass beads, broken glass, boiling stones (Carborundum), and a gas stream (particularly for vacuum work) probably find most frequent use because of their simplicity. Glass wool, as proposed by Morton (1), is one of the most effective, but a considerable quantity of the wool is required. Because of the large holdup due to the packing, as shown in Table I, it is impossible to recover small pot residues without extensive dilution by wash solvent.

TABLE I. LIQUID HOLDUP OF GLASS WOOL

Drainage Time Min.	Liquid Retained, <sup>a</sup> No Packing				Liquid Retained, <sup>a</sup> 70 Grams of Glass Wool			
	Tur- pen- Cc.	Ethyl alco- hol Cc.	H <sub>2</sub> O Cc.	Pine oil Cc.	Tur- pen- Cc.	Ethyl alco- hol Cc.	H <sub>2</sub> O Cc.	Pine oil Cc.
5	2	2	1	4	64	55	100	112
30	1	1	1	2	51	42	86	87
40	1	1	1	2	40	41	86	85
60	..	..	..	..	39	41	86	85
160	..	..	..	..	39	..	..	66
1100 (about 19 hours)	..	..	..	..	..	..	..	57

<sup>a</sup> Cc. retained = cc. added - cc. drained.

In these experiments a measured quantity of liquid was poured into a 2-liter round-bottomed flask, shaken to wet the flask and glass wool thoroughly, and then inverted and drained. The flask was shaken six times during each test to break up pockets of liquid in the glass wool, and thus speed up drainage.

TABLE II. PRACTICAL TESTS WITH PROPOSED DEVICE

Experi- ment No.	Bath for Still Type	Pot Temp. ° C.	Vapors in Still Pot ° C.	Immersion Heater		Watts	Distilla- tion Pres- sure Mm. Hg
				Temp. of Oil Bottom ° C.	Top ° C.		
1	Steam	100	88	93	95	7	60
2	Steam	100	88	89	89	0	60
3	Oil	121	88	95	100	7	60
4	Oil	122	88	96	100	16	60
5	Oil	121	91	108	121	18	10
6	Oil	194	153	176	186	20	190

The device described in this paper has been subjected to rigid experimental tests under varying conditions of use. A few experimental runs are recorded in Table II.

## Principal Features

All parts coming in contact with the liquid to be distilled are of glass.

A large promoting surface is provided, consisting of glass thread closely wound around a glass "heater tube." This tube is heated by an easily controlled external means, independent of the heat source for the distillation proper, and activates the glass thread.

The very close contact of the glass thread with the source of heat renders the thread itself comparable to a continuous "hot wire," without introducing hot metal into the distillation liquid.

The glass thread winding extends from the bottom of the distillation flask to a point well above the surface of the liquid being distilled. Boiling is thus promoted over a large surface throughout the depth of the liquid.

The device is compact. The thread does not retain any significant amount of the residual liquid, and can easily be cleaned by washing with solvent.

As the heating medium for the boiling promoter is not in direct contact with the liquid being distilled, any suitable means of supplying heat may be used. When the temperature of the liquid being distilled is not above 90° C., steam may be used very effectively. Oil heated by a rheostat-controlled electric immersion heater made of coiled asbestos-covered wire has been found to serve very well over a wide range of temperatures. In this way a satisfactory temperature differential between the heating medium of the device and the liquid being distilled can be established, and functioning of the device ensured.

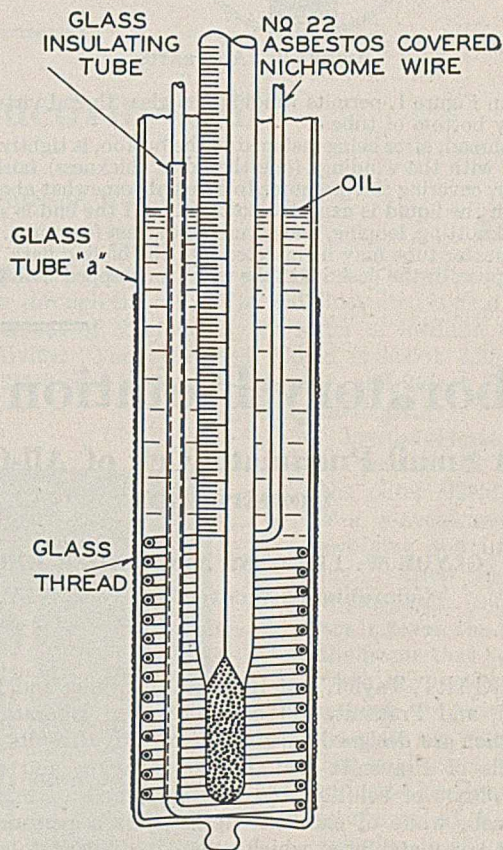


FIGURE 1. HEATER TUBE

This device may also be used in a limited way to provide heat for the distillation. It is best used, however, as a bumping preventer and boiling promoter only, the heat for the distillation proper being provided independently by an oil bath, a steam bath, an electric heater, or other suitable means.

## Construction of Boiling Promoter

The heater tube proper is essentially a wide test tube, the bottom of which is pushed up, and has a small glass button sealed to it to permit fastening the glass thread. This construction, as



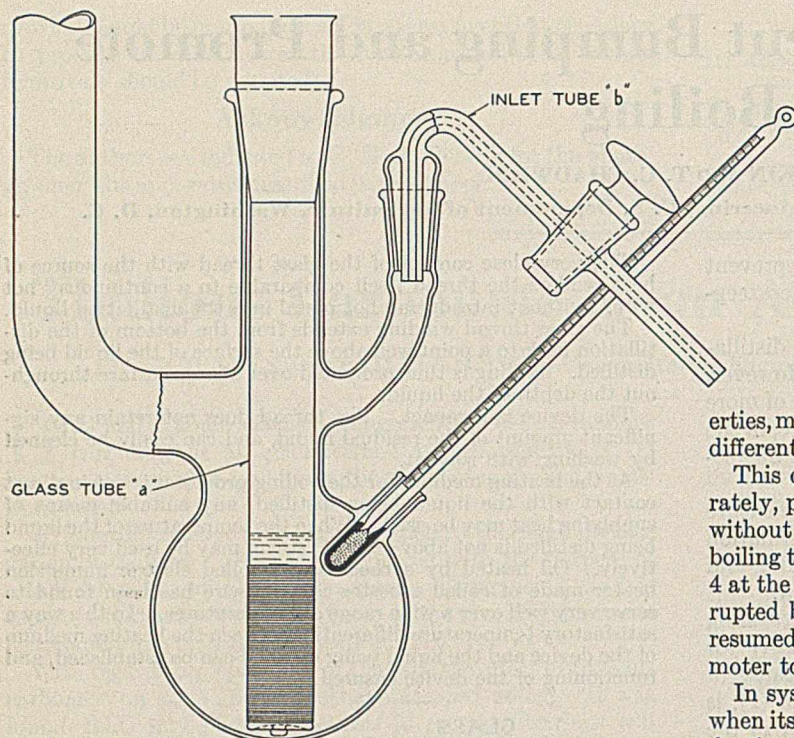


FIGURE 2. APPARATUS

shown in Figure 1, permits winding the glass thread virtually to the very bottom of tube *a*.

The thread, after being fastened to the button, is tightly wound upward with the windings (one thread in thickness) fairly close together, covering the promoter to a height somewhat above that to which the liquid is expected to reach, and the end is securely tied by knotting, looping, and reversing the last few turns.

The heater tube may be inserted into the boiling flask by way of a stopper, or the flask and tube may be equipped with ground-

glass joints, as shown in Figure 2. In that case, careful adjustment of the height of the joint on the flask will have to be made, so that the promoter will just clear the bottom of the flask.

In order to test its effectiveness the device was used not only with a number of liquids, including water, acetone, ether, ethyl alcohol, benzene, methyl chavicol, anethole, fenchyl alcohol, turpentine, terpinolene, and pine oil, in simple distillations at varying pressures, but also as a unit incorporated in a plate column assembly for systematic fractionation. Data on a few typical experiments are recorded in Table II.

As may be seen from experiments 1 and 3, the use of steam, because of its superior heat-transfer properties, makes it possible to operate at a much lower temperature differential between bath and still pot than when oil is used.

This device can also function without being heated separately, provided the distillation is not allowed to stop. Thus, without supplying electric current to the promoter, smooth boiling took place throughout experiment 2, and in experiment 4 at the beginning only. In the latter case, boiling was interrupted by addition of cold turpentine. Smooth boiling was resumed only after supplying sufficient current to the promoter to raise its internal temperatures to 96° and 100° C.

In systematic fractional distillation, the device works best when its temperature is carried sufficiently high so that introduction into the system of additional liquid will not inactivate the promoter but interrupt the boiling only long enough for the added material to be heated to the boiling point. Data were obtained in experiment 5 in a normal systematic fractionation of a high-boiling terpene hydrocarbon, during which the device functioned continuously.

#### Literature Cited

- (1) Morton, "Laboratory Technique in Organic Chemistry," New York, McGraw-Hill Book Co., pp. 104-5, 1938.

## Laboratory Flotation Cell

### A Small Pneumatic Cell of All-Glass Construction

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TAGGART, Taylor, and Ince (3), Oberbillig and Fahrenwald (1), and Prausnitz (2) have described laboratory flotation cells which are designed to give quantitative results. However, the cells of Prausnitz and Taggart, Taylor, and Ince use a large volume of solution and a large sample of mineral. The latter cell, while of excellent design, has a perforated rubber disk and a metal base which make it difficult to clean. The Prausnitz cell is constructed entirely of glass, but both it and the Oberbillig and Fahrenwald cell have flaring tops which cause the froth to collapse during operation, necessitating manual removal of the froth in order to get quantitative results.

The cell described here can be made entirely from glass, and has been designed to work in a setup such as that described by Oberbillig and Fahrenwald (1) for controlling the air flow. Compressed air has been found satisfactory as an air source, each run being made at the same pressure reading on the differential manometer. Each run requires only 50 cc. of solution in the cell, and a 5-gram mineral sample (<200 mesh) gives reproducible results. In order to keep a constant volume in the cell during the run, the solution must be added

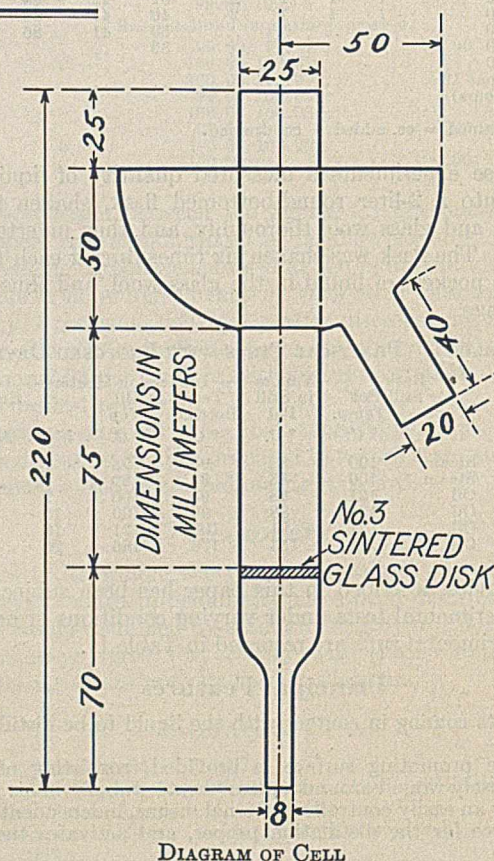




TABLE I. FLOTATION DATA

Solution	Concn. of Reagent P. p. m.	Galena Grams	Pulp Density %	Recovery %	Galena per Cc. Overflow Gram
Water	...	5.00	10	10.2	0.011
α-Naphthylamine	170	5.00	10	40.0	0.057
	170	10.00	20	22.2	0.092
	170	20.00	40	23.1	0.145
	340	2.00	4	57.8	0.020
	340	5.00	10	60.4	0.061
	340	10.00	20	63.7	0.162
Potassium ethyl xanthate	340	20.00	40	57.8	0.327
	25	5.00	10	75.9	0.118
	25	10.00	20	87.5	0.199
	25	20.00	40	87.6	0.319
	50	5.00	10	82.2	0.117
	50	10.00	20	87.5	0.208
	50	20.00	40	72.0	0.351
	100	5.00	10	84.5	0.094
	100	10.00	20	85.8	0.228
	100	20.00	40	92.7	0.501

from a dropping funnel to compensate for that lost as overflow. The volume of solution added is usually 30 or 40 cc. The duration of each run is 15 minutes.

The column of the cell is made of 2.5-cm. (1-inch) Pyrex tubing drawn out at one end to fit into the mouth of a suction flask which is used as an air reservoir. A standard No. 3 sintered-glass disk sealed into the column has been found to give good bubbling action. The recovery trough is sealed to the column and an out-

let tube is sealed into the trough at the bottom, so that the overflow can be run directly into a filtering crucible for filtering and weighing if desired.

The data given in Table I are taken from unpublished work by Knoll, Leaf, and Baker on the collecting action of α-naphthylamine on galena. The data on potassium ethyl xanthate are included to show the recovery of mineral when a better collecting agent than α-naphthylamine is used. The cell described in this paper was used in all cases, although results with the Oberbillig and Fahrenwald and Taggart, Taylor, and Ince cells are comparable.

When solutions which contained no collecting agent were used in the cell, the weight of mineral (galena) recovered depended directly upon the volume of overflow. When solutions containing collecting agents were used in the cell, the percentage recovery of mineral (galena) was independent of the volume of overflow.

Literature Cited

- (1) Oberbillig, E., and Fahrenwald, A. W., *Mining J.* (Phoenix, Ariz.), 22, No. 1, 7 (1938).
- (2) Prausnitz, P. H., "Glas- und keramische Filter," p. 129, Leipzig, Akademische Verlagsgesellschaft, 1933.
- (3) Taggart, A. F., Taylor, T. C., and Ince, C. R., *Am. Inst. Mining Met. Engrs., Tech. Pub.* 204, 25 (March, 1929).

## A Dipping-Type Conductivity Cell

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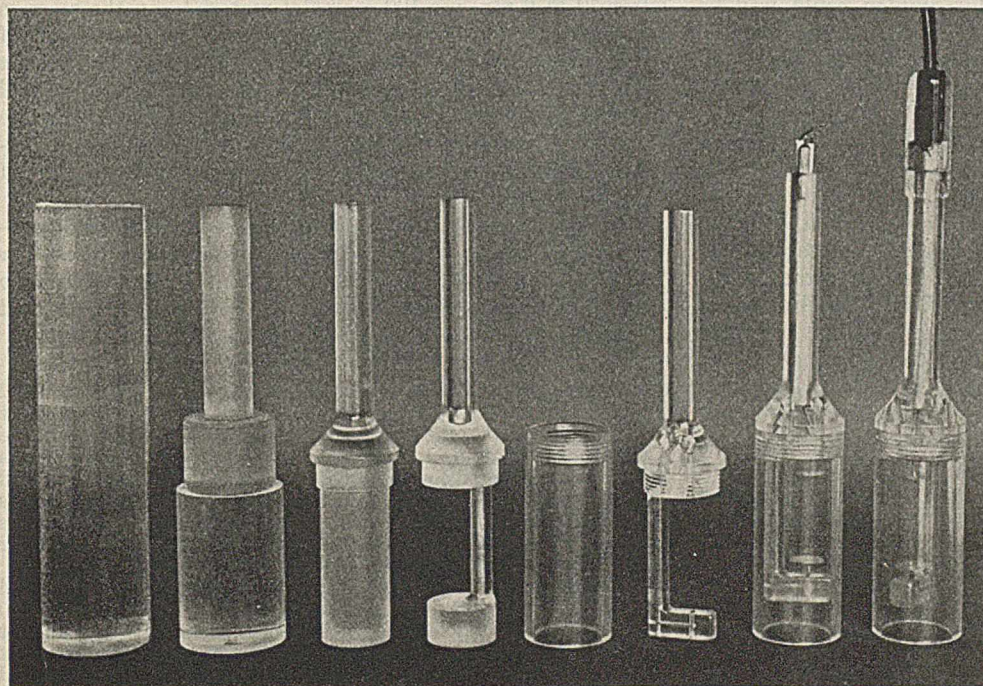
THE accompanying illustration shows steps in the manufacture of a conductivity cell, which has been found very useful in measuring the conductivity of water samples in the field and in the laboratory. The cell is made of lucite and is of the commonly used dipping type, with a full-sized opening at

the bottom and several holes at the top to permit circulation of water through the cell. The cell illustrated is used for the measurement of conductivity of water of medium to high conductivity. The cylindrical shield is about 3.25 inches long, 1.25 inches in outside diameter, and 1 inch in inside diameter.

The use of lucite makes it possible to remove the outer shield, which is a convenience in assembling and in cleaning. After the electrodes and lead wires are in place, the holes in the frame that holds the wires are sealed with a cement prepared especially for use with lucite. For field use a cylinder of lucite has been used, instead of a glass cylinder, to contain the sample during the measurement.

The platinum electrodes and the lead wires were purchased from a manufacturer and the cells were made in the Geological Survey instrument shops.

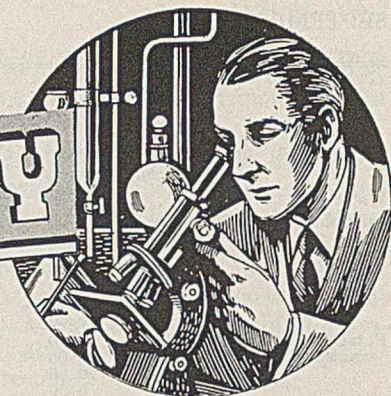
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STEPS IN THE CONSTRUCTION OF A CONDUCTIVITY CELL



# MICROCHEMISTRY



## Determination of Urea

### In Material Used for Filling in Articles of Bedding and Upholstered Furniture

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THE Massachusetts law pertaining to articles of bedding and upholstered furniture is administered by the Massachusetts Department of Public Health. This law provides in part that each article of bedding or of upholstered furniture shall be plainly marked with a statement in English of the kind of material used for filling, the name of the manufacturer or vendor, and, if the material has previously been used, the words "second hand." "Previously been used" means used as a part or portion of another manufactured article, or for any other purpose. A 1936 amendment permits the use of clippings of new cloth under the name of new material in the manufacture of upholstered furniture.

In early attempts to enforce this law it was necessary to rely upon experts from the waste trades for extremely unsatisfactory testimony regarding the secondhand nature of the material used for filling. The last such expert used by the department stated on the witness stand that very obviously secondhand material in his opinion could well be characterized as new within the understanding of the trade. The defendant was found not guilty, and the judge expressed regret that he was obliged to rely on the testimony of the expert for his decision.

The department then used an ultraviolet lamp to differentiate between new and secondhand material. The method (9) is simple and rapid, as it consists of examining the materials in a dark room by strong ultraviolet light (3130 to 4045 Å.), and noting the color and intensity of the fluorescence. In the case of new raw or bleached cotton the fluorescence ranges from red-violet to blue-violet. In the case of cotton impregnated with urine or perspiration, it is pale blue if the impregnation is fresh and ivory if the impregnation is at least a month old. The reliability of this method depends on ability to judge colors and shades of color and to interpret their significance. Colors and shades of color are difficult to describe; for that reason the chemist should familiarize himself, by actual examination, with known new and secondhand materials which he should keep on hand for comparison with unknown materials being tested. This method is best suited for the examination of raw or bleached cotton, and is obviously useless for dyed materials and for animal fibers.

However, more satisfactory methods were needed. It occurred to one of the authors (Racicot) in 1934 that it might be possible to detect the presence of urea in material that had been in contact with the human body long enough to absorb

minute quantities of urine or perspiration, and by such a method to prove that the material had been previously used. After considerable research work, qualitative methods for urea and creatinine were adopted and used successfully in a contested case where the defendant introduced expert testimony.

In July, 1935, there appeared an article (10) by Yee and Davis upon the microdetermination of urea. This method was immediately studied and modified considerably in order to utilize apparatus used in the determination of ammonia in eggs, meat, and meat products (2). This modified method has been used with success to date.

In September, 1935, the authors' attention was brought to the method of Moskowitz, Landes, and Himmelfarb (3) for distinguishing between new and secondhand cotton filling materials. This article listed analyses of thirty-six samples of so-called new cotton wastes with a urea content ranging from 0 to 9 mg. per 100 grams of material—on the average considerably higher than the values found by the authors of the present article in waste material which they had reason to believe was not secondhand. These high figures, as well as the presence of small amounts of urea in the new waste materials in somewhat constant concentration, were attributed to the presence of urease, which is a constituent of certain seeds.

In order to ascertain whether cottonseed or raw cotton contains urea, whether cottonseed contains urease, and whether the reaction under ordinary conditions is reversible, the following experiments were made with cottonseed, linters, and raw cotton.

**EXPERIMENT 1.** Ten grams of cottonseed were soaked for 2 hours in water at a temperature of about 35° C. The extract was filtered from the seeds, the seeds were washed, and the filtrate was made up to 100 cc. Five cubic centimeters of this extract were tested for the presence of urea by the Nieloux and Welter microgravimetric method (4), which gives reliable results for quantitative determination as small as 0.05 mg., or if used as a qualitative test will detect the presence of one part of urea per million. No urea was found in this solution.

**EXPERIMENT 2.** Ten grams of cottonseed were taken, soaked in warm water, and filtered, and the filtrate was made up to 100 cc. Two aliquots of 20 cc. each were then taken; to 1 aliquot were added 100 mg. of urease, and the mixture was fermented at 50° C. for 15 minutes. A blank containing the urease in distilled water was similarly treated. All three were then subjected to the Folin aerometric method (2) for the determination of ammonia,



using Nessler solution as the reagent. The blank contained 0.074 mg. of ammonia, the unfermented extract contained 4.69 mg., and the fermented extract contained 4.76 mg. Subtracting the blank from the fermented extract result gives a figure identical with that of the unfermented extract. Consequently no urea was present in the cottonseed.

Several samples of raw cotton of known purity were examined by this method, and no urea was found.

The following experiments were undertaken to determine whether or not cottonseed contains urease.

**EXPERIMENT 1.** Five grams of cottonseed were placed in a wide-mouthed flask, and 20 cc. of urea solution containing 18 mg. of urea were added, with sufficient distilled water to cover the seeds. The material was allowed to stand overnight, filtered, and washed, and the filtrate was made up to a volume of 100 cc. Twenty cubic centimeters of the urea solution containing 18 mg. of urea were placed in a 100-cc. volumetric flask, and the solution was made up to the mark with distilled water. A 5-cc. aliquot of each solution was taken, and urea determinations were made upon each by the Nicloux and Welter method. The solution containing the cottonseed extract and urea was found to contain 0.914 mg. of urea. The solution containing the urea alone was found to contain 0.900 mg. of urea.

The water extract was filtered and treated with acetone according to Van Slyke's method (6) for extracting urease from the jack bean. The residue obtained by evaporation of the acetone extract was dissolved in water, urea was added, and the solution was then incubated at 50° C. for 15 minutes in a flask. A few drops of methyl orange indicator were added; the solution remained neutral after 24 hours, showing the absence of free ammonia. From this experiment we must conclude that the cottonseed was free from urease.

The following experiments were undertaken to determine whether or not the reaction of urease or urea is reversible. Urease will convert urea into ammonium carbonate, and this when warmed will split into water, ammonia, and carbon dioxide.

In one experiment three wide-mouthed flasks were used. To one flask were added 5 grams of cottonseed covered with linters and impregnated with 100 mg. of urease powder; to the second flask, 5 grams of clean absorbent cotton impregnated with 100 mg. of urease powder; and to the third flask, 100 mg. of urease powder. To each flask was added some moistened ammonium carbonate. The flasks were stoppered and allowed to stand at

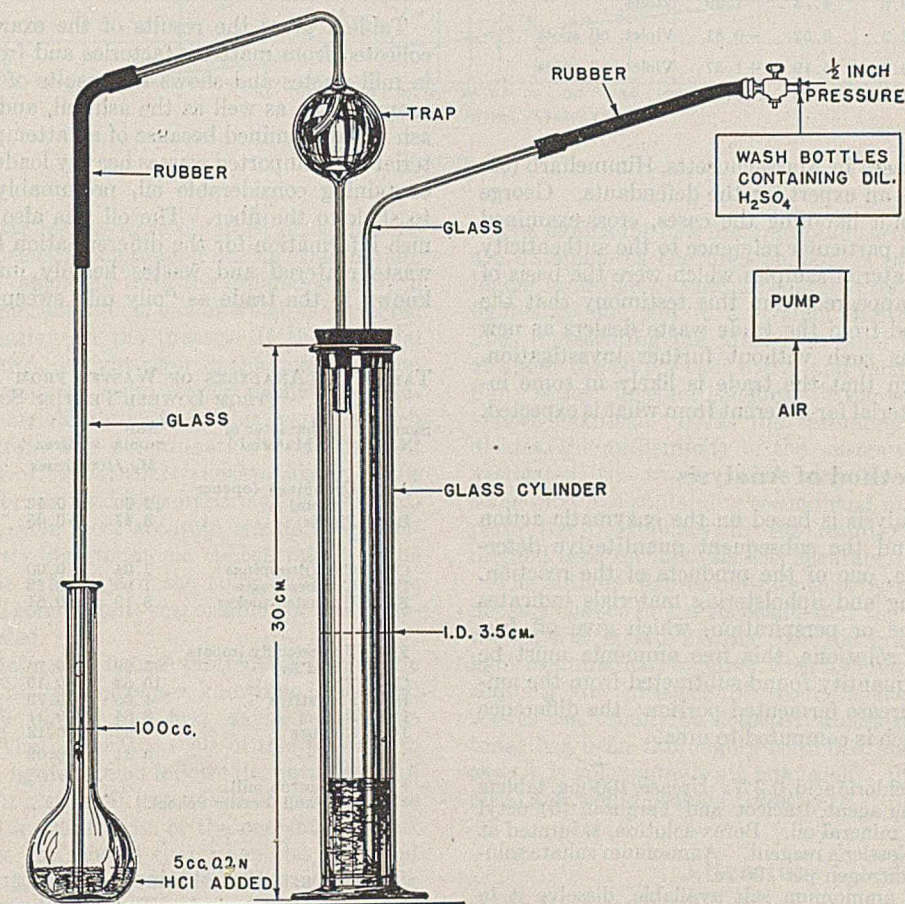


FIGURE 1. AERATION APPARATUS

If the cottonseed contained urease, part of the urea should have been hydrolyzed to ammonia and carbon dioxide, and, therefore, the urea in the solution containing the cottonseed extract should have been less instead of more than in the urea solution alone. From this experiment we must assume that there was no urease in the cottonseed at the authors' disposal.

**EXPERIMENT 2.** The cottonseed used in experiment 1 was unbroken and was covered with so-called linters. Urease when found in seeds containing this material is in the cotyledons and not in the hulls. In order to ascertain whether urease may have been present in the cotyledons, a 100-gram sample of the cottonseed was ground to a fine meal, and this meal was then extracted

room temperature overnight, and the contents were then analyzed for urea. No urea was found in any flask, in spite of the fact that the urease was exposed for several hours in an atmosphere saturated with ammonia, carbon dioxide, and water, which naturally would be most favorable conditions for reversing the reaction.

A large piece of filter paper was impregnated with 100 mg. of urease and hung up in the laboratory for 30 days. The atmosphere of the laboratory should contain at least as much ammonia, carbon dioxide, and water as is found in a cotton storage warehouse. After 30 days this filter paper was analyzed for urea; no urea was found.



TABLE I. ANALYSES OF TRADE WASTE OBTAINED FROM MATTRESS FACTORIES AND FROM TRADE WASTE DEALERS

Trade Designation	Ash %	Oil %	Ammonia Mg./100	Urea grams	Fluorescence in Ultraviolet Light
Picker	5.52	2.3	20.40	0.74	Violet, oil spots, yellow spots
Picker and fly	3.30	0.5	7.81	-1.18	Violet, dirty
	3.12	0.3	6.17	-0.83	Violet, oil spots
	5.14	1.2	10.10	-0.79	Violet, dirty
	3.32	0.8	8.33	-0.46	Violet, oil spots
	3.24	2.0	10.75	-0.11	Violet, oil spots
	2.86	0.5	4.65	+0.05	Violet, oil spots
	2.35	0.5	6.58	0.16	Violet
	3.89	0.7	7.40	0.32	Violet, few oil spots
	3.47	2.9	1.97	0.40	Violet, oil spots, dirty
	2.83	0.7	10.10	0.58	Violet, dirty
3.00	0.8	5.26	1.58	Violet, dirty	
Fly	3.84	0.8	6.94	1.48	Violet
	3.40	1.5	13.88	1.67	Violet, oil spots, dirty
Cotton felt	1.98	0.7	4.07	1.48	Violet
Garnetted felt	2.02	0.7	6.19	-1.04	Violet, oil spots
	1.87	0.4	6.57	-0.35	Reddish violet
1st grade	2.31	1.3	5.17	+0.79	Violet
	1.78	0.4	5.19	-0.09	Violet
2nd grade	1.46	0.4	3.63	+0.84	Violet
	2.05	1.0	5.19	0.70	Violet
China garnetted felt	1.65	0.7	4.67	1.69	Violet
	0.91	0.5	3.40	1.14	Violet
	0.94	0.8	4.73	1.99	Violet
Rollers	2.80	2.2	6.52	-0.81	Violet, oil spots
Strip	3.69	0.6	5.19	+1.37	Violet, oil spots
Av.	2.80	1.08	6.96	0.44	

In two contested cases in Massachusetts, Himmelfarb (co-author, 3) testified as an expert for the defendants. George L. Drury, the inspector handling the cases, cross-examined Mr. Himmelfarb with particular reference to the authenticity of the alleged new-material samples which were the basis of his publication. It appeared from this testimony that the material was obtained from the trade waste dealers as new and was accepted as such without further investigation. Experience has shown that the trade is likely in some instances to submit material far different from what is expected.

### Method of Analysis

The method of analysis is based on the enzymatic action of urease on urea and the subsequent quantitative determination of ammonia, one of the products of the reaction. Since urea in bedding and upholstery materials indicates the presence of urine or perspiration, which give off free ammonia in alkaline solutions, this free ammonia must be determined and the quantity found subtracted from the ammonia found in the urease fermented portion; the difference is urea ammonia, which is computed to urea.

**REAGENTS.** Hydrochloric acid, 0.2 *N*. Urease, 100-mg. tablets (buffered). Defoaming agent, Racicot and Ferguson (5) octyl alcohol, paraffin, and mineral oil. Borax solution, saturated at room temperature. Nessler's reagent. Ammonium sulfate solution, 1 or 0.5 mg. of nitrogen per 100 cc.

Procure the purest ammonium salt available, dissolve it in water, add sufficient saturated sodium carbonate, and, by a strong current of air, aspirate it into sulfuric acid solution. Precipitate the resulting ammonium sulfate with alcohol, filter, wash with diluted alcohol, and dry. By this method impurities which may affect the Nessler solution are removed (1).

**APPARATUS.** The apparatus is shown diagrammatically in Figure 1. It consists of 2 aeration glass cylinders and 2 receiving flasks (100-cc. volumetric flasks containing 5 cc. of 0.2 *N* hydrochloric acid diluted with 50 cc. of distilled water), the inlet tubes of the aeration cylinders being connected to the wash bottles and air pump. The air pump and the wash bottles containing dilute sulfuric acid are standard equipment.

**PROCEDURE.** Weigh 10 grams of the material and place in a 400-cc. beaker; add about 60 cc. of boiling distilled water, and knead with a heavy glass rod until thoroughly wetted. Allow to stand for 1 hour, transfer to a Büchner funnel, filter, and wash by suction. Transfer the filtrate to a 100-cc. volumetric flask,

cool to room temperature, and make to volume with distilled water.

Set up the apparatus, unstopper the cylinders, place a 100-mg. tablet of urease in one of the aeration cylinders, add about 5 cc. of distilled water, and dissolve. Then, from the 100-cc. volumetric flask containing the extract of 10 grams of the material, pipet accurately two 20-cc. aliquots, one in each aeration cylinder. Restopper the cylinders and, without disconnecting, lift the cylinder containing urease and stand it in a beaker containing water which has been warmed to 45° C. Mix the solution by gently shaking, and allow to stand for 15 minutes, shaking occasionally. A fermentation of 15 minutes at 40° C. ensures complete decomposition of urea.

At the end of this period remove the water bath, allow the cylinder to cool to room temperature, make the solutions in the two cylinders equal in volume, add defoaming agent and 20 cc. of saturated borax solution to each cylinder, stopper tightly, and start the air pump. Adjust the flow of air to at least 10 bubbles per second, and aspirate for 2 hours. Then remove the receiving flasks, add 25 cc. of diluted Nessler solution (5 cc. plus 20 cc. of water) to each flask, dilute to the mark, and compare with a standard solution of ammonium sulfate, using a colorimeter as in the Folin method for the determination of ammonia (2). An analysis should be made on a urease tablet and a correction made if necessary. Any increase in ammonia in the solution to which urease is added is due to urea. A blank determination on the reagents is also advisable.

Table I gives the results of the examination of material collected from mattress factories and from wholesale dealers in mill wastes and shows the results of the ultraviolet light examination, as well as the ash, oil, and urea content. The ash was determined because of an attempt to use as new material some imported wastes heavily loaded with clay and also containing considerable oil, presumably to cause the clay to stick to the fiber. The oil was also determined, to furnish information for the differentiation between normal new waste material and wastes heavily impregnated with oil, known in the trade as "oily mill sweepings."

TABLE II. ANALYSES OF WASTES FROM A COTTON MILL AND FROM LOWELL TEXTILE SCHOOL

Sample No.	Character of Material	Ammonia Mg./100	Urea grams	Fluorescence in Ultraviolet Light
A <sup>a</sup>	Droppings (opener room)	12.90	0.42	Violet plus dirt and chaff
B <sup>a</sup>	Picker	8.47	-0.05	Violet plus white tufts; latter violet when shredded
C <sup>a</sup>	Card droppings	7.04	0.00	Violet
D <sup>a</sup>	Comber waste	1.92	0.12	Violet
E <sup>b</sup>	Undusted picker	8.19	0.61	Violet plus white tufts; latter violet when shredded
F <sup>b</sup>	Undusted fly (moats and fly)	3.92	-0.76	Violet
G <sup>b</sup>	Fly	10.52	-0.19	Violet
H <sup>b</sup>	Flat strips	4.65	-0.79	Violet
I <sup>b</sup>	Rollers	8.84	-0.11	Violet
J <sup>b</sup>	Comber	1.62	-0.13	Violet
Av.		6.81	-0.09	

<sup>a</sup> From a cotton mill.

<sup>b</sup> From Lowell Textile School.

The department obtained a number of samples of mill wastes, which were classified as new material after careful examination by Ralph Cooper, inspector of the department, who was formerly employed in the manufacture of upholstered furniture. Ultraviolet light confirmed this opinion in each instance. Subsequently a large cotton mill was visited and samples of cotton wastes were obtained from the machines used in manufacturing cotton fabrics from the raw cotton in the bale to the finished product. Table II shows the results of the examination of samples collected in the mills and in the Lowell Textile School during the process of manufacture.

In considering the results of these analyses, it will be noted that some wastes gave a negative urea content. It was first thought that this was due to eyestrain in reading the



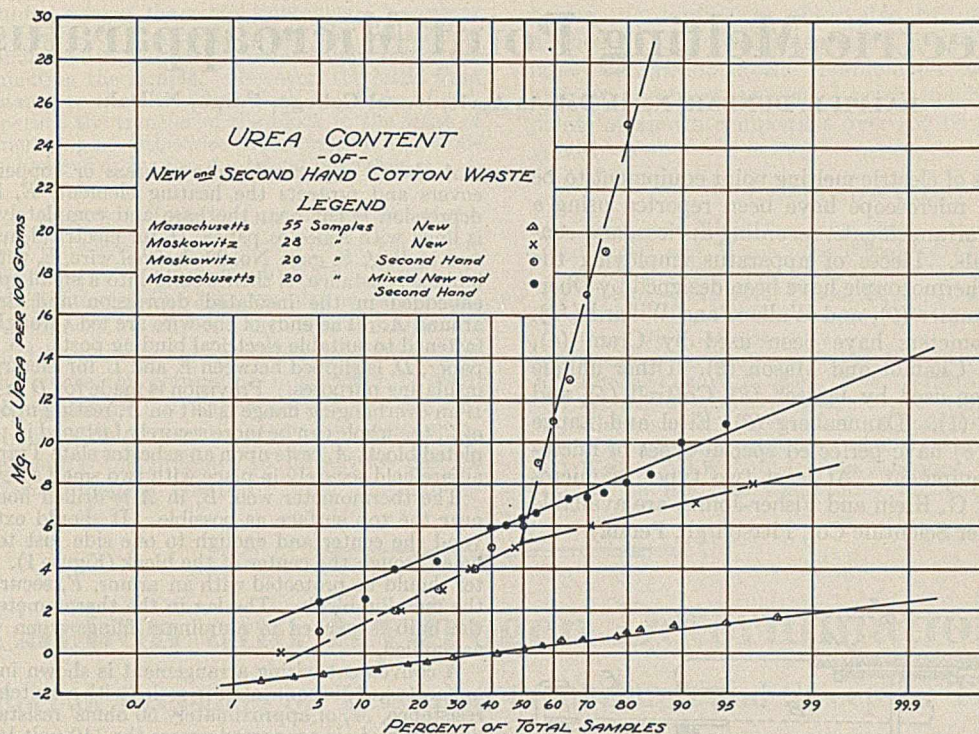


FIGURE 2

colorimeter, but similar results were obtained on additional samples, using a photoelectric colorimeter during examination.

Each urea figure is calculated from the difference between two ammonia microdeterminations, one of which is corrected by a blank determination on the urease. If the material contains little or no urea, a slight error in the determination of ammonia in either solution could readily result in a negative value for urea, particularly if, as in this instance, each analytical figure is from one determination and does not represent the average of two or more check analyses. The standard ammonia solution used for comparison with the unknown was selected to give most accurate results when analyzing material of fairly high ammonia concentration. The difference between the intensity of the color of the sample and the standard is to some extent responsible for the negative urea values reported.

Figure 2 shows certain urea figures plotted on arithmetic probability scales. This type of paper, known as Hazen and Whipple's probability paper, was first devised by Allen Hazen in 1913 (8). The percentage scale of this paper is so spaced that any set of figures which follows the natural law of probability will plot in a straight line. The 50 per cent line of this scale is placed in the middle of the percentage scale. Subsequently Whipple (7) showed that when the series did not plot as a straight line, as is usual with figures involving bacterial counts, it would frequently do so if the other scale of the paper were changed from arithmetic to logarithmic. Figures for plotting on this type of paper are arranged as a summation series in ascending order and from this arrangement a summation percentage series is calculated. If the arithmetic average of this series closely approximates the 50 per cent value, the figures are plotted upon arithmetic probability paper, but if this average exceeds to any extent the 50 per cent value, logarithmic probability paper is used. The authors' 55 samples of new material plot in a straight line, as do those of mixtures of new and secondhand material, such mixtures being identified by the ultraviolet fluorescence. Each of these series, therefore, follows the natural law of probability.

The figures for new material published by Moskowitz *et al.* are different, as the urea content is on the average much higher than that of samples collected by the authors, and the figures do not plot in a straight line on this paper. The lines representing the Moskowitz analyses are both broken at about the 50 per cent mark, and each plots as two probability series; lines for the lower 30 per cent of each series are almost identical. If, as the testimony of Himmelfarb indicates, the authenticity of the wastes was not carefully investigated, the waste dealers may have submitted as new some mixtures containing secondhand material; this will explain the discrepancy in the results, assuming that the method used for analysis was accurate.

The authors' figures indicate that by their method there is not one chance in ten thousand that the urea content of new wastes will exceed 2.8 mg. per 100 grams. By ultraviolet light examination, together with a determination of the urea content, the presence of secondhand material in cotton wastes can usually be detected, unless such secondhand material has been thoroughly scrubbed and washed, in which case it is substantially, if not legally, the same as new material and would probably cost more.

### Literature Cited

- (1) Folin, Otto, personal communication.
- (2) Folin, Otto, *Z. physiol. Chem.*, **37**, 161 (1902); *J. Biol. Chem.*, **11**, 532 (1912).
- (3) Moskowitz, S., Landes, W., and Himmelfarb, D., *Am. Dyestuff Repr.*, **24**, 463-6 (1935).
- (4) Nicoloux, M., and Welter, G., *Compt. rend.*, **173**, 1490 (1921).
- (5) Racicot and Ferguson, *IND. ENG. CHEM., Anal. Ed.*, **11**, 380 (1939).
- (6) Van Slyke, D. D., *J. Biol. Chem.*, **16**, 19, 211 (1914).
- (7) Whipple, G. C., *J. Franklin Inst.*, **182**, 37, 205 (1916).
- (8) Whipple, G. C., "Vital Statistics," p. 391, New York, John Wiley & Sons, 1919.
- (9) Winne and Donovan, *Am. Dyestuff Repr.*, **21**, 601 (1932).
- (10) Yee and Davis, *IND. ENG. CHEM., Anal. Ed.*, **7**, 259 (1935).



# Electric Melting Point Microapparatus

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VARIOUS types of electric melting point equipment to be used with the microscope have been reported using a variety of heating arrangements, recording devices, and constructional materials. Pieces of apparatus employing the application of the thermocouple have been designed by Oberhoffer (10), Niethammer (9), and Wallace and Willard (11). Laboratory thermometers have been used by Cram (5), Clevenger (3), and Chamot and Mason (2). Other unique variations have been used by Jentsch (8), Cottrell (4), and Admur and Hjort (1). Dannenberg (6), Eitel and Lange (7), and Walton (12) have perfected special types of microscopic hot-stage equipment. At least two types of microapparatus, those of G. Klein and Fisher-Johns, are available commercially (Fisher Scientific Co., Pittsburgh, Penna.).

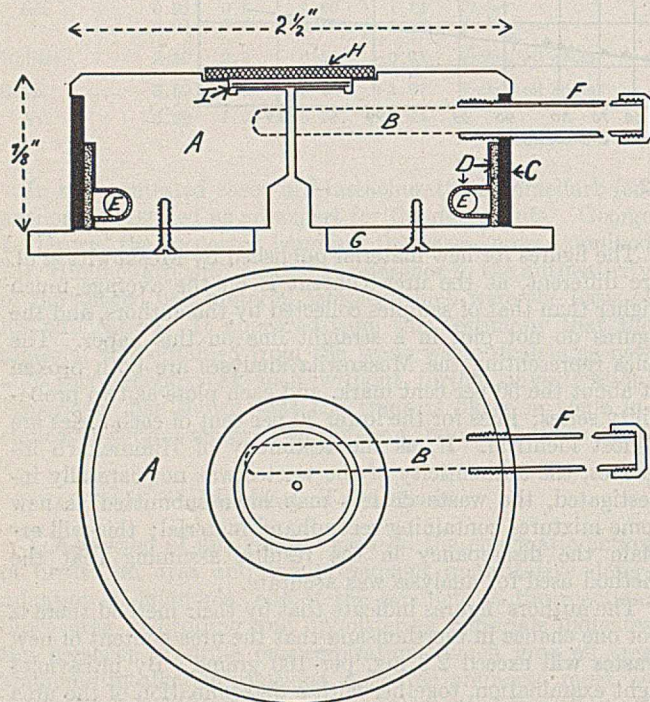


FIGURE 1. VERTICAL AND HORIZONTAL DIAGRAMS

The author's apparatus consists essentially of a solid aluminum block that has been carefully shaped or turned on a lathe, is heated by means of resistance wire, and carries a thermometer well. Figure 1 is drawn to scale.

The aluminum block, A, is cylindrical in shape and measures 0.875 by 2.5 inches. If a block of aluminum of this size is not available, smaller pieces may be melted in a muffle furnace, cast into a slightly larger block, and turned down on a lathe to the correct size. A series of concentric depressions is made on the top surface of the block, of a size to admit two circular microscope cover glasses, I, and immediately above a still larger circular piece of glass, H. H can be readily cut to any desired size by spinning a suitable sized cork borer or piece of brass pipe on a piece of clear glass, using a suspension of silicon carbide or emery dust in water for cutting purposes. A small depression at the outer edge just below I aids greatly in the removal of the cover glasses when the apparatus is in use. Some time can be saved and difficulty avoided if H and I are first prepared and then the depressions are cut to a suitable size and depth. A small hole is drilled straight through the center of the block from the bottom of these depressions and is enlarged somewhat at the base. This opening serves to illuminate the sample when melting point determinations are being made.

A should slip snugly into a brass or copper ring, C, which covers and protects the heating element, E, below. A small depression is cut near the base and completely around A, and is lined with asbestos paper, D, for electrical insulation. Three feet of B. & S. gage No. 22 chromel wire, E, with approximately 3 ohms resistance, is then wound into a small spiral coil which is embedded in the insulated depression and drawn completely around A. The ends of the wire are led through holes in C and fastened to suitable electrical binding posts. A layer of asbestos paper, D, is slipped between E and C for electrical and thermal insulating purposes. Provision is made for D in A, as illustrated. If an overhanging flange is left on A, resting upon the upper edge of C, the whole can be more securely fastened in place. The completed block, A, rests upon an asbestos slate Transite base, G, and all are held securely in place with two small screws as illustrated.

The thermometer well, B, in A is drilled horizontally and as near the top surface as possible. It should extend slightly beyond the center and enough to one side just to clear the small hole through the center of the block (Figure 1). The thermometer should be protected with an armor, F, securely screwed into the metallic block. The lag in the thermometer is much less if the bulb is packed in aluminum filings when the apparatus is assembled.

A convenient wiring arrangement is shown in Figure 2. The apparatus, A, is connected in series with a switch, K, and variable resistance, M, of approximately 50 ohms' resistance. A 10-watt light bulb, L, is connected across the 110-volt leads, with switch J in series, to be used for illuminating the sample. Convenient switches, binding posts, and similar items can be secured at radio supply stores.

Figure 3 illustrates a compact arrangement, which includes the microapparatus, source of light, and resistance. The variable

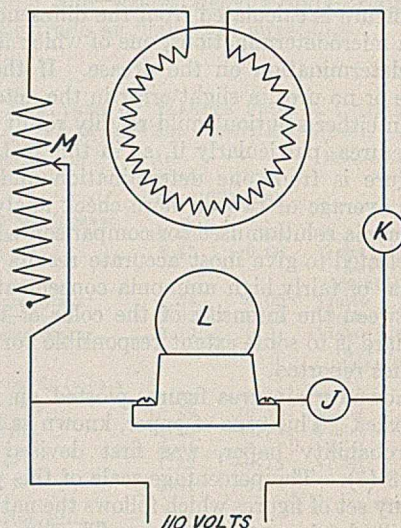


FIGURE 2. WIRING OF APPARATUS

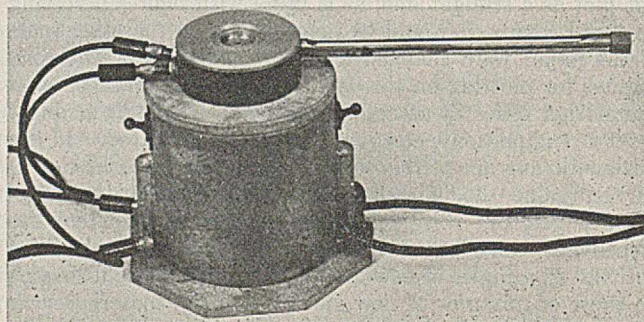


FIGURE 3. APPARATUS, LIGHT SOURCE, AND VARIABLE RESISTANCE



resistance is mounted within the metal container. Necessary insulated electrical leads are provided through the walls. The 10-watt bulb is mounted in the center, immediately below the opening for illuminating the sample. However, the leads from the variable resistance to the aluminum block should be of sufficient length to permit the transfer of the block to the stage of any compound microscope. Otherwise the samples may be observed with the naked eye or by use of a tripod magnifier.

When a melting point is to be taken a small crystal of the unknown is placed between the microscope cover glasses, *I*, and above the small opening provided for illumination. *H* is then placed in position. The temperature is raised and controlled by the amount of current provided through *M*. The sample should be illuminated by direct light from *L* or by reflected light where the compound microscope is used.

Not only melting points but any tendency for the unknown to soften or sublime can be observed under these conditions. Frequently the presence of impurities can be detected by different melting points or other unusual be-

havior, not ordinarily observable by other melting point methods. Any discrepancy from true melting points due to faulty calibration of the thermometer or thermal losses at high temperatures can easily be corrected by checking melting points of known compounds over the temperature range involved.

#### Literature Cited

- (1) Admur and Hjort, *IND. ENG. CHEM., Anal. Ed.*, **2**, 259 (1930).
- (2) Chamot and Mason, "Handbook of Chemical Microscopy," Vol. 1, p. 203, New York, John Wiley & Sons, 1930.
- (3) Clevenger, *IND. ENG. CHEM.*, **16**, 854 (1924).
- (4) Cottrell, *J. Am. Chem. Soc.*, **34**, 1328 (1912).
- (5) Cram, *Ibid.*, **34**, 954 (1912).
- (6) Dannenberg, *Kautschuk*, **3**, 104, 128 (1927).
- (7) Eitel and Lange, *Z. anorg. Chem.*, **171**, 168 (1928).
- (8) Jentsch, *Z. wiss. Mikroskop.*, **27**, 259 (1910).
- (9) Niethammer, *Mikrochemie*, **2** (2), 223 (1930).
- (10) Oberhoffer, *Z. Electrochem.*, **15**, 634 (1909).
- (11) Wallace and Willard, *J. Chem. Education*, **8**, 706 (1931).
- (12) Walton, *IND. ENG. CHEM., Anal. Ed.*, **1**, 106 (1929).

## Carbon and Hydrogen Determinations

### Effect of Pressures on Lessening Combustion and Sweeping Times

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**T**HERE has been great need for lessening the time required for microdeterminations of carbon and hydrogen. Authors of methods for microanalysis at best suggest from 45 to 50 minutes as combined combustion and sweeping times. Those who have had experience with combustions with polyhalogen compounds, compounds containing sulfur or nitrogen, or combinations of all three, know that extreme care must be taken not to get too high results for carbon. This leads to an examination of the manner of filling the combustion tube, since its function is to remove the unwanted halogens, sulfur, and nitrogen (if it is burned to oxide). Inasmuch as the trend is to semimicroanalysis, using samples on the order of three to seven times the maximum size of microsamples (when sufficient material is available), it was felt that a tube of larger cross section would be advantageous. Conditions which would speed up semimicrodeterminations should also hold true for microsamples.

Initially, with the set described (1), a tube of Pregl dimensions was used and filled in the conventional manner. Samples from 12 to 35 mg. were burned. With 20 to 25 minutes arbitrarily set as combined combustion and sweeping times, the results were much too poor. Compounds containing nothing but carbon and hydrogen, or carbon, hydrogen, and oxygen gave closer results than those containing in addition halogen, sulfur, or nitrogen. The smaller tube was soon abandoned in favor of a larger tube of 11- to 12-mm. bore.

It can be argued that a tube of wider bore will contain more filling, permit better removal of the halogen, sulfur, etc., and last longer. The filling of the tube differs in two respects from that previously described (1): The precipitated silver is supported on short-fiber asbestos, and the tube is packed rather tightly. This tight packing enables combustions to take place under pressure. The exit ends of the capillaries of the absorption tubes are further constricted to enable absorptions to take place under pressure. The pressure in the combustion tube varies with the bubble rate, but is constant for a fixed bubble rate. For example, with the particular tube the author is now using, at 100 bubbles per minute the pressure is about 5 cm. of mercury (1 pound),

and at 180 bubbles per minute, about 10 cm. (2.0 pounds). These two figures are given because combustions take place at 100 bubbles per minute, and sweeping at 180 bubbles per minute. As yet the author has found no sample up to 35 mg. that is not completely oxidized and absorbed within the time limits set. No more than 225 cc. of oxygen are required for combustion and sweeping of any sample up to 35 mg. (The pressure figures throughout this paper are approximate.)

A simple device enables one to measure the pressure in the combustion tube. With the pressure chamber (which has displaced the glass gasometer described in the previous article, 1) set to 250 cm. of mercury (50 pounds), and the set diaphragm delivering the oxygen at a head of 35 cm. (7 pounds), the delivery needle valve is adjusted to 100 bubbles per minute.

At intervals, while filling the combustion tube, the tube is checked for pressure head by inserting a three-way stopcock into the open end of the combustion tube by means of a rubber stopper. To the opposite end of the stopcock is joined an open mercury manometer. The exit end of the combustion tube is left open. The set soon comes to equilibrium and the pressure rise is noted in the manometer. The short-fiber asbestos mixed with precipitated silver and the lead peroxide supported on short-fiber asbestos are tamped until the desired pressure head is reached. The third opening of the three-way stopcock is used for regulating the pressure head in the absorption tubes. The absorption tube is connected by means of rubber tubing to the arm of the stopcock, the end of the combustion tube is plugged, and the exit ends of the capillaries of the absorption tubes are constricted until they show a pressure head of approximately 1.25 to 1.8 cm. of mercury (0.25 to 0.375 pound).

Even though pressure plugs are included in the standard Pregl set, the pressures are below those cited in this paper. Moreover, it is apparent that the absorption tubes are always under a slight vacuum due to the pull of the Mariotte bottle. This suggests the necessity for slow combustion and absorption times. Under pressure absorption is more complete than under slight vacuum.

The reproducibility of the results is indicated by Table I. Since an analytical balance of sensitivity 40 was used, the discrepancies in the last two places of decimals might be due to the inaccuracy of the balance.



With the simplification of procedure, impetus should be given to the teaching of micro- and semimicrodeterminations. All the troublesome and involved techniques are a distinct deterrent when time is a factor.

TABLE I. REPRESENTATIVE RESULTS

(An analytical balance of sensitivity 40 was used, and approximations of the fourth figure were made in the usual manner)

Substance	Sample Mg.	H <sub>2</sub> O		CO <sub>2</sub>		H		C	
		Found	Found	Found	Found	Calcd.	Calcd.	Calcd.	Calcd.
		Mg.	Mg.	Mg.	%	%	%	%	%
<i>p</i> -Nitrochlorobenzene	20.70	4.77	34.70	2.56	45.71	2.54	45.71		
	34.80	8.10	58.28	2.58	45.66				
Thiourea	20.30	9.61	11.80	5.26	15.85	5.30	15.78		
Benzoic acid	15.84	7.04	40.04	4.94	68.94	4.92	68.82		
	20.70	9.22	52.36	4.95	68.98				
	34.62	15.40	87.40	4.94	68.86				
Arsenic acid	22.60	7.58	27.54	3.73	33.23	3.71	33.18		
	33.85	11.20	40.80	3.68	33.20				
2,4-Dinitrophenol	13.40	2.60	19.18	2.16	39.04	2.19	39.12		
	15.26	2.96	21.82	2.16	39.00				
2,4-Dichloroaniline	20.40	5.71	33.26	3.11	44.46	3.11	44.45		
	22.80	6.40	37.20	3.12	44.49				
	35.64	9.90	58.10	3.09	44.46				
<i>p</i> -Dichlorobenzene	23.42	5.80	42.00	2.76	48.91	2.74	48.93		
	34.00	8.50	61.05	2.78	48.97				
Bromobenzene	18.92	5.52	31.42	3.24	45.29	3.21	45.23		
<i>p</i> -Aminobenzoic acid	25.43	11.70	57.00	5.10	61.13	5.11	61.28		

With two platinum boats and four absorption tubes, the author has had no difficulty in running as many as sixteen samples in 8 hours (the first sixteen results in Table I). The

number of samples may at first appear large, but as tubes are conditioned by means of a tube conditioner while the second combustion is run, the absorption tubes can be weighed and a new sample made ready for combustion during the sweeping out.

### Summary

A method for filling absorption tubes is discussed whereby combustion time can be materially lessened for semimicro-samples and for microsamples.

The substitution of silver supported on asbestos for silver wool increases the efficiency of the combustion tube in the removal of halogen.

Combustions under increased pressure ensure completeness of oxidation and removal of halogen, sulfur, nitrogen, etc.

Absorptions under pressure ensure complete removal of water and carbon dioxide.

### Acknowledgment

The author is indebted to Mr. Weiskopf of the Technicon Co., New York, N. Y., for his cooperation in the development of this apparatus, and for furnishing combustion tubes of various sizes.

### Literature Cited

- (1) Natelson, Brodie, and Conner, *IND. ENG. CHEM., Anal. Ed.*, 10, 609 (1938).

## A Generator for the Production of Pure Carbon Dioxide

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THE author (2, 3) has described generators which consistently produce carbon dioxide of the high purity required in Pregl's microcombustion method of estimating nitrogen. Modifications of this equipment (1, 4) have corrected some of the imperfections of the original apparatus but, unfortunately, introduced complications and other defects.

A simplified form of the apparatus is represented in the figure. Chambers *A* and *B* are conveniently made from 2- and 1-liter Pyrex flasks. The construction of the acid delivery tube, *F*, ensures a smooth feeding of small drops of solution and eliminates after-drops. The tip should be drawn down to a diameter of approximately 1 mm.

Beginning with the generator completely empty it is charged as follows:

With the generator lying on its side, 170 cc. of concentrated sulfuric acid diluted with 150 cc. of water are introduced into *B* through *E* and *C*, and the acid remaining in *C* is displaced with air and washed into *B* with 25 cc. of water. With the generator in the up-

right position, a solution of 500 grams of potassium acid carbonate dissolved in 1100 cc. of water is run into *A* through *D*, followed by 100 cc. of water to rinse out the stopcock and bubble trap. The system is evacuated with a vacuum pump through *D* and *E* simultaneously for about 15 minutes. Mercury is introduced into the manometer and trap, *C*, and the generator is set in operation as outlined in a previous publication (3).

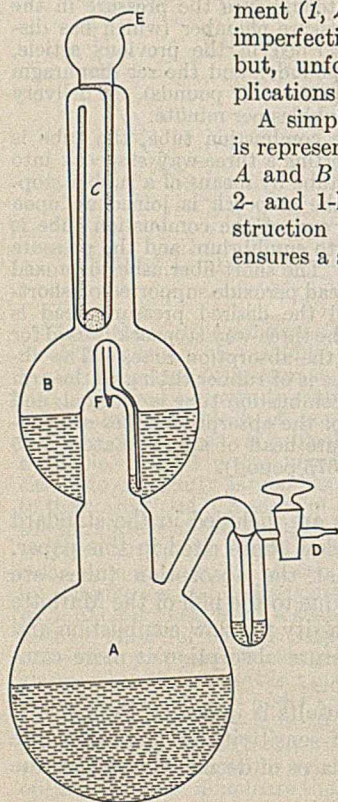
Trap *C* is constructed with the volume of the inner and outer chambers about equal. Should the pressure in the system, for any reason, fall so low as to break the mercury seal, mercury will be forced into *B*, and its presence will show that the system has been contaminated with air. In this event the apparatus must be completely emptied and recharged. Any drops of mercury which cannot be removed from bulb *B* by ordinary means should be dissolved with nitric acid, and the apparatus thoroughly washed to remove nitrates. *C* is placed in a diagonal position in such a manner that when it is forced the bubbles of gas will travel up one wall. Thus the entire column of mercury cannot be forced into the upper bulb, to prevent action of the trap.

Since the solid potassium sulfate formed in the generator is water-soluble, the generator can be cleaned by running water in at *D* and out at *E*. After emptying the generator of water, it is ready for recharging.

This generator will deliver pure carbon dioxide with small fluctuations of pressure, is compact and sturdy, and can be used for the generation of gases other than carbon dioxide. This piece of apparatus is available from E. H. Sargent and Company, Chicago, Ill.

### Literature Cited

- (1) Lowe, E. W., and Guthmann, W. S., *IND. ENG. CHEM., Anal. Ed.*, 4, 440 (1932).
- (2) Poth, E. J., *Ibid.*, 2, 250 (1930).
- (3) *Ibid.*, 3, 202 (1931).
- (4) Shelberg, E. F., *Ibid.*, 10, 704 (1938).





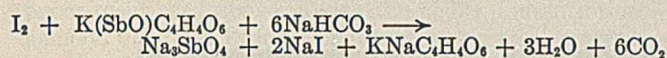
# Tartar Emetic on Leaf and Fruit Surfaces

## Distributional and Semiquantitative Analysis, Using an Iodine-Starch Paper

DONALD STARR, Bureau of Entomology and Plant Quarantine, United States Department of Agriculture, Washington, D. C.

ATTEMPTS to determine the quantity of tartar emetic remaining on citrus foliage during a spraying program led to the realization that in insect control it is sometimes more important to know how the poison is distributed than to know the exact amount present on a given surface. A simple and rapid analytical method was needed if the large number of analyses required in control work were to be handled.

A sensitive iodine-starch test paper was devised which gave a picture of the distribution of the tartar emetic over the leaf surface. The iodometric titration of tartar emetic is a well-known analytical procedure (1) in which the following reaction is involved:



The iodine-starch paper used was dark blue or brown, and the reaction with tartar emetic reduced the iodine and whitened the paper. A semiquantitative estimation of the tartar emetic was made possible by preparing, as a standard of comparison, small slips of paper containing a known quantity of tartar emetic on the surface. The tartar emetic paper

and the citrus leaves were tested with the same iodine-starch paper, and by roughly integrating and comparing the whitened area due to the standard with that due to the unknown the approximate quantities of tartar emetic on the citrus leaves were obtained. The test may also be used for roughly estimating tartar emetic residues on citrus fruit surfaces.

### Preparation of the Test Paper

The iodine-starch mixture used in coating the paper had the following composition: 6.4 grams of iodine, 13 grams of potassium iodide dissolved in a small portion of the water, 54 grams of soluble starch, 3.4 grams of sodium bicarbonate, and 1 liter of water. It is conveniently prepared by adding the starch and sodium bicarbonate to 1 liter of a stock solution of 0.05 *N* iodine. The effect of varying the proportions has not been studied extensively, but the above amounts may be altered without markedly affecting the results. Larger quantities of sodium bicarbonate increased the fading of the paper; however, when sodium bicarbonate was absent the sensitivity was decreased. The amount of water used depends upon the sensitivity of the reaction desired. The more concentrated mixtures give darker and better coats of iodine, but the reaction is less sensitive.

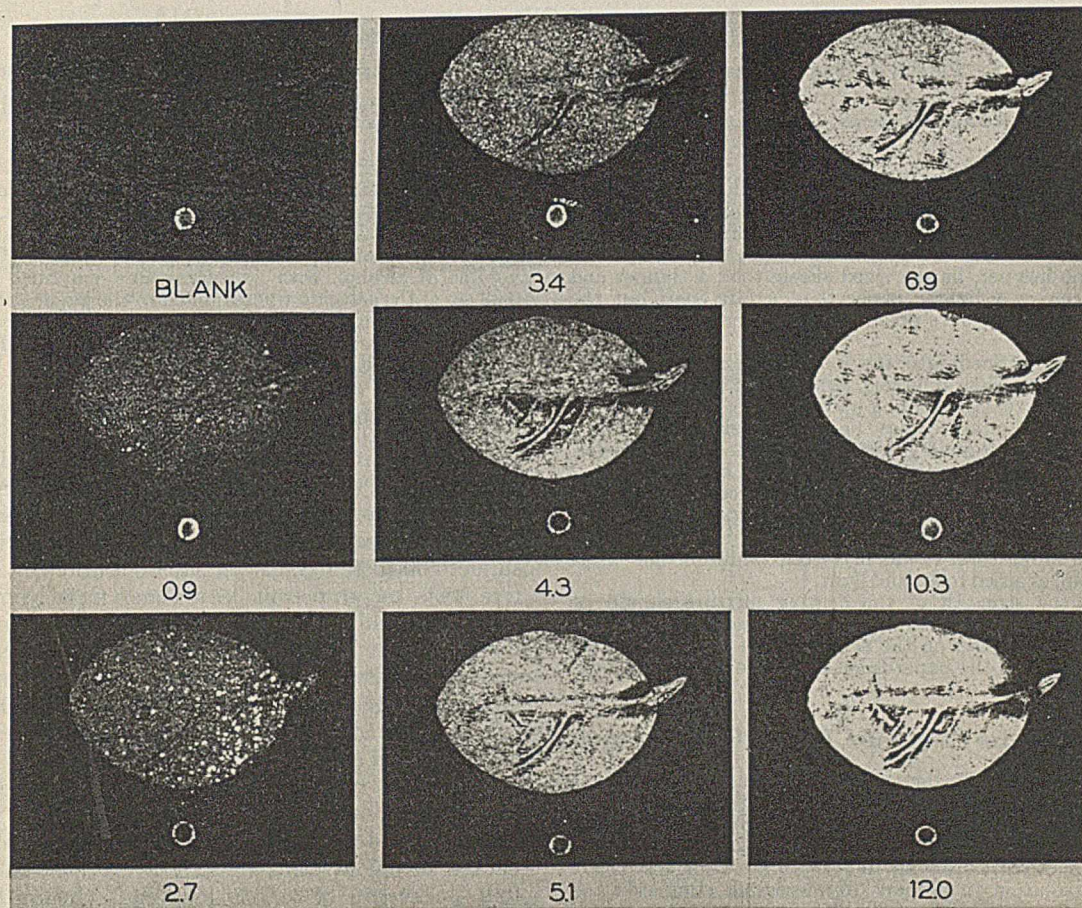


FIGURE 1. PRINTS OF TARTAR EMETIC ON GRAPEFRUIT LEAVES USING THE MORE SENSITIVE TEST PAPER. Numbers indicate tartar emetic concentration in micrograms per square centimeter. Each circle represents 10 micrograms.



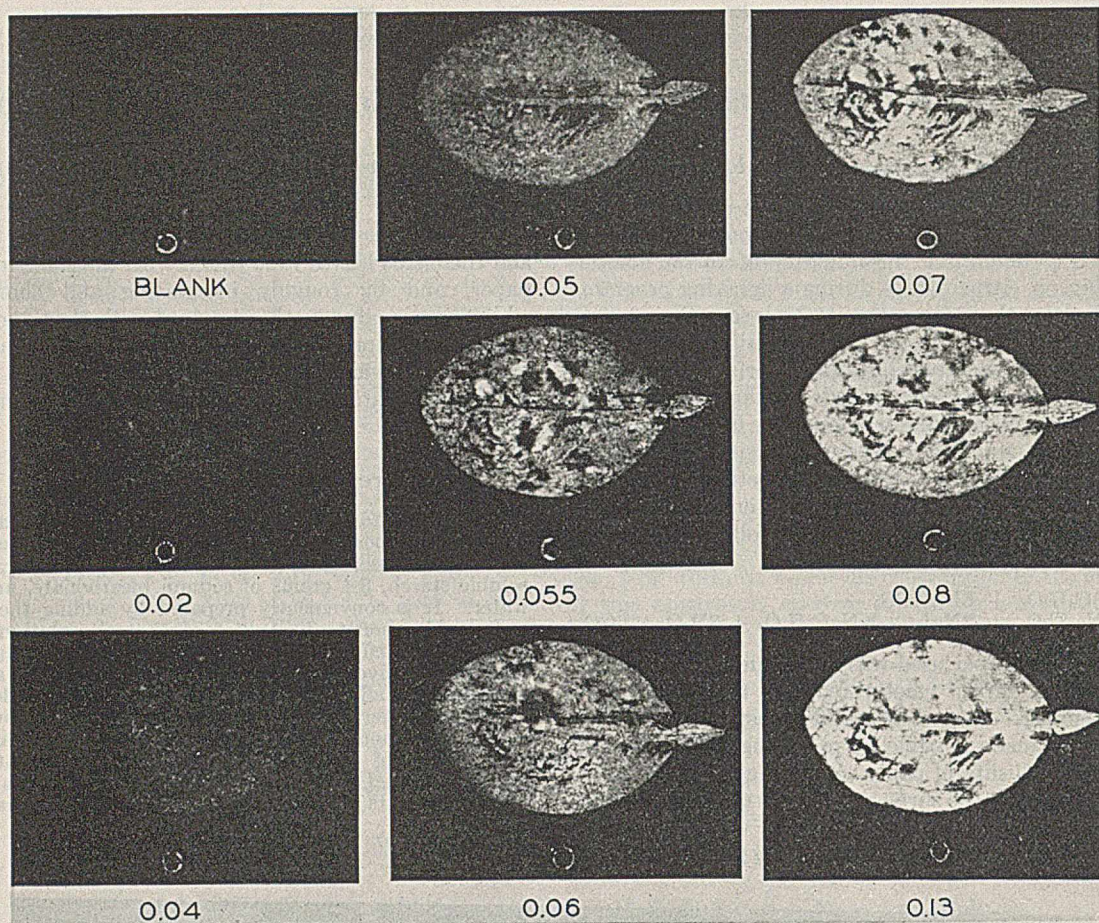


FIGURE 2. PRINTS OF TARTAR EMETIC ON GRAPEFRUIT LEAVES USING THE PAPER WITH THE HEAVIER COATING OF IODINE

Numbers indicate tartar emetic concentration in milligrams per square centimeter. Each circle represents 0.02 mg.

The paper which gave the best results in these studies was manifold typewriting paper of about 9 pounds per ream, 17 by 22 inches, containing 500 sheets. The methylene blue size test (as used at the Institute of Paper Chemistry) was about 30 seconds. Some heavier, harder sized sheets took a thinner and less uniform coat. A lighter paper took a fair coat, but the uniformity and opacity were poor. Filter paper did not take a uniform coat.

The paper was dipped into the iodine-starch mixture until thoroughly wet, and then removed, drawn over a 12-mm. glass rod to remove the excess, and hung up to dry.

The iodine-starch mixture may be used or stored for 3 or 4 weeks, but the coat obtained gradually becomes lighter in color. The paper fades noticeably after it has been kept for 1 or 2 months. Increasing the sodium bicarbonate content and exposure to sunlight accelerates fading. Iodine-starch paper kept in a small air-tight container away from the light had faded slightly after a month, but it was in better condition than when kept in the open, exposed to air and light.

In general, the strength of the coating mixture should be varied to suit individual needs, depending on the time the paper is to be stored before use, on the sensitivity of the reaction desired, and on the way the paper takes up the iodine-starch mixture.

### Preparation of the Standard Tartar Emetic Paper

Different amounts of tartar emetic were used to prepare the standard paper, but 0.01 or 0.02 mg. was found to be satisfactory.

The standard papers were prepared using a microburet which delivered a drop of distilled water having a volume of 0.045 cc. at 22° C. at a speed of 1 drop in 3 to 5 seconds. Using 0.00133 *N* tartar emetic solution to prepare 10-microgram standards and 0.00266 *N* for the 20-microgram standards, 80 drops represented 3.595 cc. in the first case and 3.615 cc. in the second. The average differences are 0.14 and 0.42 per cent from the volume on which the calculations were based.

The paper was such that the solution would stand up well and upon drying leave a ring of tartar emetic 5 to 7 mm. in diameter.

Alcohol was added to the solution in attempts to produce a spot of tartar emetic rather than a ring. Up to 50 per cent by volume of alcohol, with 20 micrograms contained in a drop of 0.02 cc. of the solution when applied to the paper still gave a ring, but 10 to 14 mm. in diameter.

Sodium thiosulfate standards equivalent to 10 micrograms of tartar emetic also gave ringed deposits.

### Recommended Testing Procedure

The degree of reaction obtained between the iodine-starch test paper and the tartar emetic standard paper increases with time, temperature, and pressure. A nearly complete reaction is obtained in 15 minutes at 20° to 25° C. with a pressure of 100 to 150 grams per square centimeter, but qualitative tests on grapefruit leaves and fruit have been very distinct in a minute or less. It has been determined experimentally that the reaction from grapefruit leaves, dorsal surface, and from glass surfaces is faster than from the standard paper. If the pressure used is less than 100 grams per square centimeter, it may be necessary to increase the time in order to get a complete reaction.

The test is run by placing the standard paper beside the leaf and pressing the test paper against them with a well-moistened pad made of about eight thicknesses of filter paper backed by about eight thicknesses of muslin toweling and four thicknesses of turkish toweling. (In the laboratory a weight of about 20 kg. was applied to thick glass plates of 160-sq. cm. area, but in the field A. C. Baker found it convenient to use a small photographic printing frame.) The



leaf can be tested on both top and bottom surfaces by placing it between two test papers with moist pads above and below.

If permanent records of the tests are desired, brown or blue prints may be made from the iodine-starch test paper. The prints must be exposed accurately to bring out the tartar emetic spots without smudging the paper. Iodine-starch prints fade considerably after one or two months.

The sensitivity of the test has been increased by diluting the coating mixture. A paper prepared as described above gave a distinct reaction with 0.0005 cc. of a solution containing 2.0 grams of tartar emetic per liter, or 1.0 microgram of tartar emetic. A more sensitive paper prepared from the above formula with the sodium bicarbonate doubled, and diluted with seven parts of water reacted to 0.1 microgram of tartar emetic.

Figures 1 and 2 are photographs of prints taken from grapefruit leaves dusted with varying known amounts of tartar emetic. It will be noted from Figure 1 that the tartar emetic concentration can be tested within the range of 0.9 to 10 micrograms per square centimeter using the more sensitive paper mentioned above. With the higher concentrations—namely, 0.02 to 0.13 mg. per square centimeter—paper prepared from the undiluted mixture may be used. The results are shown in Figure 2. The photographs indicate the degree of precision obtainable under the prescribed conditions.

The distribution of tartar emetic on citrus leaves after being

sprayed with tartar emetic solutions is much less uniform than that obtained by dusting.

### Interfering Substances

The materials that may be expected to interfere with the test are reducing substances in general. Some of the materials found to interfere are sodium arsenite, glue, and molasses. The paper is not very sensitive to arsenious oxide or Paris green, probably owing to the low solubility of these compounds. Sucrose, glucose, fructose, galactose, arabinose, and xylose were found to be nonreactive, or so nearly so that there would be no interference. Strong ammonia solution, calcium hydroxide, and potassium carbonate reacted with the paper. Strong alkalis in general react with iodine to give hypiodites.

### Summary

Iodine-starch test papers have been prepared for the purpose of obtaining distributional and semiquantitative analyses of leaf surfaces for tartar emetic. The test is sensitive to 0.9 microgram per square centimeter.

Known quantities of tartar emetic have been deposited on paper as a standard of comparison.

Substances that reduce iodine interfere with the test for tartar emetic.

### Literature Cited

- (1) Treadwell and Hall, "Analytical Chemistry," 7th Ed., Vol. II, p. 581, New York, John Wiley & Sons, 1930.

## Ejector-Type Evacuator for Wet Assay Systems

EDGAR J. POTH, Stanford University School of Medicine, San Francisco, Calif.

THE elimination of corrosive fumes evolved in wet assay methods such as Kjeldahl digestions frequently presents a problem, especially in poorly planned laboratories. One is faced with the problem of disposing of corrosive fumes as well as removing them from a given system. For the elimination of fumes created in many microanalytical procedures, a small digestion chest is presented (Figure 1, G). It is made of stainless steel, has a removable top, and, after use, can be washed out thoroughly. It can be placed on a hot plate.

The ejector or jet pump is constructed of Pyrex glass and operates with high efficiency on low-pressure steam. The fumes are brought into direct contact with live steam, which in turn is condensed by a spray of cold water. In this way the corrosive materials either react with the steam or are dissolved in the condenser water. Furthermore, they are highly diluted and can be dumped directly into the ordinary laboratory drainage system. The pump will handle liquids as readily as vapors and so it is not necessary to have traps for liquids condensing in or introduced into the system.

In the construction of this pump it is well to determine experimentally the position where any particular jet gives the greatest efficiency with the steam pressure available.

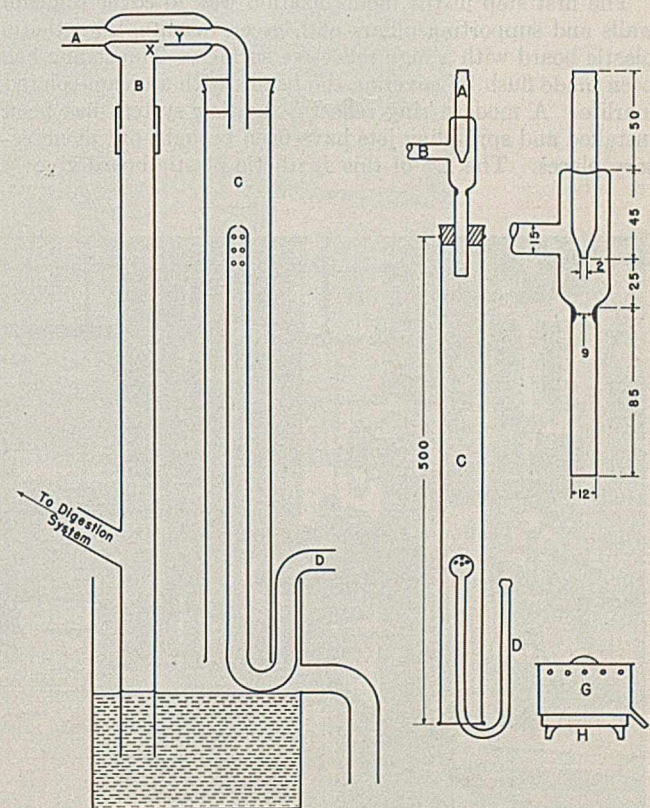


FIGURE 1. EJECTOR-TYPE EVACUATION PUMP  
(See designations at left)

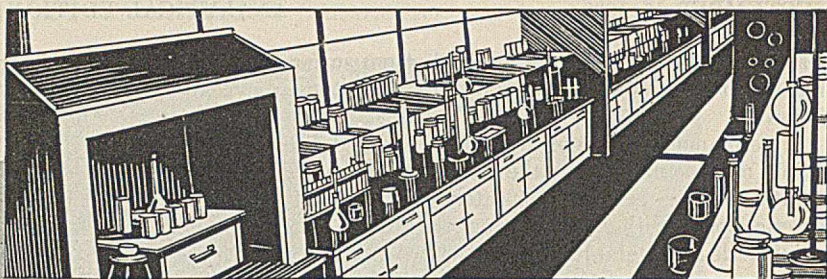
- A. Steam inlet and jet
  - B. Vacuum outlet to connect with digestion system
  - C. Condenser
  - D. Spray condenser
  - G. Digestion box made of stainless steel
  - H. Hot plate
  - I. Fume and spillway to be connected with B
  - X. Male half of steam jet, 5 mm. in inside diameter
  - Y. Female half of steam jet, 12 mm. in inside diameter, slightly tapered.
- Gap between X and Y measures 4 mm.

Dimensions in millimeters. Design on right best suited for system of small capacity; design on left, illustrated with sump and overflow water trap, best for systems of large capacity.



# MODERN

# LABORATORIES



## Modernization of Norwich Laboratories

G. W. BENGERT

The Norwich Pharmacal Co., Norwich, N. Y.

THE new laboratories of the Norwich Pharmacal Co., which were opened in March of this year and are the finishing touch to a complete plant-modernization program, are not only a marked improvement over the former laboratories of this company but present many features and innovations new to laboratory construction. The space now occupied by the laboratories was formerly the pill-coating department and is located on the third floor of a conventional brick factory building having an interior of exposed wooden beams and flooring and a double row of supporting pillars about 15 feet apart and 17 feet from the brick side walls. Yet in this typical factory setting there has evolved a modern, clean, well lighted laboratory.

The first step in the modernization was to cover the side walls and supporting pillars with green marlite, a synthetic plastic board with a high reflective surface. The ceiling has been made flush by covering the beams with a cream-colored marlite. A modern ring reflector lighting system has been installed and sprinkling jets have been brought out at necessary places. The use of this synthetic plastic board gives a

hard, fume-resisting surface which is easy to clean and because of its light-reflective properties makes the laboratory much brighter than those laboratories using the usual white flat paint.

The supporting columns have been made a part of the laboratory bench by designing equipment to fit around them. Individual bays have been made on both sides of the room, a portion of the space between columns serving as a center main aisle. The bays are U-shaped and contain a center work bench built about a column, two side work benches also built about columns, and two steel desks along the wall, or bottom portion of the U. Here the similarity to most laboratories ends and the novel features of this new laboratory start. Each bay has been separated from the next by plate glass which extends from the top of the side laboratory benches to within a few inches of the ceiling. Such plate-glass dividers increase the amount of light received in the bay, give an effect of spaciousness, and allow privacy for conversation without completely shutting off each unit; yet each worker has the necessary isolation for efficient work. By not

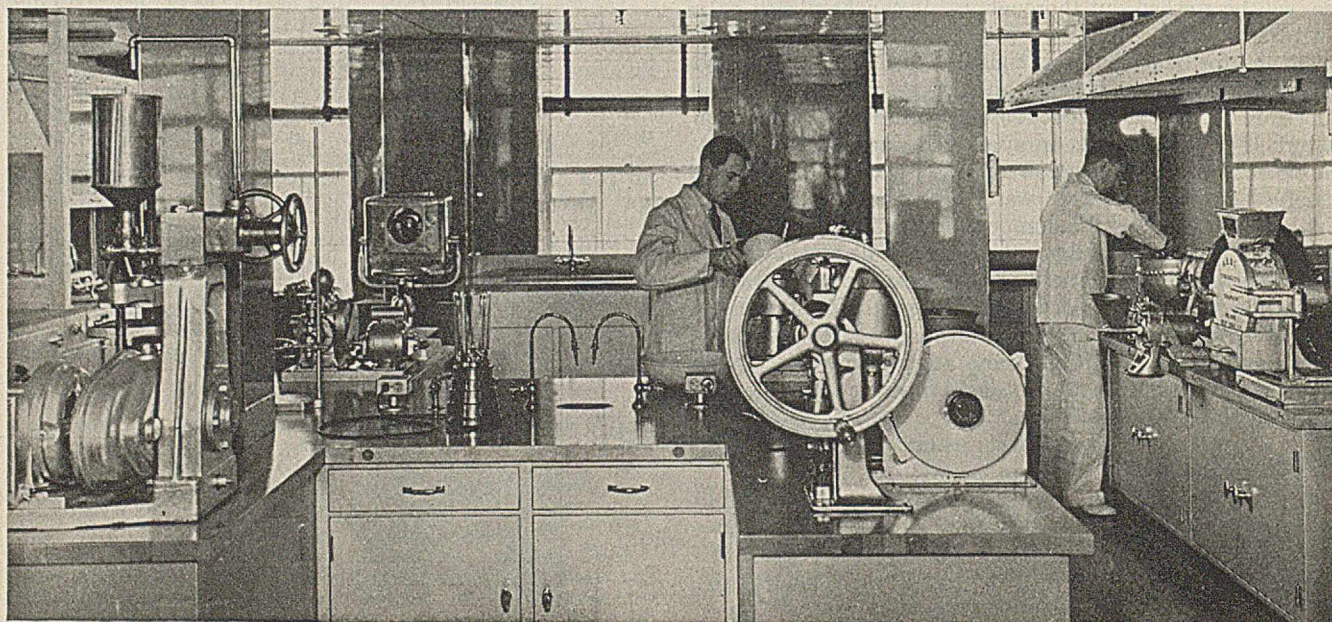


FIGURE 1. PILOT PLANT AFTER MODERNIZATION



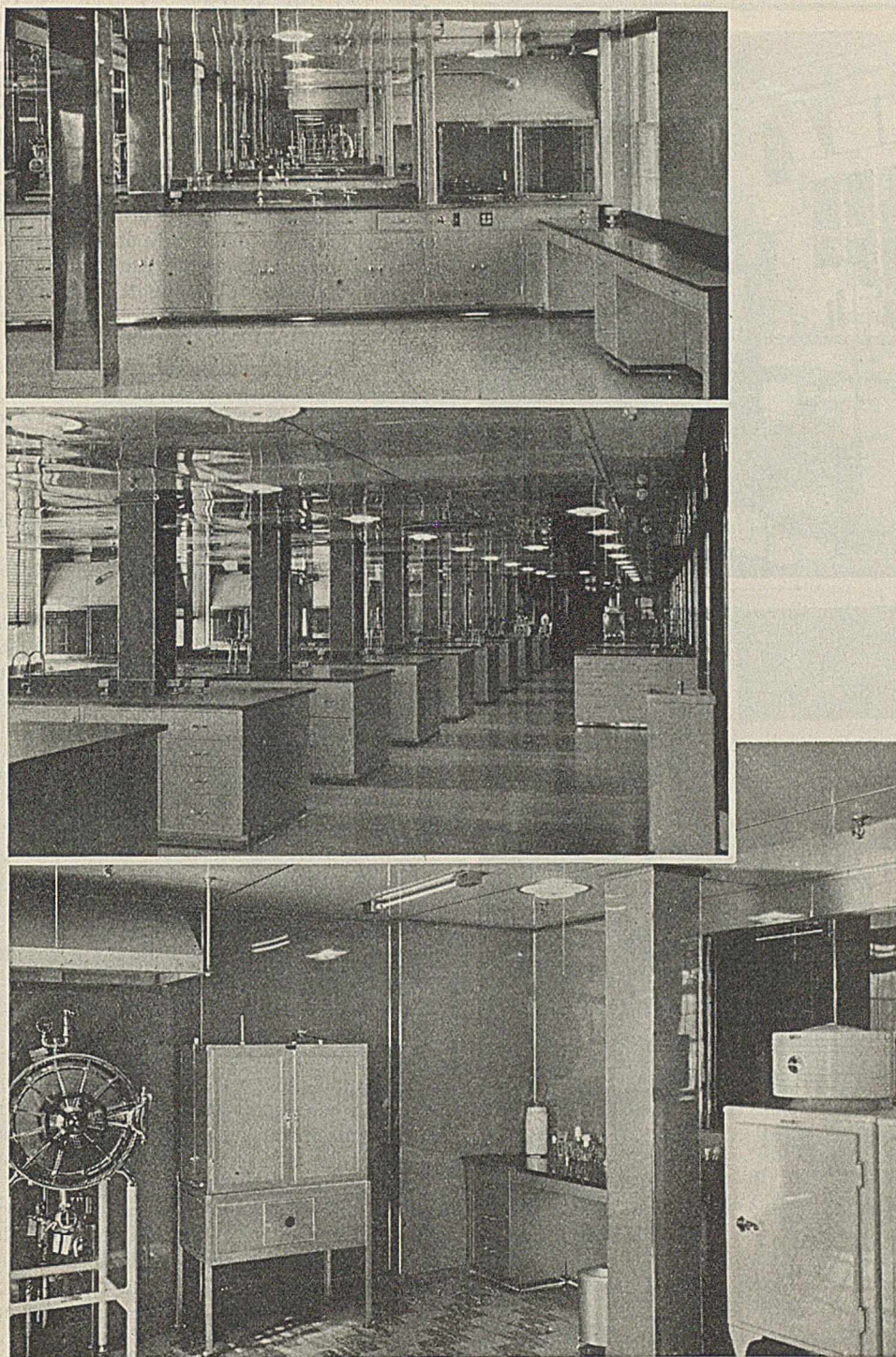


FIGURE 2. MODERNIZED LABORATORIES

*Top.* Looking towards front through plate-glass partitions, steel desk at right. *Center.* General laboratory, plate-glass dividers at left center, individual fume hoods, no reagent shelves. *Bottom.* Bacteriological laboratory. Long tube on ceiling is sterilizing lamp.

extending the plate glass to the ceiling one air-conditioning outlet may serve a number of work spaces.

Peg boards, glassware cabinets, etc., have been eliminated and all glass apparatus has its proper storage space in the specially designed steel benches. There are no drainboards or storage spaces on top of the work bench for dirty glassware. Each chemist stores his dirty utensils in a specially designed stainless steel tray which fits into one of the end drawers of the work bench. The drawer has been constructed so that

the face may be swung downward and the tray slipped out. All dirty apparatus is collected at intervals and transported to a washing room. When clean, the apparatus is returned to the bench from which it came.

Reagent shelves, chemical storage shelves, etc., have also been eliminated. Reagents have been placed in specially designed wooden trays which are also stored in a bottom drawer of the work bench. For routine analytical procedures, reagents for each type of analysis are stored in separate



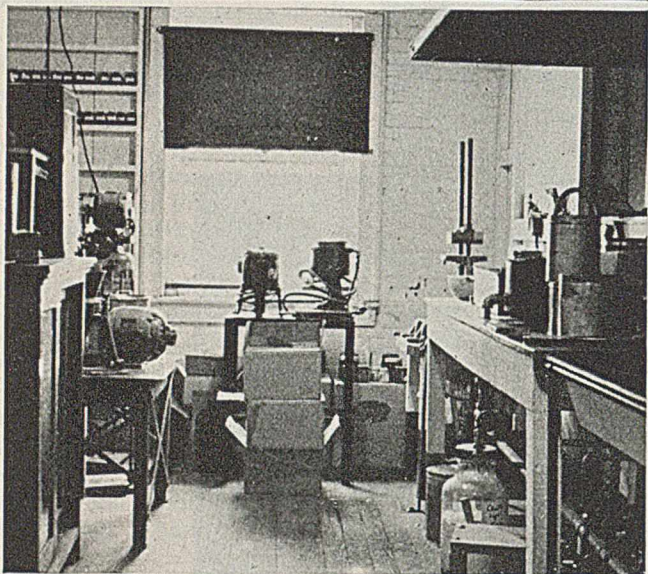
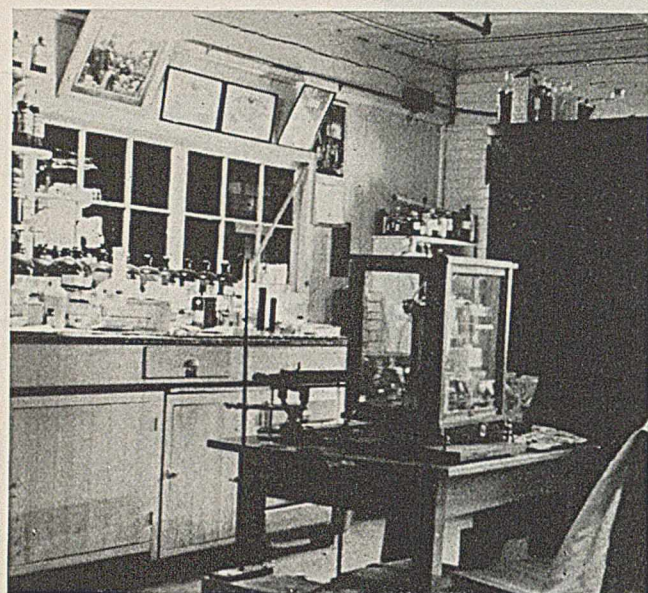


FIGURE 3. LABORATORIES BEFORE MODERNIZATION  
Pilot plant in center, bacteriological laboratory at bottom

trays and at the beginning of each work day, or at the beginning of each analysis, the proper tray is lifted out and put on the work space. As each analysis is completed the tray containing the reagents is put back into its proper space.

The equipment was designed for each type of individual project. Although storage drawers and closets are conventional there are several unique features, such as waste receptacles which have been designed to fit underneath the sinks. Slits have been cut in the bench door in front of the receptacle and a small chute or neck leads to the waste pan, assuring proper disposal. Another feature is the constant-temperature closet housing the shaking mechanism which has been installed in the bottom end of the bench devoted to routine analytical procedures.

Frogs used in biological tests have a specially designed storage tray in the pilot plant section of the laboratory. Temperatures in this tray are kept close to freezing in order to maintain these animals in their dormant state. Adjacent to the animal tray are two special units, one refrigerated in which preparations for sale in the colder sections of the world are tested, and one electrically heated for testing products shipped to tropical regions.

The pilot plant is equipped with laboratory-size production equipment such as filter presses, pill-coating machines, dryers, ball mills, fractionating apparatus, kettles, etc., and can duplicate any unit process used in manufacturing operations.

Each chemist has a fume hood adjacent to his desk. Each fume hood has a permanent, recessed, stainless steel water bath with an alberene stone top, and service facilities for hot and cold water, air, vacuum, gas, and steam. Each hood has an individual exhaust fan and an outside control for the gas line. The bottom portion of the rear partition and the top or exhaust part of the fume hoods are adjustable, thereby allowing a regulation of the draft space. For heavy gases the rear aperture could be made smaller, ensuring an increased velocity of incoming air.

All benches, desks, and cabinets are of aluminum-painted steel. Cabinets have adjustable shelves and each stone table top has several small cone-shaped drains lined with stainless steel for use on condenser water lines, and two small steam baths served with low-pressure live steam. These baths are used to warm flasks of inflammable chemicals and solvents, thereby making unnecessary the use of oil and sand baths except where high temperatures are needed.

A titration service area is located against the side wall of the bay devoted to routine analysis and with one exception partitions and superstructures have been eliminated. This exception is the bacteriological laboratory, which had to be separated from the main area, as the air is carefully filtered and sterilized. A sterilizing lamp can be seen in the picture of the bacteriological laboratory.

As a matter of convenience the center main aisle serves to separate the two activities of the laboratory, one side being devoted to control and analysis of raw and finished materials, the other to research, pilot plant, and bacteriological work.

Expensive and infrequently used apparatus has been placed on the center aisle end of the benches. In this manner equipment may be used without disturbing other workers and without requiring a special instrument room. A library and reading room are located at the end of the laboratory area.

A central main washing room and a chemical storage space serve the chemical as well as the company's animal laboratories.

#### Acknowledgment

The assistance of Francis Chilson, consulting engineer, in the modernization of the Norwich plant is gratefully acknowledged.



# Efficiency Requirements for A Laboratory Stirrer

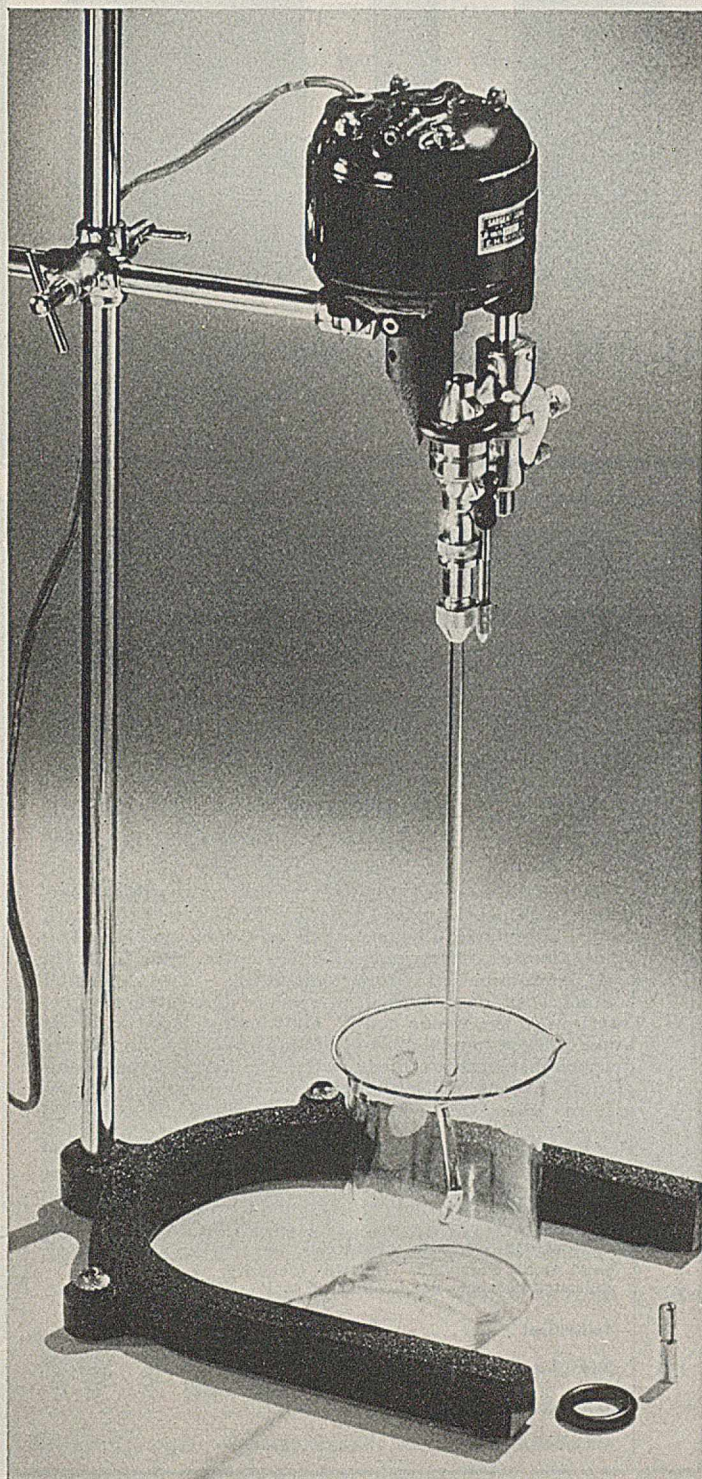
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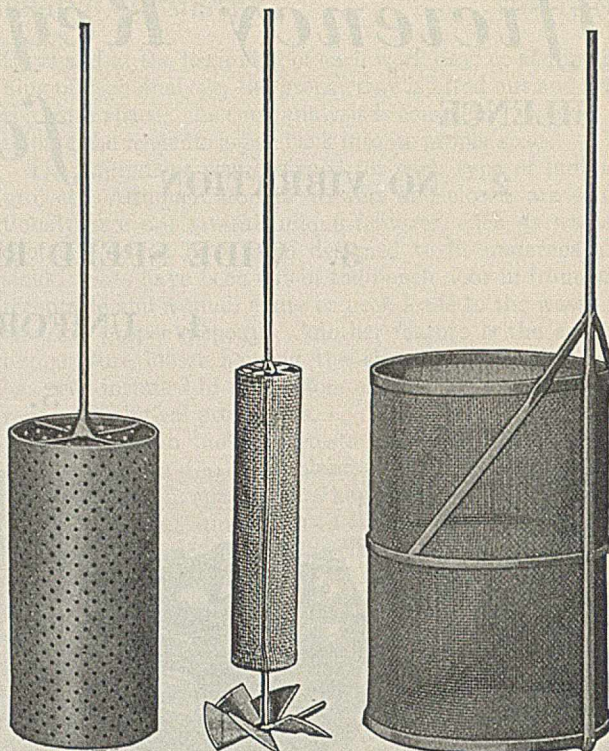
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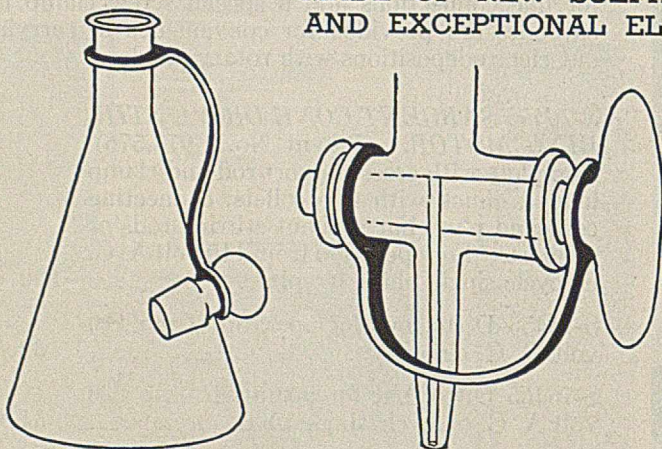
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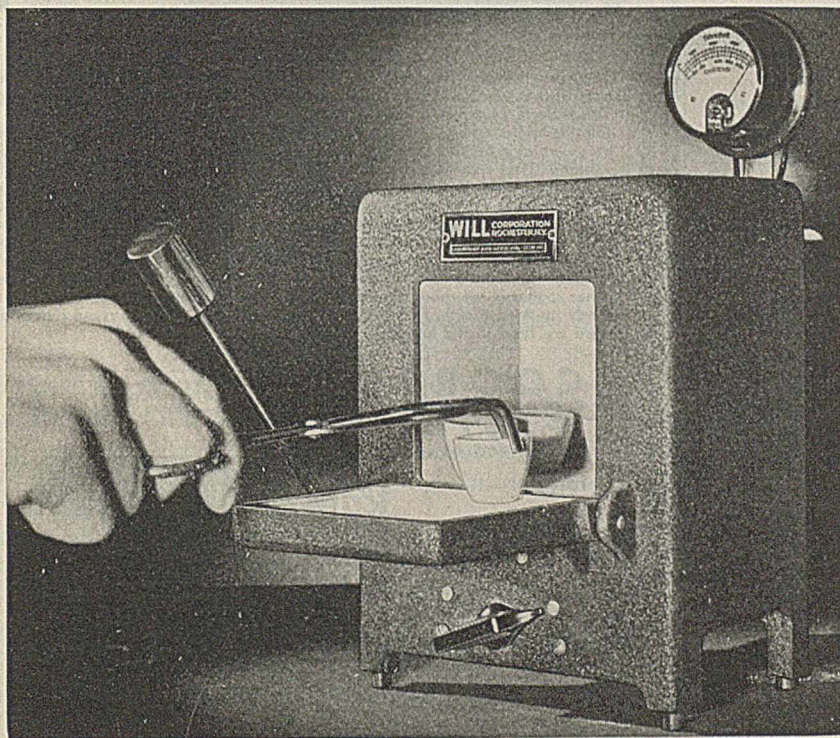


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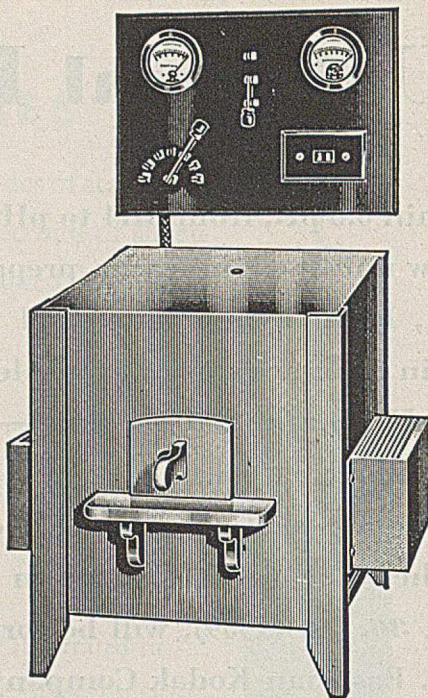
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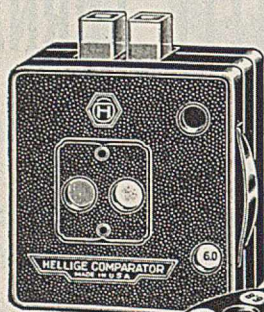
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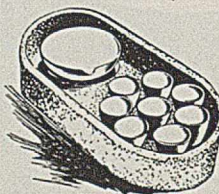
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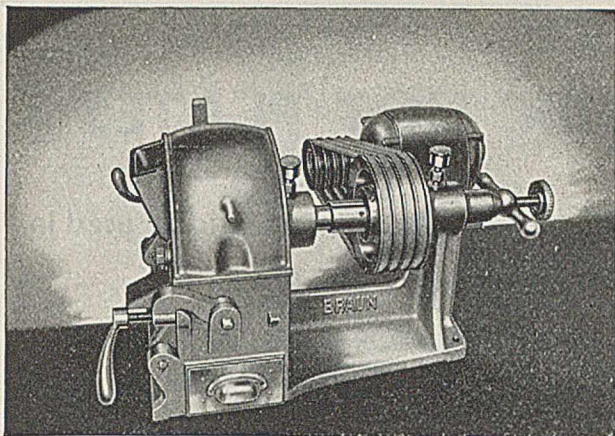
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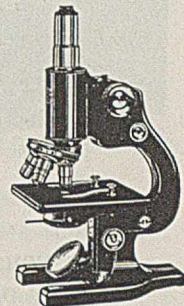


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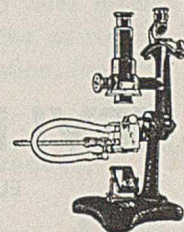
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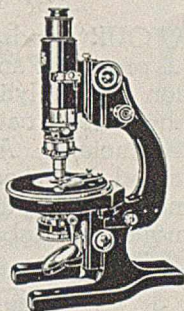
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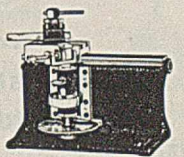
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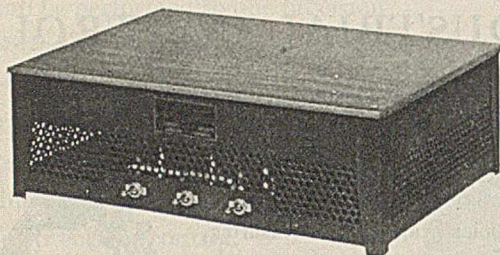


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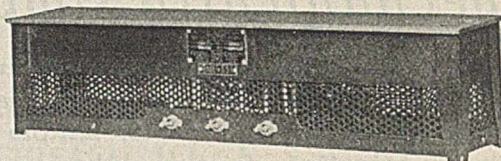
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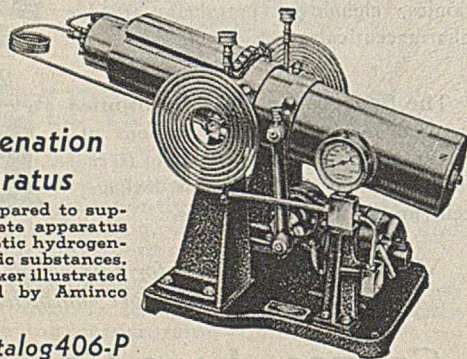
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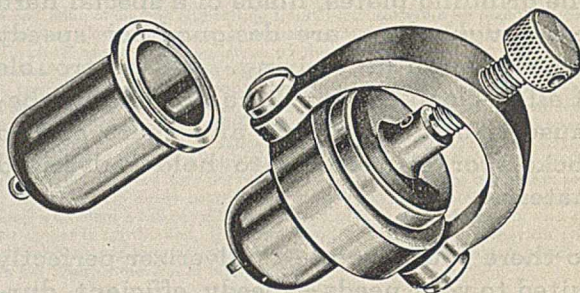
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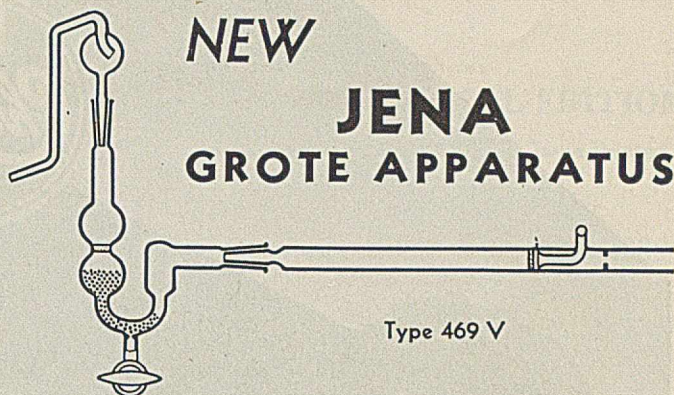
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