## INDUSTRIAL AND ENGINEERING CHEMISTRY

#### ANALYTICAL EDITION

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# Some Commercial Applications for Porous Products

#### REFRACTORIES

In the construction of electrically heated furnaces operating at high temperatures, a muffle having suitable chemical and physical qualities, is imperative.

#### The problem is to provide:

1. A muffle to be porous to allow the diffusion of hydrogen through the muffle so as to completely protect from oxidation the heating element and the work being heat-treated inside the muffle.

2. A muffle of high purity to operate satisfactorily in contact with molybdenum or tungsten wire at temperatures up to 1750° C without damage to the wire.

3. A muffle to be chemically unaffected by a reducing atmosphere, as these furnaces are generally flooded with a hydrogen atmosphere.

4. A muffle to be refractory enough to stand temperatures up to  $1750^{\circ}$  C.

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(ALUNDUM is the registered Norton trade mark for electrically fused alumina.)

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1. A porous medium having a controlled, uniform volume of pore space, depending on the requirements of the particular process.

2. A porous medium of a chemical stability and refractoriness to withstand chemical reaction with ingredients present at the temperatures of operation, which are frequently very high. 3. A porous medium of a purity necessary to avoid undesirable chemical reactions in the process.

4. A porous medium of the size and shape required by the process.

#### Solution

The solution was reached by using "controlled structure." Manufacture controlled the porosity and permeability.

Special shapes were developed to meet the "packing" requirement of the processes. In some cases, high purity ALUNDUM was necessary, whereas others could use the regular type of ALUNDUM. Carriers were, in some cases, supplied in the shape of crushed and screened porous grains controlled closely as to size. In others, porous tubes of proper size were supplied. These last are now playing a noteworthy part in the war effort. A wide combination of shapes and sizes can be produced to meet the given need. Of necessity, each



Diagram of High Temperature Electric Furnace Using ALUNDUM Tube and Operating in Hydrogen Atmosphere



Typical Shapes and Sizes of Catalytic Carriers

application must be developed in close co-operation with the user.

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#### ELECTROLYTIC DIAPHRAGMS

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The problem is to provide:

1. A diaphragm of a chemical stability to operate in the process without chemical contamination or reaction, and to meet specific electrical demands.

2. A diaphragm of refractoriness to withstand high temperatures.

3. A diaphragm of strength to give long life and a minimum of breakage. 4. A diaphragm of structural qualities to give the desired resistance to the passage of liquid, but, at the same time, maintain a minimum resistance to the passage of electric current.

5. A diaphragm of the shape required to fit into the desired cell.

#### Solution

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April 15, 1943

#### ANALYTICAL EDITION

Contraction of XY 888 Mr. Roy Troth Dept # 82 % Kimble Glass Go U.S. MC.UNIT \$300 2 PM Vineland, New Jersey SanEmacisco Cali Wed. Nov. 4, 1942 Mr. Anoth: I sav something that would probably be of some interest to you. I happened to be over at the field hospital the other day & while I was there I saw one of the technicians using one of your Inlyigette The straight pipette like Viginia graduates on the straight gigette machine. It seemed funny to see the old trade mark flown here in the vildeness of Quadelcanal. I though this would give you an idea of how Kinkle's ware gets to some gretty remote places in this World. hope the people now realize that they're r stop quiltling over shall domestic fighting a Sincerely natters, Chick Sclock Rt. Charles J. Schoch V--- MAIL





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5936-A.

SOLTYS ACTIVE HYDROGEN APPARATUS (Micro Gas Analysis Apparatus), A.H.T. Co. Specification. A micro modification of the Grignard machine, with glass parts of Pyrex throughout.

For the quantitative determination of active hydrogen atoms and of molecules or groups of molecules which react with Grignard Reagent even though methane is not evolved, i.e., where the moles of Grignard Reagent are added to the molecule. Accuracies within approximately 1% are possible but depend upon the structure of the compound. Deter-minations can be made with milligram samples.

For use in methods based on the procedure of L. Tschugaeff and Th. Zerewitinoff as modified for micro samples by A. Soltys — see Mikrochemie, Vol. 20 (1936), pp. 107-125, and J. B. Niederl and V. Niederl, "Organic Quantitative Micro-analysis," 2nd ed. (John Wiley & Sons, Inc., New York, 1942), pp. 263-272. The assembly consists of the following components:

- Components:
  Reaction Vessel A (Methane-Generator), with interchangeable ground joint for attaching Reaction Flasks F. Measuring tube for introduction of Grignard Reagent is graduated from 0 to 2 ml in 0.02 ml, with automatic zero adjustment. Side tube for aniline is graduated from 0 to 1 ml in 0.02 ml. Stopcocks are provided with special locking device to prevent leakage under pressure during shaking. Funnel G is for filling.
  Gas Burette with Manometer B (Methanometer). Burette is graduated from 0 to 7 ml in 0.02 ml, with corresponding marks on manometer tube at same level.
  Shaking Device C with pictor drive for aperation by either com-

Shaking Device C, with piston drive, for operation by either com-pressed air or vacuum. With fly wheel.

Support D, with base of Coors porcelain, 30-inch nickel plated rod and rack and pinion device for adjustment of leveling bulb. Burette Meniscus Reader E.

Water Bath K, of Monel metal, 35/s inches diameter. Micro Burner L. for artificial gas.

- Train for drying nitrogen gas, consisting of Drying Tube M and Gas Washing Bottle N; and Friedrich Gas Pressure Valve P for maintaining constant nitrogen pressure.
- Grignard Reagent Preparation Apparatus R, on Support S with Coors porcelain base and necessary Spring-Grip clamps.
   Benedetti-Pichler Drying Block T, Improved Form, modified to accommodate a measuring pipette and reaction flask F. With micro burner and thermometer.
- Ether Bottle U, 250 ml capacity; for storage of reagents.
- Storage Jar V, 125 ml capacity; for organic liquids. With special stopper to protect contents against moisture. Dropping Bottle W, 60 ml capacity.
- Wash Bottle X, 250 ml capacity, with fused-in white label. With saliva trap and movable capillary tip.
- Alber Micro Weighing Tube Y, with ground glass cap; for weighing hygroscopic substances.

5936-A. Soltys Active Hydrogen Apparatus, A.H.T. Co. Specification, as above described, complete assembly as shown in illustration, with glass parts of Pyrex and including accessories for preparing Grignard Reagent, modified Benedetti-Pichler Drying Block, two reaction flasks F, two thermometers, two pipettes 1 ml in <sup>1</sup>/<sub>10</sub>ths, Pyrex beaker 10 ml, two wash bottles labelled "Acetone" and "Alcohol 96%," respectively, with necessary Spring-Grip clamps, coil springs, rubber tubing connections, and directions for assembling. With burners for artificial gas, but without nitrogen tank or pressure reducing valve for same.......... \$193.25 Code Word.....

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## INDUSTRIAL AND ENGINEERING CHEMISTRY

#### ANALYTICAL EDITION

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## The Viscosity of Pitches

W. F. FAIR, JR., Mellon Institute, AND E. W. VOLKMANN, Koppers Company, Pittsburgh, Penna.

The viscosities of the less fluid bituminous materials are usually determined at elevated temperatures, under which conditions the consistencies may be convenient for estimation with empirical or capillarytype viscometers. To determine the viscosity of such materials at lower temperatures a simplified falling coaxial cylinder viscometer was devised, following the recommendations of Traxler and co-workers. Results obtained for a group of pitches indicate that these pitches exhibit viscous flow

THE absolute viscosities of tars and pitches may be readily determined at different temperatures by means of capillary rise viscometers as shown by Volkmann, Rhodes, and Work (6), and the change in viscosity with temperature thereby studied. However, the practical use of this method is restricted to temperature ranges in which the bituminous material under investigation is fluid enough to exhibit a measurable rise in a reasonable period of time, corresponding roughly to temperatures above the ring and ball softening point of the material. As a linear relation between log log viscosity and log absolute temperature has been found to hold for tars and pitches in this temperature interval by Rhodes, Volkmann, and Barker (3), confirming the earlier work of Ubbelohde and associates (5), it has been thought that viscosities at lower temperatures might be estimated by extrapolation of curves based on results obtained at the higher temperatures. The slope of this linear curve furnishes a convenient numerical reference for temperature susceptibility.

Because the normal use of many tars and pitches depends upon their properties at much lower temperatures than the ones at which the capillary rise method can be applied, it was determined to try to investigate the viscosities of these materials at lower temperatures by some other method, if possible, to determine whether or not the extrapolated viscosity values were of the correct order of magnitude.

After some time spent on studying the various methods which might give reliable results, it was decided to employ a simplified falling coaxial cylinder viscometer, such as has been described by Traxler and Schweyer (4). at  $25.0^{\circ}$  C., and have better temperature susceptibilities below their softening points than at higher temperatures. Viscosities calculated from the Saal viscosity-penetration relation do not agree with the results obtained with the falling cylinder viscometer.

Similar studies on a special pitch distillate demonstrate that this material changes upon standing with progressive increase in apparent viscosity and probable development of yield values.

Two instruments were made, one of brass, B, and one of aluminum, A; each set of cylinders rested upon a base equipped with detachable rods, upon which additional weights might be suspended, so that a wide range of weights could be used, and the material under examination thus subjected to widely differing stresses. The apparatus had the following dimensions: the height, L, of both inner and outer cylinders, was 2.54 cm., the inner radius, R, of the outer cylinder was 1.905 cm., and the radius, r, of the inner cylinder was 1.270 cm., as recommended by Traxler and Schweyer. The low-weight aluminum cylinder was used when the effects of relatively lower shearing stresses were being studied.

To make a determination, the space between the two concentric cylinders was filled with the molten pitch, which was allowed to cool to room temperature, then the excess material was trimmed off with a hot spatula, and the instrument was suspended in a constant-temperature bath. The viscometer assembly was placed upon a stand which supported the outside cylinder only, thus allowing the inner cylinder to fall at a slow rate, depending upon the nature of the material in the annular space, and the total weight of the inner cylinder, stem, and base, plus any suspended additional weights. The drop of this inner cylinder was observed by following a mark near the top of the upright stem attached through the inner cylinder to the base, by means of a micrometer microscope.

In Figure 1 are shown the filled B set of cylinders, three weights, two rods, the A set of cylinders, and the stem. In Figure 2 the viscometer is illustrated fully assembled but supported by a wire attached to the top of the stem to prevent any movement while the sample is coming to temperature. In Figure 3 the viscometer is presented as it appears while a determination is being made, with the inner cylinder and attached base and stem free to fall.

After observing the distance, h, in centimeters, through

TABLE I.	SOFTENING POINTS
Sample	Softening Point (Ring and Ball) ° C.
1 2 3 20 4 5	$53.4 \\ 55.1 \\ 52.2 \\ 56.8 \\ 56.0 \\ 57.0$

which the inner cylinder dropped in t seconds, under the influence of total weight, W, in grams, the viscosity is calculated by substituting in the following equation:

$$V = \left(\log_{e} \frac{R}{r}\right) \left(\frac{g}{2\pi L}\right) \left(\frac{W \times t}{h}\right)$$

For the specified dimensions of the instrument described above, this expression reduces to

$$V = (0.4055) (61.466) \left(\frac{W \times t}{h}\right) = 25.0 \left(\frac{W \times t}{h}\right)$$

From this formula the apparent viscosity for any given weight may be calculated. If the material being examined exhibits truly viscous flow, the viscosity will be constant, independent of the weight used; but if the material is nonviscous, the apparent viscosity will increase with decreasing weights. For this reason it is of value to know the shearing stress and the rate of shear, for a graph showing these functions indicates the apparent viscosity and the yield value. If the material exhibits viscous flow, the curve will be a straight line directed toward the origin.

These values may be calculated according to the following equations:

Shearing stress, $F = \frac{-Wg}{2\pi L} \left(\frac{1}{R} - \frac{1}{r}\right) = 16.1 \times$	w
Average rate of shear, $\frac{dv}{dr} = \frac{h}{l} (R - r) = (0.635)$	$\binom{h}{\overline{t}}$



FIGURE 1. CYLINDERS, WEIGHTS, RODS, AND STEM

Five different coal-tar pitches were obtained for measurement of viscosity in this apparatus and a sixth pitch, No. 20, was prepared by distilling heavy water-gas tar in the laboratory. Their softening points (ring and ball) are given in Table I.

In Table II are set forth the experimental observations and calculated results for the viscosity, shearing stress, and the rate of shear, as determined at 25° C. for these pitches. Inspection of this tabulation shows that reproducible results have been obtained, and that these pitches have constant



FIGURE 2. ASSEMBLED VISCOMETER

viscosity at 25° C. (within an experimental error of about 5 per cent) over a wide range of applied stresses. In Figure 4, the respective shearing stresses, F, are plotted against the corresponding rates of shear  $\left(\frac{dv}{dr}\right)$ ; inspection of these curves clearly indicates that these pitches exhibit truly viscous flow at 25° C.

The linear curves obtained by plotting stress against rate of shear in all cases may be extrapolated to the origin, thus emphasizing the purely viscous nature of these materials.

To obtain a rough evaluation of the temperature susceptibility of these pitches at low temperatures it was decided to

TABLE II.	Viscos	іту, Sh	EARING	STRESS,	AND	RATE	OF SHEAR
Sample	W Grams	Drop Mm.	Time Sec.	Viscos Poise	ity	F	dv/dr × 10⁵
5 Av.	87.0 169.3 216.8 300.3 435.1	$1.32 \\ 1.77 \\ 1.80 \\ 2.52 \\ 1.91$	3600 2519 1990 2033 1051	5.94 × 6.02 6.03 5.89 5.99	107	1400 2730 3500 4830 7000	2.344.565.848.1911.7
20	$\begin{array}{r} 87.0\\ 169.3\\ 216.8\\ 300.3\\ 435.1\\ 442.4\end{array}$	1.832.472.763.215.034.83	2498 1739 1392 1202 1318 1335	2.96 × 2.98 2.73 2.82 2.84 3.05	107	1400 2730 3500 4830 7000 7100	$\begin{array}{r} 4.73\\ 9.18\\ 12.9\\ 17.1\\ 24.7\\ 23.6\end{array}$
Av. 4 Av.	87.0 169.3 216.8 300.3 435.1	$1.64 \\ 2.49 \\ 3.06 \\ 3.95 \\ 3.06 \\ 3.06 \\$	3635 2842 2622 2565 1319	$2.89 \times 4.82 \times 4.83 \times 4.65 \times 4.65 \times 4.69 \times 4.77 \times 10^{-10}$	10 <sup>7</sup> 10 <sup>7</sup>	1400 2730 3500 4830 7000	$2,90 \\ 5.66 \\ 7.55 \\ 10.0 \\ 14.9$
2 Av.	87.0 170.5 217.5 300.6 435.3	3.76 4.69 3.98 5.34 5.91	3643 2269 1466 1431 1104	$2.11 \times 2.13$ 2.01 2.01 2.07 $2.07 \times 2.07 \times 10^{-10}$	107	1400 2740 3510 4830 7000	$\begin{array}{r} 6.64 \\ 12.9 \\ 17.5 \\ 24.0 \\ 33.8 \end{array}$
1 Av.	87.0 170.5 217.5 300.6 435.3	3.72 4.36 4.15 5.48 6.39	2751 1656 1188 1158 909	$1.61 \times 1.63$ 1.57 1.59 1.55 $1.59 \times 1.59 \times 1.59$	107	1400 2740 3510 4830 7000	$\begin{array}{r} 8.70 \\ 16.8 \\ 22.3 \\ 30.4 \\ 45.1 \end{array}$
3 Av.	87.0 217.5	1.19 2.60	1553 1284	2.84 × 2.69 2.77 ×	10 <sup>7</sup> 10 <sup>7</sup>	1400 3510	4.93 13.1

	TABLE III.	TEMPERATURE SUS	SCEPTIBILITY	s
Sample	Softening Point	Viscosity at Softening Point	Viscosity at 25° C.	
	° C.	Centistokes	Centistokes	
5 20 3 4 2 1	57.0 56.8 52.2 56.0 55.1 53.4	$\begin{array}{cccc} 1 & \times & 10^{6} \\ 1 & \times & 10^{6} \end{array}$	$\begin{array}{c} 4.68 \times 10^9 \\ 2.33 \times 10^9 \\ 2.25 \times 10^9 \\ 4.00 \times 10^9 \\ 1.67 \times 10^9 \\ 1.30 \times 10^9 \end{array}$	1.04 0.98 1.12 1.05 0.99

convert the above viscosities to kinematic viscosity at 25° C. and use the approximate relation of a viscosity of  $1 \times 10^6$  centistokes at the temperature of the ring and ball softening point. The values for the temperature susceptibility thus obtained are given in Table III. These values are the slopes of the straight lines obtained by plotting log log viscosity against log absolute temperature in each case.



FIGURE 3. VISCOMETER

With the exception of pitches 3 and 20, these values are somewhat lower than has previously been generally found for similar tars, where the calculation of the temperature susceptibility was based upon viscosity determinations made at higher temperatures. Assuming the softening point relation to be sufficiently accurate for these considerations, it is obvious that either the viscosity as above measured is incorrect, or the temperature susceptibility of these pitches at low temperatures is better than has been generally believed.

In continuing this investigation it was decided to determine the viscosity coefficients for some of these pitches at different temperatures by the more reliable falling cylinder and capillary rise methods. Typical results, converted to centistokes, are summarized in Table IV. From these findings it appears by indirect comparison that the falling cylinder viscometer gives values comparable to results obtained by the small capillary rise instrument. Some time after these determinations had been completed an open-end rotating cylinder viscometer as devised by Ford and Arabian (1) was available.



Results with this instrument agreed well with the coaxial viscometer referred to. The temperature susceptibility of these pitches at low temperatures thus appears to be better (lower) than has been previously suspected. If log log viscosity is plotted against log absolute temperature over the intervals discussed, it appears (Figures 5 and 6) that for two typical pitches the temperature susceptibility below the softening point is lower than it is above that temperature. Included for comparison (Figure 7) is a curve based on Pochettino's results roughly converted to centistokes (taken from 2), which also seems to indicate a break in the curve near the softening point region, but in the opposite direction than was found for the two pitches discussed above; in other words, this pitch showed a poorer susceptibility at low temperatures than at high temperatures, which is just the reverse of the results found for the pitches here described. It is believed that the results described truly represent changes in susceptibility occurring in the general region of the softening point and are not due to instrumental differences, since the results of Table IV indicate that viscosity measurements

		Та	BLE IV. VI	SCOSITY		
Sample	Tempera- ture ° C.	Method	Viscosity Centistokes	Tempera- ture ° C.	Method	Viscosity Centistokes
5	25 45	Cylinder Cylinder	$4.68 \times 10^{9}$ $1.55 \times 10^{7}$	35 45.1	Cylinder Large capillary	$2.0 \times 10^{8}$ $1.46 \times 10^{7}$
	55 70	Small capillary Small capillary	$1.43 \times 10^{4}$	55 85	Large capillary Small	1.51 × 10*
20	25 45	Cylinder Cylinder	$2.33 \times 10^{9}$ $1.40 \times 10^{7}$	35 35	Cylinder Large capillary	$1.63 \times 10^{4}$ $1.63 \times 10^{4}$
	70	Small capillary	1.23 × 10 <sup>5</sup>	85	Small capillary	1.55 × 104

made by the capillary and falling cylinder viscometers are in agreement.

Penetration measurements were made for these pitches and viscosity results were then calculated by the Saal relation. The results were much lower than were reported above, but the ratio of the viscosity determined by the falling cylinder to that calculated by the Saal formula seemed to decrease with increasing penetrations, as shown in Table V.



the second se			
	TABLE V.	VISCOSITY	
Sample	Penetration	Viscosity by Cylinder, 25° C. Poises	Ratio of Viscosities
	27.3 25.2 22.9 22.7 18.4	$1.59 \times 10^{7}$ 2.07 2.77 2.89 4.77	$     \begin{array}{r}       1.78 \\       2.00 \\       2.25 \\       2.28 \\       2.47 \\     \end{array} $
5	16.1	2.95	2.44

To learn whether or not the ratio of these viscosities might approach unity for softer pitches, as seems to be indicated, several pitches of lower softening points were prepared and investigated. The results obtained will be given in a subsequent paper.

As these results agreed well with earlier reports concerning the viscous flow of pitches, it was decided to investigate, as a possible interesting contrast, the flow properties of a highboiling pitch distillate, which is in the state of a soft paste at room temperature. Previously empirical investigations had indicated the probability of anomalous flow for this material. Viscosity determinations were therefore made at  $25^{\circ}$  C., using the falling coaxial cylinder viscometer described previously.

At first the results for pitch distillate, with a softening point (ring and ball) of approximately  $43.0^{\circ}$  C., were rather scattered, but later, when standard test procedures were arbitrarily adopted, and strictly adhered to, better agreement was obtained. A summary of the preparations, test procedures, and the experimental data is given in Table VI, and the stress-rate of shear curves is presented in Figure 8. Comments on these flow properties have been included with each set of determinations.

From these results it is obvious that the flow properties of pitch distillate will depend upon its previous treatment, and





upon the stresses to which it is subjected, as well as upon intermediate fluctuations in temperature, in all of which factors this distillate differs from residual straight-distilled tars and pitches.

#### Conclusions

In consequence of this investigation it is felt that the falling cylinder viscometer will prove to be a valuable tool for the determination and comparison of the rheological properties of tar products. Some typical pitches exhibit viscous flow and have better temperature susceptibilities below their softening points than has been previously thought to be the case from considerations based upon extrapolations from viscosity measurements at higher temperatures.

These tentative conclusions may be modified after future research. It is be-

lieved that continued experimentation along these lines will add materially to our present knowledge of the flow properties of tars and pitches.

#### Acknowledgment

The authors wish to express their appreciation to H. R. Beck and E. J. Maloney for assistance in laboratory determinations and in the preparation of the graphs.

#### $\frac{dv/dr}{\times 10^{3}}$ Drop w Sample Time Viscosity F Grams Mm. Sec. Poises 363-B $0.280 \times 10^{7}$ 0.271(dehydrated pitch distillate, poured at 100° C., in air 20 minutes, in bath 15 minutes) $3.95 \\ 4.39 \\ 4.74 \\ 4.52$ 59.9 739 963 $34.3 \\ 51.9 \\ 72.0 \\ 128.0$ 87.0 121.9 217.5 $1400 \\ 1960$ 545 0.272 193 228 3510 $0.276 \times 10^{3}$ Av. 363-C (363-B, poured at 100° C. in air 16 hours, in bath 15 minutes) $\begin{array}{r} 4.10 \\ 4.02 \\ 3.64 \\ 4.57 \end{array}$ 229.3 $0.304 \times 10^{7}$ 0.3640.424 $3510 \\ 1400 \\ 963$ 217.5 87.0 $114.0 \\ 38.6 \\ 22.7 \\ 61.7$ 670 87.0 59.9 1030 121 9 491 0 318 1960 Increased apparent viscosity, nonviscous flow, y value about 350 dynes per sq. cm. ield 363-D 217.5 87.0 121.9 (363-B, poured at 100° C., cooled, 3 falls and recoveries in air, in bath 15 $4.58 \\ 4.66$ 230.2 0.273 × 107 3510 127.0 $0.294 \\ 0.269 \\ 0.292 \\ 0.282 \\ 0.282$ 47.6 73.0 33.0 632 1400 4.86 minutes) 431 1960 59.9 834 963 × 107 Slightly increased apparent viscosity, small yield value of about 100 dynes per sq. cm. 363-F 217.5443.4573.5(363-B, in air 16 hours, then 1 hour at 60° C. in oven) 0.0 3000 $(high) \\ 2.84 \\ 1.63 \\ 1.63$ 3510 7120 9240 0 2.51 0.62 1591 1553 5.65 Greatly increased apparent viscosity, nonviscous flow, yield value of about 6000 dynes 363-H-1 217.5 87.0 3.32 $1.53 \\ 1.82$ (363-B in air 47 hours) 933 $3510 \\ 1400$ 22.9 $\times 10^{7}$ 1302 363-H-2 (363-H-1 recovered, and redeter-mined) 3.24 Increased apparent viscosity with time, decreased by "working", 1222 $1.14 \\ 1.59$ 17.2 1960 59.9 1.76 1866 1.59 963 6.05 decreased by "working", yield value unchanged, remaining about 350 dynes per sq. cm. (compare with 363-C) 363-I (363-B, poured at 100° C., cooled, 20 minutes in oven at 60° C., then determined) 87.0 217.5 59.9 121.9 $1.77 \\ 4.29 \\ 2.79 \\ 5.08$ 507 242 846 532 $\begin{array}{c} 0.625 \times 10^7 \\ 0.308 \\ 0.456 \\ 0.319 \end{array}$ $22.4 \\ 114.0 \\ 21.1 \\ 61.5$ $\frac{1400}{3510}$ 963 1966

TABLE VI. SUMMARY OF DATA

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## **Viscosity of Coal-Tar Residues**

#### Comparison of Viscosity Measurements and A. S. T. M. Penetration Tests

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The industrial chemist who examines the asphaltic and coal-tar residues commonly used for protective coatings, roofing, and waterproofing purposes determines the apparent viscosities of these materials by the A.S.T.M. penetration test. Many attempts have been made to correlate the results of this test with absolute viscosity measurements. The formula established by Saal has been accepted by many investigators as a reliable relationship as long as the materials under test do not show anomalous flow properties. A theoretical analysis of the empirical formula confirms the validity

THE penetrometer is the instrument commonly used in commercial laboratories for evaluating the flow characteristics of materials of high consistency. The equipment and procedure are specified by the American Society for Testing Materials (1). The test with this instrument has the advantage that the equipment needed is simple and relatively inexpensive, and requires little skill in its operation. The disadvantage of the penetration test is its empirical nature. Results are expressed in terms of decimillimeters which have no direct relation to accepted rheological units, thus making it impossible to correlate penetration measurements with other consistency tests.

In 1933 Saal and Koens (5) published the results of an investigation concerning the rheological properties of some asphaltic materials. On the basis of tests conducted on two steam-distilled asphalts they came to the conclusion that in the case of "nonplastic asphaltic bitumens" the relationship between penetration measurements and absolute viscosity can be expressed by

## $\eta = \frac{5.9 \times 10^9}{(\text{penetration})^{1.93}}$

where  $\eta$  is viscosity in poises and penetration is expressed in decimillimeters. This formula, known as the Saal formula, has been used by many technologists. Saal (4) indicated that it can be partly derived from theoretical considerations. Rhodes and Volkmann (3) confirmed this contention, proceeding from different assumptions.

Traxler and co-workers (9) inquired into the validity of the Saal formula by a carefully conducted study of the rheological properties of a series of steam-distilled asphalts selected as most closely approaching materials of normal, or Newtonian, flow characteristics. They found that in general a straight-line relationship resulted if the logarithm of viscosity was plotted vs. the logarithm of penetration. Each asphalt, however, gave a separate line differing from the line representing the Saal formula and from that of other asphalts. Furthermore, a closer inspection of the line resulting from connecting the experimental points for any given asphalt showed that it was actually a sinuous curve and not a straight line. In a discussion of Traxler's results Saal and Labout (6) insist that the application of the Saal formula is permissible only for materials of a purely viscous character and intimate that Traxler's asphalts do not fulfill this requirement. It is not surprising that in reply Traxler (8) claims that "this stringent limitation of the applicability of the relationship makes it worthless from an industrial standpoint...." of its general form. The results of a number of viscosity determinations and the corresponding penetration values of various pitches exhibiting viscous flow are presented and correlated on double logarithmic coordinate paper. The Saal formula seems reasonably reliable above penetration values of about 60 decimillimeters. Below this value considerable deviations are apparent. This is not surprising, since the standard penetration needle is not a simple cylindrical stem but consists of a cylindrical shank with a truncated cone 54 decimillimeters long.

It is probably correct to state that most commercial asphalts exhibit some elasticity, thixotropy, or anomalous flow properties. In contradistinction straight-distilled coaltar pitches and related materials, consisting mainly of condensed aromatic ring structures, seem to retain their normal Newtonian flow characteristics over a wider range of consistencies even upon aging. It seemed to the authors that these products should be especially suited to check the validity of the Saal formula; hence an investigation was undertaken to determine whether in the case of coal-tar pitches a definite relationship existed between penetration data and absolute viscosity measurements and, if this should be the case, to find out whether the relationship could be expressed adequately by the Saal formula.

A total of 23 samples was selected. Five of these (group A) were commercial coal-tar pitches prepared by batch-distillation of coke-oven tar in direct-fired horizontal stills. Each sample came from a different crude tar. The next four samples (group B) were coal-tar pitches prepared in the laboratory by distillation of four different crude coke-oven tars. A further group (C) of nine samples was obtained in the laboratory from one crude coke-oven tar by a single distillation, during which pitch-residue samples of increasing consistencies were withdrawn. As some of the heavy water-gas tars in their physical and chemical characteristics resemble coke-oven tars, five samples of pitches derived from such water-gas tars were also tested (group D). They were prepared in the laboratory by distillation of different crudes. Finally, as a matter of curiosity, a sample of pitch of higher softening point was also included. This pitch had a penetration (100 grams, 5 seconds, 25° C.) of 1 decimillimeter, a value below the accepted lower range limit for the instrument.

The choice of samples for the purpose at hand seemed appropriate, particularly because Traxler and Coombs (7) have indicated that the presence and magnitude of anomalous flow properties of asphalts depend upon the source, the type and degree of processing, and the temperatures and rates of shear at which the measurements of flow are made. The samples represent a wide variety in source and in the type and degree of processing. As the rate of shear changes with the depth of penetration and because the consistencies of the samples selected cover the whole practical range of the penetrometer, the factor of rate of shear is also varied. Furthermore, a few of the pitches (group A) used in this investigation have been shown (2) to exhibit normal flow characteristics at  $25^{\circ}$  C. under different stresses.

There remains the factor of temperature. Inasmuch as the investigation has been conducted primarily to determine whether penetration test results as obtained in commercial testing laboratories can be converted into absolute viscosity units, and because the penetration test is most commonly conducted at 25° C., it was decided not to vary the temperature and to determine penetration values and absolute viscosities at 25° C.

The penetration measurements have been made in accordance with the test procedure specified by the A. S. T. M. (1). At least three tests were run on each material and the average was reported.

	TABL	E I. VISCO	SITY	Deviation
Sample No. Grouj	Penetration (100 Grams; 5 Seconds, 25° C.)	Observed Viscosity	Calculated Viscosity (Saal Formula)	Deviation from Observed Value
7         B           12         C           11         C           22         D           23         D           24         D           25         D           9         B           14         A           2         A           10         B           3         A           20         D           15         C           4         A           5         A           10         C           15         C           16         C           17         C           18         C           31	$\begin{array}{c} 195\\ 186\\ 186\\ 186\\ 156\\ 156\\ 156\\ 156\\ 156\\ 156\\ 273.8\\ 69.2\\ 57.5\\ 53.1\\ 36.0\\ 27.3\\ 25.2\\ 223.4\\ 22.9\\ 22.7\\ 19.9\\ 18.4\\ 16.1\\ 14.1\\ 9.3\\ 5.2\\ 3.1\\ 1.0\\ \end{array}$	$\begin{array}{c} 1.998 \times 10^{5}\\ 2.02 \times 10^{5}\\ 2.02 \times 10^{5}\\ 2.12 \times 10^{5}\\ 2.48 \times 10^{5}\\ 2.97 \times 10^{5}\\ 3.74 \times 10^{6}\\ 1.41 \times 10^{6}\\ 1.42 \times 10^{6}\\ 2.42 \times 10^{6}\\ 2.51 \times 10^{7}\\ 2.55 \times 10^{7}\\ 3.49 \times 10^{7}\\ 4.77 \times 10^{7}\\ 5.95 \times 10^{7}\\ 7.11 \times 10^{7}\\ 1.99 \times 10^{8}\\ 4.28 \times 10^{8}\\ 7.99 \times 10^{8}\\ 3.2 \times 10^{8}\\ \end{array}$	$\begin{array}{c} 1.03828\\ 1.95\times10^3\\ 2.14\times10^5\\ 2.16\times10^5\\ 3.00\times10^6\\ 3.08\times10^5\\ 3.08\times10^5\\ 1.27\times10^6\\ 1.44\times10^6\\ 2.40\times10^6\\ 2.40\times10^6\\ 5.02\times10^6\\ 8.67\times10^6\\ 1.01\times10^7\\ 1.22\times10^7\\ 1.22\times10^7\\ 1.22\times10^7\\ 1.17\times10^7\\ 1.22\times10^7\\ 1.21\times10^7\\ 1.31\times10^7\\ 2.40\times10^7\\ 2.40\times10^7\\ 3.23\times10^6\\ 5.78\times10^6\\ 5.28\times10^6\\ 3.29\times10^6\\ \end{array}$	$\begin{array}{c} & & & & & \\ & - & 2.0 \\ & + & 5.9 \\ & - & 1.9 \\ & + & 3.7 \\ & + & 3.7 \\ & + & 3.7 \\ & + & 1.4 \\ & - & 4.4 \\ & - & 4.4 \\ & - & 4.5 \\ & - & 53.3 \\ & - & 55.2 \\ & - & 55.2 \\ & - & 55.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.2 \\ & - & 56.$

The viscosities have been determined with the falling coaxial cylinder instrument described in a previous paper (2).

The results are presented in Table I and Figure 1. In Table I the materials are listed in the sequence of their ascending consistencies. In the fifth column is shown the viscosity calculated by the Saal formula from the penetration as determined for each sample, and in the last column the deviation of the calculated from the observed viscosity is recorded.

An inspection of the values given in the last column shows that for penetration readings of more than 50 decimillimeters the data derived from the Saal formula are in fair agreement with the observed viscosity data. The greatest deviation is 21 per cent and the average deviation is 6.7 per cent. The agreement is excellent if the residues of group D are excluded—i. e., if only residues of coal-tar origin are considered. In that case the maximum deviation is only 5.9 per cent and the average deviation 3.2 per cent.

But for penetration readings of less than 50 decimillimeters there is considerable divergence between the observed viscosity data and the values derived from the Saal formula. The experimental data with one exception all seem to fall on a smooth curve (see Figure 1), indicating that the divergence is caused not by the appearance of anomalous flow properties but by factors not considered in the Saal formula. In all probability the physical shape of the penetrometer needle is responsible for the failure of the formula at readings below 50 decimillimeters. The needle consists of a cylindrical shank with a truncated cone at its lower extremity. If, in the course of a penetration measurement, the needle drops to a depth greater than the length of the truncated cone (5.4 mm.), the resistance to further immersion probably is determined principally by the cylindrical shaft. Under those conditions a simple relationship between viscosity and penetration, such as the Saal formula, may well hold,



FIGURE 1. VISCOSITY DETERMINATIONS WITH FALLING COAXIAL CYLINDER INSTRUMENT

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at least for materials of the type tested. If, however, only the conical portion of the needle is partially immersed, conditions are much more complex and the same relationship cannot be expected to apply.

#### Conclusion

It can be concluded that, in the case of coal-tar pitches and, to a less extent, of pitches from heavy water-gas tars, there is a definite relationship between standard A. S. T. M. penetration measurements (100 grams, 5 seconds 25° C.) and absolute viscosity. This relationship is well expressed by the Saal formula only for penetration readings above 55 decimillimeters. Below this value the formula is not applicable.

#### Acknowledgment

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## **Determination of Benzene**

#### Detection and Estimation of Benzene in the Presence of **Toluene**, Xylene, and Other Substances

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THE known chemical methods for the determination of benzene do not appear to be applicable in the presence of its homologs, especially toluene and xylene. The sulfuric acid-formaldehyde (4), nickel cyanide (7), dracorubin (2), levulose (10, 11), butanone extraction (13), m-dinitrobenzene reduction (5, 12, 14, 15), and Stepanow colorimetric methods (1) are not specific for benzene. Physical methods for detection of benzene, such as fractionation or ultraviolet absorption (3), likewise cannot be used to estimate the concentration of benzene when it is mixed with unknown concentrations of other substances including its homologs. The method described below was developed in order to satisfy the need (6, 8, 9) of being able to ascertain the presence and concentration of benzene in mixtures of various materials as it is commonly encountered in industry.

Briefly, the method consists of nitration, extraction with ether, development of color with butanone and alkali in alcoholic solution, elimination of the color due to interfering substances by the addition of acetic acid, and comparison of the residual color.

Benzene when nitrated in the manner described below is almost completely converted to m-dinitrobenzene. This compound when treated with butanone and sodium hydroxide in alcoholic solution produces a crimson color. Toluene, when similarly treated, is partly converted to the dinitro compound and forms a blue color which quickly turns violet; xylene forms a relatively permanent deep blue color. After addition of acetic acid, the color due to benzene remains; the colors due to toluene and xylene disappear rapidly. No color is generated with the aliphatic hydrocarbons and their derivatives such as methanol, ethanol, ethyl acetate, isopropyl alcohol, butanol, butyl acetate, acetone, and

similar substances found in such commercial products as paints, lacquers, solvents, and thinners.

#### **Reagents and Apparatus**

Nitrating mixture, equal parts by volume of fuming nitric acid, specific gravity 1.49 to 1.50, and concentrated sulfuric acid, specific gravity 1.84.

Sodium hydroxide aqueous, 1 volume of 40 per cent sodium hydroxide diluted to 4 volumes with distilled water.

Sodium hydroxide alcoholic made by diluting 1 volume of 40 per cent sodium hydroxide to 10 volumes with 95 per cent alcohol and filtering just prior to use. Acetic acid, made by diluting 1 volume of glacial acetic acid to

10 volumes with 95 per cent alcohol. Butanone (methyl ethyl ketone), practical grade. Set of test tubes of about 50-ml. capacity. These tubes should be of the same diameter (2 cm.) and equal transparency. A photoelectric colorimeter may be used if available.

Pipets graduated to 0.01 ml.

#### Procedure

A 0.50-ml. portion of the solution to be analyzed is measured into a 50-ml. Erlenmeyer flask. The flask is placed in a freezing mixture which consists of chopped ice and salt at a temperature of  $0^{\circ}$  to  $-5^{\circ}$  C. Nitrating mixture from a buret is added to the Solution at the rate of 2 drops per second while the flask is rotated. After 10 ml. have been added, the flask and contents are removed from the ice mixture and 35 ml. of distilled water are added.

The resulting mixture is cooled to room temperature and the nitrated hydrocarbons are extracted with ether, by shaking the mixture with 25 ml. of ether in a 125-ml. separatory funnel and repeating the extraction of the aqueous layer three times with 10 ml. of ether each. The ether layers are transferred into a 100-ml. volumetric flask. The combined ether solutions are poured into the separatory funnel and washed with 10 ml. of aqueous sodium hydroxide reagent, then consecutively with 2 portions of 10 ml. of



FIGURE 1. RATE OF COLOR DEVELOPMENT AND DETERIORATION

distilled water. The washed ether solution is then returned to the 100-ml. flask and 95 per cent ethyl alcohol is added to make a total volume of 100 ml. A 10-ml. aliquot of this solution is pipetted into a 50-ml. volumetric flask and 95 per cent alcohol added to the 50-ml. mark.

A 10-ml. portion of the last solution is now measured into one of a set of similar glass tubes. One or more 10-ml. samples of known concentrations of nitrated benzene made as above are also measured into other tubes of the set. To each are added 1.0 ml. of butanone and 0.50 ml. of alcoholic sodium hydroxide reagent. The tubes are agitated and after 5 minutes the colors are observed. Portions of 0.50 ml. of acetic acid reagent are now added to each tube. The tubes are again agitated and after 10 minutes the color is compared with that of the standard most closely approaching it in intensity.

The comparison may be made as follows: A measured quantity of alcohol is added from a buret or pipet to the solution of greater intensity until both tubes match exactly. If the test solution has a yellow tinge, as is found when high concentrations of xylene are encountered, a dilute solution of sodium or potassium dichromate placed in back of the tube containing the known concentration is of considerable aid in matching the two solutions. The quantity of alcohol added must be taken into consideration. If after 2.5 ml. of alcohol have been added to the test solution, it matches the standard containing the equivalent of 10 per cent benzene, the concentration of benzene in the sample =  $\frac{12 + 2.5}{12} \times 10 = 12.1$ 

per cent.

As an alternative to the above, which may be called the dilution method of comparison, a set of standards of varying concentra-tions may be used. This is known as the standards method of comparison. Standards—e. g., 12.0, 12.5, 13 per cent, etc.— may be obtained from 15 or 20 per cent benzene by diluting the alachelic solution of mitrated horzone with requisite volumes of alcoholic solution of nitrated benzene with requisite volumes of alcohol. Butanone, sodium hydroxide, and acetic acid reagents must be added to these standards at the same time and under the same conditions as in the case of the solution whose benzene concentration is to be determined. The intensity of color may be compared with the aid of an ap-

propriate colorimeter such as the Evelyn photoelectric colorimeter with filter No. 620. Readings are taken on the galvanometer scale 5 minutes after the sodium hydroxide reagent has been added (A), and again 10 minutes after the acetic acid reagent has The concentration of benzene is then read been added (B). directly on a curve previously plotted as concentration of ben-zene vs. light transmittance or readings on the galvanometer scale. If the difference in the two readings—i. e., B - A—is not very great, no correction is necessary. If, however, the difference is considerable, an empirically obtained correction is applied. If the reading A is 0, the color should be developed on a more dilute This may be obtained by taking a smaller volume of solution. alcohol-ether solution—e. g., 5 ml. instead of 10 ml.—and adding alcohol to a final volume of 10 ml. in the test tube before adding the alkali and acid reagents. This dilution must, of course, be taken into account in the computation.

The reference curve which is used with the photoelectric colorimeter is plotted from the readings obtained on solutions of varying known concentrations of benzene. These solutions are prepared by diluting c. P. benzene with purified petroleum naphtha and treating them in the manner described above and under similar conditions.

The analysis need not take more than 30 minutes. The nitration takes about 2 minutes. The dilution, cooling, extraction, and washing usually consume about 10 minutes, since the stratification of the ether and aqueous layers is prompt. Little more than 15 minutes is required for the production of color and the procurement of the necessary data when the photoelectric colorimeter is used. In the absence of a colorimeter, the additional time consumed in the use of standards is short. Once prepared, the standard solutions keep well when guarded from solvent evaporation by the use of glass-stoppered flasks. They can be used for numerous analyses, since the withdrawal of only 10 ml. is required for a determination.

#### Characteristics of Benzene, Toluene, and Xylene

The curves in Figure 1, as well as in Figures 2 and 3, represent data obtained by measuring with the aid of a photoelectric colorimeter (Evelyn with filter No. 620) the intensity of color developed by the procedure described above. All readings were taken at temperatures  $24.5^{\circ} \pm 0.4^{\circ}$  C.

Curves 2, 3, 4, 5, and 7, when representing solutions in alkaline media (broken lines, 5 to 15 minutes after sodium hydroxide reagent, but no acid, had been added) do not reach their maxima within 15 minutes. Curves 6 and 8 reach their maxima shortly before 5 minutes. However, the rate of color development which is represented by the ordinates of light transmittance is considerably decreased at the end of the 5-minute period. The rate of color deterioration in the acid media is sufficiently low 10 minutes after the acid has been added, or at a total of 15 minutes after color development was started, to require no additional delay for taking final readings.

Curve 1 in Figure 1 represents results obtained with 10 ml. of a solution of 0.190 gram of Eastman Kodak *m*-dinitrobenzene in 100 ml. of solution of 95 per cent U. S. P. ethyl alcohol. Curve 2 was derived from a solution prepared by nitrating 0.50 ml. of c. p. benzene, then adding 2.5 ml. of alcohol to 7.5 ml. of its thousandfold diluted alcoholic solution and treating it with butanone, alkali, and acid, as prescribed. This solution contains an equivalent of 75 per cent of benzene. Curve 3 was drawn from data obtained on a solution composed of 20 volumes of c. p. benzene diluted to 100 volumes with purified petroleum naphtha. Curve 5 was obtained by similar treatment of toluene. Purified petroleum naphtha, in all cases, was prepared by shaking commercial petroleum naphtha and benzine with 100 per cent sulfuric acid to remove aromatic hydrocarbons. The oil was then washed with distilled water, dried with anhydrous potassium carbonate, and distilled. Curve 6 was plotted with data from 15 per cent of xylene in purified petroleum naphtha. Curves 7 and 8 were furnished, respectively, by solutions containing 20 per cent benzene plus 20 per cent tolucne, and 20 per cent benzene plus 15 per cent xylene in purified petroleum naphtha. In this paper per cent specified is by volume, unless otherwise stated.

The rate of color development of benzene, when treated by the above procedure, is rapid at first, then gradually diminishes. After addition of the acid reagent the color remains the same, though decreased somewhat in intensity (curves 2 and 3, Figure 1). The color formed with the solution of *m*-dinitrobenzene which corresponds in concentration to that given by 100 per cent benzene, if completely nitrated to m-dinitrobenzene, shows the same characteristics (curve 1, Figure 1). In contrast, the color of the toluene complex develops slowly, does not reach the intensity produced by equal concentrations of benzene, and fades rapidly after adding the acid reagent (curves 4 and 5). Xylene, at a 15 per cent concentration, almost instantaneously exhibits a color nearly as intense as 75 per cent benzene. However, 15 seconds after adding the acid reagent, its blue color completely disappeared (curve 6).

The slight interference resulting from the presence of toluene and xylene is illustrated by curves 7 and 8 in Figure 1. In alkaline media, both curves differ considerably from curve 3, although they all contain 20 per cent benzene. After the acid reagent is added, all curves rapidly assume the form given by 20 per cent benzene despite the fact that one solution contains 20 per cent of toluene and another 15 per cent of xylene in addition to 20 per cent of benzene.

Varying concentrations of benzene, toluene, and xylene produce different colors and intensities of color when alkali reagent is added to the alcoholic solutions of butanone and the nitrated compounds. The contrast between benzene on one hand and toluene and xylene on the other becomes much more pronounced after the acetic acid reagent is added. This is illustrated in Figure 2. The broken lines here represent results 5 minutes after the sodium hydroxide reagent had been added. The solid lines represent results obtained 10 minutes after the acetic acid reagent had been added or a total of 15 minutes after color development had begun. Curves 1 and 3 demonstrate the resemblance of the xylene to the benzene reaction when in alkaline media. This resemblance is practically nullified 10 minutes after the acetic acid has been added. Benzene largely retains its properties— i. e., of an exponential curve  $y = ae^{-kx}$  (curve 4, Figure 2) whereas the curves for toluene and xylene are transformed into straight lines located at the lower section of the graph.

The concentration of either toluene or xylene can also be determined by this method, provided only one of these and no benzene or other chromogenic compound is present. Better results, however, in this case are obtained when the color comparison is made 5 minutes after the sodium hydroxide reagent has been added, and the broken line curves in Figure 2 are used.

Mixtures of these compounds can thus also be qualitatively ascertained. A solution of benzene and toluene gives a purplish violet color, whereas a solution of benzene and xylene gives an opaque violet color. After addition of the



FIGURE 2. RELATIONSHIP OF CONCENTRATION TO INTENSITY OF COLOR



FIGURE 3. REFERENCE CURVE FOR PHOTOELECTRIC COLORIMETER

acid reagent the crimson color gradually appears in the case of benzene and toluene, whereas it almost immediately emerges in the case of benzene and xylene solutions. On observation with the unaided eye, the intensity of color indicates the concentration of chromogen. When the photoelectric colorimeter is used, wide differences between the 5- and 15-minute readings indicate high concentrations of either toluene or xylene or both. The character and position of a curve plotted as light transmittance vs. time will indicate the concentration of either toluene or xylene or both.

Curve 4 of Figure 2 is the reference curve mentioned under Procedure above. Figure 3 shows this curve broken up in four sections plotted on three different scales for the abscissa. This was necessitated by the fact that the constants a and kof the curve  $y = ae^{-kx}$  are applicable for limited sections of the curve. The formula y = mx + b or a straight-line function, actually describes some sections of the curve best. Furthermore, the use of the curves in Figure 3 facilitates readings of benzene concentrations with an error no greater than the maximum error inherent in the manipulations. The complete curve is shown at the lower right corner of the graph. The complete curve obtained from similar treatment of c. p. toluene was inserted here for comparison. In view of the fact that the benzene curve rises very sharplyi. e., the difference in color intensity for a given increment of benzene is greater-from 0.01 to 30 per cent of benzene this range was plotted in the form of three different curves. The section for 25 to 100 per cent of benzene was plotted on a fourth curve to a scale coarser than that of curves 3, 2, and 1, but finer than the similar curve in Figure 2.

#### **Checking of Method**

In order to ascertain the accuracy of the method, solutions containing different concentrations of benzene and other substances were prepared. The results obtained are shown in Tables I to IV.

TABLE I.	DETERMINATION	OF BENZENE	BY	DILUTION	METHOD
	OF	COMPARISON			

		Composit	ion of San	nples			
Sample No.	Ben- zene	Tolu- ene Volun	Xylene	Other	Benzene Found	Error	Error
1 2 3 4	75.0 50.0 40.0 30.0	25.0 20.0 60.0 70.0	30.0	Petroleum	77.0 50.8 39.8 30.7	2.0 0.8 -0.2 0.7	2.7 1.6 0.5 2.3
5 6 7 8 9	$25.0 \\ 20.0 \\ 10.0 \\ 5.00 \\ 1.00$	25.0 90.0 95.0	25.0 80.0 	naphtha 25.0 99.0 Butyl	24.8 19.7 10.0 5.00 1.00	$   \begin{array}{c}     -0.2 \\     -0.3 \\     0.0 \\     0.0 \\     0.0 \\     0.0 \\   \end{array} $	0.8 1.5 0.0 0.0 0.0
10 11	1.00 0.25	10.0	69.0 	acetate 20.0 52.50 Ethyl acetate 25.85	1.04 0.24	0.04 -0.01	4.0 4.0
12	0.20			alcohol 21.40 Petroleum naphtha 99.80	0.19	-0.01	5.0

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TABLE II. DETERMINATION OF DENZENE BY STANDARDS											
Method of Comparison											
(S	(Standards used: equivalents of 1 to 10% benzene by volume)										
	C	omposition	n of Samj	ples							
Sample No.	Ben- zene	Tolu- enc	Xylene	leum naphtha	Benzene Found	Error	Error				
		Volume	per cent		Vol. %	Vol. %	%				
1 a 2 a 3 a 4 a 5 6 7 8 9 10 11	$\begin{array}{c} 50.0\\ 40.0\\ 30.0\\ 20.0\\ 10.0\\ 5.00\\ 3.00\\ 2.00\\ 1.00\\ 1.00\\ 1.00 \end{array}$	50.0 60.0 90.0 95.0 98.0 99.0 99.0	70.0 80.0 97.0	90.0	50.0 39.0 31.0 20.0 10.0 9.9 5.0 2.9 2.0 1.0 1.05	$\begin{array}{c} 0.0 \\ -1.0 \\ 1.0 \\ 0.0 \\ -0.1 \\ 0.0 \\ -0.1 \\ 0.0 \\ 0.05 \end{array}$	$\begin{array}{c} 0.0\\ 2.5\\ 3.3\\ 0.0\\ 0.0\\ 1.0\\ 0.0\\ 3.3\\ 0.0\\ 0.0\\ 5.0\\ \end{array}$				
a Dilu	ted 10 fir	nes with a	leahol be	fore comp	arison						

on Dummun

The standards used for visual comparison of the test solutions in Table I were those corresponding to 0.2, 1.0, 5.0, 10.0, 20.0, and 50.0 per cent benzene. The standard used in each case was that most closely approaching in color the test solution. In the case of Nos. 1, 2, 4, 5, 9, and 11 a small quantity of alcohol gradually added to the test solution produced a color that matched the standard. Alcohol greater than this quantity reduced the intensity of color. The formula used in these cases was  $B = \frac{12 + a}{12}S$ , where B = volume per cent of benzene, S = ben-

zene concentration of standard used, and a = ml. of alcohol added to match the color of the standard solution. In the case of Nos. 3, 6, and 12 the standards had to be diluted. The formula used in the latter case was  $B = \frac{12}{12 + a}S$ . Table II illustrates the results obtained with test solutions com-

Table II illustrates the results obtained with test solutions compared by the alternative visual method of standards comparison. A series of standards corresponding to the range of 1 to 10 per cent benzene with unit intervals was first used. The color was then reproduced simultaneously with several standards of concentrations with increments corresponding to 0.1 per cent of benzene varying from the standard most closely matching the test solution. Whenever the concentration of the test solution appeared to be greater than 10 per cent benzene, the test solution was diluted tenfold with alcohol, the color redeveloped, and the compari-

son repeated. The determinations listed in Tables III and IV were made with the aid of the graph in Figure 3. The errors found when differences in readings between the 5- and 15-minute intervals were considerable were greatly minimized by the use

terences in readings between the 5- and 15-minutes considerable were greatly minimized by the use of empirically derived corrections. The correction applied in Table IV as well as the final results was multiplied by 10, since the test solutions were diluted tenfold. The formula used in computation for the series in Table III was benzene % = C - (B - A - 25) 0.005; the formula used for the series in Table IV was benzene % = 10[C - (B - A - 25) 0.005]. C is benzene per cent corresponding to reading B on galvanometers. B and A are as given under Procedure.

#### Accuracy and Sensitivity

The presence of petroleum naphtha, ethyl acetate, butyl acetate, isobutyl alcohol, acetone, toluene, and xylene did not interfere with the determinations of benzene in the experiments tabulated. Reasonable accuracy, with a mean error of 1.6 per cent, was attained when the intensity of color produced was matched without the aid of a colorimeter. Greater accuracy was attained with the aid of a photoelectric colorimeter where a mean error of 0.9 per cent for a similar range of concentrations was in evidence. Concentrations less than 0.2 per cent benzene could not be determined with the naked eye, whereas concentrations down to 0.01 per cent benzene could be determined by the use of a photoelectric colorimeter. The errors involved at concentrations less than 0.2 per cent benzene, however, were considerable and amounted to 10 per cent at 0.05 per cent benzene and more at lower concentrations.

The 10-ml. aliquot of solution used for color development represents 0.01 ml. of the sample of 0.50 ml. taken for analysis and diluted to  $100 \times 5$ . Since 0.01 per cent benzene can be detected, the method appears to be sensitive to  $1 \times 10^{-6}$  ml. or  $8.8 \times 10^{-7}$  mg. of benzene. By visual comparison, in the absence of a photoelectric colorimeter or when an error above 1 per cent is not permissible, the sensitivity is reduced to  $2 \times 10^{-5}$  ml. or  $1.8 \times 10^{-5}$  mg. of benzene.

The concentration of benzene vapor in air may be determined by the above method after the vapor has been transformed from the gaseous to the liquid phase. This may be accomplished by adsorbing or dissolving the vapor in petroleum naphtha or alcohol. The concentration of benzene in the resulting solution may then be determined as prescribed. By sampling 5 liters of air, as little as  $1.8 \times 10^{-5}$  mg. per liter or 0.0056 part per million of benzene in air should be possible of detection. Concentrations of 0.018 mg. or more of benzene per liter of air (5.6 p. p. m.) can thus be determined with an error less than 1 per cent on a sample of 100 ml. of air.

Greater accuracy for concentrations lower than 0.2 per cent benzene or 0.018 mg. per liter of air may be obtained by decreasing the dilution. If the ether extract of nitrated solution is diluted only to 50 ml. and a 10-ml. aliquot is taken from it for the butanone reaction, 0.02 per cent, and 0.018 mg. or more per liter of air may accurately be determined on a sample of only 10 ml. of air. Concentrations down to as low as  $8.8 \times 10^{-4}$  mg. per liter of air or 0.27 p. p. m. may be detected on 10-ml. samples of air. The significance of this may be realized when it is perceived that numerous samples of air may thus be taken in a comparatively short time and that many small portable containers may be used.

#### Sources of Error

The products formed on treating benzene with nitrosulfuric acid depend not only on the volume of acid used

TABLE	III. D	ETERMI	NATION	OF BENZ	ENE WITH	1 Рнотое	LECTRIC	Colori	METER
		-Compo	osition of	Samples- Petro-		Benzene As read	Found		
Sample No.	Ben- zene	Tolu- enc	Xylene	leum naphtha	Other	on curve	Cor- rected	Error	Error
		Ve	olume per	cent		Vol.	%	Vol. %	%
$\frac{1}{2}$	75.0 50.0	25.0		50.0	Butyl	75.3 50.2		0.3 0.2	0.4 0.4
3 4 5 6	5.00 2.00 1.00 0.250	40.0 50.0 99.0	10.0 48.0	5.00	40.0 52.5 Ethyl acetate 25.85 Isobutyl alcohol	5,08 2,29 1,12 0,25	4.99 2.01 0.99	$\begin{array}{c} -0.01 \\ 0.01 \\ -0.01 \\ 0.00 \end{array}$	$0.2 \\ 0.5 \\ 1.0 \\ 0.0$
7	0.050		in a datan in a datan in a datan in a datan	80.0	4.28 Butyl acetate 10.50 Ethyl acetate 5.17	0.065	0.055	0.005	10.0
8	0.010	0.06	0.03	81.9	4.00 Butyl acetate 5.00 Isobutyl alcohol 4.00 Acetone 5.00	0.030	0.020	0.01	100

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TABLE IV.	DETERMINATION OF BENZENE WITH PHOTOELECTRIC COLORIMETER

Sample No.	Ben- zene	-Comp Tolu- ene	Xylene	of Samples Petro- leum naphtha er cent	Other	Benzene As read on curve Vol.	Found Cor- rected	Error Vol. %	Error %
1 2 3	$75.0 \\ 50.0 \\ 25.0$	$25.0 \\ 20.0 \\ 25.0$	30.0 25.0	25.0		7.49 5.16 2.67	$74.9 \\ 50.1 \\ 24.9$	-0.10 0.10 -0.10	$   \begin{array}{c}     0.1 \\     0.2 \\     0.4   \end{array} $
4 5 6 7 8	$20.0 \\ 20.0 \\ 10.0 \\ 10.0 \\ 1.00 \\ 1.00$	40.0 90.0 85.0	20.0 90.0 14.0	20.0	Acetone 80.0	$\begin{array}{c} 2.03 \\ 2.19 \\ 1.00 \\ 1.21 \\ 0.305 \end{array}$	$20.3 \\ 19.8 \\ 10.0 \\ 9.70 \\ 1.05$	$\begin{array}{r} 0.30 \\ -0.20 \\ 0.00 \\ -0.30 \\ 0.05 \end{array}$	$1.5 \\ 1.0 \\ 0.0 \\ 3.0 \\ 5.0$
9	1.00	50.0	10.0	9.00	acetate 30	0.250	1.00	0.00	0.0

and the temperature surrounding the solution but also on the rate of adding the acid. The heat formed in the reaction must be allowed sufficient time to dissipate. Too rapid addition of the nitrating acid tends to form undesirable by-products with a lower yield of *m*-dinitrobenzene.

m-Dinitrobenzene is soluble in ether to the extent of 6.7 grams per 100 ml. at 15° C. It is soluble in water to the extent of 0.047 gram per 100 ml. at 15° C. Although most of the nitrated compound enters the ether layer on extraction, some of it tends to remain in the aqueous layer. The favorable distribution of m-dinitrobenzene between ether and water is probably adversely affected by the mutual miscibility of the two solvents. However, even with this effect, a single extraction might be sufficient were it possible to separate the two phases completely. To ensure reasonably complete extraction, four ether extractions are made, and only small volumes of water are used to wash the ether extract.

Increase in temperature, as is often the case in chemical reactions, hastens the production of color in alkaline media and the disappearance of color in the acid media in the case of the dinitrobenzene as well as the nitrated toluene and xylene. Light also has some effect on the rate of color development and deterioration. The temperature should be within 0.4° C., and light conditions and the time elapsed should all be the same when the readings are taken with the photoelectric colorimeter as when the reference curve was prepared. When the color is compared by visual inspection, the unknown and standard are subjected to the same conditions and the effect is the same on all solutions. A series of permanent standards made from dyes or inorganic salts is not recommended because this would be applicable for only one given set of conditions.

The sensitivity of the individual observer to fine gradations of color and color intensity will influence the magnitude of error resulting from visual color comparison. This personal error, which inevitably accompanies all colorimetric determinations, may be eliminated by the use of the photoelectric colorimeter.

The photoelectric colorimetric determinations listed in Tables I and II show mean errors of 0.4 and 1.2 per cent, respectively, for concentrations above 0.2 per cent of benzene. The lower apparent accuracy in Table II is not due so much to the added manipulation of additional dilution as to the resultant decrease in benzene concentration of the test solutions. This dilution, necessitated by the fact that the solutions tested developed too intense a color in the  $\times$  1000 dilution, may perhaps be obviated by the substitution of a more appropriate filter than that used in the above experiments.

Since the galvanometer scale used can be read only to the nearest 0.25 division, the accuracy of the apparatus is

limited in the presence of very high or very low concentrations of chromogen. The probability of an error of 2 per cent in 95 per cent benzene, for example, is high, even if all precautions are carefully taken. In the case of high transmittance or low concentrations of benzene, an experimental error of the magnitude of 0.005 per cent may produce an error of 10 per cent in material containing 0.05 per cent benzene. It would thus seem advisable to read the concentration of benzene at light transmittance between 20 and 80 per cent in order to avoid the upper and lower extremes of the reference curve. This may be attained by adjusting the dilution of the test solution after a preliminary determination.

#### Summary

A method developed for the estimation of benzene in the presence of toluene, xylene, and other substances requires little material for analysis, is rapid, and is sensitive to 8.8 imes10<sup>-7</sup> mg. of benzene.

Concentrations varying from 0.25 to 75 per cent of benzene by volume have been determined with a mean error of 0.9 per cent.

The method may be used for the determination of small air samples.

Means for the identification of toluene, xylene, and benzene have been given.

The accuracy of the method, the sources of error, and the precautions to be taken in order to minimize the effect of the errors are discussed.

#### Acknowledgment

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## **Rapid Determination of Soluble Nutrients** in Soil and Plant Extracts

#### By Means of a Photoelectric Colorimeter

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KNOWLEDGE of the amounts of soil and plant nutrients soluble in weak acids, buffered salt solutions, or solutions of buffered salts and acids helps materially in explaining crop production. Because of the number of samples usually involved and the immediate need for the information, rapid tests for the soluble nutrients have been used (1-9, 11,12). The majority of these methods depends upon a visual comparison of colors or turbidities and as such can only differentiate between certain levels of nutrients, such as low, medium, etc.

In the course of studies on the correlations of crop yields with soluble nutrients, it became necessary to define the amounts of nutrients more accurately, and to obtain quick results with large numbers of samples. Consequently, the rapid methods herein described have been adopted, and have been used satisfactorily to determine soluble nutrients in over 1000 soil samples and a similar total number of bean, pea, tomato, asparagus, and cover crop samples.

The methods employed are variations of tests already in use. They are adapted to a photoelectric colorimeter with a resulting increase in accuracy without too great a loss in speed. The nutrients in both soil and plants are extracted with Morgan's Universal extracting solution (8) and are determined directly in separate aliquots of the extracts. Essentially, the tests for potassium, calcium, and magnesium are variations of those employed by Morgan (8); the tests for nitrate nitrogen and phosphorus are those used by Carolus (1) and Emmert (2, 3).

#### Apparatus

Photoelectric colorimeter with filters. A Fisher electrophotometer was used with success, and the amounts of extracts and reagents indicated are based on this machine.

Photometer tubes. Specimen vials,  $80 \times 25$  mm., are satisfactory, if proper selection is made. Photometer readings of tubes filled with distilled water should not vary more than 0.5 unit (arithmetic scale). Tu should be marked at 25 ml. Tubes for nitrate nitrogen determination

Water bath with 3 removable racks, each to hold 24 photometer tubes (Figures 1 and 2). Wooden racks, each to hold 25 photometer tubes.

Automatic burets for dispensing solutions.

Drying oven.

Glass stirring rods. Pointed rods  $12.5 \times 0.3$  cm.  $(5 \times 0.125)$  inch) are satisfactory for the nitrate, phosphorus and calcium tests. Rods,  $12.5 \times 0.47$  cm.  $(5 \times 0.188)$  inch), with a flat bottom 0.94 cm. (0.375) inch) in diameter are desirable for the magnesium tests.

Pipets, 1-, 5-, and 10-ml., marked at 0.1 ml. A 10-ml. bac-teriological pipet is desirable for pipetting plant extracts for cal-cium or phosphorus determinations. Funnel vials, Arthur H. Thomas Co., blueprint No. 2132-1. Wooden racks to hold 12 funnel vials.

Waring Blendor.

#### **Reagents and Solutions**

All reagents are of c. P. grade unless otherwise indicated. Wherever possible Baker's analyzed reagents were used. EXTRACTION. Morgan's Universal extracting solution  $(\mathcal{S})$ , normal sodium acetate buffered at pH 4.8 with acetic acid. Carbon, activated, Darco grade 0-97. DETERMINATION OF NITRATES. Phenoldisulfonic acid. So-dium hydroxide, 15 per cent. Standard nitrate, 0.2428 gram dis-solved and made up to 1 liter with extracting solution = 40 p. p. m. of nitrate nitrogen.

DETERMINATION OF PHOSPHORUS. Ammonium molybdate, 2.5 per cent in 6 N sulfuric acid. Aminonaphtholsulfonic acid. Fifteen grams of sodium bisul-fite, anhydrous, are dissolved in 100 ml. of distilled water and 0.5 hte, anhydrous, are dissolved in 100 ml. of distilled water and 0.5 grams of pure, dry 1 amino-2 naphthol-4 sulfonic acid and 1.5 grams of anhydrous sodium sulfite, are added. The contents are shaken, made up to 500 ml., and stored in a brown bottle (15). Standard phosphorus. Monosodium phosphate, monohydrate (0.0890 gram) dissolved and made up to 1 liter with extracting solution = 20 p. p. m. of phosphorus. DETERMINATION OF POTASSIUM. To make sodium cobalti-nitrite, 25 grams of cobalt nitrate and 150 grams of sodium nitrite are dissolved in 250 ml. of water containing 12.5 ml. of glacial

are dissolved in 250 ml. of water containing 12.5 ml. of glacial acetic acid. The volume is diluted to 500 ml. with distilled water. The solution is allowed to stand 24 hours, then filtered, and stored in a brown bottle at 5° C.

Isopropyl alcohol, 900 ml. mixed with 100 ml. of formaldehyde (35 per cent).

Standard potassium. Potassium chloride (0.0955 gram) dissolved and diluted to 1 liter with extracting solution = 50 p. p. m. of potassium.







TOP VIEW FIGURE 1. TRAY

TABLE I.	TABLE I. DETERMINATION OF NUTRIENTS FOR STANDARD CURVES AND IN SOIL AND PLANT EXTRACTS								
Nutrient Determined	Material	Useful Range P. p. m.	Volume of Aliquots <i>Ml</i> .	Diluted to Ml.	Filter Used	Null Adjustment with Blank to			
Nitrate nitrogen	Standard solution Soil extract Plant extract	0 to 20 0 to 40 0 to 40	0 to 2.5 2.5 or 5 2.5 or 5	5	425	100			
Phosphorus	Standard solution Soil extract Plant extract	0 to 10 0 to 40 0 to 10	0 to 20 5 20	20	425	0 (log scale)			
Potassium	Standard solution Soil extract Plant extract	0 to 50 0 to 250 0 to 250	0 to 10 1 1	10	650	100			
Calcium	Standard solution Soil extract Plant extract	0 to 100 0 to 600 0 to 30	0 to 20 1 20	20	425	100			
Magnesium	Standard solution Soil extract Plant extract	0 to 10 0 to 200 0 to 200	0 to 10 1 1	20	525	90			

DETERMINATION OF CALCIUM. Sodium oxalate, 2 per cent, prepared daily, kept in a stoppered bottle and shaken before use. Standard calcium. Calcium acetate, dihydrate (0.4395 gram) dissolved and diluted to 1 liter with extracting solution = 100

p. p. m. of calcium. DETERMINATION OF MAGNESIUM. Titan yellow (0.2 gram) is dissolved in 200 ml. of 50 per cent methyl alcohol solution and stored in a brown bottle. The solution will keep for about 3 months.

Sodium hydroxide, 15 per cent (same as for nitrate nitrogen).

Standard magnesium. Magnesium acctate, tetrahydrate (0.0881 gram) dissolved and diluted to 1 liter with extracting solution = 10 p. p. m. of magnesium.

#### Methods

EXTRACTION OF SAMPLES. Soil. Twenty-five milliliters of ex-tracting solution are added to 12.5 grams of sieved (2-mm.), air-dry soil placed in a 50-ml. Erlenmeyer flask. The contents are shaken for 1 minute and filtered on a Whatman No. 1 filter paper placed on a funnel vial. The filtrate is reserved for the tests.

placed on a lunnel vial. The hitrate is reserved for the tests. *Plant.* Fresh or frozen minced plant tissue (2.5 grams), usually stems, is placed in a Waring Blendor and 100 ml. of ex-tracting solution and 1 level teaspoonful of carbon are added. The mixture is agitated for 5 minutes and the pulp is filtered on a Whatman No. 1 filter paper. The filtrate is reserved for rapid tests ( $\delta$ ). At the same time, 2.5 grams of the minced tissue are selected for moisture determinations. CALIBRATION OF STANDARD CURVES. Alignets of the stendard

CALIBRATION OF STANDARD CURVES. Aliquots of the standard solutions are diluted with extracting solution to the designated level (Table I) and are then treated as in the determination of nutrients in soil and plant extracts. Photometer readings are taken using the appropriate filter and adjusting the blank to designated values (Table I). Deflection-concentration curves for each nutrient are drawn from the resultant data.

DETERMINATION OF NUTRIENTS IN SOIL AND PLANT EXTRACTS. Nitrate Nitrogen. Either 5 or 2.5 ml. of soil or plant extracts (depending on the concentration present) are pipetted into a series of photometer tubes (previously marked at 25 ml.). The 2.5-ml. portion is diluted to 5 ml. with extracting solution and 1 ml. of 15 per cent sodium hydroxide solution is added to each tube. The contents are evaporated to dryness on the steam bath. The racks are removed, the tubes cooled, and 2 ml. of phenoldisulfonic acid are added to each. The salts are broken up quickly with a stir-ring rod, and are allowed to stand until cool. The contents are diluted to 25 ml. with 15 per cent sodium hydroxide, stirred, and allowed to cool to 35° C. Photometer readings are immediately taken using the 425 blue filter, and adjusting the null to give a reading of 100 with the blank.

Phosphorus. Four milliliters of ammonium molybdate and 2 ml, of aminonaphtholsulfonic acid are added to each tube containing 20 ml. of plant extract or 5 ml. of soil extract diluted to 20 ml. The contents are stirred. After 15 minutes, the contents are again stirred, and photometer readings are taken on the log scale using the 425 blue filter and a null adjustment to give a zero reading with the blank.

*Potassium.* One milliliter of soil or plant extract is brought to 10-ml. volume with extracting solution. The contents of the tubes are cooled to 10° C., and 1 ml. of cooled sodium cobalti-nitrite solution is added to each. Ten milliliters of isopropyl alcohol solution are run in quickly down the sides of the tubes.

The tubes are stoppered and after 2 minutes are rotated, slowly at first but increasing in speed until the contents are thoroughly mixed. After 5 minutes, photometer readings are taken using the 650 red filter and a null adjustment giving 100 per cent transmission with the blank.

Calcium. Four milliliters of sodium oxalate are added to each tube, containing 20 ml. of plant extract or 1 ml. of soil extract diluted to 20 ml. The contents are stirred, allowed to stand for 15 minutes, and restirred, and photometer readings are taken using the 425 blue filter and a null adjustment giving a reading of 100 with the blank.

Magnesium. One milliter of soil or plant extract is diluted to 20 ml. with extracting solution, and 1 ml. of Titan yellow and 3.5 ml. of 15 per cent sodium hydroxide are added to each tube. The contents are mixed by means of a flatbottomed rod. Readings are taken after

5 minutes using the 525 green filter and a null adjustment giving a reading of 90 per cent transmission with the blank.

#### **Discussion of Methods**

SELECTION AND PREPARATION OF SAMPLES. Soil. The selection and preparation of soil samples have been fully discussed elsewhere (7, 8, 12).

Plant. The concentration of soluble nutrients in plants varies with the concentrations and relative proportions of nutrients in the soil, with prevailing climate, with the portion of the plant tested, and with age. It is important, therefore, that the latter two factors, which are controllable, be kept constant in order to enhance reliability. Until criteria are established for every nutrient and for every plant of all physiological ages, it is important that the concentration of test plants be compared with those of normal plants grown under the same climatic conditions.

Any portion of the plant can be used for testing. However, it is felt that the concentration of soluble nutrients in the older portions of the stem is the best general index of the supplying power of the soil (2). Concentrations in this portion of the plant are not usually excessive, and no large dilution errors are introduced (14). However, the portion



FIGURE 2. WATER BATH

TABLE II. RECOVERY FROM MIXTURES OF STANDARD SOLUTIONS AND OF SOIL AND PLANT EXTRACTS PLUS STANDARD SOLUTIONS

Substance	Found P. p. m.	Caled. P. p. m.	Diff. P. p. m.	Found P. p. m.	$\begin{array}{c} P \\ \hline Calcd, \\ P, p, m, \end{array}$	Diff. P. p. m.	Found P. p. m.	Calcd. P. p. m.	Diff. P. p. m.	Found P. p. m.	Calcd. P. p. m.	Diff. P. p. m.	Found P. p. m.	Caled. P. p. m.	Diff. P. p. m.
Mixed solutions Soil extract Soil extract +	5.2 6.2 27.5	5.0 28.2	+0.2 -0.7	4.9 8.0 17.0	5.0 18.0	-0.1 -1.0	$50.0 \\ 40.0 \\ 150.0$	50.0 140.0	0 +10.0	$26.0 \\ 194.0 \\ 212.0$	25.0 244.0	+ 1.0 -32.0	$26.6 \\ 19.0 \\ 30.2$	25.0 34.5	+1.6 +1.7
Plant extract + mixed solutions	2.5 40	37.5	+2.5	7.8 9.2	8.9	+0.3	$\begin{array}{c}150.0\\175.0\end{array}$	175.0	····· 0	$\begin{array}{c}13.1\\34.0\end{array}$	31.5	+2.5	$\begin{array}{c} 33.4\\ 39.2 \end{array}$	41.7	-2.5

TABLE III. CONCENTRATION OF SOLUBLE NUTRIENTS IN SOILS AND PLANTS AS DETERMINED BY RAPID TESTS<sup>4</sup>

Field No.	NO3-N	P	K	Ca	Mg	NOJ-N	р	K	Ca	Mg	Yield No. of Pods
		Pounda	s per a	cre		<i>P</i> .	p. m.	of drice	t tissue		
M-10	40	8.8	134	1720	209	4000	2270	1815	8400	6800	10
M-10	20	11.2	104	1800	209	3100	1470	1220	7000	6100	2
C-82	50	16.0	172	1168	272	3080	1490	2980	8760	6200	31
C-82	25	16.0	232	1064	252	2200	1550	2700	7050	7400	2
M-2	50	15.2	224	1456	145	3620	1320	1470	7240	5300	17
M-2	25	10.0	224	1456	145	2250	1885	1350	6510	5700	1

of the plant tested will depend to a certain extent on the type of plant and the purpose of the investigation. The various interrelationships of some of the nutrients in the plant and their possible importance in selection of samples have recently been discussed (9, 13).

After collecting the samples, extracts should be prepared as soon as possible. These extracts, if placed in tightly stoppered flasks, will keep for several months without appreciable change. If impossible to prepare extracts immediately, the plants should be frozen without delay and kept in cold storage until time is available. The frozen material is then minced, weighed, thawed, and extracted as before.

TESTS. A blank should be run with all determinations. In the final part of the nitrate analysis, samples should be cooled quickly and read immediately for best results.

The time consumed in running the nitrate nitrogen tests can be materially reduced by using three trays. The tubes in the second tray are prepared while the first tray is on the steam bath, etc. By the time the samples in the first tray have been tested, the tubes in the second tray will be almost ready for the additions of the phenoldisulfonic acid. Using such a system, it is a simple matter to determine quantitatively the nitrate nitrogen content of 72 samples in a day.

In the phosphorus determination, full color is not developed for several hours. However, comparative repeatable results can be obtained after 15 minutes.

The precipitate formed in the potassium determination may be of variable composition (10) and is influenced a great deal by temperature, rate of shaking, and ammonia present. The temperature of the solution at time of precipitation and the rate of shaking should be kept as uniform as possible. Concentrations of ammonia up to 100 p. p. m. in the extracts do not interfere, providing formaldehyde is used. Since the amounts of ammonia in the extracts are usually less than this amount, no correction for ammonia need be made.

In the calcium determination, the results are more accurate if the sodium oxalate reagent is prepared daily. The oxalate reagent undergoes changes in concentration upon standing, with a corresponding change in the calcium oxalate precipitate formed. Even with a fresh sodium oxalate reagent, it is desirable to stir the reagent thoroughly before adding it to a batch of extracts.

The determination of magnesium is complicated by the fact that the Titan yellow reaction is appreciably influenced by changes in pH and salt concentration. Plant and soil extracts add some buffering effects and salts. The errors are reduced to negligible factors by using small samples of extracts for analysis.

CALCULATIONS. Concentrations in parts per million can be read directly from the deflection-concentration curves or from charts prepared from such curves.

It is desirable to report soil nutrients in pounds per plowed acre (assuming 2,000,000 pounds of air-

dry soil per acre to a plowed depth), and concentrations of plant nutrients in parts per million on a dry weight basis.

ACCURACY. The methods proposed give results not entirely comparable to longer methods of analysis, but of definite value in determining relative differences between the soluble nutrients in soils and plants. Recoveries of added nutrients are good (Table II). Determinations can be repeated within 0.75 p. p. m. of nitrate nitrogen, 0.1 p. p. m. of phosphorus, 0.2 p. p. m. of potassium, 0.5 p. p. m. of calcium, and 0.1 p. p. m. of magnesium. Using the recommended aliquots, these variations would represent about 150 p. p. m. of nitrate nitrogen, 20 p. p. m. of phosphorus, 400 p. p m. of potassium, 100 p. p. m. of calcium, and 400 p. p. m. of magnesium per dry weight of plant. For soils, it would represent 3 pounds of nitrate nitrogen, 1.6 pounds of phosphorus, 8 pounds of potash, 40 pounds of calcium, and 8 pounds of magnesium on an acre basis. In most cases, the above values represent an accuracy of  $\pm 10$  per cent in duplicate analysis of the same extracts of one sample. Analysis made on duplicate samples of soil or plants will have greater variations. The variations in concentrations within samples from the same field are often associated with different types of growth (Table III).

ADAPTATIONS. The methods presented are based on the use of a Fisher electrophotometer and of Morgan's Universal extracting solution. They may readily be adapted to other photoelectric colorimeters and other types of extracting solutions.

#### Conclusions

Rapid methods for the determination of soluble nutrients in soils and plants are presented. A photoelectric colorimeter is used to determine accurately concentrations of nutrients in separate aliquots of extracts. Only one extract of either soil or plant is made, using one extracting solution for all determinations. Determinations on the same extract in most cases can easily be repeated within  $\pm 10$  per cent.

#### Acknowledgment

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## Photometric Determination of Benzene, **Toluene, and Their Nitro Derivatives**

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Certain factors relating to the production of maximum color from nitro compounds with butanone and alkali have been studied and modifications of existing procedures arc recommended. The analysis of mixtures of benzene and toluene, such as occur in some new commercial solvents, has been improved by introducing a differential oxidation of the nitro derivatives.

THE fundamental reaction between certain nitro com-pounds and ketones in the presence of concentrated alkali has been studied by many workers (1, 2, 4-7, 9, 11). A summary of their findings leads to the following conclusions:

Mononitro derivatives of benzene and its homologs do not give the reaction. Among the dinitro derivatives tested, only those of the meta series (nitro groups meta to each other) respond. When further substitution in the ring occurs, only those compounds retaining ketone solubility give color. At least one position para to one of the nitro groups must be unsubstituted. Blues or reds signify the presence of aromatic polynitro derivatives of this class. Certain substitutions, such as hydroxyl and amino groups, change these colors to yellows and oranges and indicate a different reaction. The concentration of alkali used determines the intensity of the color obtained and the rapidity of its production.

The evidence indicates a condensation between the enol form of the ketone and the aci-nitro form of the nitro compound with the elimination of a molecule of water:



The colors gradually fade, and brown insoluble compounds are produced (11). In some cases, one of the nitro groups is replaced (13).

Quantitative procedures have been described by Pearce, Schrenk, and Yant (10, 12, 14, 15) and by Kay (8) but are not entirely satisfactory regarding the strength of alkali used or the development and measurement of the colored compounds produced. The analysis of mixtures of benzene and toluene was only approximate (14). The present report describes some improvements which were made in these procedures.

#### Experimental

**REAGENTS.** Furning nitric acid, specific gravity 1.50; chromic acid  $(CrO_2)$ , saturated aqueous solution; potassium hydroxide, 70 per cent (one pound of pellets, dissolved and diluted to 650

ml.); and butanone. APPARATUS. Nitration of hydrocarbons is carried out in a small U-tube filled with beads. The sample is transferred to the tube from a gas buret by means of mercury if vapors are being analyzed, or, if the hydrocarbons are in aqueous solution, they may be blown over by means of a current of air. Rubber con-nections and greased stopcocks may not be used. A suitable lubricant for stopcocks may be made from starch and glycerol (3). A Bausch & Lomb visual spectrophotometer with 5- and 10-

mm. cells was used, although any other suitable instrument could be substituted.

PROCEDURE. The sample containing 10 to 100 micrograms of a mixture of hydrocarbons is collected in 2.0 ml. of fuming nitric acid in the nitration tube filled with beads. The tube and contents are heated in an oil bath at 90° C. for 15 minutes. If benzene only is to be determined, 1 drop of a saturated chromic acid solution is added and the sample is mixed by bubbling a little air through it. If benzene, toluene, and xylene are to be determined, the chromic acid is omitted.

The tube and sample are returned to the oil bath for another period of 15 minutes.

Beads and sample are transferred to a 60-ml. glass-stoppered bottle with the aid of three 2.0-ml. portions of water. The mixture is cooled in ice water and carefully neutralized with 70 per cent potassium hydroxide until the dichromate orange changes to chromate yellow-green. In the toluene determination, where no oxidation is required, 1 drop of chromic acid solution may be added after dilution and cooling without loss of toluene.

Ten milliliters of butanone are added to the neutralized sample, and the bottle is firmly stoppered and shaken vigorously. It is placed in a water bath at 60° C. to prevent crystallization of potassium nitrate and shaken occasionally during 5 to 10 minutes.

The sample is poured into a jacketed buret kept at about 60° C. and allowed to separate. The beads are caught in a funnel which is fitted with a wire to prevent closure of the stem by the beads.

The lower aqueous layer is carefully withdrawn and discarded and the upper butanone layer is carefully withdrawn and discarded and the upper butanone layer containing the nitrated sample is drained into a 25-ml. glass-stoppered cylinder. Ten milliliters of 70 per cent potassium hydroxide are added and the mixture is shaken vigorously for 2 minutes. A motor-driven shaker has been found convenient if a large number of analyses are required. The colored butanone layer is allowed to converte and is trans-

The colored butanone layer is allowed to separate and is trans-ferred to the cell of the photometer. If the color is too dark for satisfactory measurement, the butanone may be quantitatively diluted or a shorter cell may be





substituted. Owing to fading of the colors, not more than 5 to 10 minutes should elapse between the shaking of the mixture and the reading of the instrument.

A calibration curve should be prepared relating milligrams of hydrocarbon to color density for each substance determined, and since losses occur in the several steps, standards must be treated exactly as the samples are treated. Color density =  $\frac{1}{1}$ 

#### $\log \frac{1}{\text{transmission}}$

Since the density-milligram curve is linear, it is convenient to express the relation by a factor.

Table I gives the factors calculated when nitro compounds and hydrocarbons are analyzed by the procedures described. They are expressed as density per milligram of hydrocarbon for a 10-mm. cell. The corrected values are obtained by making allowances for loss of butanone in extraction and loss of water in dehydration. Comparison of these corrected values with those obtained with dry butanone standards gives a measure of the losses of nitro compound sustained in nitration and extraction. The small increase shown upon heating nitric acid solutions of dinitrobenzene indicates that traces of mononitrobenzene are present in the preparation. The dinitrotoluene sample is purer, as judged by the identity of the values for heated and unheated samples.

Some interesting comparisons regarding the nitration of benzene and toluene can be made. The values obtained indicate that 86 per cent of benzene and 76 per cent of toluene are converted to *m*-dinitro compounds by fuming nitric acid when liquid hydrocarbons are used. The corresponding figures for the vapors are 77 and 78. The losses may be due to the formation of ortho and para isomers and to oxidation. That no appreciable loss was due to inefficient trapping of vapors by the nitration tube was shown by introducing a second tube in series with the first.

ABSORPTION CURVES. Figure 1 shows the absorption curves for several of the compounds studied. The wave length selected for quantitative comparison was 560 millimicrons.

PREPARATION OF BUTANONE EXTRACTS. It is not possible to develop these colors quantitatively in the presence of water or potassium nitrate (14); therefore, the nitro compounds formed during nitration of aromatic compounds must be extracted from the nitration mixture. Butanone is fairly soluble in acid solutions, and nitro compounds are only partially extracted from alkaline solutions of pH greater than 10.

The most convenient indicator to use for adjusting the pH for extraction is the chromic acid solution used as oxidant in differentiating benzene from toluene. A sharp change from orange to yellow-green occurs at about pH 7.

#### **Factors Affecting Color Development**

According to the mechanism of the reaction proposed, the alkali serves several functions: converts ketone to enol form, converts nitro compound to aci-nitro salt, and removes water formed by condensation. Figure 2 shows the effect of increasing concentration of alkali on density of color obtained from nitrated benzene and toluene. Owing to losses of butanone during extraction without corresponding losses of nitro compound, the densities were too high. A correction was therefore made and these values were plotted. The increase in density obtained by increasing concentrations of alkali is best explained as an increase in efficiency of

the alkali as a dehydrating agent. Almost the maximum density is obtained with 50 per cent alkali and dinitrobenzene, whereas only about one third of the maximum density is obtained with dinitrotoluene and this concentration of alkali.

Further confirmation of the dehydrating action of the alkali is shown in Figure 3, where the larger volumes of 70 per cent alkali solution give greater color densities than the smaller volumes.

Potassium nitrate inhibits color development, as shown in Figure 4. Seventy per cent potassium hydroxide solution was saturated with dry potassium nitrate and the resulting



FIGURE 2. COLOR DENSITY AT VARIOUS CON-CENTRATIONS OF POTASSIUM HYDROXIDE

#### TABLE I. COLOR DENSITY PER MILLIGRAM OF HYDROCARBON

04 - 1 - 1-	Ber	zene	Toluene		
Standards		Alter Crus		Atter Crui	
Butanone $+$ <i>m</i> -dinitro	$30.3 \pm 0.7$		$20.9 \pm 0.4$		
HNO: + m-dinitro (unheated)	$32.1 \pm 0.8$		$24.0 \pm 0.9$		
HNO: + m-dinitro (corrected)	$26.3 \pm 0.7$		$19.7 \pm 0.7$		
HNO <sub>1</sub> + m-dinitro (heated)	$35.2 \pm 1.4$	$33.4 \pm 1.6$	$23.8 \pm 0.9$	0.0	
$HNO_s + m$ -dinitro (corrected)	$28.8 \pm 1.1$	$27.4 \pm 1.3$	$19.5 \pm 0.7$	0.0	
HNO: + liquid (heated)	$30.1 \pm 0.5$	$28.8 \pm 1.2$	$18.2 \pm 1.4$	0.0	
HNO: + liquid (corrected)	$24.7 \pm 0.4$	23.6 = 1.0	$14.9 \pm 1.2$	0.0	
HNO: + vapor (heated)	$27.0 \pm 1.6$	$27.6 \pm 2.0$	17.4 = 0.5	0.0	
HNO: + vapor (corrected)	$22.1 \pm 1.3$	$22.6 \pm 1.6$	$14.3 \pm 0.4$	0.0	
Butanone + trinitro	$8.8 \pm 0.3$		9.6 = 0.4		



FIGURE 3. COLOR DENSITY AND VOLUME OF 70 PER CENT POTASSIUM HYDROXIDE

solution mixed in various proportions with 70 per cent potassium hydroxide solution. Ten milliliters of these mixtures were shaken with the butanone extract of nitrated toluene and the densities determined.

This experiment emphasizes the importance of making a clean separation of the butanone extract from the aqueous phase in the determinations. It also supports the need for larger volumes of potassium hydroxide solution used to develop the colors than were recommended by Pearce et al. (10).

#### **Differentiation of Benzene and Toluene**

When mixtures of benzene and toluene are nitrated with fuming nitric acid, heated, diluted, neutralized, and extracted with butanone, the density obtained is equal to the sum of those obtained with the individual substances separately. If, however, the mixture is oxidized with chromic acid after

TABLE II.	ANALYSIS OF	BENZENE AN	ND TOLUENE	MIXTURES	
	_ Tal	ken	For	ind	
Sample	Benzene	Toluene	Benzene	Toluene	
	Micro	grams	Micrograms		
1	71.5	00.0	71.9	00.0	
2	57.2	15.7	59.2	15.7	
3	42.9	31.4	42.8	34.6	
4	28.6	47.1	27.4	48.1	
5	14.3	62.8	13.7	65.0	
6	00.0	78.5	2.3	73.3	

nitration, only the color of the benzene derivative is obtained.

A paired series of mixtures was prepared by dissolving various amounts of standard benzene and toluene solutions in 2.0 ml. of fuming nitric acid. One set of mixtures received 1 drop of a saturated aqueous solution of chromic acid in each sample; the other set served as controls. Both sets were placed in an oil bath at 90° for 15 minutes and then diluted, neutralized, and extracted as usual. The results in Table II show an average error of  $\pm 5.0$  per cent.

> Analyses of benzene and toluene vapors and of mixed solvents have shown the methods to be equally satisfactory.

The differentiation probably depends upon the loss of butanone solubility of the oxidized products. Experiments with 2,4-dinitrobenzoic acid indicate that dinitrotoluene is oxidized to this substance. m-Dinitrobenzene is not oxidized under the conditions selected but is lost with permanganate oxidation and with longer heating periods with the oxidant chosen,

#### Summary

The colored compounds formed by shaking m-dinitrobenzene and its homologs with ketones and alkali are probably quinoids formed by condensation of the aci-nitro and enol forms with the elimination of water.

Various factors concerned with the production of these colors have been studied, and

certain modifications recommended for their quantitative determination. The use of 70 instead of 50 per cent alkali greatly hastens and increases color production.

Mixtures of benzene and toluene have been satisfactorily analyzed by oxidation of dinitrotoluene, presumably to dinitrobenzoic acid, which gives no color under the conditions chosen. m-Dinitrobenzene is not attacked and gives its usual color with undiminished intensity.

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## **Colorimetric Determination of Alkyl Benzene Sulfonates**

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Simple colorimetric quantitative method for the estimation of alkyl benzene sodium sulfonates is described which is sensitive to one part per million of pure sulfonate. The analysis may be made visually or photometrically.

ETHODS for the determination of the active ingredient content of commercial surface-active agents, including alkyl benzene sulfonates, have been the subject of several papers (3, 4, 5). Few of these methods are entirely satisfactory, because they include impurities such as sodium sulfate, or are inoperative with dilute solutions of surface-active agents. The determination of surface tension depression is easily accomplished, but does not lend itself to strictly quantitative estimation.

The need for a rapid method for the quantitative estimation of alkyl benzene sodium sulfonates in dairy cleansing processes is described by Scales and Kemp (6), who outline a qualitative test based upon the formation of a blue coloration when a solution of alkyl benzene sulfonate is added to a solution of o-tolidine and sodium hypochlorite. However, not all detergents undergo this reaction, since they found that soap, Turkey red oil, lauryl sodium sulfate, and three related compounds failed to produce the iodo-blue color characteristic of this test. Under their conditions a flocculent precipitate obscured the test, so that it was not considered sufficiently accurate for quantitative purposes.

Re-examination of their data and further investigation proved that the test could be made quantitative in character.

#### **Visual Method**

EQUIPMENT. 50-ml. Nessler tubes (or 50-ml. graduates), pipets, and a 10.0-ml. buret graduated in 0.05-ml. divisions. SPECIAL SOLUTIONS. o-Tolidine Solution. Add 1.0 gram of o-tolidine to 5 ml. of 20 per cent hydrochloric acid (100 ml. of hydrochloric acid, specific gravity 1.18-1.19, to 500 ml. of dis-tilled water) and grind to a thin paste. Add 150 to 200 ml. of distilled water to produce a solution. Transfer to a 1-liter distilled water to produce a solution. Transfer to a 1-liter graduate and make up to 505 ml. with distilled water, then make to 1 liter by adding the balance of the 20 per cent hydrochloric acid solution. Store in an amber bottle out of direct sunlight.

Sodium Hypochlorite. Prepare a solution of sodium hypochlorite by slurrying 5 grams of high test calcium hypochlorite and 4 grams of anhydrous sodium carbonate in 334 ml. of distilled water. Let the insoluble matter settle, then decant the solution through a filter. Analyze it for available chlorine content accord-ing to the A. O. A. C. (2) arsenious oxide titration method. Prepare a standard solution containing 300 p. p. m. of available chlorine.

Alkyl Benzene Sodium Sulfonate, or Unknown. Prepare a 0.05 per cent solution of the alkyl benzene sulfonate by suitably Prepare a diluting a stronger solution with distilled water. Dilute a wash solution 1 to 5 or more, depending upon the approximate concen-tration of the alkyl benzene sulfonate. This solution must be as dilute as indicated, or if stronger must be measured accurately

dilute as indicated, or if stronger must be measured accurately from a suitably calibrated buret or pipet. PROCEDURE. Transfer 40 ml. of distilled water to each of two Nessler tubes. Add 1 ml. of 300 p. p. m. sodium hypochlorite solution to each tube, and invert to mix. Add 2 ml. of o-tolidine solution to each, and invert to mix. Make the blank up to 50 ml. with distilled water and invert several times to mix thoroughly. Add the unknown solution of alkyl benzene sulfonate of definite

Add the unknown solution of alkyl benzene sulfonate of definite dilution carefully in known amounts to a fresh mixture of reagents, until a color change just appears. Make the tube up to volume and compare with the blank. From the volume of un-known added, and the fact that 1 p. p. m. of alkyl benzene sodium sulfonate is required for a color change, calculate the strength of solution.

Used in the manner described above, the method is suitable for determining the strength of dilute solutions by visual observation where photometric equipment is not available.

#### Experimental

The experimental information developed for the visual method is applicable to use in photometric equipment. The several variable factors involved were investigated.

Benzidine and diamidine were tested to find whether they would produce a more suitable color for analytical purposes, but o-tolidine produced the most satisfactory results.

Tests were made to determine the effect of quantities of reagents upon the color formation.

To show the effect of available chlorine, a standardized solution of 300 p. p. m. of sodium hypochlorite was used, and known incre-ments were added to 50-ml. Nessler tubes containing 30 ml. of distilled water, 5 ml. of o-tolidine solution, and 0.5 ml. of 1 per cent alkyl benzene sodium sulfonate solution. The volume was made up to 50 ml. and the colored solutions were examined. The results, shown in Table I, indicate optimum color formation at 6 p. p. m. of available chlorine in the final test solution. To determine the optimum amount of *a*-tolidine solution, 1-ml.

To determine the optimum amount of o-tolidine solution, 1-mi. increments of o-tolidine solution were added to aqueous solutions containing 300 p. p. m. of available chlorine and 0.5 ml. of a 1 per cent solution of alkyl benzene sulfonate. The 1-ml. increment produced a brownish blue coloration, with very little precipitate; 2 ml. gave a deep blue; and increasing amounts of o-tolidine produced a greenish blue color with a greater amount of precipi-tate. tate.

The order of addition of reactants had a profound effect upon the formation of the undesirable surface precipitate. Addition of the alkyl benzene sulfonate solution just before making up to volume minimized this difficulty.

#### TABLE I. OPTIMUM AMOUNT OF AVAILABLE CHLORINE

(Varying increments of NaOCl solution, 5.0 ml. of o-tolidine solution, 0.5 ml. of 1% alkyl benzene sulfonate solution, q. s. water)

No Chlorine (Control)	1 p. p. m.	Available Chlor 3 p. p. m.	ine in Test Solu 6 p. p. m.	tion24 p. p. m.
Yellow solu- tion	Yellow pre- cipitate	Blue solution, precipitate on surface	Deep blue so- lution, pre- cipitate on surface	Brownish blue solution, large amount of precipitate on surface

Utilizing the optimum amounts of available chlorine (300 p. p. m.) and o-tolidine solution (2 ml.), the desired dilution of alkyl benzene sulfonate was ascertained with varying amounts of pure alkyl benzene sulfonate solution: 0.0005 gram of sulfonate produced a suitable coloration, whereas 0.004 gram resulted in a deep brown color. This indicated that somewhat less than 80 p. p. m. of alkyl benzene sulfonate should be present in the test solution.

Time (up to 15 minutes) had no effect upon the end point, but it is preferable to make the test shortly after all the ingredients have been mixed.

Tap water (ca. 300 p. p. m. hardness) produced no visible effect.

TABLE	II.	EXAMINATION	OF	SOLUTION	FOR	OPTIMUM	WAVE
		LENGTH A	ND '	TRANSMITT.	ANCE		

Wave Length	Transmittance
Millimicrons	%
500	8.8
600	0.3
700	17.0
800	13.0
900	21.5
1000	16.0

Alkalies in wash solutions have little effect upon the test under the conditions observed—i. e., if the alkyl benzene sulfonate solution is alkaline, the degree of dilution will be such that final pH will be adjusted by the *o*-tolidine solution.

A color change is produced by as little as 0.00005 gram of pure sulfonate in 50 ml. of solution according to test. This is equivalent to 1 part per million. Alkyl benzene sodium sulfonates diluted with sodium sulfate are detected in proportionally small amounts, dependent upon the degree of dilution of the active ingredient.

TABLE III.	PHOTOMETRIC TRANSMITTANCE DATA
Sample A, 40% alkyl	benzene sodium sulfonate; sample B, 100% alkyl
benzene sodium sulfor	nate; sample C, 100% n-butyl diphenyl sodium

Parts per Mil- lion	Sam Photel- ometer B filter	ple A Spectro- photom- eter, 600 mµ	Photel- ometer B filter	-Sample B- Spectropl 525 mµ	hotometer 600 mµ	Sample C Photel- ometer B filter
$\begin{array}{c} 0.25\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 3.0\\ 4.5\\ 5.0\\ 7.5\\ 10.0\\ 20.0\\ 25.0\\ 30.0\\ 40.0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0$	96.5 96.5 97 95 92 93 91  84.5 84.5 85 65 85 65 85 65 47 45 33	97 96 95 95 94 95 94 93 91 91 88 84.5 88 84.5 83.5 30.5 20.5 20.5	$\begin{array}{c} 97\\ 97\\ 94.5\\ 91.5\\ 87.5\\ 85\\ 77.5\\ 74.5\\ 69\\ 60.5\\ 56.5\\ 43.5\\ 32\\ 43.5\\ 32\\ 17\\ 12 \end{array}$	99 98 96 92 88 84 80.5 78 74.5 71.5 68  44 19 13 8.5 4.5	$\begin{array}{c} 97\\ 95.5\\ 92\\ 87\\ 84\\ 78\\ 73.5\\ 70.5\\ 66.5\\ 63.5\\ 59.5\\ 52.5\\ 42.5\\ 32.6\\ 18.0\\ 11.5\\ 6.0\\ 3.5\\ 1.7\\ \end{array}$	95 94 92 92 92 91 91 91 89 81 79 71 66 55

#### **Photometric Method**

The analytical procedure used is exactly the same as that for visual observation. In this case, however, a suitable filter must be chosen with instruments such as the Cenco-Sheard-Sanford photelometer, or a wave length of maximum color absorption with instruments such as the Coleman spectrophotometer. Once this factor has been ascertained by examination of the blank and of a test portion which contains the maximum expected amount of alkyl benzene sulfonate, the problem is to prepare sufficient data to graph percentage transmittance vs. concentration. If such a curve substantially conforms to Beer's law, it may be used as reference for samples of unknown concentration.

A filter which produced satisfactory results with the Cenco-Sheard-Sanford photelometer was the B filter with maximum transmission at 525 millimicrons. Examination of the solutions with the Coleman spectrophotometer indicated that satisfactory results could be obtained in a range lying between 500 and 600 millimicrons.

Typical data developed by this method of analysis are shown in Table III. The data for sample B at 525 millimicrons and with the B filter are plotted in Figure 1. The curves closely approach straight lines, hence conform to Beer's law. Solutions of alkyl benzene sulfonates of unknown strength can be prepared for test as described in the procedure, and then submitted to photometric analysis. From the percentage transmittance of such test solutions, the concentration may be ascertained by reference to the curve. The concentration of active alkyl benzene sulfonate in the original sample of unknown strength can be calculated from the size of the sample used in the test, and its degree of dilution. It is suggested that such a dilution of unknown be chosen that an appreciable coloration be formed, and obviously, that it fall within the limits of the curve.

Tests were made with sodium sulfate-containing products which were calculated to contain  $40 \pm 1$  per cent of active ingredient as alkyl benzene sodium sulfonate.

A more or less usual method for determining the active ingredient is to extract a 1.00-gram sample of the product with 200 ml. of neutral 95 per cent alcohol in a 400-ml. beaker on the water bath, for at least an hour, replacing the alcohol which evaporates. The residue is then quantitatively transferred to a tared Gooch crucible, washed with 100 ml. of boiling alcohol, and dried at 105° C. to constant weight.

The moisture content of the sample was determined by the xylene distillation method (1). The active ingredient content was determined by difference: 100 minus the sum of the alcoholinsoluble plus moisture yielding the active ingredient content.

It is recognized that the alcohol-insoluble method will yield low results because of the difficulty of removing all the alcohol-soluble active ingredient from the residual sodium sulfate. The results with three samples are shown in Table IV.

The photometric method was used for analyzing the same samples by adding 5 ml. of a 0.05 per cent (dry basis) solution of the sample to the mixture of reagents described in the procedure. The percentage transmittance of the unknowns was measured with a B filter using the photelometer. The per-





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TABLE IV.	COMPARISON OF GRAVIMETRIC ALOCHOL-INSOLUBLE
	METHOD WITH PHOTOMETRIC METHOD

			Active			
4601633	Moisture		From alcohol-	From photel-		
Sample	(Xylene	Alcohol	insoluble method	ometer B filter,		
No.	Distillation)	insoluble	by difference	sample B		
	%	%	%	%		
1	5.0	59.25	35.75	41.0		
2	4.0	59.07	36.93	39.6		
3	6.0	60.05	33.95	38.6		

centage of active ingredient for each of the samples was calculated from the concentration of the sample, and reference to the photelometer curve for sample B, Figure 1. This information is shown in Table IV. It is obvious from this that the photometric method gives more nearly correct results than does the alcohol-insoluble method.

There was a possibility that certain other alkyl aryl sulfonates might be amenable to this method of estimation. Tests were made with two alkylhydroxydiphenyl sulfonates and n-butyldiphenyl sodium sulfonate (Table III). Apparently the hydroxy group interferes with this particular color

formation, since only the latter compound produced a color approaching the characteristic iodo-blue. Improved characteristics of this curve could have been obtained by using a more suitable wave length for examination of the test solutions. This method of analysis may be suitable for other alkyl aryl sulfonates.

#### Acknowledgment

The constructive suggestions made by Carroll A. Hochwalt and Ross W. Moshier have been of great assistance in the preparation of this paper.

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## **Identification of Carbon Black by Surface Area** Measurements

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ARKINSON (6) has suggested that the particle size of lampblack recovered from a tire tread stock by means of nitric acid is unchanged from that of the original supply. His conclusions were drawn from sedimentation experiments. The authors have found (8) that the low-temperature ni-trogen-adsorption method of Emmett and his co-workers (1, 2, 3) for determining surface areas of finely divided substances is a comparatively rapid and accurate method of measuring the total surface of commercial carbon blacks. The object of the present investigation was to expand Parkinson's observation to a variety of commercial carbon blacks, employing the nitrogen-adsorption technique. Since the surface area of most of the standard carbon blacks has been previously determined (3, 8), a method of identifying the carbon black present in an unknown rubber stock can be readily devised if it is first established that the carbon black can be recovered from a rubber stock with unchanged surface

The present paper reports the surface area values determined by the nitrogen-adsorption method for a number of commercial carbon blacks recovered from vulcanized tread stocks.

#### **Experimental Details**

The technique and apparatus for determining the surface area of carbon black by the low-temperature nitrogen-adsorption iso-therm have been described in a previous publication (8). An oxyliquid nitrogen bath during a run. From this temperature, the appropriate saturation pressure,  $p_0$ , of the adsorbate nitrogen is obtained and employed in calculating the final surface area value

(3). The carbon blacks studied were compounded in the following recipe:

Ingredient	Parts by Weight	Ingredient	Parts by Weight
Smoked sheet	100	Captax	0.9
Zine oxide	5	Steario acid	4.0
Sulfur	3	Agerite Hypar	1.0
Pine tar	3	Black	45

One stock was made from Grade 6 carbon black in Buna S:

Buna S	100
Zine oxide	5
Sulfur	2
Pine tar	2
B-L-E (antioxidant)	1.0
B-J-F (accelerator)	1.
Laurex	2
Grade 6 black	50
	a state of the sta

The smoked sheet stocks were cured for 30, 60, and 90 minutes at 134° C., and the Buna S stock at 144° C. The 60-minute cure was nearly optimum in the majority of cases, and was the only cure selected for study.

The following commercial carbon blacks were selected for study:

GASTEX, a nonimpingement-type black manufactured from natural gas. A semireinforcing black of the "soft" type widely used in rubber goods.

ACETTLENE BLACK (Shawinigan), prepared by thermal decom-position of acetylene. A soft-type black which does not possess the marked rubber-reinforcing properties of channel blacks. Its electrical conductance in rubber stocks is very high.

SPHERON, grades 9 through 1, a series of rubber-reinforcing carbon blacks prepared by impinging natural gas flames on metal surfaces. Their essential difference is particle size, grade 9 being the coarsest and grade 1 the finest of these typical rubber blacks.

SPHERON N, a channel black of fine particle size with superior electrical conducting properties when compounded in rubber stocks.

The free carbon in the vulcanized rubber stocks was separated by means of nitric acid. The procedure followed was essentially that of Oldham and Harrison (5).

In the authors' laboratory it is the practice to employ a 0.75to 1.00-gram sample of rubber stock instead of the 0.15-gram sample suggested by Oldham and Harrison ( $\delta$ ). While larger samples increase the time required for washing and filtering, it is the authors' experience that greater accuracy and repro-ducibility are attained thereby. Jacob Gabry, to whom the

TABLE I. EXPERIMENTAL RESULTS							
Black	Original Area	Area after Treating with HNO:	Area after from I By HNO <sub>3</sub>	Recovery Rubber By cresol	Carbon in HNO <sub>3</sub> method	n Rubber Cresol method	Carbon Calculated
	Sq. m./g.	Sq. m./g.	Sq. m./g.	Sq. m./g.	% b	%	%
Gastex Acetylene Cabot grade 9	26 ª 64 99	67	22 63 100	21 70 99	28.4	27.7	27.8
Cabot grade 6 Cabot grade 4 Cabot grade 1	109 143 210	112 181	110 175 203	107 125 156	27.7 27.9	27.4 27.7	27.8 27.8
Spheron N Grade 6 in Buna S	330 109	316	326 113	204 ¢	29.9		30.3
<sup>a</sup> A previous publication (8) reported 40 sq. m. per gram as the surface of standard Gastex. C. W. Snow, General Atlas Co., has kindly stated that this material was actually CS-3 carbon. The present							

value is that of standard Gastex. <sup>b</sup> Ash-free basis. <sup>c</sup> Not completely soluble.

authors are indebted for the analytical results reported here, also points out that it is essential to control the time of digestion of the rubber stock and nitric acid to 3 to 4 hours at the specified tem-perature of  $60^{\circ}$  to  $70^{\circ}$  C. While in the case of channel blacks, the weight of carbon black recovered by this method is generally reported (5) to be 105 per cent of its original weight, under the conditions reported here a value of 108 per cent has been found more general. Consequently, a correction factor of 1.08 is employed instead of the value 1.05 recommended by Oldham and

Harrison (5). One to 0.75 gram of the vulcanized stocks was digested for one hour with 15 cc. of concentrated acid. After the addition of another 35 cc. of acid, digestion was continued for 2 hours more. In order to avoid contamination of the black for the subsequent surface area determination, a Selas sintered filter crucible FS-20-100 was used in place of the usual asbestos Gooch. The crucible and black were washed according to the standard method, then dried at 110° for 2 hours. The per cent carbon in the rubber stock was determined directly without ignition. The surface area of the dried sample of recovered black was then determined by low-temperature nitrogen adsorption. The ash was deter-mined on a duplicate sample by ignition. In all compounds studied, it amounted to about 0.4 per cent by weight of the whole rubber stock. Thus the recovered black as weighed out for the surface area determinetion contained 144 per cent ash. The surface area determination contained 1.44 per cent ash. The surface values in column 4 of Table I are accordingly 1.44 per cent lower than if they had been calculated on ash-free basis. However, in the absence of data on the surface area of ash itself, such a simple correction is not justified. The correction in any case would not amount to more than 1 or 2 square meters per gram, a value too small to cause any confusion in the identification of the black.

It was necessary to establish that no appreciable change in sur-face area of the carbon black was brought about by the nitric acid during the separation of the black from the rubber stock. In order to establish this, "blanks" of 0.5-gram samples of carbon black alone were subjected to the same treatment employed with the compounded rubber stock and the surface areas of the blacks were then determined.

The use of cresol for the separation of carbon black from rubber stocks has been described by Roberts (7). In natural rubber stocks, this method gives excellent results for free carbon. It was felt that there would be less opportunity for alteration of the carbon surface during separation by this method than with concentrated nitric acid. The carbon black was separated from the stocks by cresol according to the method of Roberts (7). The surface area of the recovered carbon was then measured.

A single determination of the area of a grade 6 carbon black recovered from a Buna S stock with nitric acid was carried out. As it was not possible to get complete solution of this stock in cresol, the method had to be abandoned in this instance.

#### **Experimental Results**

Table I presents a summary of the data collected. With the exception of the Gastex and grade 9 channel black, which are values for single recoveries, the surface area values re-

ported are the average of at least two independent recoveries. The deviation in all cases was not more than 3 per cent.

The data indicate that carbon black undergoes no appreciable alteration in surface area during incorporation in, or vulcanization of, a rubber stock. With but a single exception, the surface areas of the carbon blacks studied are substantially the same before in-corporation and after removal from the rubber stock by means of nitric acid.

It is not possible to offer any ready explanation for the 25 per cent increase in surface of the grade 4

sample. This is not due to any peculiar effect of the rubber on the carbon black, since the black alone in nitric acid showed an appreciable increase in surface. There was nothing peculiar in the method of manufacture or properties of this particular sample to account for its apparent increased activity toward nitric acid. In any case, the alteration in the surface area of the recovered carbon is still not sufficient to confuse its identity.

In general, both the nitric acid and cresol methods gave excellent results for the amount of free carbon in the stocks. The surface areas of the blacks recovered by the cresol method show satisfactory agreement with the original supply in the case of the coarser blacks. However, with the finer particle blacks, the surface is considerably reduced. Thus, grade 1 black has an original surface of 210 square meters per gram. After recovery from the tread stock, by cresol extraction this value was only 156. After treating a 0.5-gram sample of this type black with cresol according to the standard procedure, the surface was 165 square meters per gram. Evidently a small amount of material is retained by the carbon in spite of the extensive washings and heating described in the procedure. The amount is not sufficient to alter the weight of the sample appreciably, but it is sufficient to block off certain interspaces in the black that were formerly accessible to the nitrogen molecule. Such an effect should become more pronounced the finer the particle size of the black. Accordingly, the cresol method of recovery is not satisfactory for separating carbon black from "unknown" rubber stocks for identification by surface area measurements.

The Buna S stock showed little solubility in cresol and quantitative recovery of carbon was not possible. It was possible, however, to get a satisfactory recovery of the carbon from the Buna S stock with nitric acid. In order to obtain complete solution, it was necessary to digest this stock with nitric acid somewhat longer than the specified 3 hours. This more drastic procedure is reflected in the slight increase in surface area of the recovered carbon.

#### Conclusions

In general then, we may conclude that carbon black can be recovered from rubber stocks with unchanged surface area. The nitric acid technique is the most effective method of effecting the separation. The digestion temperature must be controlled to between 60° and 70° C. for a total of not more than 3 to 4 hours. This method of identifying the carbon black in an unknown rubber stock is directly applicable only in the presence of a single type of carbon black. If blends of blacks are employed in the material under investigation, some secondary identification is also required. The nonimpingement-type blacks, for example, are readily identified

by microscopic observation. From the known surface areas of these materials and the total per cent carbon present in the stock, a fairly positive identification of the blend can be made.

The fact that carbon black can be recovered quantitatively and with unchanged surface area from vulcanized rubber stocks appears to lend impetus to a physical concept of carbon black reinforcement. This point of view implies that any chemical combination between the ingredients of the rubber stock and the carbon black would be evidenced by some alteration in the surface of the latter. A few experiments were performed in an attempt to establish to what extent this concept was valid.

One hundred grams of grade 6 carbon black were intimately mixed with 6.6 grams of sulfur. This is about the ratio in which they are present in a standard rubber batch. Samples of this mixture were subjected to the standard curing temperature of 134° C. for 30, 60, and 90 minutes. The free sulfur was then 134° C. for 30, 60, and 90 minutes. The free sulfur was then extracted for 40 hours with acetone and the combined sulfur on the carbon was determined. Values of 0.16, 0.21, and 0.4 per cent combined sulfur were obtained. The original sample of grade 6 carbon black had a surface area of 108 square meters per gram. The extracted sample of black containing 0.4 per cent of combined sulfur had a surface area of 109 square meters per gram. These values are identical within experimental error.

While unaltered surface area need not necessarily be interpreted as evidence of complete lack of surface reactions, it is the authors' opinion that the extent of chemical combination at the carbon black surface is very small. This interpretation is in accord with the views expressed in a previous publication (9), where it was suggested that the chief role of carbon black in rubber reinforcement may rest on its ability to orient the chains of rubber molecules (4) and thus alter the extent and type of rubber-sulfur bonds normally formed in nonreinforced rubber stocks.

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## **Rapid Iodine Number Determinations**

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F THE numerous iodine number methods described in the literature for determining the unsaturation of fats and oils, the Wijs and Hanus methods are used most extensively (4), although the Rosenmund-Kuhnhenn method, especially in its micromodification, is used to a considerable extent in biological work. The Wijs reagent, official with the American Oil Chemists Society, gives theoretical values for pure nonconjugated unsaturated fatty acids, but it is sensitive to light and is not recommended for use when more than 30 days old. The Hanus reagent, on the other hand, usually gives results about 2 to 4 per cent lower than those obtained with the Wijs method, but it is stable and when protected from light will remain in a satisfactory condition for a year or longer. The Rosenmund-Kuhnhenn reagent is also stable but gives results appreciably low for all oils of iodine number greater than 100 (2). The reaction time for all three methods is usually 0.5 to 1 hour, depending upon the degree of unsaturation of the sample.

Some time ago, Hoffman and Green (3) suggested the addition of mercuric acetate to the Wijs reagent in order to cut the reaction time to 3 minutes without any change in the iodine number. This convenient rapid method has apparently escaped much attention. One of the present authors (5), however, has used this modified procedure on oils containing conjugated double bonds. Results obtained on tung oil are shown in Figure 1. Here the standard Wijs, rapid Wijs, and standard Rosenmund-Kuhnhenn methods are compared. Results obtained with the standard Hanus method are not shown, since they are known to be erratic when the reagent is employed in its normal concentration (0.2 N). [Theoretical iodine numbers on pure conjugated fatty acids have been reported by von Mikusch (6), using an

approximately double strength Hanus reagent. However. normal strength Hanus reagent usually gives high and erratic results (1).]

Standard (slow) Wijs values are largely dependent upon the excess of reagent employed, the iodine number varying 43 units in an excess range of 25 to 272 per cent. Rapid Wijs values, however, vary only insignificantly in the reagent excess range of 30 to 225 per cent, permitting much greater latitude in sample weights. The 55 == 3 per cent excess re-


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TABLE I.	COMPARISON	OF	STANDARD	AND	RAPID	HANUS	IODINE
	VALUES	ON	UNCONJUG	ATEL	FATS		

	Iodine Value					
Fat	Standard Hanus	Rapid Hanus				
Sardine oil	187.0	186.6				
Linsecd oil	173.4	174.0				
Soybean oil	127.0	126.2				
Corn oil	125.4	124.9				
Cottonseed oil	109.2	109.5				
Castor oil	84.0	90.7				
Olive oil	84.6	85.0				
Rendered pork fat	65.7	65.7				

agent recommended for tung oil (1) in the standard Wijs method gives values located on the steep part of the curve and hence susceptible to maximum error. An excess range of 125 to 150 per cent would be a better choice if the standard Wijs method is used. The Rosenmund-Kuhnhenn method (1 hour) is second to the rapid Wijs in utility but the values obtained are slightly low, and if reaction time is shortened to 15, 30, or 45 minutes a further lowering of the iodine value is obtained, values tending to decrease gradually with decreasing reaction time below one hour.

Recently, the authors had need of an iodine number reagent suitable for intermittent use over fairly long periods of time. The stability of Hanus solution and the catalytic effect of mercuric acetate on iodine absorption of conjugated fats indicated that this combination be tried on nonconjugated materials. Their results are summarized in Table I.

With the single exception of castor oil, the standard and rapid Hanus iodine number methods check within the allowable experimental error (one unit). The anomalous result with castor oil is due to its content of ricinoleic acid, as indicated by experiments on a ricinoleic acid concentrate. With conjugated materials the rapid Hanus method is not satisfactory, since the iodine number varies with excess of reagent used in the determination. Representative results on a sample of tung oil are shown in Table II.

### Experimental

RAPID HANUS METHOD. The iodine numbers were determined in the manner usually employed for the Hanus reagent (4) except that the 25 ml. of reagent were followed by 10 ml. of a 2.5 per cent solution of mercuric acetate in glacial acetic acid. The mixture was then shaken and titrated, after 3 to 5 minutes' standing. Rapid Hanus blanks were consistently found to be about 3.2 per cent lower than those of the standard Hanus method. Thus, the omission of mercuric acetate solution from the blank would in-crease the apparent iodine number of linseed oil by about two units.

Theoretical reagent excesses were calculated on the basis of an assumed iodine value of 170 for tung oil. For example, if the blank titration was 50.25 ml. and a 55 per cent excess of reagent was desired at the end of the reaction, then the titration of the sample should amount to  $\frac{50.23}{1.55}$  or 32.41 ml. Assuming an iodine value of 170, then

$$170 = 32.41 \frac{(\text{grams of } I_2 \text{ per ml. of thiosulfate})}{\text{weight of sample}} \times 1$$

00

If 1 ml. of thiosulfate is equivalent to 0.013 gram of I<sub>2</sub>,

Weight of sample = 
$$\frac{32.41 \ (0.013)(100)}{170} = 0.248 \text{ gram}$$

Excesses calculated in this way are the only safe ones to use for conjugated fats, since otherwise the excess may be calculated on the basis of an incorrect experimentally obtained iodine value. This calculation is especially valuable for pure conjugated fatty acids since, in this case, the iodine value is known and need not be assumed.

PREPARATION OF A RICINOLEIC ACID CONCENTRATE. The limited solubility of ricinoleic acid and its glycerides in petroleum ether was utilized in this preparation.

Castor oil (180 grams) was extracted five times with 100 ml. of petroleum ether (30° to 60°) at about -30° C. The residue (146.5 grams), freed from solvent, was saponified with 400 ml. of 20 per cent alcoholic potassium hydroxide, and the free fatty of 20 per cent alcoholic potassium hydroxide, and the free fatty acids were liberated in the usual manner. Petroleum ether (200 ml.) was then added to dissolve the nonricinoleic acid unsaturated constituents, and the lower fatty acid layer was re-extracted with 100 ml. of petroleum ether. Following this, six cold extrac-tions were made using petroleum ether at  $-65^{\circ}$  C. (this warmed to about  $-10^{\circ}$  or  $-20^{\circ}$  C. after mixing with the fatty acids in a separatory funnel). The residue was then taken up in ethyl ether, washed free of sulfuric acid, the solution dried with an-hydroug acdium sulfate, and the other removed in yacuo hydrous sodium sulfate, and the ether removed in vacuo.

The ricinoleic acid concentrate, melting point 6°, C. exhibited a rapid Hanus iodine number of 85.4 (theoretical, 85.1) and a standard Hanus value (0.5 hour) of 80.3, showing that ricinoleic acid is the substance responsible for the divergent results obtained on castor oil with the rapid and standard Hanus methods. Which of the two methods most nearly measures the true degree of unsaturation cannot be stated at this time, since it was not feasible to carry the purification procedure further. However, the product obtained by the method just outlined is likely to be contaminated with saturated and possibly some dihydroxy acids rather than with oleic or linoleic acids. Hence, the iodine number may be lower than expected on the basis of pure ricinoleic acid. Consequently, the low value obtained by the standard Hanus method may be due partly or entirely to contamination.

TABLE	II.	Effect	OF	REAGENT	Excess	ON	RAPID	HANUS
		IOD	INE	VALUES OF	TUNG O	IL		

	Excess Re	arent	
Sample Weight	Theoretical	Actual	Iodine Value
Gram	%	%	
0.0600	540	395	220.0
0.0600	540	392	220.3
0.1013	278	209	207.8
0.0996	284	213	207.3
0.1496	156	138	183.0
0.1492	157	138	183.7
0.2145	78.6	91.2	158.3
0.2140	78.8	93.4	157.1
0.2490	53.7	78.3	146.5
0.2485	54.1	78.2	146.8

### Summary

The combination of mercuric acetate and Wijs solution provides a rapid iodine number method suitable for use on conjugated fats.

A rapid iodine number method involving the use of easily prepared and stable solutions comprises the combination of mercuric acetate with Hanus solution. This reagent gives values identical with those obtained in the standard Hanus method on nonconjugated fats, with the notable exception of castor oil, where the ricinoleic acid content is responsible for higher values obtained by the rapid method. On conjugated fats the method is unsatisfactory.

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# Determining Glycerol in Crude Glycerin and in Soap Lyes

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A SIMPLE, rapid method for determining glycerol in crude glycerin and soap lyes has been needed for a long time. The international acetin method (3), though accurate, is lengthy and is applicable only to samples containing a maximum of 60 per cent water. The dichromate method (1)requires a preliminary purification and filtration, and its results tend to be high. The Bertram-Rutgers method (2), though simple and rapid, is lacking in accuracy. Distillation methods are usually lengthy and require special apparatus.

Experimental data (5) showed that the loss of glycerol from boiling aqueous glycerol solutions was negligible from a quantitative standpoint, and that the loss of glycerol from anhydrous 0.5-gram samples in small glass beakers at 100° C. was on the order of 2 mg. per hour. This latter fact indicated that a margin of safety could be expected for a quantitative method of removing water from aqueous glycerol solutions by evaporation. An accurate, quick method (4) had already been found for removing both water and glycerol from an aqueous glycerol sample. It was reasoned that, if water alone could be evaporated from an equal aliquot portion of the same sample, the percentage of glycerol could be calculated from the difference in weight of the two residues. The evaporation of water from an aqueous glycerol solution at 100° C. would be slow work at best. Therefore, to speed up the evaporation, many combinations of low-boiling solvents such as ethyl alcohol, ethyl ether, methyl alcohol, and benzene were tried. Methyl alcohol and ethyl ether were finally adopted as the most satisfactory.

# **Preparation of Sample**

SOAP LYE CRUDE GLYCERIN AND SAPONIFICATION CRUDE GLYCERIN. Eight to  $10 \pm 0.001$  grams are weighed into a tared 100-ml. measuring flask and about 50 ml. of water are added. The contents are well mixed, adjusted to the phenolphthalein end point with dilute hydrochloric acid or sodium hydroxide, made up to the 100-ml. mark with more water, and thoroughly mixed.

point with dilute hydrochloric acid or soulum hydroxide, made up to the 100-ml. mark with more water, and thoroughly mixed. SoAP LYE. Thirty-five to 50 grams of lye are weighed into a tared 100-ml. measuring flask, the smaller sample for lyes of high salt content. The sample is adjusted to the phenolphthalein end point with hydrochloric acid or sodium hydroxide. One to 2 ml. of a 10 per cent aqueous solution of a wetting agent (Aerosol OT) are added, and the sample is made up to the 100-ml. mark with water and thoroughly mixed. The use of a wetting agent tends to reduce spattering.

# **Removal of Water from Aliquot Portions**

Two 5-ml. aliquot portions of the sample are pipetted into tared 60-ml. Erlenmeyer weighing bottles (the bottles have a diameter of 50 mm. at the base, are 75 mm. high, and take a 24/12 \$ stopper), and 5 ml. of methanol are added. The unstoppered bottles are placed in a natural convection drying oven maintained at  $100^{\circ} \pm 2^{\circ}$  C. The oven must have ample top and bottom vents for quick heat transfer, and its make and break contact points must be located below the samples for safety. Narrow strips of 0.6-cm. (0.25-inch) asbestos millboard placed on the metal shelf of the oven are effective in preventing spattering. The Sargent electric drying oven S-63995 has been found satisfactory.

When the residue in the bottles is reduced to a thin sirupy consistency by evaporation and the characteristic sweet odor obtained when glycerol is heated under these conditions is faintly perceptible, the bottles are removed from the oven. (The time varies between 65 and 80 minutes.) Five milliliters of ethyl ether are then added and swirled in the bottom of the bottles for 2 minutes. The bottles are put back into the oven and dried at 100° C. for about 25 minutes, until the acrid odor of ether is no longer perceptible and the odor associated with glycerol vapor is again noticeable. The bottles are then brought to room temperature in a desiccator over concentrated sulfuric acid, stoppered, and weighed to the fourth decimal place. The drying with the addition of 5 ml. of ether is repeated until the loss in weight is less than 0.002 gram. Usually, only one extra drying is necessary. The final weight, minus the tare, may be termed "residue at 100° C."

# Removal of Both Water and Glycerol from Aliquot Portion

For this determination an infrared drying oven is used, either as described in a previous paper (4) or in the following manner: The top and bottom of an ordinary tin can, 15 cm. (6 inches) in diameter and 17.5 cm. (7 inches) high, are cleanly cut out, and four inverted V notches, about 2.5 cm. (1 inch) in height, are cut from the base. The can is mounted on its notched end upon a porcelain or asbestos surface. A 250-watt infrared reflectordrying lamp (General Electric R-40) is supported directly over the top opening of the tin can. A thermometer is inserted into one of the notches, so that its bulb rests directly beneath the center of the drying lamp.

of the drying lamp. Two 5-ml. aliquot portions of the sample are pipetted into tared, shallow, flat-bottomed evaporating dishes of about 70-mm. diameter. The tin can is set aside and the evaporating dishes are placed adjacent and on each side of the thermometer bulb. The tin can is replaced and current to the lamp is switched on. Preliminary evaporation is done with the lamp at a distance of about 20 cm. (8 inches) from the dishes. When the residue is almost dry, the lamp is raised slightly to prevent spattering of salt crystals. The temperature up to this point is disregarded. When the fumes of glycerol are scarcely to be seen coming off, the reading of the thermometer is brought to 160° C. by adjusting the height of the lamp. This temperature is maintained for 30 minutes, after which the evaporating dishes are removed, cooled to room temperature in a desiccator over concentrated sulfuric acid, and weighed rapidly to the fourth decimal place. This weight minus the tare may be termed "residue at 160° C." The over-all drying time rarely exceeds 90 minutes. CALCULATION.

# $\frac{\text{(Residue at 100° C. - residue at 160° C.)} \times 100}{1/20 \text{ original sample}} = \% \text{ of glycerol}$

Samples 1 and 2 are American Oil Chemists Society standard sample crude glycerin (February 1, 1929). The figure 83.33 per cent is the "true glycerol" content and represents the averaged findings of the laboratories of several soap companies. Samples 3 to 9, inclusive, are crude glycerins, both saponification and soap-lye, obtained from five different soap companies. The figures in the first column represent

L A	-Not Glussrol	CAREATAB TEESOB.	
Sample No.	Acetin method	Evaporation method	, Difference
1 2 3 4 5 6 7 8 9	70 83.33 85.04 79.62 78.23 88.20 88.07 89.56 90.37	20 83.66 83.51 85.20 79.80 78.39 88.45 88.26 89.85 90.38	$\begin{array}{c} 70\\ 0.33\\ 0.18\\ 0.16\\ 0.18\\ 0.16\\ 0.25\\ 0.25\\ 0.19\\ 0.29\\ 0.20\\ 0.01\\ \end{array}$
	Glycerol expected Gram	Glycerol found Gram	Difference Gram
10	0.1655	0.1646	0.0009

independent analyses by the acetin method. Samples 10 and 11 are "synthetic soap lyes", made from weighed amounts of the standard A. O. C. S. crude glycerin, salt, and water, to simulate the average soap lyes found in practice.

### Summary

This method offers many advantages. The over-all time is about 4 hours, and the applied time is less than 1 hour. The technique is simple and the apparatus is readily available. The deviation from accepted or independent analyses of crudes is less than 5 parts per thousand, a fact that recommends it as a cost-accounting tool.

Although the method has not been perfected to the degree

that the author would like, he feels that it is essentially useful as it stands and that refinements may be added when it is generally tried out.

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# **Determination of Tin in Babbitts, White Metal** Alloys, and Bronze

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WHILE seeking a more satisfactory method for the determination of small amounts (<0.05 per cent) of tin in steel (3), the authors found that Stanreduce (Harshaw Scientific Co., Cleveland, Ohio) is an excellent reductant for the larger amounts of tin in bronze and white metal alloys.

This paper presents the noteworthy features of the improved methods developed for these alloys: simplicity, speed of reduction, and elimination of the use of rubber tubing and external gas supply. The three methods outlined should serve as a guide in developing a method adaptable to virtually any kind of alloy containing tin.

The authors make no claim to originality of method, the chemistry presented being essentially that first used by Low (2). They felt, however, that sufficient contradiction existed in the literature to merit a detailed study of the effects of the various manipulative procedures involved. The methods outlined are direct applications of data derived from this study.

#### **Determination of Tin in Lead-Base Bearing Metal**

The following procedure applies to lead-base bearing metal of the type of National Bureau of Standards sample No. 53, which contains: lead, 78.87 per cent; tin, 10.91; antimony, 10.09; bismuth, 0.06; copper, 0.05; iron, 0.05; and arsenic 0.02 (see Table I).

Place 2.0000 grams of a finely divided sample in a 300-ml. Erlenmeyer flask, add 5.00 grams of potassium sulfate and 15 ml. of concentrated sulfuric acid, and heat the mixture on a hot plate of concentrated sulfuric acid, and heat the mixture on a hot plate until the lead sulfate turns white. Cool the mixture, first in air and then for a moment with tap water, and dilute with 10 ml. of water followed by 150 ml. of 2 to 1 hydrochloric acid. Add 10 grams of Stanreduce and place a one-hole rubber stopper, through which passes a short capillary tube, lightly on the mouth of the flask. Place the flask on a hot plate at 150° C. and bring to a boil. Boil gently, maintaining the height of the foam at between 0.925 and 1.25 cm. (0.375 and 0.5 inch). Stopper the flask tightly, cover the capillary tube with a rubber policeman, and quickly remove the flask from the hot plate. Allow it to stand for about 2 minutes, during which time the hydrogen formed re-places the condensing steam, then place the flask in a water bath and cool to 30° C. or lower. and cool to 30° C. or lower. Into a 500-ml. Erlenmeyer flask pour 10 ml. of 1 to 2 hydro-

chloric acid and 5 ml. of starch solution, and add one 2.1-gram compressed sodium carbonate tablet. While the carbon dioxide is forming, fill a 100-ml, buret with standard potassium iodate solution, add a second bicarbonate tablet to the 500-ml. flask, withdraw the 300-ml. flask from the water bath, and remove the rubber policeman and then the rubber stopper. Now add 135 ml. of cold water to the 500-ml. flask and into it quickly decant TABLE I. DETERMINATION OF TIN IN LEAD-BASE BEARING METAL

(National Bureau of Standards sample 53, 10.91 per cent tin. 0.2182 gram of tin present)

Determination			Determination			
No.	Tin F	ound	No.	Tin Found		
	Gram	%		Gram	%	
1 2 3 4	$\begin{array}{c} 0.2168 \\ 0.2182 \\ 0.2186 \\ 0.2186 \\ 0.2186 \end{array}$	10.84 10.91 10.93 10.93	6 7 8 9	0.2196 0.2186 0.2192 0.2192	$     \begin{array}{r}       10.98 \\       10.93 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\       10.96 \\     $	
5	0.2196	10.98	10 Mean	0.2182	10.91	

the solution from the 300-ml. flask. Immediately wash the 300-ml. flask and Stanreduce with 1 to 2 hydrochloric acid and decant the washing into the 500-ml. flask. Add another sodium bicarbonate tablet as needed; a total of three or four tablets will suffice. Titrate at once to a blue end point. Without delay wash the Stanreduce with 10 ml. of 1 to 2 hydrochloric acid, decant into the 500-ml. flask, and again titrate. Repeat this latter procedure until a permanent end point is obtained.

STANDARDIZING. Weigh out 0.2000-gram portions of pure tin, or use 2.0000-gram portions of National Bureau of Standards sample, and treat by the appropriate method.

Notes. Solution of the sample is obtained best at a tempera-ture of 440 °C. on a heater like the Gilmer. If a lead-base babbitt contains sufficient copper to interfere, tin should be determined as directed below for a tin-base babbitt. As a safety precaution, all flasks should be vacuum-tested and examined for flaws. The strong hydrochloric acid (2 to 1) is necessary to prevent the precipitation of antimony when large amounts are contained in the sample. The Stanreduce may be recovered for re-use by washing and drying. It should be sifted and the portion finer than 65-mesh discarded.

# **Determination of Tin in Tin-Base Bearing Metal**

The following procedure applies to tin-base bearing metal of the type of National Bureau of Standards sample No. 54a, containing: lead, 0.21 per cent; tin, 88.61; antimony, 7.32; bismuth, 0.019; copper, 3.75; iron, 0.041; and arsenic, 0.031 (see Table II).

Place 0.5000 gram of the finely divided sample in a 300-ml. Erlenmeyer flask, and add 10 ml. of 1 to 1 nitric acid. When Entenmeyer mask, and add 10 ml. of 1 to 1 mitric acid. When dissolved, evaporate the solution to dryness on a hot plate at  $125^{\circ}$ to  $140^{\circ}$  C. Bake for 15 minutes, digest the residue with 20 ml. of 1 to 1 nitrie acid for 5 minutes, and then decant onto a 9-cm. No. 42 Whatman paper. By decantation, wash the metastannic acid in the flask three times with hot 2 per cent nitric acid, wash the contents of the filter paper three times with hot 2 per cent nitric acid discard the filteria and return the filter paper to the flock acid, discard the filtrate, and return the filter paper to the flask.

TABLE II. DETERMINATION OF TIN IN TIN-BASE BEARING METAL

(National Bureau of Standards sample 54a, 88.61 per cent tin. 0.4431 gram of\_tin present)

Determination	Tin F.	- un d	Determination	(T) T) 1		
INO.	Crem	ound m	190.	111 P	ound	
	Gram	70		Gram	70	
1	0.4437	88.74	G 7	0.4437	88.74	
3	0.4437	88.74	8	0.4432	88.63	
4	0.4432	88.63	9	0.4432	\$8.63	
5	0.4426	88.52	10	0,4432	88.63	
			Mean	0.4434	88.67	

To the flask add 15 ml. of sulfuric-perchloric acid mixture (666 ml. of concentrated sulfuric acid, specific gravity 1.84, and 333 ml. of 72 per cent perchloric acid) and 2.0 grams of potassium sulfate, heat the mixture on a hot plate at 150° C. until all the carbon is oxidized, and then gradually increase the temperature to 400° C. to drive off the perchloric acid. Cool the solution, first in air and then for a moment with tap water, and dilute with 10 ml. of cold water, followed by 180 ml. of 1 to 2 hydrochloric acid. Starting with the addition of Starteduce and increasing the time Starting with the addition of Stanreduce and increasing the time of reduction to 15 minutes, complete the determination as in the case of lead-base bearing metal, but omit the addition of the 135

ml. of cold water. NOTES. When the sample is dissolved in 1 to 1 nitric acid and evaporated to dryness, the product formed is a granular, sandlike precipitate of metastannic acid which filters out well. If concen-trated nitric acid is used, the metastannic acid tends to become colloidal, and upon filtering may pass through the paper. In dissolving the metastannic acid, completion of solution is indi-cated when the flask clears. At this point, fumes of sulfuric acid only come from the mouth of the flask.

# **Determination of Tin in Bronze**

The following procedure applies to bronze of the type of National Bureau of Standards sample No. 124, containing: copper, 83.77 per cent; zinc, 5.46; tin, 4.69; lead, 4.78; iron, 0.38; nickel, 0.45; and antimony, 0.23 (see Table III).

Place 1.0000 gram of the sample in a 300-ml. Erlenmeyer flask, and add 15 ml. of 1 to 1 nitric acid. Dissolve the sample on a hot plate at 150° C., add one half of a 9-cm. soft filter paper, and continue to heat and swirl until the paper is macerated. Dilute to 50 ml. with water and heat to boiling. Filter through a 9-cm. No. 42 Whatman paper containing a small amount of pulp, wash the flask once with hot 2 per cent nitric acid, and pour the washings

flask once with hot 2 per cent nitric acid, and pour the washings into the filter paper. Wash the filter paper five times with hot 2 per cent nitric acid, discard the filtrate, return the filter paper with its contents to the flask, and add 15 ml. of sulfuric-perchloric acid mixture. Then add 2.0 grams of potassium sulfate, heat the mixture on a hot plate at 150°C. until all the carbon is oxidized, gradually increase the temperature to 400°C., and continue heating until the per-chloric acid is driven off. Cool the solution, first in air and then for a moment with tap water, and dilute with 10 ml. of cold water, followed by 180 ml. of 1 to 2 hydrochloric acid. Complete as in lead-base bearing metal, starting with the addition of Stan-reduce, but omit the addition of the 135 ml. of cold water. The time of reduction can be reduced to 6 minutes. NOTES. Since metastannic acid is a colloidal precipitate, con-

Notes. Since metastannic acid is a colloidal precipitate, con-tamination is increased if the solution is evaporated to dryness, as some authors recommend (1). The process of evaporating to dryness consumes an excessive amount of time, and if the evaporation is hastened by overheating, cupric nitrate may be decomposed, with consequent contamination of the metastannic avid. If the analysis is carried out as directed with respect to acid concentration and filtration, the filtrate will be perfectly clear. Sufficient copper may remain in the metastannic acid to give a yellow tinge when hydrochloric acid is added, but the authors have found this insufficient to do any harm.

TABLE	III. DET	ERMINA	TION OF TIN IN	BRONZE						
(National Bureau of Standards sample 124, 4.69 per cent tin. 0.0469 gram of tin present)										
Determination			Determination							
No.	Tin Fe	bund	No.	Tin Found						
	Gram	%		Gram	%					
1	0.0467	4.67	6	0.0462	4.62					
2	0.0467	4.67	7	0.0462	4.62					
3	0.0462	4.62	8	0.0462	4.62					
4	0.0462	4.62	9	0.0462	4.62					
5	0.0462	4.62	10	0.0462	4.62					
			Mean	0.0463	4.63					

#### Literature Cited

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# Sugar Analysis by Alkaline Ferricyanide Method

Determination of Ferrocyanide by Iodometric and Other Procedures

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NE of the problems of special interest when reducing sugars are to be estimated by oxidation with alkaline ferricyanide solutions is the selection of the method for determination of the amount of reagent which has been consumed. The reduction product, ferrocyanide, is frequently estimated volumetrically by titration with one of the stronger oxidizing agents.

Burriel and Sierra (2) titrated ferrocyanide satisfactorily with potassium dichromate in 0.3 N hydrochloric acid solution, using benzidine acetate as indicator. Muller and Diefenthaler (5) em-ployed permanganate in a solution acidified with sulfuric acid. Furman and Evans (5) used ceric sulfate in hydrochloric acid solution with o-phenanthroline as indicator. However, as they have shown, cerous compounds may be oxidized to ceric by ferri-cyanide in 30 per cent potassium carbonate solution. Where only ferrocyanide is to be considered, the use of some one of these stronger oxidizing agents generally is to be preferred. The pres-ence of the oxidation products of the sugars along with the ferro-

cyanide raises the question as to whether these substances may not also have reducing action upon the reagent used to titrate the ferrocyanide.

Strepkov (8) reports that oxidizing of dextrose and levulose with Ost's solution, removing the cuprous oxide, then adding a definite amount of ferrocyanide to the residual solution containing the oxidation products of the sugars, and titrating the mixing the oxidation products of the sugars, and thrating the ina-ture with potassium dichromate gave results which were in good agreement with the blanks containing only the ferrocyanide. On the other hand, parallel experiments in which the sugars were oxidized by a Fehling's alkaline-tartrate mixture showed a greater

oxidized by a Fehling's alkaline-tartrate mixture showed a greater consumption of dichromate than was given by the blanks. Use of a weaker oxidizing reagent to estimate ferrocyanide would ap-pear to be advantageous in many instances where other reducing products than ferrocyanide are present. Of the weaker oxidizing reagents, iodine has been employed for the titration of ferrocyanides. Considerable controversy is apparent as to the conditions under which the reaction should be carried out. In neutral or weakly acid solution the reaction goes to the right, while in solutions more strongly acidified it is reversed:

# $2K_{\bullet}Fe(CN)_{\bullet} + I_{\bullet} \stackrel{H^+}{\longrightarrow} 2K_{\bullet}Fe(CN)_{\bullet} + 2KI$

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	[Undation of Mire(CN)	16 WICH 0.02 IV	ioainej	
	Reagents Used	K.Fe(CN): Taken Milliegu	K.Fe(CN). Found	Error
(a)	NaHCO: 10 ml. of K4Fe(CN), 20 ml. of I: 50 ml. of water, and enough NaHCO: to make the solution 1% in this reagent	0.2068	0.1165	43.7
	Same as above except acidified with 20 ml. of 20% acetic acid before titrating	0.2068	0.1990	3.8
(b)	No complexing reagent used 10 ml. of K4Fe(CN)s and 50 ml. of water heated to 40° C. before 20 ml. of 1 solution added	0.2355	0 1889	19.8
	Same as above except acidified as in (a)	0.2328	0.2055	11.7
(c)	Rochelle salt 10 ml. of K <sub>4</sub> Fe(CN) <sub>5</sub> , 20 ml. of I <sub>2</sub> , 50 ml. of water, and 5 grams of Rochelle salt	0.2355	0.1726	26.7
	Same as above except acidified as in (a)	0.2068	0.2018	2.4
(d)	Na;HPO: 1211:0 10 ml. of K.Fe(CN); 20 ml. of Iz, 25 ml. of water, and 25 ml. of 10% Na;HPO: 121:0	0.2343	0,1650	29.6
	Same as above except acidified as in (a)	0.2179	0.2178	0.0
(e)	K <sub>3</sub> F <sub>3</sub> 10 ml. of K <sub>4</sub> Fe(CN) <sub>5</sub> , 20 ml. of I <sub>2</sub> , 30 ml. of water, and 20 ml. of 37 K.F.	0 2284	0 1854	97 B
	Same as above except acidified as in (a)	0.2284	0.2274	0.4

TABLE	I.	EFFECT OF BUFFER AND COMPLEXING AGENTS IN	N
		NEUTRAL AND ACETIC ACID SOLUTIONS	
		IO-idation of W. Fa(ON), with 0.00 Mindinal	

Rupp and Schiedt (7) have reported good results by the addition of an excess of the standard iodine to a bicarbonate-buffered solution of the ferrocyanide, then titration of the excess of iodine with thiosulfate. Muller and Diefenthaler (5) object to the use of the sodium bicarbonate. These authors believe the results obtained by the previous workers were apparently satisfactory because of a compensation of errors. One factor, an oxidation of sodium thiosulfate to sodium sulfate by hypoiodite, tends to require too little thiosulfate, while the conversion of some iodine to iodate in the slightly alkaline solution, not requiring thiosulfate, tends to offset the first effect. The degree of alkalinity, amount of excess iodine, and period of reaction affect the results. They report fairly satisfactory data if the excess iodine in the bicarbonate-buffered solution is titrated with an arsenious reagent, provided the solution does not stand so long that iodate formation has taken place. In a second article Rupp (6) recommends the use of sodium potassium tartrate instead of bicarbonate. Muller and Diefenthaler were unsuccessful with this procedure also. More recently Kolthoff (4) has reviewed the general problem, emphasizing in addition to the factors already mentioned, the effect of complexing the Fe<sup>+++</sup> to shift the equilibrium in the desired direction and titration of the excess iodine in acid solution. Furthermore, the danger of error as a result of atmospheric oxidation is pointed out. Kolthoff proposes a method in which the ferrous solution is treated with potassium bromate and later potassium iodide in phosphoric acid solution containing a trace of molybdate as a catalyst. Very good results are reported.

Kolthoff states that no benefit was observed from the presence of sodium potassium tartrate in neutral solution. In fact, better results were obtained when it was left out but the results were still 2 per cent too low. By first heating the solution to  $40^{\circ}$  C., then adding iodine in excess, and back-titrating with thiosulfate, he reported good results.

In view of the somewhat uncertain state of affairs with regard to the iodometric determination of ferrocyanide, further work in this connection was undertaken with particular reference to the application of the determination in processes of sugar analysis.

### Experimental

All the chemicals used were of analytical grade and the reactions were carried out in glass-stoppered flasks with all the usual precautions observed in iodometric work. Preliminary experiments with the bicarbonate buffer method of Rupp and Schiedt (7) confirmed the observations of later workers as to low results. In all cases more nearly correct results were obtained by slightly acidifying with acetic acid just before titration of the excess iodine with thiosulfate, but the results were still low because of the slight reversibility of the reaction. The clevated temperature method of Kolthoff in the authors' hands was also unsatisfactory. Use of tartrate in the reaction mixture as proposed by Rupp (6) gave low results in the nearly neutral solution, but if acidified before the excess iodine was titrated the results were only slightly low. A precipitate of potassium acid tartrate caused the solution to become cloudy and interfered somewhat with the indicator reaction.

The improvement in results noted when the tartrate was present may be assigned to the complexing of the ferric ion and shift of the equilibrium in the desired direction. The effect is similarly emphasized by the satisfactory results reported by Kolthoff with his procedure using the bromate-iodide mixture, acidifying with phosphoric acid, and then titrating the excess iodine with thiosulfate. Tests with phosphate and fluoride as complexing agents were also included in the preliminary experiments and sample results are shown in Table I.

Although the concentration of phosphate or fluoride and that of the acetic acid of acidification did not appear to be critical, the effect of the excess of iodine solution added for the oxidation and the time which it stood in contact with the ferrocyanide solution did seem to be important.

These factors were studied in a series of tests in which 10.00 ml. of 0.02179 N potassium ferrocyanide solution, 25 ml. of 20 per cent acetic acid, and 25 ml. of 10 per cent disodium hydrogen phosphate dodecahydrate were used with varying amounts of the 0.02 N standard iodine solution. The solutions were permitted to stand in a 150-ml. glass-stoppered flask for varying lengths of time and then titrated to the starch end point with a standard thiosulfate solution. From the results of Table II it is apparent that when there is a 65 to 70 per cent excess of the iodine reagent the oxidation of the ferrocyanide is accomplished within 15 minutes. The use of elevated temperature is not necessary, since the reaction is complete at room temperature in this relatively short time.

TABLE	II.	EFFECT	OF TI	ME,	TEMPER	ATC	TRE,	AND	Excess	OF
0.0	02	N IODINE	UPON	Ox	IDATION	OF	FER	ROCY	ANIDE	

[10 ml. of 0.02179 N K4Fe(CN), 25 ml. of 10% NatHPO. 12HO, and 25 ml. of 20% acetic acid used in each determination]

<sup>o</sup> C. Min. Ml. 50 15 25 26 15 10	e Consumed	Taken	(CN): Found	Error
50 15 25 26 15 10 26 15 15	%	Millieg	uivalents	%
26         15         13           26         15         20           26         15         25           26         5         15           26         5         15           26         15         15           26         5         15           26         15         15           26         15         25           26         15         25	$     \begin{array}{r}         115 \\         10 \\         65 \\         119 \\         174 \\         72 \\         65 \\         65 \\         174 \\         74     \end{array} $	$\begin{array}{c} 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\\ 0.2179\end{array}$	$\begin{array}{c} 0.2163\\ 0.2163\\ 0.2178\\ 0.2185\\ 0.2178\\ 0.2076\\ 0.2178\\ 0.2174\\ 0.2178\\ 0.2178\end{array}$	$ \begin{array}{r} -0.7 \\ -0.7 \\ 0.0 \\ 0.3 \\ 0.0 \\ -4.7 \\ -0.2 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ $

When the same procedure was applied to 0.1 N ferrocyanide and iodine solutions, the results were consistently 1 per cent too low and the end point was somewhat fugitive. However, by using a 300-ml. flask and adding 100 ml. of water to the reaction mixture before the thiosulfate titration, theoretical values and a stable end point were obtained. This fact is demonstrated in the following experiments:

Large crystals of potassium ferrocyanide trihydrate were split apart and portions of the center section which showed no evidence of dehydration were used for a series of determinations. The weighed portion of ferrocyanide (not in excess of 0.6 gram) in a 300-ml. glass-stoppered flask was dissolved in about 35 ml. of water and then 25 ml. of 20 per cent acetic acid, 25 ml. of 10 per cent disodium phosphate solution, and 25 ml. of standard 0.1 N iodine solution were added. After the flask had stood in a dark place for 15 to 20 minutes, 100 ml. of water were added and the excess iodine was titrated with thiosulfate to a starch end point. In a second series of experiments 3 per cent potassium fluoride

In a second series of experiments 3 per cent potassium fluoride was substituted for the phosphate.

The results are given in Table III.

and has been a second and	States of the second states of the second states	And the second second second
TABLE III.	DETERMINATION OF POTASSIUM I	FERROCYANIDE
K <sub>4</sub> Fe(CN) <sub>6.3</sub> Taken	H2O K4Fe(CN)4.3H2O Found	Error
Gram	Gram	%
0.1 N iodine as	oxidizing agent in slightly acid solution, plexing agent	Na1HPO: as com-
$\begin{array}{c} 0.4631\\ 0.4760\\ 0.4650\\ 0.4710\\ 0.3290\\ 0.3361\\ 0.4708\\ 0.4329\\ 0.3361\\ 0.4708\\ 0.4327\\ 0.4798\\ 0.4327\\ 0.3492\\ 0.2608\\ 0.3832\end{array}$	$\begin{array}{c} 0.4636\\ 0.4788\\ 0.4638\\ 0.4638\\ 0.4717\\ 0.4627\\ 0.4113\\ 0.3203\\ 0.3360\\ 0.4708\\ 0.4339\\ 0.4751\\ 0.3482\\ 0.2621\\ 0.3831\\ \end{array}$	$\begin{array}{c} 0.0\\ 0.6\\ -0.3\\ 0.1\\ -0.3\\ 0.3\\ 0.1\\ 0.0\\ 0.0\\ 0.0\\ 0.3\\ 0.2\\ -0.3\\ 0.5\\ 0.0\end{array}$
0.1 N iodine as o	xidizing agent in slightly acid solution,	K <sub>1</sub> F <sub>1</sub> as complexing
	agent	
0.3854 0.3942 0.4126	0.3858 0.3934 0.4124	$   \begin{array}{r}     0.1 \\     -0.2 \\     0.0   \end{array} $

0.4124	0.0
Ce(SO <sub>4</sub> ): as oxidizing agent	
0.8814 0.8964	$     \begin{array}{r}       0.1 \\       -0.1     \end{array} $
	0.4124 Ce(SO4); as oxidizing agent 0.8814 0.8964

#### TABLE IV. COMPARISON OF METHODS FOR DETERMINING Amount of Ferricyanide Reduced after Oxidation of Sugars

[5 mg. of levulose or dextrose heated at 50° C. with 25 ml. of a reagent containing 4 grams of K<sub>3</sub>Fe(CN)<sub>6</sub>, 80 grams of Na<sub>2</sub>HPO<sub>6</sub>.12H<sub>1</sub>O, and 150 grams of Na<sub>2</sub>CO<sub>3</sub> per liter]

Heat- ing	K <sub>4</sub> Fe(C Iodometri Dextrose	N): by c Method Levulose	K4Fe(C Cc(SO4)2 Dextrose	N). by Method Levulose	Excess Ka by KI Dextrose	Fe(CN) Method Levulose
Min.		Milliequival	ent of appar	ent ferrocya	nide formed	NOV SHEET
15 30 45 60 75	$\begin{array}{c} 0.0034\\ 0.0106\\ 0.0161\\ 0.0224\\ 0.0280\\ \end{array}$	0.0826 0.1305 0.1539 0.1645 0.1727	$\begin{array}{c} 0.0053 \\ 0.0115 \\ 0.0178 \\ 0.0233 \\ 0.0285 \end{array}$	$\begin{array}{c} 0.0810 \\ 0.1305 \\ 0.1550 \\ 0.1663 \\ 0.1721 \end{array}$	$\begin{array}{c} 0.0051 \\ 0.0110 \\ 0.0167 \\ 0.0226 \\ 0.0290 \end{array}$	$\begin{array}{c} 0.0810 \\ 0.1305 \\ 0.1552 \\ 0.1667 \\ 0.1740 \end{array}$

Variations of the experimental value from the quantity taken are small in all cases and deviate slightly in both directions from the theoretical. Better consistency can, of course, be obtained by using aliquots from a standard solution where slight errors in weighing and variation in composition of sample are eliminated. It is apparent that the potential of the ferric complex is lowered to the point at which iodine is not formed from iodide at room temperature even in acetic acid solution.

The hydrofluoric acid liberated by the acetic acid when potassium fluoride was used as a complexing agent was without effect upon Pyrex flasks over a period of several weeks, but a soft-glass stirring rod and the bulb of a thermometer were noticeably etched during this time. There seems to be no preference as to the use of the disodium phosphate or the potassium fluoride with respect to complexing ability. The solutions were about 0.03 M with respect to each of these salts.

The low results at first encountered when 0.1 N reagents were used were never observed when 0.02 N reagents were employed nor were end-point difficulties encountered in the latter case. That the trouble was due in the first case to a concentration effect is demonstrated by the fact that the addition of water made possible satisfactory results.

#### **Recommended Procedure**

The ferrocyanide content of an unknown sample is determined in the following manner:

The ferrocyanide or material containing the ferrocyanide must be put into solution if it is a solid. If it is necessary to use acid for this purpose, the solution must be neutralized before the analysis is started. The volume of the ferrocyanide solution should be from 25 to 50 ml. and should contain not over 1.5 milliequivalents of ferrocyanide (0.6 gram of  $K_4Fe(CN)_6.3H_2O$ ). To this amount of the approximately neutral ferrocyanide solution in a 300-ml. glass-stoppered flask are added 25 ml. of 10 per cent disodium phosphate dodecahydrate (or 25 ml. of 3 per cent potassium fluoride), 25 ml. of 20 per cent acetic acid, and 25 ml. of 0.1 N standard iodine solution. The flask is set in the dark for 15 to 20 minutes and then 100 ml. of water are added before the excess iodine is titrated to a starch end point with thiosulfate.

The strength of the iodine solution can be varied to cover different concentrations of ferrocyanide, as long as the volume of solution is large enough to keep the ferricyanide concentration in the reaction mixture below 0.01 M and a 65 to 100 per cent excess of iodine is used.

# Determination of the Extent of Reduction of Alkaline Ferricyanide after Use of the Reagent for Oxidation of Dextrose and Levulose

Having confirmed the practicability of the iodometric estimation of ferrocyanide, a series of experiments was planned to determine the nature of the agreement of the results when the extent of reduction of alkaline ferricyanide by sugars was estimated by several methods. Three methods were employed: the iodometric procedure described above; the ceric sulfate titration of ferrocyanide as used by Becker and Englis (1); and, indirectly, determination of the excess ferricyanide.

The last-mentioned was carried out according to Kolthoff (4) by making the solution 3 N with hydrochloric acid, adding a 1 N potassium iodide solution, and titrating the iodine with thiosulfate after the mixture had stood for about 5 minutes in a glass-stoppered flask. The conditions for the sugar oxidation were those previously described for the selective oxidation of levulose (1). Since under these conditions dextrose is only slightly oxidized and the products of oxidation left might be expected to respond somewhat differently from those after oxidation of levulose, the results are given in Table IV.

On the whole, the agreement among the methods is very good and is of the order of precision to be expected in sugar analysis. Slight variations may be assigned to probable variation in the sugar oxidation itself rather than to the estimation of the ferrocyanide. If there is any slight further oxidation of the by-products of the action of the ferricyanide on the sugars by the ceric sulfate, it is within experimental error.

### Summary

The oxidation of ferrocyanide with iodine may be accomplished by carrying out the reaction in slightly acid solution in the presence of a reagent such as phosphate or fluoride to complex the iron and prevent the reverse reaction.

The oxidation may be carried out at room temperature with a 60 to 75 per cent excess of iodine and a time interval of about 15 minutes The volume of the reaction mixture must be such that the ferricyanide concentration is below 0.01 M. The excess iodine is titrated with standard thiosulfate.

A comparison of results obtained when the reduction of alkaline ferricyanide by dextrose and levulose was made by direct oxidation of the ferrocyanide with iodine, indirect estimation by determination of ferricyanide iodometrically, and direct oxidation of ferrocyanide with ceric sulfate showed good agreement and indicates that the by-products of the primary oxidation of the sugars have a negligible effect upon any of the methods used to estimate the ferricyanide consumed.

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# Determination of Chloride in the Presence of Hydrosulfide or Sulfide Ion

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A method is proposed for the determination of chloride in the presence of hydrosulfide (or sulfide) ion. The procedure involves the precipitation of the hydrosulfide as cupric sulfide, removal of the latter by quantitative filtration, and determination of the chloride gravimetrically as silver chloride. Results are reported of analyses of several samples ranging from 94 to 99 per cent sodium chloride, the remainder being sodium hydrosulfide. The average error is -0.08 per cent; the greatest error is -0.19 per cent.

IN THE course of an attempted synthesis of a heretofore unknown alkyl mercaptan, it was naturally desired to calculate the yield of finished product. Two paths were open: to calculate the yield from the weight of the purified sulfur compound obtained, or to base calculations on the amount of sodium chloride recovered as a by-product. As a result of using the former and customary procedure, extraordinarily high yields of mercaptan were obtained. It was decided, therefore, to check these yields by employing the alternative method.

Surprisingly, there is very little information in the literature bearing directly on the determination of chloride in the presence of sulfide, hydrosulfide, or both.

Wyler (4) determined the concentration of chlorides, including sodium chloride, in mixtures containing the sodium salt of the sulfide, hydrosulfide, thiosulfate, sulfate, carbonate, and chloride. His method consists principally in the oxidation of the sulfide and hydrosulfide to sulfate by means of chromic acid. precipitation of the sulfate together with the chloride with silver ion, and subsequent isolation of the precipitate. The precipitate is then dissolved in aqueous ammonia and the silver chloride is reprecipitated by means of nitric acid. The silver sulfate remains in solution.

Topsöe (2) developed a method for the estimation of chlorides, bromides, or iodides in the presence of hydrogen sulfide. His procedure consists essentially in the oxidation of hydrogen sulfide to sulfate by means of acidic potassium permanganate, conversion of the liberated halogen into the corresponding hydrogen compound by sulfurous acid, reduction of the excess permanganate by the same reagent, and determination of the haloids in the usual way.

Another method (1) suggests acidification with nitric acid, with subsequent expulsion of the hydrogen sulfide generated by boiling. The halide is then determined by means of the Volhard method (3).

(3). Wyler's method (4) was tried several times in this laboratory and was found to give satisfactory results. However, the method is time-consuming and was therefore objectionable. Khadanov's method (1) gave excellent results with synthetic mixtures of sodium chloride and sodium hydrosulfide, but failed to yield precise values with the impure sodium chloride obtained from the synthesis of the mercaptan. The treatment was the same in each case. It is possible, however, that traces of mercaptan, which were undoubtedly present in the impure sodium chloride, were responsible for the discrepancies. Check determinations varied by as much as 0.3 per cent.

It was desirable for the authors' purpose to develop a shorter method, in view of the fact that many analyses were contemplated. The method described below involves precipitation of the hydrosulfide or sulfide as cupric sulfide. This is separated from the soluble chlorides by filtration and the latter, in turn, are precipitated with silver nitrate. The silver chloride may then be determined gravimetrically.

Known mixtures of sodium chloride-sodium hydrosulfide ranging from 94 to 99 per cent of the former were prepared. This range was selected because it corresponded to the expected "purity" of the sodium chloride precipitated from the authors' experiments.

In several preliminary experiments, it was found that lead nitrate may be substituted for the cupric salt, if certain precautions are observed. The lead sulfide must be filtered from a hot solution ( $60^{\circ}$  to  $70^{\circ}$  C.), otherwise lead chloride, which is fairly insoluble in the cold, will also be removed. It is advisable to precipitate the silver chloride from a hot solution to prevent occlusion. Oddly, no occlusion effects were observed.

If desired, the silver chloride may be determined volumetrically in the usual way (3) by adding an excess of standard silver nitrate, filtering the silver chloride, and titrating the excess silver ion with standard ammonium thiocyanate solution, using ferric ammonium sulfate as the indicator.

### Reagents

Chemically pure sodium hydrosulfide dihydrate, reagentquality sodium chloride, a 5 per cent aqueous solution of c. P. cupric nitrate trihydrate, a 5 per cent aqueous solution of c. P. nitric acid, and a 5 per cent aqueous solution of reagent-quality silver nitrate.

# **Experimental Procedure**

99 PER CENT SODIUM CHLORIDE-1 PER CENT SODIUM HYDRO-SULFIDE MIXTURE. Samples of sodium chloride and sodium hydrosulfide dihydrate in the ratio of 19.8083 to 0.2018 gram were weighed directly into a 500-ml. volumetric flask. Distilled water was added to the mark and solution effected. A 100-ml. aliquot was taken and acidified with 5 per cent nitric acid to a pH of 4 on Universal indicator paper. Next 10 ml. of 5 per cent cupric nitrate solution were added immediately with stirring to precipitate cupric sulfide. The mixture was then allowed to stand for 15 minutes and filtered quantitatively at the end of this time. The filtrate was transferred, again quantitatively, to a 500-ml. volumetric flask, made up to the mark with distilled water, and the solution was mixed thoroughly. A 25-ml. aliquot was diluted to 100 ml., 5 ml. of 5 per cent nitric acid were added, and the chloride ion was precipitated as silver chloride upon the addition of 15 ml.

	Та	BLE I. DET	ERMINATION (	OF CHLORIDE	
Sample	70	Composition	Amount Calculated Gram	of AgCl Experimental Gram	Error %
1	99 1	NaCl NaSH.2H <sub>2</sub> O	0.4859	0.4859 0.4855 0.4855	$0.00 \\ -0.08 \\ -0.08$
2	97 3	NaCl NaSH.2H <sub>2</sub> O	0.4759	0.4750 0.4754 0.4758	-0.19 -0.11 -0.02
3	94 6	NaCl NaSH.2H <sub>2</sub> O	0.4611	0.4609 0.4605 0.4607	$-0.04 \\ -0.13 \\ -0.08$
				A۱	0.08

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of 5 per cent silver nitrate. The mixture was allowed to stand for several hours and filtered. The precipitate was dried to constant weight at 110° C .:

Weight of NaCl  $\times \frac{100}{500} \times \frac{25}{500} \times \frac{M. W. \text{ of AgCl}}{M. W. \text{ of NaCl}}$ weight of NaCl  $\times$  0.02453 = weight of AgCl (calculated)

### $19.8083 \times 0.02453 = 0.4859$ gram of AgCl (calculated)

97 PER CENT SODIUM CHLORIDE-3 PER CENT SODIUM HYDRO-SULFIDE MIXTURE. The procedure was the same as that out-lined above, except that the mixture was obtained by weighing out 19.4000 and 0.6000 gram of sodium chloride and sodium hydrosulfide, respectively:

 $19.4000 \times 0.02453 = 0.4759$  gram of AgCl (calculated)

94 PER CENT SODIUM CHLORIDE-6 PER CENT SODIUM HYDRO-SULFIDE MIXTURE. The procedure was again the same as that outlined above, with the exception that the original mixture was

composed of 18.8000 grams of sodium chloride and 1.2000 grams of sodium hydrosulfide:

### $18.8000 \times 0.02453 = 0.4611$ gram of AgCl (calculated)

The results are given in Table I. The average error of nine analyses on three samples is -0.08 per cent; the greatest individual error is -0.19 per cent. The reproducibility and accuracy, as seen from these results, are excellent.

Work is now in progress on the quantitative determination of the sulfide content of these mixtures. These results will be published at a later date.

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# **Determination of Carotene in Vegetable Oils** without Saponification

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THE increasing research on carotene and its use in vegetable oil solutions has called attention to the desirability of a simple, accurate method for determining the carotene content of such solutions. The methods at present available are either too long and tedious or are subject to errors which may in some cases be large.

The more rapid methods depend upon the determination of total color by simple dilution of the oil sample with a suitable solvent and measurement of the percentage of light transmission by the solution. Data presented in this paper show that this method may be in considerable error because of the presence of colored substances that form during storage of the carotene solutions and which are included with the carotene in the analysis.

The longer methods, which are the more accurate, all require that the sample be saponified. The Guilbert method (4) as modified by Peterson et al. (10) and by Peterson (9) may be regarded as representative of the saponification methods. Following the saponification approximately 12 phasic partitions are made in separatory funnels. Caution is necessary to prevent the formation of rather stable emulsions in this process. The noncarotene chromogens are removed by partition between nonmiscible solvents or by use of chromatographic adsorption columns (11).

# Selection of Adsorbent

A rapid chromatographic method without the timeconsuming saponification and phasic separations is desirable.

Vegetable oil solutions of carotene and noncarotene chromo-gens were dissolved in petroleum ether and analyzed for carotene, using the adsorbents suggested by Moore (7), Kernohan ( $\mathscr{O}$ ), and Wall and Kelley (14) for the analysis of plant extracts. It was found that these adsorbents were not directly applicable to oil solutions, as the presence of the oil interfered with the ad-sorption of the noncarotene chromogens by the dibasic calcium phosphate, soda ash, and magnesium oxide-Celite columns. In the method of Fraps, Kemmerer, and Greenberg ( $\mathscr{S}$ ) special techniques are required for preparing the adsorbents, and the degree of activation may vary on storage, so that their activity must be redetermined each time they are used. For these reasons no attempt was made to apply the method to analysis of solutions containing oil. Vegetable oil solutions of carotene and noncarotene chromosolutions containing oil.

Seaber analyzed oil samples for carotene by saponification, removal of alkali and alcohol, transference of carotene by saponification, removal of alkali and alcohol, transference of carotene to petro-leum ether and adsorption of the carotenoids on aluminum oxide standardized according to Brockman, and eluting the carotene with 3 per cent acetone in petroleum ether. Thaler (13) prepared chromatograms of various fats and oils on Tswett columns of aluminum oxide in order to detect the pres-ence or absence of artificial colors in the oils, but mede no attempt

ence or absence of artificial colors in the oils, but made no attempt at a quantitative separation of the carotene from the other associated pigments.

This work suggested that aluminum oxide (<80-mesh aluminum oxide activated especially for chromatographic analysis, manufactured by the Aluminum Ore Company, East St. Louis, Ill.) might be used for separating carotene directly from other chromogens present in oil, thus avoiding saponification. With solutions of purified crystalline carotene, aluminum oxide columns caused no detectable destruction of carotene. Various amounts of acetone in petroleum ether were tested as eluents. Two per cent acetone in petroleum ether was found to remove carotene quantitatively from the aluminum oxide column and permit its separation from the colored oxidation products of carotene, xanthophylls, and chlorophylls. Higher concentrations of acetone did not permit as sharp a separation of carotene from the colored impurities, as they followed the carotene through the column too closely.

#### Procedure

Tswett tubes having an inside diameter of 11 mm. are packed with 12 grams of the aluminum oxide. Columns of uniform height of about 10 cm. are obtained by applying gentle suction and tamping lightly with a heavy glass rod spread and flattened on one end. The column is covered with about 1 gram of anhy-drous sodium sulfate. A 10-ml. aliquot of a petroleum ether (boiling point 30° to 60° C.) solution, containing 0.1 gram of the oil per ml. of solution, is run onto the column. After all the solution has passed into the aluminum oxide the column is developed and the carotene is simultaneously eluted with the required amount of petroleum ether containing 2 per cent acetone (no pressure or vacuum is required to hasten the per-colation). Tswett tubes having an inside diameter of 11 mm. are packed colation).

The volume of eluent needed must be determined for each batch of aluminum oxide. As the commercial preparation of aluminum oxide may vary somewhat in activity from one lot to

		App Carot Dilu	arent ene by ution	Car by Col	otene Al <sub>2</sub> O <sub>2</sub> umn	Carotene by CaHPO <sub>4</sub> Column
Sam- ple	Description of Sample	No oil	Oil added <sup>a</sup>	No oil	Oil added <sup>a</sup>	No oil
1 1	0 ml. of a solution of			1.1.1		
2 1	pure carotene 0 ml. of a petroleum ether solution of caro- tene containing a small amount of oxi-	140	142	138	140	138
3 1	dized carotene 0 ml. of a petroleum	134	139	127	127	128
4 1	ether solution of caro- tene containing a large amount of oxi- dized carotene ml. of a petroleum ether solution of xan- thorbull (X) diluted	173	175	100	100	90
5 1	with petroleum ether to 10 ml. ml. of a petroleum ether solution of caro- tene and oxidized	26		<1		<1
6 2	to 10 ml. ml. of solution (C) +	61		53		53
7 4	diluted to 10 ml. ml. of solution (C) + $2$ ml. of solution (X)	301	308		107	107
	diluted to 10 ml.	270	275		211	212
a 1 gram	of corn oil was added	to thes	e samples	before	e dilution	to 10 ml.

#### TABLE I. SEPARATION OF CAROTENE FROM OXIDATION PROD-UCTS OF CAROTENE AND FROM XANTHOPHYLL (Micrograms of carotene in 10-ml. aliquot)

another, a preliminary determination of the volume of eluent is required. The required calibration may be readily made as follows: A 10-ml. aliquot of a petroleum ether solution of crystalline carotene, containing 0.1 gram of oil per ml. of solution, is run onto the column. Several columns are prepared in this manner. Columns are then washed with various amounts of 2 per cent acetone in petroleum ether to determine the minimum amount of eluent necessary to remove all the carotene. This volume is then used in the analyses for eluting the carotene and leaving the other colored impurities on the column. The columns prepared from the first three 2.27-kg. (5-pound) lots of aluminum oxide required 45 ml. of eluent to remove the carotene, while the columns prepared from the fourth 2.27-kg. (5-pound) lot required 65 ml. of eluent. The aluminum oxide must be protected against the adsorption of moisture to keep its activity constant.

The carotene eluate is caught in a 100-ml. volumetric flask and made to volume, and the carotene concentration is determined colorimetrically in an Evelyn photoelectric colorimeter with a  $440-m\mu$  filter. This measures beta-carotene together with any alpha- or neo-beta-carotene that may be present. Both alpha- and neo-beta-carotene are more readily eluted from the aluminum oxide column than beta-carotene. Methods are available for the individual estimation of these components by spectrophotometric technique (12, 15).

The method can also be used to separate carotene from other pigments in a petroleum ether solution that is free of oil. More eluent is needed to remove the carotene from the column when no oil is present. The volume of eluent required may be readily determined as described above by use of a petroleum ether solution of carotene containing no oil. The volume of eluent required for columns prepared from various lots of aluminum oxide ranged from 75 to 90 ml.

# Comparison with Simple Dilution and Moore Method

The proposed method was tested and evaluated in the following manner:

Petroleum ether solutions of pure carotene and carotene containing some oxidized carotene were analyzed by three methods: (1) by simply diluting with petroleum ether to a suitable volume, (2) by the proposed method, and (3) by using a column of dibasic calcium phosphate as recommended by Moore (7). Moore (8) has shown that the dibasic calcium phosphates

Moore (8) has shown that the dibasic calcium phosphates obtained commercially vary considerably in activity and that potassium hydroxide will activate the commercial product. These results were confirmed in this laboratory and extended to show that commercial dibasic calcium phosphate from two manufacturers could be activated to the same degree by the following process: 500 grams of commercial dibasic calcium phosphate and 40 grams of potassium hydroxide are added to 5 liters of water in a 6-liter boiling flask. The flask is immersed in boiling water for 45 minutes, and the contents are stirred every 5 minutes. The calcium phosphate is then filtered on a Büchner funnel. Suction is applied until the mass is sufficiently dried so that the surface just begins to crack. The mass is then washed five times with 100-ml. portions of distilled water. The phosphate is dried for 24 hours at 105° C. Each batch so activated is tested with a pure solution of carotene in petroleum ether, to which a known amount of oxidized carotene is added. The proper activation is reached if the column retains all the impurity without retaining or destroying any carotene.

The same solutions of carotene, with the addition of 0.1 gram of vegetable oil per ml., were analyzed by the first and second methods. The data (Table I, sample 1) showed that neither the aluminum oxide nor the calcium phosphate column caused any destruction of carotene and that all the carotene could be recovered. Samples 2 and 3 were solutions of purified carotene in petroleum ether that had developed colored oxidation products of carotene during storage. Therefore, analysis by simple dilution (first method) gave higher value than the other two methods which removed these noncarotene chromogens. Analyses of oil-free solutions of carotene containing some oxidized carotene, by the proposed method and by the dibasic calcium phosphate column, gave the same values. Analyses of oil-containing solutions (0.1 gram of oil added per ml.) by the proposed method also gave the same values.

Analyses of petroleum ether solutions containing carotene, oxidized carotene, xanthophyll, and oil, are shown in Table I, samples 6 and 7. Analyses of these samples, using the aluminum oxide column, gave the same carotene content as was obtained by the analyses of similar solutions containing no oil, using the dibasic calcium phosphate column. The oil, therefore, did not interfere with the removal of these noncarotene chromogens by aluminum oxide when the analyses were made as described.

TABLE II. COMPAN REMOVAL OF NONC	rison of Aluminum O arotene Chromogens Peterson and Moore	vide Column for with Methods of
(Petroleum ether extra stored a year.	ct of dehydrated alfalfa lea Micrograms of carotene in 1	f meal that had been 0-ml. aliquot)
AhO: Column, Triplicato	Moore Method, I Triplicate	Peterson Method, Triplicate
180, 180, 179	182, 185, 185 gram of oil added to aliquots	
180, 181, 180		207, 218, 214

# **Comparison** with Moore and Peterson Methods

A sample of alfalfa that had been in storage for almost a year was extracted with petroleum ether, and 10-ml. aliquots of the solution were analyzed for carotene by the proposed method and by passage through a column of dibasic calcium phosphate. The results by the two methods were very similar. Aliquots of 10 ml., to which 1 gram of refined corn oil was added, were analyzed by the proposed method and by the Peterson method (9). The method of Moore was not used because it is not directly applicable to solutions containing such large amounts of oil. The Peterson method gave appreciably higher results than the aluminum oxide method. Results with the latter agreed with the analyses made before the addition of the oil. The data are given in Table II. It has been previously shown (1, 2, 5, 7) that methods based on phasic separation do not remove all noncarotene chromogens.

Cottonseed oil solutions of carotene that had been in storage under various conditions were analyzed (1) by simply diluting with petroleum ether to a suitable volume, (2) by the

TABLE III.	COMPARISON OF PROPOSED METHOD WITH DILUTION
	AND PETERSON METHODS

(Samples consist of cottonseed oil solutions of crystalline carotene after 7 months' storage under various conditions. Micrograms per 1 ml. of oil)

	Apparent Carotene, Obtained by	True Ca	arotene
Sample	Dilution Only,	Proposed method,	Peterson method,
No.	Duplicates	duplicates	duplicates
8 127	171, 170	151, 157	156, 155
S 128	173, 175	160, 158	156, 160
S 129	175, 177	161, 160	160, 158
S 130	198, 199	175, 176	175, 176
S 132	198, 198	175, 175	175, 175
S 138	155, 155	139, 139	139, 139
S 139	178, 178	163, 165	160, 165
S 140	186, 186	170, 170	176, 176

proposed method, and (3) by the method of Peterson. The data, given in Table III, indicate that colored oxidation products of carotene may develop during the storage of oil solutions of carotene and, therefore, analyses made without their removal may be in error. Very close agreement with the Peterson method was obtained in these samples, which were prepared with crystalline carotene (90 per cent beta and 10 per cent alpha) and refined cottonseed oil. As noted above, this agreement was not obtained in the analyses of oil containing the chromogens extracted from alfalfa that had been in storage for some time. It appears that the Peterson method is more efficient in removing colored oxidation products of carotene than it is in removing some of the other noncarotene chromogens that may be present in a plant extract.

Satisfactory analyses were also made by the proposed method on solutions of carotene in refined corn, refined soybean, raw coconut, and raw rice bran. It may be assumed that the method will be satisfactory for other vegetable oils.

### Summary

A rapid method is described for the determination of carotene in vegetable oil solutions without saponification. The colored oxidation products of carotene that develop during storage are removed by this method. The carotene is separated from the other chromogens by passing a petroleum ether solution of the oil containing the mixed chromogens through a Tswett column of aluminum oxide and eluting the carotene with 2 per cent acetone in petroleum ether. The method will also separate carotene from the pigments extracted by petroleum ether (30° to 60° C.) from dehydrated alfalfa, as well as from very large amounts of xanthophyll. The volume of sample and eluent must be controlled to ensure accurate separations of carotene by the column of aluminum oxide prepared as described.

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# **Detecting Adulteration of Ethylvanillin with Vanillin**

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would be expected to behave alike in chemical reactions because of their similar structures. Their main functional groups, -OH and -CHO, are identical, and their less active functional groups, -OCH<sub>2</sub> and -OCH<sub>2</sub>CH<sub>3</sub>, differ only by one -CH<sub>2</sub> grouping. Tests for distinguishing between them are therefore not very common, much less those for detecting the presence of one in the other. In fact, only one really satisfactory test has been published (2) for detecting ethylvanillin in the presence of vanillin, and none for detecting vanillin in the presence of ethylvanillin.

The two compounds, together with coumarin, are widely used in the manufacture of imitation vanilla flavors. The compound used must be stated on the label of the product, and if only vanillin is claimed by the label, the presence of ethylvanillin in the mixture must be considered adulteration. However, because ethylvanillin is much more expensive than vanillin and three times as much vanillin as ethylvanillin must be used to produce comparable products, adulteration of this type is not to be expected. When ethylvanillin is declared on the label, federal specification EE-E-911a calls for at least 0.33 gram of that substance per 100 cc. of imitation

vanilla flavor. It would then be very profitable to substitute vanillin for some ethylvanillin.

Testing laboratories which examine imitation vanilla flavor for prospective purchase of the merchandise could use the following procedure to test for adulteration of ethylvanillin with vanillin.

#### Reagents

1. Two per cent alcoholic solution of potassium hydroxide, to

which excess ammonium thiocyanate has been added. 2. A mixture of 1 cc. of 7 per cent aqueous cupric sulfate pen-tahydrate, 4 cc. of 3 per cent alcoholic ferric chloride dodecahydrate, and 5 cc. of 95 per cent ethyl alcohol.

### Procedure

The ethylvanillin-vanillin fraction of the product is extracted with alcohol-free ether, and if not crystalline is purified accord-ing to the method of the A. O. A. C. (1). Twenty-five milligrams of the residue, dried in a sulfuric acid desiccator, are placed in a medium-sized test tube. For comparative purposes, 25 mg. of pure ethylvanillin may be placed in another test tube and put through the same procedure as the unknown. Three to 4 cc. of 95 per cent ethanol are added to the solid and the tube is shaken. A drop of reagent 1 and then a drop of reagent 2 are added and the mixture is gently shaken for a minute. In the presence of vanillin a red color is produced, which fades very slightly during several hours. If only ethylvanillin is present, a light yellow color will result from a very rapidly fading reddish solution.

The test tubes used must be perfectly clean and it is advisable to rinse them with alcohol before the test. If a quantitative estimate of the amount of vanillin present is desired, the color produced by the unknown may be compared in the colorimeter with those produced by known mixtures of vanillin and ethylvanillin during the same period of time.

The method has been found to detect the presence of at least 1 mg. of vanillin in the specimen taken for analysis. Coumarin does not interfere. Fresh reagents should be prepared after 2 days, since too much water and the tendency of reagent 2 to separate will cause a decrease in the sensitivity of the test. The procedure must be carefully followed, since the addition of too much reagent or of reagent 2 before reagent 1 may lead to erroneous results.

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# **Analysis of Constant-Pressure Filtration Data**

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 $\mathbf{R}^{ ext{UTH, Montillon, and Montonna (1) developed the}$  equation

$$(V+C)^2 = K(\theta+\theta_0) \tag{1}$$

relating the volume, V, of filtrate produced during a given filtration at constant pressure, to the filtering time  $\theta$ , the terms C and  $\theta_0$  representing, respectively, the theoretical amount of filtrate and filtering time required to develop the initial press resistance. To evaluate the constants of this equation they plotted  $d\theta/dV$  against V, securing the straight line

$$d\theta/dV = 2(V+C)/K \tag{2}$$

the slope and V-intercept of which determine K and C, from which  $\theta_0$  is found by substitution in Equation 1. They showed how the determination of the constants may further be simplified by the assumption of a parabolic V- $\theta$  relation, permitting determination of the constants from the data of any three instants during the filtration.

Herewith is presented an alternate method of evaluating the filtration constants, applicable to any filtration represented by Equation 1. The working assumptions are that at  $\theta = 0$ , V = 0, and that the quantities of filtrate are  $V_1$ and  $V_2$  at times  $\theta_1$  and  $\theta_2$ , with  $\theta_2$  chosen to be twice  $\theta_1$ .

Substitution of these conditions successively in Equation 1 gives

$$C^2 = K\theta_0 \tag{3}$$

$$(V_1 + C)^2 = K(\theta_1 + \theta_0) \tag{4}$$

$$(V_1 + C)^2 = \Lambda(o_2 + o_0) \tag{3}$$

Subtraction of Equation 3 from 4 and 5 and substitution of  $nV_1$  for  $V_2$  give, following some manipulation,

$$C = V_1(n^2 - 2)/2(2 - n) = F_1 V_1$$
(6)

$$K = V_1^2 n(n-1)/\theta_1(2-n) = F_2 V_1^2/\theta_1$$
(7)

$$0 = \theta_1 (n^2 - 2)^2 / 4n(2 - n)(n - 1) = F_3 \theta_1$$
(8)

The relations between  $F_1$ ,  $F_2$ , and  $F_3$  and n are shown in Figure 1 for 1.2 < n < 1.9, with the inset covering the values for n in the neighborhood of  $\sqrt{2}$ .

A

To evaluate the constants of any constant-pressure filtration by the use of this method it is necessary to know the amounts of filtrate at two elapsed times of filtration for which  $\theta_2 = 2\theta_1$ . The ratio of the two values of V gives n, from which



the quantities F can be found for substitution in Equations 6, 7, and 8 for direct determination of C, K, and  $\theta_0$ .

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# The Chemistry of Indium

# A Colorimetric Method for the Estimation of Small Amounts of Indium

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THE suitability of 8-hydroxyquinoline as a reagent for the estimation of small amounts of indium was pointed out by Geilmann and Wrigge (5), who reported that quantitative precipitation of the compound  $In(C_9H_6ON)_3$  could be effected at 70° to 80° C. from a sodium acetate-acetic acid buffer, and indium then determined either by direct weighing of the precipitate after drying at 120° or by application of the usual bromometric titration procedure after solution of the compound in warm 10 to 15 per cent hydrochloric acid. Accurate results in the concentration range 0.83 to 70.8 mg. of indium were obtained.

The possibility of utilizing the 8-hydroxyquinoline derivative of indium for the colorimetric estimation of the element has, apparently, escaped consideration. The compound  $In(C_{9}H_{6}ON)_{3}$  dissolves readily in chloroform (a not unexpected fact, since chelate linkages within the molecule completely satisfy the coordination number of six which is normally shown by indium) yielding bright yellow solutions, the colors of which are of sufficient intensity to be readily detectable even at indium concentrations below 1 mg. per liter of solvent. Consequently, it seemed advisable to investigate this possibility, and the results here reported summarize a spectrophotometric examination of the system and a procedure for the extraction of the metal and its subsequent colorimetric estimation as the 8-hydroxyquinoline complex.

# **Apparatus and Materials**

All colorimetric measurements reported herein were made with a Cenco-Sheard spectrophotelometer (9), using cells of 1-cm. ( $\pm 0.5$  per cent) thickness and employing a slit width of 5 mµ. Measurements of pH were made with a Beckman Laboratory Model G pH meter, the glass electrode of which was calibrated against a standard phthalate buffer.

A standard indium sulfate solution containing 11.64 mg. of indium per milliliter as determined gravimetrically by hydroxide precipitation (8) was prepared from anhydrous sulfate obtained originally from a sample of the metal of 99.98 per cent purity (8). From one portion of this solution, the indium derivative of 8. hydroxyquinoline was prepared according to the directions of Geilmann and Wrigge (5). The washed and dried product analyzed 20.81 per cent indium as compared with 20.97 per cent calculated for  $In(C_9H_6ON)_3$ . From a second portion of the sulfate solution, a stock indium solution containing the equivalent of 1 mg. of the metal in 10 ml, was obtained by dilution.

rate solution, a stock indum solution containing the equivalent of 1 mg. of the metal in 10 ml. was obtained by dilution. Chloroform, containing 1 per cent ethanol by volume, was of analytical reagent quality. During the investigation, it was found convenient to recover chloroform containing 8-hydroxyquinoline or its indium derivative by shaking with 6 N sulfuric acid, which completely extracts these materials, distilling from lime, and adding ethanol in the same fashion as recommended for recovery from dithizone extractions (2). Chloroform so recovered was colorimetrically indistinguishable from the original material. Indium can be recovered after destruction of the quinoline material  $(\delta)$ .

The 8-hydroxyquinoline used was an Eastman Kodak preparation, and other chemicals were of the best qualities obtainable. Gallium and thallic sulfate solutions were obtained from the pure oxides.

# Spectrophotometric Examination of Chloroform Solutions of the Indium Derivative of 8-Hydroxyquinoline

Spectral transmittancy studies over a wave-length range of 350 to 700 m $\mu$  were made upon solutions prepared by dilution to appropriate concentrations of a stock solution containing the indium derivative of 8-hydroxyquinoline in quantity corresponding to 1000 mg. of indium per liter of chloroform. Characteristic data are given in Figure 1.

Measurements at concentrations greater than 50 mg, of indium per liter are not included, but the curves obtained differ only in a marked broadening of the absorption band. Maximum absorption is noted at 395 m $\mu$  for most samples, with a tendency to shift to 400 m $\mu$  at higher concentrations. Inasmuch as this absorption band is rather broad, differences in transmittancy between 395 and 400 m $\mu$  are in no instance particularly great. Because of this fact and because 400 m $\mu$ represents the lower limit on some instruments, all further measurements were made at 400 m $\mu$ .

# Extraction and Colorimetric Estimation of Indium

Indium, like aluminum and ferric iron (1), can be extracted from aqueous salt solutions by shaking with a chloroform solution of 8-hydroxyquinoline. The procedure followed in all extractions amounted to vigorous shaking of a 25-ml. aqueous solution of the indium salt with four successive 5ml. portions of a 0.01 M solution of 8-hydroxyquinoline in chloroform. The combined extracts were then diluted to 50 ml. with chloroform before colorimetric examination. At optimum pH values, usually the third, and always the fourth, extract appeared colorless.

The marked effect of pH upon precipitations with 8-hydroxyquinoline (3, 4, 6) is also apparent in these extractions (1). The most suitable pH for complete extraction of indium was found by extracting solutions containing the equivalent of 20 mg. of indium per liter of chloroform and adjusted



FIGURE 1. TRANSMITTANCY CURVES FOR INDIUM DERIVATIVE OF 8-HYDROXYQUINOLINE IN CHLOROFORM

TABLE I.	ESTIMATION OF SOLU	Indium in Ini tions	NUM SULFATE
	Mg. of Inc	dium per Liter of	Chloroform
No.	Taken	Found	Deviation
12	0.10	0.20	+0.10
3	0.70	0.60	-0.10
5	4.00	4.00	-0.05
6 7	8.00 12.0	7.90 11.9	-0.10 -0.1
8	16.0 20.0	16.0 20.0	0
10 11	24.0 32.0	23.5 33.8	-0.5 + 1.8

to various pH values by the addition of either 0.1 N sodium acetate or sulfuric acid, determining the per cent transmittancies at 400 m $\mu$ , and comparing these values (through the use of a calibration curve) with the sample showing maximum absorption. In this manner, the degree of extraction was obtained at each pH value.

Reference to the plot of these results given in Figure 2 indicates that while extraction begins slightly above pH 1.9, it is complete only at pH 3.2. Complete removal of indium occurs within the pH range of 3.2 to 4.5, and in all subsequent extractions a pH of 3.5 was employed.



FIGURE 2. EFFECT OF pH UPON EXTRACTION OF INDIUM

The pH values given in Figure 2 are for the aqueous solutions before shaking with the 8-hydroxyquinoline reagent. During the extraction process, some of the amine enters the aqueous phase with an attendant increase in pH, but under standard conditions of extraction, the initial pH appears to be the more readily attainable and therefore the more important. When the pH is 1.9 or less, 8-hydroxyquinoline is completely extracted from the chloroform owing to combination with the acid, and at pH values above 4.5, precipitation of hydrous indium hydroxide both decreases the amount of extractable indium and renders layer separation difficult through emulsification of water in chloroform. Plotted in Figure 3 are data obtained from transmittancy studies at 400 m $\mu$  upon extracts made at pH 3.5 from indium sulfate solutions of varying concentrations prepared from the stock solution containing 1 mg. of indium in 10 ml. Beer's law is obeyed at concentrations up to 18.0 mg. of indium per liter of chloroform, but at larger concentrations deviations become increasingly great. Intersection of the curve with the zero axis of concentration at a point below that corresponding to 100 per cent transmittancy is due to the fact that a chloroform solution of 8-hydroxyquinoline, although apparently colorless, shows a slight absorption at 400 m $\mu$  (1, 7). Use of constant conditions of extraction obviates this difficulty.



FIGURE 3. RELATION BETWEEN TRANSMITTANCY AND INDIUM CONCENTRATION

The reproducibility and accuracy of the method are indicated by the data in Table I. In the range of 0.30 to 20.0 mg. of indium per liter of chloroform, deviations are small, but at higher and lower concentrations they become marked. If concentrations be expressed in terms of actual indium content instead of per liter of chloroform, the sensitivity of the method is apparent. Since given concentrations were obtained from 50-ml. chloroform solutions, accurate measurements resulted with actual indium contents in the range 0.015 to 1.00 mg.

# Interferences

Nitrate, chloride, or sulfate solutions containing in 25-ml. portions the equivalents of 20 mg. of various metals per liter of chloroform (on the basis of complete extraction) were extracted at pH 3.5 by the above procedure, transmittancies at 400 m $\mu$  being determined. The following ions were not extracted under these conditions: magnesium, calcium, strontium, zinc, cadmium, mercuric, stannic, lead, manganous, chromic, and silver. The following ions yielded extracts showing transmittancies below that for 8-hydroxyquinoline and were, therefore, extracted (at least in part): aluminum, gallium, thallic, stannous, bismuth, cupric, ferric, ferrous, nickel, and cobalt (slightly). Ions of the latter group would interfere with the estimation of indium by this method.

Estimation of indium should be possible in the presence of any ion not extractable at pH 3.5. In Table II are summarized data for determinations made in the presence of varying quantities of zinc, cadmium, and lead ions, concentrations again being expressed relative to 1 liter of chloroform. The feasibility of the procedure is apparent.

Since the most persistent impurity in indium is iron, a method for the estimation of indium in the presence of iron would be of value. Application of the present procedure

TABLE II. ESTIMATION	OF INDIUM IN ADMIUM, OR LEAD	PRESENCE OF ZINC,
(20.0 mg. of indium p	er liter of chloroform	m taken in all cases)
Impurity Add	led	Indium Found
Ion	Mg.	Mg.
Zn++	20 100 200	20.0 20.0 20.0
Cd++	20 100 200	20.0 20.0 20.0
Pb++	20 100 ª	20.0 20.0
<sup>a</sup> Some precipitation of les	d sulfate noted.	

would be feasible if it were possible to extract either ferric iron or indium to the exclusion of the other at an appropriate pH. However, since the extraction of the ferric derivative of 8-hydroxyquinoline is complete only at pH values above 1.9 to 2.0 (1, 7) whereas extraction of indium begins in this pH interval, such a procedure would not appear to be suitable. Furthermore, the extensive absorption of the ferric complex at 400 m $\mu$  (7) would cause any iron unextracted at a pH lower than 1.9 to interfere with indium extracted at pH 3.5. Attempts at successive extractions of iron and indium have fully demonstrated the lack of reliability of such a procedure.

### Summary

The 8-hydroxyquinoline derivative of indium dissolves readily in chloroform, yielding yellow solutions which show a fairly broad absorption band in the region of 395 to 400 m $\mu$ . At 400 m $\mu$ , such solutions obey Beer's law in concentrations up to 18.0 mg. of indium per liter of chloroform and lend themselves to the colorimetric estimation of the element.

Indium ion can be completely extracted from aqueous

solutions in the pH range 3.2 to 4.5 by shaking with a chloroform solution of 8-hydroxyquinoline. Of the commoner ions, only the following are extracted at pH 3.5 and therefore interfere with the colorimetric estimation of indium in the chloroform extracts: aluminum, stannous, bismuth, ferric, ferrous, cobalt, nickel, and cupric. Gallium and thallic ions also interfere.

Indium can be estimated accurately in the presence of considerable quantities of zinc, cadmium, and lead ions, but it appears impossible to determine indium accurately in ferricindium ion solutions by extraction of ferric iron at a low pH and subsequent extraction of indium followed by colorimetric examination.

The colorimetric procedure yields accurate results for indium concentrations in the interval of 0.3 to 20 mg. per liter of chloroform or 0.015 to 1.00 mg. of the metal in a 25-ml. aqueous solution. Analyses of samples containing larger amounts of indium should be possible through sufficient dilution of the chloroform extract.

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# The Dead-Stop End Point

# As Applied to the Karl Fischer Method for Determining Moisture

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HE chemical reaction involved in the Karl Fischer method (2) for determining water was given originally as follows:

 $2H_2O + I_2 + SO_2 C_6 H_6 N + 2C_6 H_6 N =$  $(C_5H_5N)_2H_2SO_4 + 2C_5H_5N.HI$ 

Smith, Bryant, and Mitchell (4) have shown that the reaction is not so simple as this and that it occurs in two distinct steps:



The second reaction does not involve water and this makes it necessary to control all conditions with care during the titration in order to get reproducible results. No equation can be written to represent the stoichiometric relation between the water consumed and the amount of Fischer reagent used up. This is not a serious drawback, however, because the Fischer reagent is readily standardized against pure water or a standard solution of water.

Fischer, as well as Smith, Bryant, and Mitchell, detected the end point visually by the appearance of brown iodine when all the water had reacted. This is often difficult because the products of the reaction are yellow and the brown color of iodine is not easily seen under these conditions. Starch does not serve as an indicator for iodine in these nonaqueous solutions.

Almy, Griffin, and Wilcox (1) used a potentiometric method with platinum and tungsten electrodes for detecting the end point which was more precise than the visual method. The authors have been able to duplicate their results, although the manipulation difficulties are a little greater than when the end point is detected visually.

The authors have found that the dead-stop method of Foulk and Bawden (3) gives a sharp and reproducible end point in these nonaqueous solutions with fewer manipulation difficulties than the potentiometric method and better precision than the visual method. It depends upon the fact that when an electromotive force of 10 to 15 millivolts is impressed upon two platinum electrodes immersed in the Fischer reagent, sufficient current flows through the solution to deflect a galvanometer off the scale. During the titration of the Fischer re-



FIGURE 1. TITRATION APPARATUS

agent with a standard solution of water in methanol, the galvanometer remains deflected until the end point is approached. Near the end point the galvanometer is affected by each addition of water solution, and at the end point the galvanometer suddenly comes to a steady reading near its rest point. The reverse titration—that is, the addition of Fischer reagent to a solution containing water—was found to be less satisfactory and was not used in these experiments.

The dead-stop apparatus is continuous-reading, and requires practically no adjustment from day to day, while the potentiometric apparatus must be adjusted before each individual titration.

### Apparatus

The two standard solutions were dispensed from automatic burets, protected from atmospheric moisture by means of Drierite.

The apparatus for stirring the solutions was similar to that of Almy, Griffin, and Wilcox (1) and is shown in Figure 1. The stirrer, buret tip, and platinum electrodes pass through a Bakelite stopper which has been turned to fit a No. 27 standard taper, 250-ml., glass-stoppered Erlenmeyer flask. The stirring propeller and its bearing are made of stainless steel.

The dead-stop apparatus was similar to that used by Wernimont and Hopkinson (6).

A small weighing pipet for standardizing the solutions consisted of a 2-ml. medicine dropper with a rubber bulb and a Nichrome suspension wire.

#### Reagents

FISCHER REAGENT. A 700-ml. portion of pyridine, Eastman reagent No. 214-H, was measured into a 1-liter Erlenmeyer flask and tared on a platform balance. Gaseous sulfur dioxide was passed from a cylinder into the pyridine through a gas-dispersion tube until 380 grams had been added. When the solution had cooled to room temperature, 1 liter of pyridine, 200 ml. of anhydrous methanol, and 500 grams of resublimed iodine were added; it was immediately cooled in an ice bath and shaken occasionally until all the iodine was dissolved. The reagent was stored in a glass-stoppered bottle and dispensed from an automatic 50-ml. buret, protected from atmospheric moisture by means of Drierite. STANDARD WATER SOLUTION. Twenty milliliters of distilled water were added to 3.8 liters of commercial methanol and this

STANDARD WATER SOLUTION. Twenty milliliters of distilled water were added to 3.8 liters of commercial methanol and this solution was dispensed from an automatic buret, protected from atmospheric moisture by means of Drierite, directly into the titration flask in the stirring apparatus. The ratio, R, between this solution and the Fischer reagent was first determined by direct titration to a dead-stop end point. Then 25-ml. portions of anhydrous methanol were titrated for their moisture content by adding Fischer reagent until the brown color of iodine appeared and back-titrating with standard water solution to a dead-stop end point. The milliliters of standard water solution, b, equivalent to the water in the methanol were calculated as follows:

 $b = (ml. of Fischer reagent \times R) - (ml. of standard water solution)$ 

Finally, 0.13- to 0.15-gram portions of water were weighed from a small weighing pipet into dry Erlenmeyer flasks containing 25 ml. of anhydrous methanol. Fischer reagent was then slowly added to these solutions until an excess was present and the excess was immediately back-titrated with standard water solution to a dead-stop end point. The water factor, W, of the standard water solution was calculated as follows:

 $W = \frac{\text{grams of water weighed}}{(\text{ml. of Fischer reagent } \times R) - (\text{ml. of standard water solution}) - b}$ 

An alternative method for standardizing the solutions and making the analysis was devised after this work was completed which made the calculations somewhat simpler. The distilled water was weighed into Erlenmeyer flasks containing 25 ml. of anhydrous methanol. Several extra flasks containing 25 ml. of methanol were also set up to serve as blanks. Exactly 25.00 ml. of Fischer reagent were added to the first blank and titrated with the standard water solution to a dead-stop end point. The remaining blanks were titrated in a similar manner, using the same volume of Fischer reagent; if they agreed within 0.1 ml., the water standards were then titrated. The difference between each standardization titration and the average titration of the blanks is equivalent to the amount of water weighed out. The water factor, W, of the standard water solution in this case is:

$$W = \frac{\text{grams of water weighed}}{\text{net ml, of standard water solution}}$$

This procedure automatically corrects for the water in the solvents used to dissolve the standards or samples and it has been most satisfactory when the samples all have about the same water content.

ANHYDROUS METHANOL. Commercial methanol was allowed to stand over Drierite for several days and was then distilled from Drierite and collected in a receiver, protected from atmospheric moisture by means of Drierite. It usually contained 0.03 to 0.05 per cent of moisture as determined by this method on a 25-ml. sample.

Methanol which is to be used as a solvent for analyzing traces of moisture in other materials should be as dry as possible, or the uncertainty of the blank determinations becomes appreciable.

# **Stability of the Standard Solutions**

The stability of the two standard solutions was tested by determining the ratio, R, between them at various intervals and checking the water factor, W, of the standard water solution against weighed amounts of water. The results, given in Table I, are the average of four to five determinations. The range of the individual determinations never exceeded 6 parts per thousand and the average deviation was about 2 parts per thousand. The factor, W, remained constant within experimental error; but it was necessary to determine the ratio, R, whenever the solutions were used.

Date	Ra	W b
1-5-40	1.106	0.00524
1-8-40	1.030	
1-9-40	1.020	
1-11-40	0.984	AFT DELLET
1-17-40	0.921	0.00523
2-16-40	0.919	0.00526

# **Experimental Results**

The precision and accuracy of determining water in the presence of methanol were determined by weighing various amounts of water from a small weighing pipet into Erlenmeyer flasks containing 10 ml. of anhydrous methanol. The resulting solutions and the original solvent were analyzed for their water content by adding Fischer reagent until the brown color showed that an excess was present. The excess was immediately titrated with standard water solution to a dead-stop end point. The results given in Table II, show that the - recovery of water was satisfactory. Similar experiments in which the methanol was replaced by acetone gave the results shown in Table III. In every case the agreement between water found and water present is satisfactory up to about 200 mg. of water.

TABLE II. ANALYSIS OF WATER IN PRESENCE OF 10 MILLILITERS OF METHANOL

Sample No.	Fischer Reagent Added <i>Ml</i> .	Standard Water Solu- tion Back- Titrated <i>Ml.</i>	Standard Water Solu- tion, Net <sup>a</sup> Ml.	Wa Found Mg.	ter Present <sup>b</sup> My.	Differ- ence Mg.
1	5.00	6.20	0.70	3.74	3.74	
2	5.00	6.20	0.70	3.74	3.74	100
3	8.00	6.60	4.43	23.7	23.3	+0.4
4	8.00	6.40	4.63	24.7	24.4	+0.3
5	10,00	4,55	9.24	49.3	50.1	-0.8
6	15.00	8.30	12.38	66.1	65.5	+0.6
7	15.00	6.85	13.83	73.9	74.0	-0.1
8	20.00	9.05	18.53	99.0	99.1	-0.1
9	20.00	4.20	23.38	124.8	125.6	-0.8
10	25.00	7.55	26.93	143.8	144.3	-0.5
11	25.00	6,00	28,48	152.1	152.5	-0.4
12	30 00	5 70	35 67	190 5	191 6	-11

R = 1.379 ml. of standard water solution per ml. of Fischer reagent. W = 0.00534 gram of water per ml. of standard water solution.

<sup>a</sup> (Ml. of Fischer reagent  $\times R$ ) - ml. of standard water solution back-titrated. Sum of water added to and found in 10 ml. of methanol

TABLE I	II. ANA	LYSIS OF	WA	TER IN	PRESENC	CE OF	10	MILLI-
LITERS OF ACETONE								

		Standard				
	Fischer	Water Solu-	Standard			
Sample	Reagent	tion Back-	Water Solu-	W	ater	Differ-
No.	Added	Titrated	tion, Netª	Found	Presentb	ence
	Ml.	Ml.	Ml.	Mg.	Mg.	Mo.
1	5.00	5.00	1.65	8.8	8.6	
2	5.00	5.10	1.55	8.3	8.6	
3	5.00	3.00	3.65	19.5	21.7	-2.2
4	5.00	2.90	3.75	20.0	21.4	-1.4
5	10.00	6.10	7.20	38.4	38.1	+0.3
6	00.01	5.50	7.80	41.7	42.2	-0.5
7	15.00	9.55	10.40	55.5	54.2	+1.3
8	15.00	9.05	10.90	58.2	57.0	+1.2
9	15.00	6.45	13.50	72.1	72.1	0.0
10	15.00	6.05	13.90	74.2	77.7	-3.5
11	20.00	7.40	19.20	102.5	106.2	-3.7
12	20.00	4.50	22.10	118.0	117 1	+0.9
13	25.00	5.80	27.45	146.6	148.9	-2.3
14	30.00	8.20	31.70	169.3	168.7	+0.6

R = 1.330 ml. of standard water solution per ml. of Fischer reagent. W = 0.00534 gram of water per ml. of standard water solution.

<sup>a</sup> (Ml. of Fischer reagent  $\times R$ ) - ml. of standard water solution backtitrated.

<sup>b</sup> Sum of water added to and found in 10 ml. of acctone.

TABLE IV. ANALYSIS OF KNOWN SOLUTIONS OF WATER IN METHANOL							
Sample Weight	Fischer Reagent Added	Standard Water Solu- tion Back- Titrated	Standard Water Solu- tion, Net <sup>a</sup>	Wa	ater Present		
Grams	Ml.	Ml.	Ml.	%	%		
19.8 19.8	10.00 10.00	6.90 6.80	2.29 2.39	0.061 0.063	0.059		
19.8 19.8	15.00 15.00	5.45 5.45	8.33 8.33	$0.22 \\ 0.22$	0.218		
7.92 7.92	$15.00 \\ 15.00$	5.80 5.75	7.98 8.03	0.53 0.53	0.525		
$1.580 \\ 1.575$	20.00 20.00	2.90 2.85	15.48 15.53	$\substack{5,13\\5.17}$	5.02		

R = 0.919 ml. of standard water solution per ml. of Fischer reagent. W = 0.00524 gram of water per ml. of standard water solution.

<sup>a</sup> (M1. of Fischer reagent  $\times R$ ) – ml. of standard water solution back-titrated.

Known solutions of water in methanol and in ethanol were made up by weighing various amounts of water from a small weighing pipet into 100-ml. volumetric flasks and making up to the mark with anhydrous solvent. Suitable amounts of these known solutions were then analyzed for their water content. The solvents were also analyzed and the "water present" column includes the water which came along with the solvent. The results, given in Tables IV and V, also show satisfactory recovery of water by this procedure.

The dead-stop apparatus and method have been used for the routine determination of moisture in lower alcohols, in 1,4dioxane, and in mixtures of alcohols containing acetone up to about 15 per cent. It has not been used to determine water in mixtures of high acetone content because the acetyl chloride method of Smith, Bryant, and Mitchell (5) has been found more satisfactory in these cases. Some organic liquids, such as esters, hydrocarbons, and chlorinated hydrocarbons, do not dissolve readily in the Fischer reagent; but they have been analyzed with satisfactory results when mixed with anhydrous methanol.

TABLE V. ANALYSIS OF KNOWN SOLUTIONS OF WATER IN ETHANOL							
Sample Weight Grams	Fischer Reagent Added <i>Ml.</i>	Standard Water Solu- tion Back- Titrated <i>Ml.</i>	Standard Water Solu- tion, Net <sup>a</sup> Ml.	W Found %	ater Present %		
19.8 19.8	20.00 19.15	5.15 4.70	10.25 10.06	0.29 0.28	0.28		
7.92 7.92	31.00 32.85	4.85 6.15	19.02 19.14	1.35 1.36	1.35		
1.610 1.610	36.50 35.40	6.20 5.40	21.90 21.86	$7.63 \\ 7.62$	7.52		

R = 0.770 ml. of standard water solution per ml. of Fischer reagent. W = 0.00561 gram of water per ml. of standard water solution.

<sup>a</sup> (Ml. of Fischer reagent  $\times R$ ) - ml. of standard water solution backtitrated.

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# **Modification of Cenco Spectrophotometer**

Permitting Measurements of Reflection and Fluorescence Spectra

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METHODS for the determination of color of opaque objects fall, essentially, into three categories: (1) those employing color charts or standards for comparison, (2) those employing colorimeters and comparators which synthesize colors similar to the colored samples, and (3) those employing spectrophotometers. Of these three classes of apparatus, only the spectrophotometers have the advantage of resolving color into fundamental physical units.

The investigator who does not have available a reflection spectrophotometer, but does have the Cenco type transmission spectrophotometer (3), may readily modify that instrument to permit the measurement of reflection spectra. Fluorescence spectra may also be measured with this instrument through the use of a nearly identical optical system. The required modifications are described in the present paper.

# **Reflection Measurements**

The spectrophotometer is rotated  $60^{\circ}$  counterclockwise from its normal position when viewed from above, as shown in Figures 1 and 2. The spring plate which holds filters in front of the slit



FIGURE 1. OPTICAL SYSTEM OF THE CENCO SPECTROPHOTOM-ETER AS MODIFIED FOR MEASURING REFLECTANCE SPECTRA L, light source. Q, quartz lens. M1, M2, plane mirrors. R, samples for reflectance measurements. S1, entrance elit. S2, exit slit. P, photocell. G, grating

is removed and a back-silvered mirror  $(1 \times 2 \text{ cm.})$  is attached at the side of the slit nearer the light source at an angle of approximately 37.5° to the optical bench. By means of the collimating lens, the image of the lamp filament is brought to a focus 1 cm. after reflection from the mirror. At this point the light strikes the objects from which reflection measurements are to be made. These solids, along with the magnesium oxide standard, are fastened by means of spring clips to a circular disk. This disk is rotated in a plane parallel to that of the entrance slit of the spectrophotometer, bringing successively the magnesium oxide standard and the individual samples into the reflecting position. Thus the light strikes the surface of the sample with an angle of incidence of 45°, and only the light reflected diffusely and in a direction normal to the surface passes through the monochromator to the photocell. The reflectance of the samples at the various wave-length scale settings is measured by the usual method in terms of the ratio of galvanometer deflections for the samples to those for the standard white.

The standard white reflector was prepared by pressing magnesium oxide powder into a circular pad in a Carver press, and then roughening its surface with fine emery paper. Samples of finely divided materials may also be prepared for color measurements by pressing them into a similar pad. In this form they are readily attached to the sample disk. In order to obtain sufficient intensity of reflected light upon the photocell, using the lens furnished with the instrument, an entrance slit width of 2.5 mm. is used with an exit slit width of a nominal value of 20 m $\mu$ . In the region of maximum photocell sensitivity (approximately 585 m $\mu$ ), a galvanometer deflection of 45 mm. was obtained for the standard. At wave lengths shorter than 430 m $\mu$  and longer than 660 m $\mu$ , deflections of less than 10 mm. are obtained and as deflections decrease the per cent error in reading the galvanometer increases. If the effective apperture of the collimating lens system is increased by the introduction of a second component similar to that furnished with the instrument, the intensities on the photocell are increased about 2.5 times. (The theoretical fourfold increase is difficult to attain because of space limitations.) This added intensity permits the extension of the effective range of the spectrophotometer to 400 m $\mu$  in the red region of the spectrum, and permits the range.

When a disk holding three samples and the magnesium oxide standard is used and readings are taken at  $10-m\mu$  intervals, the data for three samples may be obtained in less than an hour. Calculation of the data requires an additional half hour.

The curves in Figure 3 show the reflectance spectra of colored papers and make possible a comparison of results with those obtained upon a Hardy recording spectrophotometer. (The colored papers upon which the authors' measurements were made and reflection spectra data with which they are compared have been reproduced by the General Electric Co., 2.)

# Fluorescence Measurements

Fluorescence spectra are measured with the same optics, except that a General Electric (H-6) water-cooled mercury are replaces the tungsten lamp as a source of excitation and an absorption cell containing the fluorescing solution replaces the reflecting samples. However, in this case, the intensity of fluorescence as a function of wave length is desired, rather than the intensity related to a standard reflector as above. Since the sensitivity of the photocell varies considerably with wave length, it was necessary to correct the instrument to a constant sensitivity value. A correction factor for the spec-



FIGURE 2. CENCO SPECTROPHOTOMETER AS MODIFIED FOR MEASURING REFLECTANCE SPECTRA

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trophotometer at each wave length was obtained by dividing the intensity of light isolated by the spectrophotometer from a tungsten source radiating at 3250° K. by a value calculated from Planck's equation for the intensity of light emitted at that wave length from a black body radiator at the same temperature.

The optical system is characterized by an arrangement in which the fluoresced light is observed from the direction of the source. A system which has been used frequently for exciting fluorescence utilizes a beam of exciting light 90° from the line of observation of the fluoresced light (4). Another arrangement is that of observing the fluoresced light in line with the exciting light through appropriate filters which remove the exciting light but transmit the fluorescence (1). In the two latter arrangements it can be shown algebraically, and it has also been observed experimentally (5; see also Figure 4), that the shape of the curve representing the spectral distribution of energy and position of the maximum vary with the concentration of the fluorescing substance as a result of reabsorption of the fluoresced light of shorter wave lengths. In the present arrangement in which the fluoresced light is observed from the direction of the source, the position of the maxima and shape of the curve are independent of concentration. The algebraic description of this arrangement is as follows:

Consider the intensity of fluoresced light of wave lengths between  $\lambda$  and  $\lambda + d\lambda$  coming from an elementary volume,  $dx \, dy \, dz$ , in a fluorescing solution of infinite depth and excited by monochromatic light of incident intensity ( $I_0$ ) uniform over the incident surface. Let the angle of the path of fluoresced light be 180° with respect to the exciting beam and 90° with respect to the plane of the window of the containing cell. When several constants (the quantum efficiency factor for the wave-length band  $d\lambda$ , the specific absorption coefficient of the solution for the exciting light, and the ratio of the energy values of the quanta corresponding to the wave lengths of exciting and fluoresced light) involved in the excitation of fluorescence are grouped into a single constant, K, the intensity of the fluoresced light,  $dI_f$ , reaching the measuring instrument from the elementary volume,  $dx \, dy \, dz$ , may be expressed as the product of (1) constant K, (2) the concentration of the fluorescing substance, (3) the intensity,  $(I_{ee}^{-\alpha_n cz})$ , of exciting light reaching depth x, and (4) the fraction of the intensity of fluoresced light transmitted back in the direction of the exciting beam through x cm. of solution  $(e^{-\alpha_f cz})$ :



FIGURE 4. FLUORESCENCE SPECTRUM OF THIOCHROME Solid curve, fluorescence received at approximately 180° to exciting beam. Broken curve, fluorescence received in line with exciting beam

# $dI_f = K c I_0 e^{-\alpha_a cx} \times e^{-\alpha_f cx} dx dy dz$

where  $\alpha_f$  = specific absorption coefficient for fluoresced light  $\alpha_a$  = specific absorption coefficient for activating (exciting) light

c = concentration of fluorescing material in grams per liter x = depth in cm.

Upon integrating this function with respect to x between the limits x = 0 and  $x = \infty$  and substituting for  $\int \int dy dz$  its equivalent, the cross-sectional area, A,

$$I_f = \frac{K}{\alpha_a + \alpha_f} \times I_0 A$$

the concentration factor cancels out and therefore the intensity of the fluoresced light of any given wave length is independent of concentration.

In practice, an absorption cell of 1-cm. depth was used instead of the theoretical cell of infinite depth and the concentration of the fluorescent material was increased to give total absorption of the exciting light in a depth of 1 cm. In certain cases—e. g., that of thiochrome described below—90 per cent of the exciting light was absorbed in passage through the first millimeter of solution.

An example of the type of data taken with the apparatus and optical system just described is given in Figure 4 as the solid curve—the fluorescence spectrum of thiochrome (the alkaline oxidation product of vitamin  $B_1$ ). The dotted line represents data taken with the optical system in which fluorescence is observed in line with the exciting beam. As explained above, the shift of the maximum toward the longer

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wave lengths is due to the reabsorption of the shorter wave lengths of fluoresced light.

# Summary

A simple modification of the Cenco spectrophotometer permits the measurement of reflection and fluorescence spectra with moderate resolution. The arrangement whereby fluorescence is observed from the same direction as the exciting light is superior to other possible arrangements, in that the shape of the curve representing the spectral distribution of energy and the position of the maximum are independent of concentration of the fluorescing substance.

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# **Ultraviolet Photometer for Analysis of Solutions**

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A simple and inexpensive ultraviolet photometer, suitable for the analysis of solutions, is outlined in detail. Results obtained with phenol, sulfanilamide, and potassium nitrate are described, and applications to other substances, particularly aromatic compounds, are discussed.

MANY instruments and methods of analysis based on the absorption of light have been described in the literature of the past few years. Photometric procedures have been found to be very convenient, particularly in routine testing and control, because of their sensitivity and rapidity. A description of some common types of apparatus using visible light has been given recently by Müller (6).

Some instruments have also been developed to utilize the absorption of ultraviolet light to measure concentrations in solutions. Demarest (2), for example, has described a photometer which uses light of about 3300 Å. for the analysis of vitamin A. Similarly, Buswell and Dunlop (1), using a spectrograph and photographic plate, measured the concentrations of aqueous solutions of phenol by the absorption of

radiation of approximately 2700 Å. This paper describes a photoelectric photometer which may be used in the analysis of solutions which absorb light of 2537 Å. The construction of such an apparatus has been facilitated recently by the development of inexpensive ultraviolet-sensitive photocells and high-silica, ultraviolet-transmitting glass. These have been combined with a commercial germicidal lamp, a convenient source of 2537 Å. radiation, to yield a simple instrument composed of readily available materials.

Instruments similar in principle to the one described in this paper have been developed by Woodson (7) and by Hanson (4) for the determination of concentrations of vapor in air.

### Design and Operation of Apparatus

A schematic diagram of the optical and electrical system is given in Figure 1.

LIGHT SOURCE. A General Electric T-10 germicidal lamp was used in the manner described by Hanson (4). After a preliminary warm-up period of about an hour, the lamp maintained an intensity of radiation constant to within 0.1 to 0.2 per cent. PHOTOELECTRIC DETECTOR. An RCA C-7032 phototube served as the light-sensitive element. The photocurrents were amplified by an RCA 054 accm tube used in the manner de-

PHOTOELECTRIC DETECTOR. An RCA C-7032 phototube served as the light-sensitive element. The photocurrents were amplified by an RCA 954 acorn tube used in the manner described by Gabus and Pool (3), but in a somewhat modified circuit (5). With a potentiometer in the grid circuit and a galvanometer in the plate circuit, the amplifier can be used as a sensitive null point indicator, and difficulties due to nonlinearity in response may be eliminated. The changes in the plate resistance and the elimination of a separate battery for the photocell have increased the stability of the electrical system. The light interview.

The light intensities are measured by the following procedure. With the shutter closed and the potentiometer, P, set at zero, the plate resistances are varied until the galvanometer shows a null reading. One of the absorption cells is then placed in the path of the light beam and the shutter is opened. The potential drop across the grid leak produced by the flow of the photocurrent through the high resistance is counterbalanced by increasing the potential imposed by the potentiometer until the plate meter has returned to its original reading. The reading of the potentiometer is then directly proportional to the intensity of the light incident on the phototube.

light incident on the phototube. For a precision of 0.1 to 0.2 per cent, a Leeds & Northrup student potentiometer may be used to measure grid potentials. For less precise work a rheostat-potentiometer is suitable.



FIGURE 1. DIAGRAM OF ULTRAVIOLET PHOTOMETER

ABSORPTION CELLS. The body of the cells consisted of Pyrex tubing with suitable side arms for the introduction of solution. The windows, however, were cut from Corning No. 791 ultraviolet-transmitting glass, which transmits about 50 per cent of radiation of 2500 Å. wave length, and were sealed to the body of the cell by means of Sealstix cement.

The absorption cells were 10.02 cm. in length.

# Calibration

To avoid frequent calibrations with mixtures of known composition, the author used the exponential relationship between light intensity and concentration

$$\log I_0/I = \epsilon c d \tag{1}$$

where  $I_0$  = intensity of light leaving pure solvent I = intensity of light leaving solution  $\epsilon$  = extinction coefficient

- = concentration of solute C
- d =length of absorption cell

The transmission,  $I/I_0$ , was determined from the ratio of the potentiometer readings with solution and solvent, respectively, in the path of the light beam. With d and cknown, one can calculate  $\epsilon$  very readily.

The "effective" extinction coefficient observed with the photometer differed somewhat from that determined with a spectrophotometer because of the large amount of stray radiation in the light source of the photometer. With sulfanilamide, for example, the "effective" e was 10,100 liter mole<sup>-1</sup> cm.<sup>-1</sup>, whereas that determined with monochromatic radiation of 2537 Å. was 14,700. Nevertheless, this discrepancy has no significant effect on the order of magnitude of the sensitivity obtained.

The presence of stray light was also exhibited by the variation of the extinction coefficient with concentration. Since Beer's law was not applicable, it was necessary to construct a calibration chart of log  $I_0/I$  vs. concentration for each substance of interest.

TABLE I. DEPENDENCE	E OF	SENSITIVITY ON EXTINCTION
	COEFI	FICIENT
Extinction Coefficient		Minimum Detectable Concentration
Liter mole <sup>-1</sup> cm. <sup>-1</sup>		Mole liter <sup>-1</sup>
10,000 1,000 100 10 10		$3 \times 10^{-4}$ $3 \times 10^{-7}$ $3 \times 10^{-8}$ $3 \times 10^{-8}$ $3 \times 10^{-4}$

# Applications

Figure 2 shows three typical calibration curves obtained with the ultraviolet photometer.

The sensitivity of the ultraviolet photometer toward phenol is probably comparable with that of any chemical method, for with a precision of 0.2 per cent in the light intensity it is possible to determine changes of approximately  $3 \times 10^{-5}$  gram of phenol per liter of water. This type of instrument may be very useful, therefore, in the analysis of phenol in water.

The limit of detection of sulfanilamide is even lower than that for phenol and is of the order of  $2 \times 10^{-6}$  gram per liter. A direct analysis of biological fluids is not possible, however, because of the presence of many other interfering substances which also absorb ultraviolet light. Nevertheless, the instrument will be very useful in a study of the adsorption and diffusion of sulfa compounds in various artificial media.

The results obtained with phenol and sulfanilamide are typical examples of the sensitivity one may expect with aromatic substances. Ultraviolet photometry would also be applicable to the analysis of organic substances such as ketones, conjugated hydrocarbons, heterocyclic compounds, and other ultraviolet-absorbing substances when they are dissolved in nonabsorbing solvents.



FIGURE 2. CALIBRATION CURVES A. Phenol B. Sulfanilamide C. Potassium nitrate

An application to inorganic analysis, the calibration curve for potassium nitrate, is also illustrated in Figure 2. In this case the sensitivity, about  $3 \times 10^{-3}$  gram per liter, is not so high as that obtained with aromatic compounds, but the instrument would still afford a very rapid and convenient method for the analysis of nitrates.

These examples are only a few illustrations of the applications of this photometer. Many other involved and tedious chemical analyses, particularly of aromatic substances, can be replaced readily by ultraviolet photometry. To determine the sensitivity toward any particular substance, it is merely necessary to estimate the extinction coefficient from data usually available in the literature and to apply Equation 1 to calculate the minimum detectable concentration. A series of such estimates has been summarized in Table I to enable one to tell at a glance whether the desired sensitivity can be attained with a given compound.

# Acknowledgment

The author is indebted to H. Campaigne, Chemistry Department mechanic, for advice and assistance in the construction of the carriage for the absorption cells.

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# Determination of Specific Gravity of Dry Paint Pigments

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DIFFICULTY has been experienced in getting accurate, reproducible results in determining the specific gravity of dry paint pigments by the pycnometer bottle method when using oil, water, kerosene, or alcohol as a wetting medium (1). The errors encountered were: evaporation of liquid from glass joints of the pycnometer bottle, incomplete removal of surface-adsorbed air, and moisture condensation on the exterior of the pycnometer bottle. This procedure requires a very long treatment under vacuum, presents a hazard due to possible collapse of the desiccator under high vacuum, and is too complicated for routine tests for specific gravity of paint pigments.

TABLE	I.	SPECIFIC GRAVITY	OF TITANIUM	Dioxide	PIGMENTS
Sample		Specific Gravity	Variation from Average		% Variation from Average
1	Av.	3.859 3.849 3.850 3.851 3.850 3.850 3.850 3.853 3.852	$\begin{array}{r} +0.007\\ -0.003\\ -0.002\\ -0.001\\ -0.002\\ +0.004\\ +0.004\\ +0.001\\ 0.003\end{array}$		$\begin{array}{c} 0.18\\ 0.08\\ 0.05\\ 0.03\\ 0.05\\ 0.10\\ 0.03\\ 0.07 \end{array}$
2	Av.	3.854 3.854 3.851 3.852 3.853 3.853	$\begin{array}{c} +0.001 \\ +0.001 \\ -0.002 \\ -0.001 \\ 0.00 \\ 0.001 \end{array}$		0.03 0.03 0.05 0.03 0.00 0.00
3	Av.	3.851 3.850 3.853 3.858 3.858 3.854	$\begin{array}{r} -0.003 \\ +0.002 \\ -0.001 \\ +0.004 \\ 0.0025 \end{array}$		0.08 0.05 0.03 0.10 0.06

A rapid, accurate, reproducible method for the determination of specific gravity of such materials is presented here. Using heat and a high-speed centrifuge, pigments may be deaerated and wetted and their specific gravities determined rapidly with a minimum of equipment and skill, and with an accuracy of 5 parts per thousand.

### Procedure

Fill a 600-ml. Berzelius beaker with kerosene oil. Prepare a suitable specific gravity tube by reducing a test tube 3.5 cm. in diameter to a length of 7 cm. At opposite sides of the tube and close to the top, punch two small holes through which a fine platinum or steel wire can be attached to act as a handle, so that the tube may be suspended from the hook above the analytical balance pan. Prepare a small glass stirring rod, slightly longer than the tube. Wash the tube and stirrer with cleaning solution followed by an alcohol wash, heat, and cool in a desiccator to remove moisture. Insert the stirrer in the tube, place in the 600-ml. beaker of kerosene, and bring the entire contents to 25° C. in a thermostat-controlled water bath. Wipe the kerosene from the suspending wire, support the beaker over the balance pan, and weigh the tube and stirrer completely submerged in kerosene at 25° C, after making certain that the temperature inside the test tube has had sufficient time to come to equilibrium with the surrounding temperature.

Remove the tube from the kerosene bath and weigh into it, by difference, from 1.5 to 25 grams of the paint pigment, depending on the specific gravity of the pigment, the pigment being previously dried at 105° C. for 2 hours. For pigments of low specific gravities, such as blacks and blues, weigh about 1.5 grams; for opaque white pigments, about 12 grams; for red lead, about 25 grams. Add sufficient kerosene to the pigment to wet it entirely and leave about 0.6 cm. (0.25 inch) of clear liquid above the pigment. Place the tube containing the pigment and stirrer in another beaker of kerosene and heat for 0.5 hour on a hot plate at a temperature of 65° to 70° C. with frequent stirring to remove air and other occluded matter and entirely wet the pigment. (This produces a small change in the specific gravity of kerosene and a negligible change in the final weight of the pigment in kerosene.)

how on a not plate at a transference of 0.5 to 7.6 C. when frequent stirring to remove air and other occluded matter and entirely wet the pigment. (This produces a small change in the specific gravity of kerosene and a negligible change in the final weight of the pigment in kerosene.) Remove the tube from the kerosene bath, fill with kerosene to about 0.6 cm. (0.25 inch) from the top, and centrifuge at about 2000 r. p. m. for 0.5 hour. Remove the tube and carefully fill with kerosene. Place the tube and its contents again in the original 600-ml. beaker and place in the water bath at 25° C. When the temperature of the entire contents, inside and surrounding the tube, is 25° C, weigh the tube as before. The increase in weight represents the weight of the pigment in air and the weight in kerosene represents the weight of kerosene displaced. Accurately determine the specific gravity of the kerosene at 25° C. (It is not necessary to determine the specific gravity of kerosene after testing each of several pigments.) The specific gravity of the pigment is calculated from the formula:

Specific gravity of pigment =

weight of pigment in air

weight of pigment in air-weight of pigment in kerosene  $\times$  sp. gr. of kerosene

TABLE II.	Specific Gravity	OF TITANIUM-CAL	CIUM PIGMENT
Sample	Specific Gravity	Variation from Average	% Variation from Average
1	3.197 3.201	-0.002 + 0.002	0.07
Av.	3.199	0.002	0.07
2 Av.	3.207 3.206 3.2065	+0.0005 -0.0005 0.0005	0.02 0.02 0.02

# Discussion

The method outlined is direct and easily performed, and involves no detailed, difficult procedures. The errors of the pycnometer method have been eliminated since evaporation or moisture condensation is prevented by the fact that the apparatus is weighed both times submerged in the same liquid at the same temperature. Air and other occluded gases are removed more thoroughly by the double process of heating and centrifuging than by the single process of vacuum treatment. The accuracy of the results, as noted in Tables I and II, is 5 parts per thousand or better.

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THE views presented in this article are those of the writers and should not be construed as the official views of the Navy Department.

# Laboratory Deodorizer for Fats and Oils

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S TEAM deodorization is one of the fundamental processes in edible oil and fat technology and is practiced commercially on a very wide scale. It is, however, a relatively troublesome operation to conduct in the laboratory.

The operation involves blowing a heated batch of oil with steam under reduced pressure. Because the pressure required for the best operation is somewhat below the vapor pressure of water at ordinary temperatures, it is somewhat difficult to maintain vacuum upon the system. Multiplestage steam ejectors such as are used commercially are not practicable for laboratory use. Mechanical oil-sealed vacuum pumps are not generally used because of the difficulties involved in completely condensing and trapping relatively large amounts of water vapor. Water ejectors operating on ice water or cooled brine are effective, but considerable auxiliary equipment is required for the constant delivery of large quantities of a cold liquid at high pressure. During the deodorizing operation, steam must be delivered to the apparatus at a constant and easily controllable rate. The generation and delivery of the steam also present some difficulty and require the use of a steam generator of special and usually rather elaborate design.

The laboratory deodorizer described here is greatly simplified, in comparison with the conventional apparatus. It should be of particular interest to oil and fat laboratories which have only limited or occasional use for such equipment, and consequently have hesitated to devote space and funds to the usual deodorization setup. The entire apparatus, including the steam generator, is made of Pyrex, and may be fabricated by a glassblower of average ability. Vacuum for the apparatus is supplied by an ordinary rotary oil-sealed pump.

The distinctive feature of the apparatus, and the one which makes possible its simple design, is the relatively high



FIGURE 1. DIAGRAM OF APPARATUS

vacuum under which it operates—namely, about 1 mm. of mercury, instead of the usual 5 to 10 mm. under which most installations operate. Since steam requirements in deodorization are directly proportional to the total pressure (1), the amount of steam which must be generated and condensed is extremely small. This condition permits the use of a steam generator of novel design, and makes it feasible to condense all vapors in simple dry ice traps.

All volatile substances removed from the oil are quantitatively recovered in the condensers. The apparatus is useful for certain high-vacuum steam-distillation work other than deodorization and has been successfully used to reduce the free fatty acid content of crude vegetable oils, to strip out unreacted glycerol or free fatty acids after re-esterification reactions, and to separate degradation products from heattreated oils.

The apparatus is illustrated in Figure 1. It is composed entirely of small Pyrex units equipped with standard groundglass joints which permit the use of duplicate units in the original assembly. Spherical joints at certain points lend flexibility and make the apparatus easy to assemble. The ground joints may be lubricated with the oil or fat which is to be deodorized. The charm composed of the apparatus energy of the apparatus of the second by

The steam generator, G, consists of two bulbs connected by capillary tubing. One bulb serves as a water reservoir. The other bulb is partially filled with asbestos, the top layer of which is covered with a film of carbon black, to enhance the absorption of heat. The carbon coating is conveniently applied to the asbestos by suspending a quantity of carbon in water and dropping the suspension on the asbestos surface from a pipet, while maintaining suction on the opposite end of the system. The rate at which water is admitted from the reservoir and at which steam is generated is easily controlled by the grooved stopcock between the two bulbs. Heat necessary to generate the steam by evaporation from the surface of the asbestos is supplied by a 250-watt infrared lamp, H. For critical work the water in the reservoir may be boiled to remove dissolved oxygen and then kept in an oxygen-free atmosphere by means of a hydrogen- or nitrogenfilled expansion bulb connected to the reservoir outlet. The steam delivery tube, D, is provided with a fritted-glass tip to distribute the steam flow.

The flask, F, which contains the oil to be deodorized, is fabricated from a Claisen-type distilling flask, and may be of any desired capacity within the range of about 1 to 3 liters. The flask is preferably heated by means of an oil bath, B, with the thermometer, T, indicating the temperature of the bath. A good deodorization rate is attained at temperatures of 425° to 475° F. (218° to 246° C.). If the apparatus is to be used for any purpose where it is important to know the exact temperature of the contents of the flask, a thermometer or thermocouple well should be inserted through a ground-glass joint directly into the body of the flask.

The spray trap, A, may be insulated or provided with an electrical resistance heater to prevent excessive reflux when stripping large quantities of fatty acids or other volatile constituents from the oil.

Pressure on the system is indicated by the manometer, M, which is connected to the spray trap by means of heavy rubber tubing. It is essential that all vapor passages be made large, as indicated in Figure 1, to avoid an appreciable pressure gradient through the apparatus.

through the apparatus. Condensers C and C' are cooled with a dry ice-acetone mixture or with powdered dry ice. Single-hole rubber stoppers serve to keep warm air away from the interior of the condensers and permit the escape of gaseous carbon dioxide.

A single charge of dry ice will generally suffice for a dcodorization. The dry ice is well insulated from the warm air of the room by the evacuated space surrounding the inner shell of each condenser. It will be found that practically all vapors from the flask will be retained in the first condenser. The second condenser functions largely as a safety device, to protect the pump in the case of accidental failure of the first condenser. The proper sequence of congrations in starting the deodorization

The proper sequence of operations in starting the deodorization operation is more or less obvious. After the apparatus is charged with oil, water, and dry ice, the vacuum pump is started, the heating lamp is turned on, the stopcock of the steam generator is gradually opened until the desired rate of steam generation is attained, and the oil bath is then heated to the operating temperature.

After deodorization is completed (usually 30 to 60 minutes), the hot oil bath is removed. The flask is then cooled by cold oil, a current of cool air, or other means, until the deodorized oil has reached a temperature of  $100^{\circ}$  to  $150^{\circ}$  F. (38° to 66° C.). The stopcocks leading to the manometer and the water reservoir are then closed, the manometer is disconnected, the vacuum pump is stopped, and vacuum on the system is broken by cautiously and simultaneously opening the stopcocks leading to A and D. This procedure avoids drawing oil back into the steam generator or blowing excessive quantities of air through the deodorized oil.

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# **Mayonnaise and Salad Dressing Yolk Content**

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THE circulation in commerce of liquid and frozen egg yolk products varying in egg yolk solids content, and, more particularly, the recent promulgation of a definition and standard of identity for "egg yolk" by the Food and Drug Administration (2), call for a reconsideration of the analysis for "egg yolk" of such food products as mayonnaise and salad dressing.

The Association of Official Agricultural Chemists (1) gives an equation which expresses the per cent of yolk in the sample as a function of the per cent of nitrogen and the per cent of phosphorus pentoxide.

$$\% \text{ yolk} = 75.69 P - 1.802 N$$
 (1)

when P equals per cent of total phosphorus pentoxide and N equals per cent of total nitrogen. The per cent of egg yolk calculated from this equation is in terms of egg yolk having a total solids content of 50.5 per cent. Such a yolk can be prepared in the laboratory only and has been called "theoretical" yolk. Commercially produced egg yolk material contains various proportions of adhering egg white and has, therefore, a total solids content substantially below 50.5 per cent. The equation and other directions of the Association of Official Agricultural Chemists (1) do not give sufficient data to enable one to express the analytical results in terms of commercial yolk, and do not indicate that the percentage of yolk content calculated by the equation is the percentage of yolk of 50.5 per cent solids content.

How much egg white is admixed with the 50.5 per cent yolk in a commercial yolk depends on the definition of the commercial yolk; as defined by the provisions and regulations of the Federal Food, Drug and Cosmetic Act of 1938 (2), commercial yolk contains 43 per cent total solids. This 43 per cent commercial yolk can be considered to be a mixture of 80.42 parts of yolk of 50.5 per cent solids content and 19.58 parts of white of 12.2 per cent solids content.

In this discussion, as well as in the publications of the Association of Official Agricultural Chemists, it is assumed that all nitrogen and phosphorus pentoxide determined by an analysis of the mayonnaise or salad dressing are derived from egg yolk and egg white only (3).

Because of the need for determining the content of commercial yolk in salad dressing or other food products, the

following equations are presented. The numerical basis of the equations is the following analytical data taken from a paper by Mitchell (4):

	Total N %	Total PrOs %
In theoretical yolk (50.5% solids content)	2.61	1.38
In egg white (12.2% solids content)	1.72	0.04

The same analytical fundamental data are the bases for the equations of the Association of Official Agricultural Chemists (1).

The equation which expresses the analytical results as per cent of egg yolk of 43 per cent solids in the sample is

$$\% \text{ yolk } _{(43)} = 94.26 P - 2.192 N \tag{2}$$

when P is the per cent of phosphorus pentoxide and N the per cent of nitrogen present in the sample. The per cent of egg white of 12.2 per cent solid content present in the sample outside of the egg white present in the commercial yolk of 43 per cent solid content is

$$\%$$
 white = 61.24 N - 133.48 P

when P is the per cent of phosphorus pentoxide and N the per cent of nitrogen present in the sample.

The equation which gives the per cent of commercial yolk of any (g per cent) solids content in the sample is

% yolk (a) 
$$= \frac{2899 P}{g - 12.2} - \frac{69 N}{g - 12.2}$$
 (3)

The relation of this equation to the equation for 50.5 per cent yolk content

$$\% \text{ yolk } (50,t) = 75.69 P - 1.802 N$$
 (4)

can be seen by writing Equation 3 as follows:

% yolk (
$$_{g}$$
) = (75.69  $P - 1.802 N$ )  $\frac{50.5 - 12.2}{g - 12.2}$  (5)

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# **Ground Glass for Spot Testing in Solvent Extractions**

**AUGUST EDELER** 

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ABOUT five or six years ago the writer noted the ease with which a ground-glass plate, such as is used in photography, becomes soiled in handling. Application of this observation led to a simple spot test for determining the completeness of extraction of fatty oils, or other nonvolatile liquids, with volatile solvents.

The test depends on the transparency which an oil or other nonvolatile liquid produces on ground glass, and is analogous to the familiar transparency which an oil produces in paper. The most plausible explanation is, briefly, that the oil film, by its refractive power, suppresses both the reflection of the incident light rays and the spreading of the emergent refracted rays, causing the latter to assume more nearly parallel courses, such as would have occurred had they passed through plate glass with polished surfaces. This hypothesis predicts maximum transparency when the liquid and glass have the same refractive index, a condition which is approached in the case of most fatty oils and ordinary ground glass of the grade commonly used for photographic focusing.

PROCEDURE. Drops of the solution under test and of the solvent are placed on a clean ground-glass surface and allowed to evaporate. Depending on the amount of solute present, the transparencies formed vary from that of the clean plate with the pure solvent to a disk of clear transparency of about the same area as that of the spot before evaporation. Between these ex-tremes lies a wide variety of intensities, and at low concentra-tions of solute one or more circular lines of approximately hair-line thickness are formed. The residue can also be viewed against a dark background, when it will appear dark instead of as a clear transparency. When the solvent is impure, the blank test may show a slight hairline transparency of varying intensity, depending on the impurity in the solvent, and this should be taken into consideration when making a spot test on an extraction. PROCEDURE. Drops of the solution under test and of the

### Sensitivity

As described, the limit of sensitivity of the test is about one part of solute in 20,000 parts of solvent (0.005 per cent). Greater sensitivity can be obtained by allowing two or more drops of solution to evaporate on the same spot, or by dusting the spots with a dark powder, such as a fine carbon bleach, and shaking off the excess. This procedure brings out the residual solute in sharp relief, as in fingerprint detection. A magnifying glass frequently can be used to advantage, but for most purposes it will suffice to examine, with the unaided eye, the transparency produced by a single drop of solution.

# Applicability

Though originally devised for, and used on, solutions of fatty oils in petroleum ether, ethyl ether, etc., this test may be applied to most solutions of nonvolatile liquids in volatile solvents, such as glycerol and sulfuric acid in water solution. In these cases the test is not quite so rapid as in the case of the more volatile solvents, and may be hastened by the gentle application of heat in the early stages of the evaporation. Much care must be taken, however, near the end of the evaporation to avoid loss of glycerol or sulfuric acid, both of which are somewhat volatile at relatively moderate temperatures.

This test should be found useful in gaging the extraction of oils and fats, glycerol, and other substances. A typical application is its use as an index to completeness of extraction with petroleum ether in the determination of unsaponifiable matter.

### Precautions

The solution tested must be free from nonvolatile material other than that which is to be detected or estimated, regardless of whether such extraneous nonvolatile matter produces a transparency or an opacity. Salts and similar solids produce opacities, and if present in sufficient quantity, obscure the test. Fortunately, such substances are rarely extracted by the usual solvents employed in the extraction of fats and oils.

# **A Mercury-Balance Pressure Regulator**

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OF THE numerous pressure regulator designs reported, the large majority involve elaborate and costly apparatus which permits neither rapid assembly and easy adjustment nor portability and application to different operations involving reduced pressure.

Broadly, pressure regulators can be classified as intermittent or continuous in operation. Most of the elaborate electrical assemblies maintain the pressure at an average value by intermittent pumping, or intermittent leaking with constant pumping. Basically, all these intermittent devices would appear to produce pressures which oscillate above and below the average value, the degree of oscillation depending upon the ballasting effect of the entire system and the sensitivity of the compensating device. Continuous regulators, on the other hand, adjust the amount of leakage so that the sum of gas from the vacuum system plus the controlled leakage equals the capacity of the pump. The precision of pressure regulation then depends on the precision of the proportioning valve-i. e., the sensitivity of the regulator-which is a compound factor determined by the smallest change which causes compensation, the rapidity of compensation, and the magnification of the compensation. Ideally, a continuous regulator should react swiftly and to an exaggerated degree to a minute departure from established pressure.

The designs involving direct control of leakage by mercury balance appeared to offer a precise method of obtaining continuous regulation with all three of these characteristics. The precise types devised by Schierholtz (4) and Thelin (6) used the translation of mercury in a manometer to actuate a lever which controlled the magnitude of the leak. The mercury control of Emerson (3) employed mercury entrained in the stream of leakage to obtain the final degree of throttling. The designs of Swayze (5) and Watts, Riddick, and Shea (7) are examples of intermittent operation of pump and leak, respectively. The apparatus of Caldwell and Barham (2) employed a glass valve operated directly by the mercury in a manometer. Numerous other devices, including many of considerable complexity, have been reported.

### Apparatus

Apparatus patterned originally after those of Schierholtz and Thelin was improved through four successive models. The use of a mercury column to balance the excess pumpage by leakage was found to be precise, rapidly responsive to disturbance of equilibrium, and capable of indefinite magnification of compensation.

Two modifications of the final device are presented here. They employ the same principle as those of Schierholtz and Thelin, but have the mechanical beam eliminated and incorporated in the manometer; one has a loop type of manometer which permits wide range and easy adjustment. Both require only elementary glassblowing technique to construct. The construction is shown in Figures 1 and 2.

Three sizes of tubing were used: 1-mm. capillary, 8 mm. in outside diameter, and 19 mm. in outside diameter, as indicated by A, B, and C, respectively, in Figures 1 and 2 (lettered identically). The glass manometer was supported in two places: by the spring, D, and the pivot, E. The spring contained 90 turns of 26-gage piano wire coiled on a 4-mm. rod and was connected by a swivel, F, to the thumbscrew, G, which adjusted the tension in the spring. Pivot E was a glass tube at right angles to the manometer, which served both as the vacuum connection and the shaft about which the manometer rotated. The thumbscrew is the thumbscrew is the state of the manometer rotated.

screw and pivot were supported by the cold-rolled iron rod, H, which was attached to a ring stand by a right-angle clamp. To this rod was attached a rubber stopper, I, which served as the valve seat. The stopper was preboiled in dilute alkali and the glass scat was ground flat with a fine pocket whetstone.

#### Operation

The regulator in Figure 1 was operated by connecting to the vacuum system with the spring relaxed. When evacuated to the proper degree, the spring was tightened until the valve barely opened. While the actual opening was not usually easily visible, the effect was noted on a separate manometer. Once adjusted, a decrease in pressure in the system caused the mercury in the manometer to flow into the reservoir, unweighting the manometer-deam and opening the valve. An increase in pressure caused opposite effects.



FIGURE 1. PRESSURE REGULATOR WITH CLOSED MER-CURY MANOMETER

The regulator in Figure 2 was similar in operation, except that the stopcock was left in the open position while the proper degree of vacuum was established roughly by adjusting the spring tension. The stopcock was closed and the final adjustment made by adjusting the spring tension. A decrease in pressure then caused the mercury to flow out of the closed end of the manometer, unweighting the manometer-beam and allowing the spring tension to open the valve.

# **Precision of Regulation**

The precision obtained with the regulator shown in Figure 1 was about 0.1 mm. of mercury; that of the type in Figure 2 was not readable with the naked eye. Many factors influence precision. The precision obtained with these regulators was the algebraic sum of these variables under given conditions and was by no means the ultimate precision of which the device was capable.

Spring tension affected sensitivity greatly. A spring having a small load-deflection ratio was more sensitive than



FIGURE 2. PRESSURE REGULATOR WITH LOOP TYPE OF MANOMETER

a stiffer spring. The diameter of the tubing in the closed limb of the manometer controlled the weight of mercury shifted for a given pressure change, hence larger tubing in the closed limb of the manometer greatly increased sensitivity; because of location the size of the open limb was unimportant. A bubble of air was always trapped in the closed end of the manometer in the Figure 2 type of regulator; a larger bubble resulted in increased sensitivity. A bubble trapped above the mercury in the Figure 1 type of regulator increased the sensitivity and increased the pressure range over which the device was operative. While the pivot bearing on these regulators was the glass tube, better practice would be to sheath this tube with a machined, split metal bushing, since glass tubing is rarely round and is apt to stick in the bearing. It would likewise be better practice to connect to the vacuum connection, E, with a loop of thin-walled rubber tubing, prevented from collapsing by Raschig rings inserted at intervals, and with the other end of the loop fastened permanently to the support bar, H, so that torque on the regulator by changing the position of the suction tubing would not change the adjustment of the regulator.

Both regulators were independent of variations in atmospheric pressure. Adjustment to a predetermined pressure by means of the thumbscrew, G, having 32 threads per inch, was easily effected. Both regulators controlled pressure with uniform facility over the entire pressure range. Both regulators were susceptible to "bouncing" under certain conditions-i. e., an oscillation of the mercury column and concomitant movement of the manometer-beam, causing intermittent admission of air. It was found to be due to parallelism of valve seat and face, and was eliminated by an imperceptible bending of the valve seat support, so that valve seat and face were not quite parallel and hence the valve could not close completely. The bouncing apparently was due to complete closure of the valve. In order to open the valve, pushing against atmospheric pressure required overcompensation of the mercury-balance, and then rapid overcompensation in the opposite direction resulted owing to the sensitivity of the device, again causing sealing of the valve. This bouncing phenomenon has been noted in other

regulating devices (1) using a mercury column and is due to similar causes.

Generally speaking, the Figure 2 type of regulator was more flexible and sensitive, but no stopcock under vacuum can be considered completely dependable under long periods of operation. Either regulator may be made capable of increased sensitivity by increasing the diameter of the tubing in the closed manometer limb, lengthening the beam, using a more elastic spring, or trapping a larger volume of air in the closed end of the manometer. Where great sensitivity is not required, a rubber cushion can be used to replace the spring suspension, but all attempts to use rubber have necessitated continual adjustment, owing to the fatigue of the rubber cushion.

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# **Electrolytic Preparation of Quinhydrone**

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N ELECTROLYTE used extensively in pH measurements A is quinhydrone, which consists of bright platinum immersed in a saturated solution of quinhydrone. In view of the fact that quinhydrone is an equimolecular compound of hydroquinone and quinone, it was thought possible that hydroquinone, a relatively cheap product used in photography, might be oxidized to quinone by the use of an electric current. The resulting product would be free of foreign materials.

The apparatus consists of an outer cup of nonporous material 20 cm. (8 inches) high and 20 cm. (8 inches) in diameter and an

inner cup of porous material 17.5 cm. (7 inches) high and 7.5 cm. (3 inches) in diameter. A carbon electrode, obtained from a dry battery such as those used in residential doorbell circuits, is placed in the outer cup (anode) and another is placed in the inner cup (cathode).

I	ABLE I. PREP	ARATION OF	QUINHYDRONE	R. I.
Expt. No.	Electrolysis Time Hours	Amperage Amperes	Hydroquinone Grams	Yield %
1 2 3 4 5	$\begin{array}{r} 4.82\\ 2.41\\ 1.61\\ 1.21\\ 0.96\end{array}$	1 2 3 4 5	10 10 10 10 10	72.674.274.875.374.1

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The hydroquinone has an equivalence of 2; therefore one mole of hydroquinone would take 2 faradays for complete oxidation. As only half the quantity of hydroquinone used is to be oxidized, half of the required faradays for complete oxidation should be used, or one faraday per mole of hydroquinone.

should be used, or one faraday per mole of hydroquinone. The hydroquinone (20 grams) was dissolved in a suitable amount of water and poured into the outer cup of the electrolytic apparatus. Two to 3 grams of sodium sulfate were added and the level of the liquid was raised to within 2.5 or 5 cm. (1 or 2 inches) of the top of the cup. The inner cup was half filled with distilled water, 5 ml. of glacial acetic acid were added, and the cup was filled with distilled water to within 1.9 cm. (0.75 inch) of the top. The current was then turned on at various amperages and for various times (Table I). Sodium sulfate was added to the outer cup liquor in small amounts from time to time to maintain a constant amperage. At the completion of the required oxidation period, the solution in the inner cup was concentrated and cooled, and the quinhydrone was filtered off. The yield was about 75 per cent of the theoretical.

The purity of the quinhydrone in each experiment was 98 per cent or better in each case. In the opinion of the author a higher yield may be obtained by using the mother liquor repeatedly.

# **Accurate Low-Pressure Gage**

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OW-PRESSURE gages commonly found in physics and chemistry laboratories are either of the Bennert closed U-type, or one of the many modifications of the McLeod type. The Bennert type is satisfactory for pressures above 1 cm. of mercury, but is not very accurate for lower pressures. For the low-pressure range the McLeod gage is usually used, but its application is limited by the fact that it depends on increasing the pressure in one part of the system. This increase in pressure will, in the case of vapors from liquids having high boiling points, lead to a condensation of the vapors, which will make the measurements useless. Thus in the case of measuring the vapor pressure of water of crystalline hydrates, the pressure cannot be increased above that over pure water at the same temperature without bringing about dew formation.

A number of methods have been used for increasing the accuracy of such measurements, one of which involves the replacement of mercury by a liquid of low density and negligible vapor pressure, always being certain that the vapors being measured are not soluble in the confining liquid.

The floating tube barometer described by Caswell (1) in 1704 and later adapted to use in what has been called the steelyard barometer (3) embodies the basic principles of a recent instrument known as the Dubrovin (2) gage, which may be purchased from scientific apparatus houses. Since there appears to be no published description of the theoretical background of the floating barometer, it seemed worth while to develop the equation for the magnification factor, and to give directions for making a gage which would be useful in vacuum distillation work, as well as around physical chemistry and physics laboratories.

Figure 1 shows an inverted closed cylinder floating freely over mercury. Its lateral motion is controlled by three point guides at top and bottom lightly touching the inside walls of the containing vessel. The device is placed on its side and a high vacuum is created by means of a good oil or diffusion pump. This removes all the air and adsorbed gases from the inside and outside of the floating tube. It is then set up on end and atmospheric pressure is slowly restored. If the density of the tube material is less than that of mercury, the tube will float and the inside of the floating tube will be entirely filled with mercury. Now if the external pressure is gradually reduced, the tube remains stationary until the external pressure becomes equal to the height of the mercury column inside the tube above the outside level. (Capillary forces are for the moment neglected.)

Reducing the pressure still further results in the condition shown in the figure. The height, N, measures the pressure in the large cylinder. As the pressure is progressively reduced, the mercury column drops while the tube itself rises. Thus a drop of 1-cm. pressure results in a drop of 1 cm. in height N, while Hmay increase 10 or 20 cm., corresponding to multiplying factors of 10 or 20.



Regarding the tube as a freely floating body at equilibrium, constrained by guides to move only in a vertical direction, and assuming the gas pressure inside the floating tube to be zero, we may equate the sum of the downward forces to the sum of the upward forces. Height N of the liquid inside the tube depends only on the external pressure, P. The pressure in the liquid at the base of the floating tube is

The pressure in the liquid at the base of the floating tube is made up of the sum of the gas pressure,  $P = Ng\rho$ , and the pressure of the liquid column, K, which is  $Kg\rho = (L - H)g\rho$ , in which g and  $\rho$  represent the force of gravity and the density of the liquid. This total pressure  $g\rho(N + L - H)$  over the annular ring area of

the tube  $\frac{\pi}{4} (D_2^2 - D_1^2)$  exerts an upward force  $\frac{\pi g\rho}{4} (D_2^2 - D_1^2) (N +$ L - H).<sup>4</sup> To this we add F, the algebraic sum of all other constant forces exerted by surface tension, floats, etc. Hence:

Total upward force = 
$$\frac{\pi g \rho}{4} (D_2^2 - D_1^2)(N + L - H) + F$$

The downward force is made up of W, the weight of the tube, and the pressure,  $P = Ng\rho$ , over the sectional area of the tube  $\frac{\pi}{4} D_{2}^{2}$ :

Total downward force = 
$$\frac{\pi N g \rho D_2^*}{4} + W$$

For such a body in equilibrium we may equate the upward to the downward forces and obtain

$$\frac{\pi g\rho}{4} (D_2^2 - D_1^2)(N + L - H) + F = \frac{\pi N g\rho D_2^2}{4} + W$$

Simplifying and grouping the constant terms as C, this becomes

$$-H = \frac{ND_1^2}{D_2^2 - D_1^2} + C$$

Differentiating, we obtain

$$-\frac{dH}{dN} = \frac{D_1^2}{D_2^2 - D_1^2}$$

This equation states that as N increases, H decreases and vice versa. It also states that the rate of change of H with respect to N is constant, since it depends only on the con-stant tube dimensions. The numerical value of this rate of change for a given instrument with constant tube diameter and constant wall thickness is accordingly the same for infinitesimal and for finite changes in H and N. Since the weight of the tube, the density of the liquid, surface tension forces, etc., included in the constant term, C, do not appear in the final equation, the rate of change of H with respect to N is independent of all such constant terms.

The absolute value of N depends on the pressure, P, in the outer tube and on capillary forces. The absolute value of H depends on the densities of the tube and the liquid, pressure P, and surface forces. In view of these facts it is evident that the ratio of the absolute value of H to N is meaningless. On the other hand, a decrease in the pressure, P, of 1 mm. of mercury is accompanied by a decrease in N of 1 mm. if the confining liquid is mercury. If simultaneously the tube rises 10 mm., then H has increased by 10 mm. and the change of H with respect to N is 10. This is then the true value of the multiplying factor or magnification. As indicated in the equation for the rate of change of H with respect to N, it can be calculated from the internal and external diameter of the floating tube, and is independent of all other factors. Both theory and experiment show that as the liquid inside the tube falls and the tube rises, the level of the outside liquid does not change. This means that the volume of the cylinder that comes out of the liquid equals the volume of the liquid that drops into the body of the fluid.

The instrument has the very distinct advantage over other mechanical and optical magnifying devices of not magnifying the error, if any, due to capillarity, adhesion to the tube, etc.

reading is to be made, a light tap on the side of the outer tube momentarily releases contact, permitting the floating tube to rise or fall freely about its equilibrium position, which is easily reproducible to less than 0.2 mm. If we have a tube with a magnification factor of 20, a barometric change of 1 mm. of mer-cury is accompanied by a 20-mm. change of H. An error of 0.2 mm. in reading the height of H is an error of 1 per cent. Stated another way a 0.01-mm change in barometric pressure is the another way, a 0.01-mm. change in barometric pressure is the minimum change which can be observed directly without the use of a vernier. Since the accuracy of reading is independent of H,  $10^{-2}$  mm. of mercury is the lowest pressure that can be read on an instrument whose magnification factor is 20 when the liquid used is mercury

If in place of mercury we use Apiezon B oil, whose density at 25° C. is 0.861 gram per cc., the accuracy is greatly increased. With the above instrument having a magnifying factor of 20, and a minimum observable pressure change of 0.01 mm, the minimum observable pressure change becomes 0.01/15.7 = 0.00064 mm. of mercury, in which 15.7 is the ratio of the densities of mercury and Apiezon B oil at 25°.

The above considerations show that for mercury as a confining liquid the useful range of the gage lies between  $10^{-2}$  and  $10^{3}$  mm. of mercury, whereas with Apiezon B oil the lower range is extended to  $6.4 \times 10^{-4}$  mm. A relatively high accuracy is achieved over a very large pressure range without the use of a vernier. Readings are made directly and are instantly observable. No operation such as changing volumes as in the case of the McLeod gage is necessary.

Mercury as a confining liquid has the great advantage of dissolving very few vapors of either organic or inorganic substances. It has the disadvantage of high density and accompanying inaccuracy in reading small pressure changes. It is this latter difficulty which the floating tube overcomes.

A concrete illustration of its use in the authors' laboratory of physical chemistry: In the determination of gas densities by direct weighing, the student is instructed to evacuate the bulb to 0.1 mm. or less and then weigh. This involves the use of a gage of the McLeod type. However, by including the floating gage in the system the pressure can be read directly. the system the pressure can be read directly.

Although the equation enables the calculation of the dimensions of the tube for any specific multiplying factor, the following have been found practical.

$D_1$	Dı	Wall Thickness	L	Magnification
Inch	Inch	Inch	Inches	04.05
0.3576	0.1250	0.00125	10	24.25 10.03

Stainless steel, nickel, platinum, and glass tubes may be used with mercury. Since a uniform bore and wall thickness are essential to a uniform pressure scale and the thin-walled tubes which are necessary are stronger when made of metal, metal tubing is especially satisfactory. Strength is often necessary, since a rapid restoration of pressure in the outside container may cause the resulting mercury hammer effect to break out the top of the floating tube. To obviate this, the lower part of the tube may be made with a rather small opening, and thus avoid a rapid entry of the mercury.

# Acknowledgment

The authors wish to thank the Superior Tube Company, Norristown, Penna., and the Summerill Tubing Company, Bridgeport, Penna., for their kindness in making up special tube sizes for use in the above studies.

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The apparent density of the tube may be changed either by making the lower submerged part of tube itself of a double-walled sealed cylinder or by attaching a separate float made of glass at its base. In this way even a platinum tube can be made to have the absolute value of H greater than the barometric height of 76 cm. of mercury, using mercury as the confining liquid. We then have a direct-reading magnifying barometer. The guides serving to hold the tube erect make only slight con-tact with the outer tube, some clearance being allowed. When a

# Automatic Apparatus for Determination of Small Concentrations of Sulfur Dioxide in Air

# Application to Hydrogen Sulfide, Mercaptan, and Other Sulfur and Chlorine Compounds

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MANY units of the automatic apparatus described in earlier papers (6, 7, 8) have been in continuous operation during the last twelve years and they have provided complete records of sulfur dioxide concentrations in the atmosphere. The machines have required very little attention for servicing, and have given long periods of satisfactory operation.

Three years ago the authors experimented with a multipleport stopcock-type metal valve to replace the numerous camoperated poppet valves, and this innovation has given complete satisfaction, resulting in simple construction and trouble-free operation. Making use of this new valve, the authors have constructed an autometer which determines the sulfur dioxide (plus sulfur trioxide) and also independently

the total volatile sulfur content of the atmosphere. The latter may also include hydrogen sulfide, carbon disulfide, mercaptan, and even substances like thiophenol or thiophene. Preliminary observations have shown that this apparatus is also applicable to volatile chlorine compounds like chloroform, carbon tetrachloride, ethylene chloride, and chlorobenzene, all of which can produce hydrochloric acid that is absorbed as readily as sulfur dioxide, and affects the conductivity like sulfuric acid.

# **Construction of Apparatus**

The multiple-port stopcock, as used on the combined sulfur dioxide-total sulfur machine, is shown in Figure 1. For sulfur dioxide alone planes 3, 5, and 2 of the ports on plane 6 may be eliminated and the valve made correspondingly smaller. Stainless steel and bronze, or bronze and brass, have been used in its construction. The body and core are machined, then lapped with suitable steel blanks before lapping them carefully together to produce a smooth close fit. Finally the ports and grooves are made without disturbing the fit.

ports and grooves are made without disturbing the fit. The valve is mounted in a vertical position on the support, C. It is operated, using a heavy stopcock grease and adjusting the collar, B, so that a minimum clearance is maintained to prevent the surfaces from binding. Adequate pressure is given by the cap and spring, A. The core is turned from below by a reduction gear system with which it is connected by means of a universal drive pin, D, that allows the core to remain centered in the valve body. A well-made valve of this type will run for many months without any attention.

Figure 2 is a diagram of the assembly. The valve, reduction gear system, pump, and motor are mounted on a bed plate. The absorbers are placed on a light-iron framework so that they will drain by gravity through the lowest ports of the stopcock. On an upper shelf is a 20-liter bottle containing the absorbing solution, and at a level between the supply bottle and absorbers are placed the pipets. Thus the solution passes through the valve three times by gravity: first into the pipets, then into the absorbers, and finally to waste. Accessory apparatus is the same as that described earlier (6, 7).

# Application

It has been known for a long time that appreciable amounts of hydrogen sulfide would pass through the sulfur dioxide absorber without producing a measurable effect on the conductance of the absorbing solution. The same has now been found to be true of the other sulfur and chlorine compounds mentioned above. Accordingly, if these compounds could be quantitatively oxidized or pyrolyzed to sulfur dioxide or



FIGURE 1. MULTIPLE PORT STOPCOCK-TYPE METAL VALVE, FOR CONTROLLING FLOW OF GASES AND LIQUIDS

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hydrochloric acid, they could be determined with the same precision and sensitivity that characterize the sulfur dioxide analysis, for which the limit of detection is about 2 parts per billion.

The application of the sulfur dioxide autometer to the determination of hydrogen sulfide has long been envisioned, but until recently only a few preliminary experiments had been carried out.

In 1939-40 Philip Drinker borrowed an autometer from this laboratory and used it to determine carbon disulfide and hydrogen sulfide in the Lewistown Plant of the American Viscose Corporation. The results of this study were described as satisfactory by Reece, White, and Drinker (4). The carbon disulfideair and hydrogen sulfide-air mixtures "were passed over heated platinum foil and the sulfur completely oxidized to sulfur dioxide." Evidence of completeness of oxidation was not presented, but this probably was not important because the authors state, "The instrument must be calibrated against known concentrations of sulfur dioxide, furnished, in our case, by the oxidation of carbon disulfide." The sampling rate was 5.5 liters per minute. The authors have been unable to attain complete oxidation of hydrogen sulfide at 15 liters per minute in a silica tube containing platinum foil and heated externally in an electric tube furnace.

Analysis of chlorinated hydrocarbons has been accomplished by several investigators using combustion methods.

Olsen, Smyth, Ferguson, and Scheflan (3) passed the vapors of carbon tetrachloride in air together with some water vapor, through a silica tube at 1000° to 1100° C., and determined the liberated hydrochloric acid by titration. They suggested the possibility of an automatic method based on conductivity, but did not try it out. Their procedure has been modified by Tebbins (5) who used a platinum catalyst in the combustion tube and re-



The new sulfur dioxide-total sulfur autometer is really a double sulfur dioxide analyzer.

It has four identical absorbers, two of which are used for sulfur dioxide exactly as in the simpler machine. The other two receive an equal volume of air in a parallel line from the same source. To secure continuous operation, one pair of absorbers is aspirated while the other pair is recharged with solution. The second air stream is passed through a well-insulated 25-mm. silica tube in which a platinum wire, spirally wound and elec-trically heated, serves to oxidize other sulfur com-pounds to sulfur dioxide. The reaction is partly a pyrolysis, since carbonaccous material gradually deposits beyond the heater. The use of the internally heated tube results in a great saving of power with the large air flow employed (15 liters per minute) as compared with an externally heated tube, and also gives a quantitative oxidation. With smaller rates of air flow still less power would be required.

The hot end of the silica tube is connected to a Pyrex adapter by a ground joint which is maintained by holding tube and adapter together with a spring. The adapter tube is partly water-cooled, but extreme cooling of the gas is avoided, since there is some tendency to produce sulfuric acid in the heater, and this



FIGURE 2. DIAGRAM OF ASSEMBLY FOR SIMULTANEOUS DETERMINATION OF SULFUR DIOXIDE AND TOTAL SULFUR IN AIR

TABLE I. DETERMINATION OF SULFUR AND CHLORINE COMPOUNDS							
Compound	No. of Analyses	Energy	Gas Temperature	Ele	ment Calculated	Compound Calculated	Recovered
And the second second is		Watts	° C.	Mg. S . 100	or Cl per 00 l.	P. p. m. vol.	%
Hydrogen sulfide	1 1 1 2 1 2 6 3 1 2 7 6 1	$100 \\ 100 \\ 108 \\ 160 \\ 160 \\ 160 \\ 160 \\ 240 \\ 255 \\ 255 \\ 258 \\ 260 \\ 366 \\ 470 \\ 490 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 $	390 390 395 395 470 470 470 470 555 570 573 575 650 715 715 715 725	$\begin{array}{c} 0.51\\ 0.98\\ 1.17\\ 1.97\\ 0.035\\ 0.080\\ 0.77\\ 0.91\\ 0.135\\ 0.67\\ 1.07\\ 2.22\\ 3.58\\ 0.20\\ 0.180\\ 0.74\\ 3.76 \end{array}$	$\begin{array}{c} 0.78\\ 1.37\\ 1.82\\ 3.30\\ 0.034\\ 0.075\\ 0.88\\ 1.07\\ 0.130\\ 0.70\\ 1.10\\ 2.36\\ 3.60\\ 0.195\\ 0.179\\ 0.75\\ 3.82 \end{array}$	$\begin{array}{c} 0.68\\ 1.19\\ 1.58\\ 2.87\\ 0.030\\ 0.065\\ 0.076\\ 0.93\\ 0.11\\ 0.61\\ 0.96\\ 2.05\\ 3.14\\ 0.170\\ 0.156\\ 0.65\\ 3.33\end{array}$	65 71 64 60 103 107 88 85 104 96 97 94 99 99 90 103 100 99 98
Carbon disulfide	1	250 250	565 565	1.69	1.68 1.77	0.73 0.77	101 98
Ethyl mercaptan (C <sub>2</sub> H <sub>6</sub> SH)	1 1 1 1 1	250 250 250 250 250 250	565 565 565 565 565 565	$\begin{array}{c} 0.050 \\ 0.085 \\ 0.72 \\ 2.55 \\ 3.59 \end{array}$	$\begin{array}{c} 0.049 \\ 0.085 \\ 0.70 \\ 2.54 \\ 3.61 \end{array}$	$\begin{array}{c} 0.043 \\ 0.075 \\ 0.61 \\ 2.21 \\ 3.24 \end{array}$	102 100 103 100 99
Thiophenol (CtHsSH)	11	240 240	555 555	0.65 1.08	0.69 1.08	$     \begin{array}{c}       0.60 \\       0.94     \end{array} $	94 100
Thiophene (C:H4S)	1 1 1 1 1	250 265 265 250 375	565 575 575 565 660	0.175 1.95 2.87 5.90 3.65	$\begin{array}{c} 0.173 \\ 1.79 \\ 2.81 \\ 6.25 \\ 3.68 \end{array}$	$\begin{array}{c} 0.15 \\ 1.56 \\ 2.25 \\ 5.45 \\ 3.20 \end{array}$	101 109 102 95 99
Chloroform	1 1 1 1 1	240 235 235 455 610	555 550 550 710 790	0.11 0.15 8.9 0.40 0.69	$\begin{array}{c} 0.31 \\ 0.50 \\ 24.7 \\ 0.51 \\ 0.63 \end{array}$	$\begin{array}{c} 0.041 \\ 0.065 \\ 3.12 \\ 0.067 \\ 0.082 \end{array}$	35 30 36 78 107
Carbon tetrachloride	1 1 1 2	108 164 225 610	395 475 540 790	0.36 8.2 0.20 0.55	30.0 35.2 0.64 0.565	$\begin{array}{r} 2.94 \\ 3.45 \\ 0.063 \\ 0.055 \end{array}$	1 23 32 97
Ethylene chloride (C2H4Cl2)	1 1 1 1 1	168 260 260 600 567	475 570 570 785 770	$3.15 \\ 0.08 \\ 3.60 \\ 1.19 \\ 1.62$	85.5 0.31 7.55 1.12 1.58	16.8 0.061 1.48 0.22 0.31	4 26 47 106 103
Chlorobenzene (C <sub>0</sub> H <sub>4</sub> Cl)	1	257 630	570 800	0.17 1.98	0.36 1.89	0.14 0.74	48 105

will condense before reaching the absorber if the gas is cooled to room temperature. The warm air from the heater causes an amount of evaporation and also a resultant temperature in the absorber somewhat higher than that caused by the colder air in the parallel line. This discrepancy can be compensated for by using a larger volume of solution in the "total sulfur" absorber.

A line-drawing recorder and a suitable switching mechanism give the conductivities of the two solutions at 1-minute intervals during the absorption period of 30 minutes. The increment of conductivity of the absorber receiving unheated gas represents sulfur dioxide; any additional increment in the other absorber represents other sulfur compounds, since the same calibration applies to both absorbers (see Figure 3). This calibration is based on different dilutions of standard sulfuric acid.

In Table I are summarized the results of analyses of known mixtures with air of the substances listed above.

Hydrogen sulfide of tested purity was displaced from a mercury pipet into a large measured air stream. The various liquids were handled in weighed Nesbitt bulbs, and they were volatilized by means of controlled air streams. The table also shows the wattage of the heater and the approximate exit temperature of gases. In all cases the air volume was 15 liters per minute. A current consumption of 250 watts was adequate to cause the oxidation of all these sulfur compounds to sulfur dioxide. The platinum wire was red and the gas temperature about 580° C. Even at 100 watts (390° C.) there was considerable oxidation of hydrogen sulfide, but the process was not quantitative. The reaction was nearly complete at 160 watts (470° C.).

Thiophene showed a distinct tendency to form sulfuric acid, and it was necessary to maintain the adapter at a higher temperature with this substance than with the others.

For the decomposition of the chlorine compounds it was

necessary to use 500 to 600 watts. At 250 watts the yield of hydrochloric acid was only about 25 to 50 per cent. Evidently water vapor supplies the hydrogen to enable a substance like carbon tetrachloride to form hydrochloric acid (3). Some acid condensation in the adapter has been noted with the chlorine compounds, presumably as chloric or perchloric acids. At normalities below 10<sup>-3</sup> all these acids, as well as sulfuric acid and nitric acid, have nearly the same conductivities, and practically the same calibration applies to them all. When large amounts of chlorine compounds were put through the heater at 400° to 600°C. some retention occurred in the silica tube, which caused a long continued low level evolution of hydrochloric acid when the temperature was raised to about 800° C. This condition is being investigated further.

The agreement between the theoretical and analytical concentrations is satisfactory. In many of these analyses sulfur dioxide was also present in variable amounts, but there is nothing to suggest that it interfered with any of the determinations. It was merely subtracted from the total sulfur or chlorine values. Some of the values in Table I represent the upper limit of the recording system under the chosen conditions of operation. Higher concentrations could readily be determined by changing the time or rate of sampling, or the cell constant.

The apparent lack of specificity of the proposed method suggests itself as a drawback. This difficulty can be resolved in some cases by preliminary absorption of certain constituents of mixtures. For example, hydrogen sulfide was absorbed by Reece, White, and Drinker (4) to enable



FIGURE 3. PORTION OF A FIELD CHART SHOWING PRESENCE OF SULFUR DIOXIDE WITH OTHER SULFUR COMPOUNDS

them to determine carbon disulfide. The hydrogen sulfide was then found by difference. Doubtless there is a practical limit to which the resolution of a complex mixture could be carried, but it would be entirely feasible to add another parallel combustion and absorption train to the assembly proposed here, by merely adding two more planes of ports to the valve.

The possibility of oxidizing nitrogen compounds to nitric acid, which would also be readily absorbed and determined, was explored for the most part without success. Ammonia was practically completely destroyed at 250 watts, but a trace of nitric acid was produced at higher temperatures. This destruction of ammonia would remove interference by this gas in the sulfur dioxide analysis (2). Pyridine, which interferes like ammonia, was not so completely destroyed in the heater. Hydrocyanic acid and aniline were without appreciable effect on either absorber, as was also nitrobenzene.

A unit of the sulfur dioxide-total sulfur apparatus has now been in continuous operation for several months in the field near an industrial district and has given a complete and satisfactory record. Figure 3 is a portion of the chart, showing the presence of sulfur dioxide, together with an approximately equal amount of other sulfur compounds, presumably hydrogen sulfide and possibly some mercaptans. It is improbable that any chlorine compounds were present.

Finally, it may be of interest to record a few observations on the physiological detection of some of these compounds. Under very favorable conditions, sulfur dioxide has been detected by sensitive persons at this laboratory at 0.3 p. p. m. by the sense of taste, and at 0.5 to 0.6 p. p. m. by smell. Hydrogen sulfide has a distinct odor at 0.3 p. p. m., and is detectable at 0.025 p. p. m. Ethyl mercaptan has a "very strong" odor at 0.6 p. p. m., and a distinct odor at 0.03 to 0.07 p. p. m. Its odor is detectable at approximately 0.002 p. p. m.

# Summary

The automatic apparatus for the determination of small concentrations of sulfur dioxide in air has been modified by the substitution of a simple multiple-port stopcock-type valve for the numerous poppet valves of the older assembly. This equipment has also been modified to enable the simultaneous determination of the total volatile sulfur compounds in the air, with the same precision and sensitivity as characterized the sulfur dioxide analysis. Carbon disulfide, hydrogen sulfide, ethyl mercaptan, thiophenol, and thiophene have been so determined. The method is also applicable (at a higher operating temperature) to organic chlorine compounds, such as chloroform, carbon tetrachloride, ethylene chloride, and chlorobenzene. Nitrogen compounds could not be oxidized to nitric acid in this equipment.

Some observations are given on the physiological limits of detection of sulfur dioxide, hydrogen sulfide, and ethyl mercaptan.

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# An Efficient Low-Holdup Laboratory Column

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IN THE hydrogenation studies on lignin being carried out in these laboratories a highly efficient, low-holdup laboratory fractionating column was urgently needed. Although the problem of devising such a column has been a common one throughout the history of organic chemistry, it has only been in the past few years that successful investigations have been carried out in this field. Of the several recent comprehensive articles concerning laboratory frac-tionation columns, those of Whitmore *et al.* (11) and Podbielniak (8) are the most important, since these two articles contain a critical discussion of all recently developed fractionating columns.

The specific problem faced in these laboratories was the separation of a mixture of aliphatic and cyclic alcohols (6 to 10 cc. in volume) which boiled over a range of 90° C. at 20 mm. to 180°C. at 1 mm. This required maximum theoretical plate efficiency accompanied by a total liquid holdup of less than 1.0 cc. Of the columns reported in the literature, the Purdue spiral screen (6) and the Podbielniak Heli-Grid (8) types of packing appeared to be the most satisfactory. The only objections to the use of these two designs were the difficult task of making a spiral screen with an outside diameter of 5

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mm. or less, and the prohibitive cost of the excellent Podbielniak column.

Other excellent columns were considered inapplicable. The high-efficiency low-holdup column described by Selker, Burk, and Lankelma (concentric-tube packing, 9) presents construction difficulties, requires a long time to attain equilibrium conditions (9 to 12 hours), and requires expensive temperature control equipment. The low-holdup spinning-band column developed by Baker, Barkenbus, and Roswell (1) has too low an efficiency (H. E. T. P., 7.8 cm.), while the efficient, small-diameter Stedman column (2) is difficult to construct and has a relatively high liquid holdup (0.18 cc. per plate).

A suggested alternative was the use of a type of packing proposed by D. F. Stedman of the National Research Council of Canada. According to this authority, an efficient packing for small-scale work should be obtainable by use of a narrow strip of wire gauze twisted to produce a series of vertical plates at an angle of 90° to each other. An investigation was carried out, therefore, on the applicability of such wiregauze spirals as packings in fractionating columns.

# **Normal Fractionation Column**

WIRE PACKING. After several attempts to prepare a satisfactory packing, the following method was adopted:

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A strip of 50 (or  $60 \times 40$ ) mesh Monel metal wire gauze (1.5 times the length of the glass column) was cut from a sheet of this material with heavy scissors. The width of the gauze should be approximately two wire strands greater than the diameter (4 to 6 mm.) of the tube to be packed. The two outside longitudinal strands were then removed and the projecting lateral strands bent back in one direction strains but has been in the strip fitted tightly in the glass column. The gauze strip was then ready for twisting. This was accomplished by use of two pairs of round-nosed pliers, the nose of one pair of which had been ground to a thickness of about 0.15 cm. (0.06 inch). The top of the gauze strip was gripped tightly with the thing nosed pliers and 0.3 cm. thin-nosed pliers and 0.3 cm. (0.125 inch) away with the standard pliers, and the strip was then twisted through 90° with a simultaneous compression force, so that when the two pliers were at an angle of 90° they were touching each other. This resulted in the formation of two flat vertical planes at 90° to each other separated by two horizontal, opposed quadrants. The further twisting of the gauze strip was accomplished by gripping it just below the first bend with the thin-nosed pliers and 0.3 cm. (0.125 inch) below that point with the standard pliers. The twisting (in the same direction as the first turn) and compression as the first turn) and compression motions were then carried out as de-scribed above. This entire process was repeated until the whole strip had been converted into a series of about 0.3-cm. (0.125-inch) vertical gauze platelets as shown in

Figure 1. It is essential that the vertical axis of each platelet coincide with the line of axes of the adjoining platelets if a perfect fit is to be obtained, and it is therefore necessary to make certain that each platelet is properly centered before proceeding to the next. When the entire strip had been so treated it was found that the previously flattened horizontal strands had spread some-what and that the strip no longer fitted the column. This was remedied by rolling the twisted strip back and forth on a hard flat surface and tapping gently with the flat side of a hammer until the packing just fitted the glass column. The simplest method for inserting the modified spiral was to lubricate it with oleic acid and pull it through the glass tube with the aid of a strand of cop-per wire tied to the end of the packing. The oleic acid was re-moved with ethanol and the copper wire dissolved in concentrated nitric acid.

If the packing has been properly constructed, a continuous film of liquid will be formed at the two lines of contact between the glass and the gauze when alcohol is poured down the column. If there are no more than a few (up to about five) breaks in the gauze-glass liquid film, the packing is considered satisfactory. If many such breaks occur, it is advisable to prepare a new packing. If the packing is made up of more than one continuous strip, it is not necessary to join the component strips, as two or more strips touching each other firmly have been found to give satisfactory results.

GLASS COLUMN. The glass portion of the fractionating column was of very simple design, as shown in Figure 2.

Although the sketch of the apparatus as used in these labora-tories is drawn to scale, the only dimensions which are of sig-nificance are: (a) packed section,  $5.0 \pm 0.5$  mm. in inside diam-eter; (b) cold-finger condenser,  $10.0 \pm 1.0$  mm. in outside diam-eter; (c) reflux head,  $15.0 \pm 1.0$  mm. in inside diameter. The delivery tube should be as small as possible, the limiting factor generally being that of the viscosity of the condensate. In this investigation tubing 5 mm. in inside diameter was found to be investigation tubing 5 mm. in inside diameter was found to be

### ANALYTICAL EDITION

Although the packed sections of the columns consatisfactory. Although the packed sections of the columns con-structed in these laboratories have varied in size from 37.5 to 112.5 cm. (15 to 45 inches) lengths of 60 to 90 cm. (24 to 36 inches) are most satisfactory with regard to ease of construction of the packing and total plate efficiency of the column.

The specially tapered and drilled ground-glass joint was made from a 12/30 male joint and was so constructed as to eliminate flooding at the joint. The flasks (still pots) were pear-shaped and it was found that 15-, 30-, 60-, and 100-cc. sizes were most convenient. All the flasks were equipped with 12/18 female grounds, so that the tapered end of the male ground projected below the closed area of the joint. The still head was of the "partial condensation" type with cold-finger condenser. The inlet tube to the condenser was connected

finger condenser. The inlet tube to the condenser was connected to a hot (90° C.) and cold water supply by means of a T-tube, so that it was possible to control the temperature of the condenser within the range of 20° to 90° C.

Adiabatic conditions were approximated by the use of an electrically heated vacuum jacket

The column was heated by means of COLUMN HEATING UNIT. a spiral of 8 mm. (1/z) inch) Nichrome ribbon wrapped uniformly around the vacuum-jacketed column, so as to produce a resistance of 12 to 20 ohms per foot. The Nichrome ribbon was carried beyond the packed, vacuum-jacketed portion of the column as far as the take-off side arm and the spirals were placed closer together in this area. The temperature outside the vacuum

together in this area. The temperature outside the vacuum jacket was determined by means of a thermometer placed inside the air jacket. The control circuit for the column heating unit consisted of a sensitive variable rheostat providing a range of 0 to 40 volts across the column heater. The bath consisted of an asbestos-wrapped, 400-cc. beaker wound with 24-gage (B. & S.) Nichrome wire (40 to 50 ohms) through which a variable resistance circuit operated, providing a range of 0 to 110 volts. The fraction receiver, also shown in Figure 2, was a modifica-

The fraction receiver, also shown in Figure 2, was a modifica-

15 mm.I.D. 0.D mm.I.D. 5 COLUMN HEATER RUBBER SLEEVE VACUUM VACUUM JACKET AIR JACKET CENTRAL TUBE -5 mm.I.D. SCALE: CENTIMETERS 111 11 8 10 6 0 2 4 12/30 STANDARD GROUND BEVELLED TO 45° AND WITH HOLE AS SHOWN





FIGURE 1. COLUMN PACKING

tion of the Ellis type (3) in which the receiving tubes are held on the movable axis, A, at points B-B with rubber bands and the size of the tubes is governed by the size of the fractions to be collected (0.4 cm. in diameter  $\times$  5 cm. in length for 50- to 300-mg. samples, or 0.6 cm.  $\times$  8 cm. for 0.50- to 1.5-gram samples).

OPERATION OF THE COLUMN. In an actual fractionation the procedure was divided into three stages—namely, flooding, establishing equilibrium conditions, and collecting fractions. In order to simplify the regulation of the bath and column temperatures during the equilibrium stage it was found advisable to make certain observations during the flooding operation. The following procedure proved most satisfactory:

The product to be fractionated (8 to 30 cc.) was placed in one of the still pots containing glass wool, this serving as an excellent antibumping agent at both atmospheric and reduced pressures. The contents of the flask were heated slowly by means of the electrically heated oil bath until distillate appeared in the lower 5 to 7.5 cm. (2 to 3 inches) of the packed section, whereupon the current passing through the bath heater was so adjusted that the bath temperature,  $T_1$ , remained constant. The voltage (or amperage, depending upon whether current control is maintained with a voltmeter in parallel or an ammeter in series with the bath heater) was recorded as  $V_1$ , since the bath temperature at this stage was generally the same as that used in the equilibrium stage. As soon as this voltage value was attained the current through the column heater was gradually increased from zero until the point at which the liquid film at the base of the packed section almost disappeared. The voltage across the column heater at this point was recorded as  $V_2$ .

Floading was now accomplished by increasing the bath temperature rapidly (110 volts across the bath), the column voltage being maintained at  $V_2$ . When all the packing had been flooded the current across the bath heater was lowered to  $V_1$ . The bath was cooled to  $T_1$  by inserting a Pyrex test tube containing cold water into the bath, and the bath surrounding the still pot was lowered cautiously in order to allow the packed section to drain slowly. There was so little tendency for the packing to dry during the draining operation that the bath frequently could be removed completely until the final traces of excess liquid had drained into the flask.

When all the excess liquid had drained from the packed section, the bath was raised again and the bath temperature then regulated to give a reflux rate (condensate return from drip point of cold finger) of approximately 30 drops per minute (38 to 40 cc. per hour) for 30 minutes in order to reach equilibrium. Although this period may appear short, test runs at total reflux showed an increase of less than one theoretical plate (23-plate column) when the time was extended to 90 minutes.

The actual fractionation was carried out either continuously or in batches. In the continuous method, which required careful control of the cold-finger temperature, distillate was collected continuously at a rate of about 100 to 200 mg. per hour. In the batch method 100-mg. samples of distillate were collected every 45

continuously at a rate of about 100 to 200 mg. per hour. In the batch method 100-mg. samples of distillate were collected every 45 minutes by rapidly increasing the temperature of the cold finger. As soon as the sample appeared in the side arm the cold finger was cooled down to total-reflux temperature again and the system permitted to attain equilibrium (30 minutes at total reflux).

The column was found to operate satisfactorily either at atmospheric or reduced pressure, and materials boiling as high as 200° C. at 1 mm. could be distilled successfully.

EFFICIENCY OF THE COLUMN. The theoretical plate values on the column were determined by use of methylcyclohexane-nheptane mixtures according to the procedure described by Ward (10). The liquid holdup was determined by the method of Fenske (4). The results of efficiency measurements on a pre-flooded 43-cm. (5 mm. in inside diameter) packed section are shown in Table I.

The flood point was found to be slightly more than 110 cc. per hour reflux (measured at top of column). This value was fairly constant at atmospheric or reduced pressures except where the viscosity of the liquid was relatively high.

Other columns, packed and operated as described above and having efficiencies of 28 to 45 plates (length of packing, 50 to 90 cm., 20 to 36 inches), have been used extensively in these laboratories.

SAMPLE FRACTIONATION. Beta-hydroxypropiovanillone was hydrogenated in dioxane solution over CuCrO at 280° C. Three grams of the product were fractionated in a Monel metal-packed, 51-cm. (20.5-inch), 28-plate column constructed as described above. The results are shown in Figure 3. The identity of the products (3-cyclohexylpropanol-1 and 4-n-propyleyclohexanol) was proved by preparation of their phenyl urethanes. The fractionation conditions were as follows: distillation pressure, 20 mm.; bath temperature, 120° to 150° C.; column temperature, 70° to 100° C.; reflux rate (at top of column) 30 drops per minute; total pressure drop at the above reflux rate, 0.7 mm. (0.025 mm. per plate); flood point, 110 cc. per hour reflux; take-off rate, 0.2 cc. per hour. When the quantity of residual, unfractionated material became less than the holdup of the column, it was forced over into the receiver (last point on fractionation curve) by raising the column temperature.

SUMMARY. An efficient, easily constructed, low-holdup fractionating column having an H. E. T. P. of 1.88 cm. and a liquid holdup of 0.045 cc. per plate is described. This apparatus compares favorably with the larger, Purdue spiral-screen column ( $\beta$ ), but is less efficient than the more expensive Podbielniak Heli-Grid column ( $\beta$ ). Columns of varying lengths (5 mm. in diameter) having theoretical plate values from 23 (42.5 cm., 17 inches) to 45 (90 cm., 36 inches) have been constructed and employed for the fractionation of small quantities (6 to 15 cc.) of liquids boiling from 100° C. at 760 mm. to 200° C. at 1 mm.

### Semimicro Fractionating Column

When wood meal is treated with ethanolic hydrogen chloride, a portion of the lignin is converted into a mixture of

TABLE I.Efficiency Tests on 43-Cm. (17-Inch)Fractionating Column					
Reflux Rate (at Cc./hour	Top of Column) Drops/min.	Theoretical Plates	Н. Е Ст.	. T. P. Inches	Operating Holdup Cc./plate
38,5 63.0 84.0 110.0	32 52 70 92	23 19 17 15.5	$1.88 \\ 2.28 \\ 2.54 \\ 2.79$	$\begin{array}{c} 0.74 \\ 0.89 \\ 1.00 \\ 1.10 \end{array}$	0.045



FIGURE 3. FRACTIONATION CURVE OF PRODUCTS FROM HYDROGENATION OF  $\beta$ -Hydroxypropiovanillone

TO «

0

TUBING

5 mm.I.D



WELL D COLUMN HEA TER CENTRAL TUBE 4 mm.I.D. JACKET RUBBER SLEEVE SCALE: CENTIMETERS 1 2 3 4 5

SEMIMICROCOLUMN FIGURE 4.

relatively high-boiling phenols, ketones, and aldehydes (5), which, in the past, have been laboriously separated on the basis of their chemical properties. Although the applicability of fractional distillation to this problem was considered frequently, there was no highly efficient apparatus available for the fractionation of very small quantities (0.5 to 1.5 cc.) of high-boiling (85° to 150° C. at 1 mm.) materials. [Since this article was submitted for publication it has been called to the authors' attention that a very efficient semimicrocolumn is described in a recent paper (7).]

The development of the packing described above, however, led to the construction of an efficient "semimicro" fractionating column of simple design and operation which has proved to be of great value in the separation of the phenolic and ketonic products obtained in the ethanolysis of wood meal. Examples of such fractionations using this semimicrocolumn will appear in forthcoming papers by Hibbert et al.

OPERATION OF THE COLUMN. It is unnecessary to give a detailed description of the construction of the column which is shown in Figure 4. The packing is described in detail above, and the Pyrex portion can be built by the average amateur glass-blower from the sketch.

The operation of the semimicrocolumn, although relatively simple, does require a fair degree of care if optimum results are to be attained.

The liquid sample (0.6 to 1.5 cc.) dissolved in a low-boiling solvent was placed in the bulb, A, together with a wad of glass wool. The side arm was closed with a glass rod plug, B, as shown in Figure 4 and the solvent was removed at atmospheric Until equilibrium was attained the procedure was the pressure. same as that described above—flooding, draining, then slow, con-trolled reflux for 30 minutes. The vapor was condensed for reflux by means of an air jet directed on the top of the column.

The sample-collecting procedure was similar to the "batch" method described above. In order to collect a fraction, a current of approximately 1 ampere was sent through the 4-ohm heating unit, C, in the column head. As soon as distillate appeared in the side arm the current through C was shut off, the bath lowered, and the bath temperature raised. While the temperature of the bath was being raised to the flood point the fraction was removed from the receiver, D, as follows:

Air (or better, nitrogen) was admitted to the system and the liquid in D removed through side arm E to a tared test tube with the aid of a clean medicine dropper. The residual liquid in D and that remaining in the medicine dropper were washed into a second tared test tube by use of a pure low-boiling solvent (ether or (In washing D, it was important that some solvent be ethanol). forced back into the column in order to remove all traces of the first fraction from the condensing area.) After the washing operation the system was closed and re-evacuated, the bath was raised, and the procedure of flooding, draining, and refluxing was repeated.

The fractions obtained by this procedure, using the apparatus shown in Figure 4, weighed approximately 50 mg. If larger samples were desired-e. g., 100 mg.-the procedure was modified as follows:

After the first fraction had been forced over, the current in Cwas shut off, but the liquid in the pot was allowed to reflux at the same bath and column temperatures as were used prior to the collection of the first fraction. After refluxing had been continued for about 30 minutes, a second fraction was collected and the total contents of receiver D were removed as described above.

The column, as shown in Figure 4, was designed for the fractionation of high-boiling materials (85° to 150° C. at 1 mm.). For lower-boiling compounds (100° C. at 760 mm. to 100° C. at 10 mm.) it would be necessary to modify the head by removing the asbestos shield and to employ cooling (for total reflux) with a current of air. Both systems have been employed successfully in these laboratories. No plate determinations have been made on the semimicrocolumn, but on the basis of the previously described determinations on this new type of packing, the column shown in Figure 4 (13-cm. packed section) should have a 7-plate efficiency.

These "semimicro" columns are excellently suited for the final purification of "fractions" obtained from the larger columns described above. Frequently the "flat" portion of a fractionation curve (obtained from 10 to 15 cc. of a mixture) contained traces of lower- and higher-boiling impurities but the total volume of the fraction was too small (1 to 3 cc.) to permit refractionation. Such a material could often be purified readily by refractionation in the semimicrocolumn with a recovery as high as 80 to 90 per cent.

# Acknowledgment

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# A Colorimetric Method for the Determination of Sodium

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**F**OLLOWING the publication of the method for the gravimetric determination of sodium as a hydrated triple salt,  $NaZn(UO_2)_3(C_2H_3O_2)_3 \cdot 6H_2O$ , by Barber and Kolthoff (1) and the corresponding magnesium salt by Caley and Foulk (3), a number of colorimetric methods based on the color conferred on the solution by the uranyl ion have been described in the literature.

Caley and Foulk suggested dissolving the triple acetate in water and comparing the yellowish solutions colorimetrically. They mention that "best results are obtained when the solutions (known and unknown) show a fairly deep straw color". This is equivalent to saying that the sensitivity is limited.

It has been suggested by Barrenscheen and Messinger (2) that a water solution of the triple acetate treated with potassium ferrocyanide gives a stable brownish red color due to a potassium uranyl ferrocyanide which may be used as the basis of a colorimetric method. This procedure has been criticized by several authors on the basis that the color intensity varies with such external conditions as temperature and excesses of reagents.

Rosenheim and Daehr (4) while investigating the hydrates of



uranium tetroxide found that if a solution of hydrogen peroxide is added to a solution containing the uranyl ion, a white amorphous precipitate forms which they took to be a hydrated uranium tetroxide. If, however, the solution is first made alkaline with sodium or ammonium carbonate and the hydrogen peroxide is then added, a true solution is formed which varies in color from an intense yellow to orange to red, depending upon the concentration of the uranyl ion.

It occurred to one of the authors that this color might be made the basis of a colorimetric method for determining sodium.

This method is basically only a method for estimating the triple acetate of sodium uranyl and zinc or magnesium acetate and therefore assumes all of the precautions and interferences of the methods of Barber and Kolthoff and of Caley and Foulk.

Preliminary experiments using a Duboscq colorimeter indicated that the intensity of color was somewhat dependent upon the amounts of ammonium carbonate and hy-

drogen peroxide used. At this time a Coleman spectropho-

tometer became available and the transmission curves shown in Figure 1 were taken. Curve A shows the transmission of a solution prepared by treating an amount of the triple zinc acetate equivalent to 0.308 mg. of sodium, with an excess of 3 per cent hydrogen peroxide and saturated ammonium carbonate solutions, and diluting the whole to 25 ml. Curve B is the same curve for a solution containing an amount of triple acetate equivalent to 1.300 mg. of sodium, again diluting the whole to 25 ml. Both curves show transmissions of suitable size for wave lengths from 5200 Å. to about 5500 Å.

Therefore, using a 30 mµ fixed slit in the spectrophotometer, a band at 5200 Å, was chosen for all succeeding measurements. The procedure involved making a stand-

The procedure involved making a standard triple acetate solution in a known weight of water and making comparison solutions from this by weight. The required amounts of 3 per cent hydrogen peroxide and saturated ammonium carbonate were added and the whole was made up to a volume of 25 ml. in calibrated flasks. It is important to add the ammonium carbonate solution first, followed by the hydrogen peroxide. If the order is reversed, the amorphous precipitate

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TABLE I.	EFFECT C	F AMM	ONIUM	CARBONATE	ON
TRANSM	ITTANCE OF	TRIPLE	ACETA	TE SOLUTION	15

Sodium Taken	Saturated (NH4)2CO3	Transmittance
Mg.	Ml.	%
0.03	0.5	71.0
0,03	1.0	84.5
0.03	2.0	95.5
0.03	5.0	97.5
0.03	6.0	99.6
0.03	10.0	99.6
0.15	0.5	50.6
0.15	1.0	55.2
0.15	3.0	58.8
015	5.0	58.9
0.3	0.5	13.8
0.3	1.0	14.2
0.3	3.0	14.2
0.3	5.0	14.2

TABLE II. EFFECT OF HYDROGEN PEROXIDE ON TRANSMITTANCE OF TRIPLE ACETATE SOLUTIONS

Sodium Taken Mg.	3% H1O2 Ml.	Transmittance %
$\begin{array}{c} 0.15 \\ 0.15 \\ 0.15 \\ 0.15 \\ 0.03 \\ 0.03 \end{array}$	$\begin{array}{c} 0.5 \\ 1.0 \\ 3.0 \\ 5.0 \\ 0.5 \\ 1.0 \end{array}$	12.7 13.7 14.8 14.9 58.6 63.8
0.03	5.0	63.8

referred to by Rosenheim and Daehr tends to form. Because the ordinary hydrogen peroxide of commerce stabilized with acetanilide was not satisfactory, a fresh 3 per cent solution of this reagent was made each time by diluting 30 per cent perhydrol.

Table I shows the effect of ammonium carbonate on the color. It can be seen that the transmittance varies somewhat with the amount of ammonium carbonate, but for the amounts of sodium taken for ordinary determinations, 6 ml. of a saturated solution seemed to be a sufficient excess to develop maximum color rapidly.

Table II shows the corresponding variation for the number of milliliters of 3 per cent hydrogen peroxide. The standard conditions were then chosen to give sufficient excess of each reagent—namely, 6 ml.

The following experiments were run to test the fading of the color:

The proper amounts of the stock solution of the triple acetate were weighed into 25-ml. volumetric flasks, to each flask separately the ammonium carbonate and hydrogen peroxide were added, the solution was diluted to volume and the color comparison was made immediately. About 5 minutes were required for this and for the necessary adjustments on the spectrophotometer, so that the readings taken at zero time were in error about 5 minutes.

LABLE III.	ACETATE SOLUTION	SMITTANCE OF IRIPL
Sodium	Time after Development	Transmittance
Mg.	Hour	%
0.22	0	75.2
0.55	02	51.2
0.88	02	35.8
1.02	02	30.9 30.8
1.40	0	21.2
1.66	21 0 1	21.5 17.2 17.3
1.90		17.4 15.2 15.0
2.09	21 0 1 21	15.1 12.3 12.1 11.8

Table III shows the effect of time on the per cent transmittance. Within the time necessary to make a colorimetric determination, there is no appreciable fading. This appears to be true in spite of the fact that on standing for some time, the decomposition of the hydrogen peroxide is evidenced by the appearance of bubbles in the solution. But after shaking to remove the bubbles, the transmittance appears to be unchanged when measured in the spectrophotometer.

An attempt was made to determine the minimum amount of sodium distinguishable by this method, by making a number of pairs of solutions from the stock solution which differed from each other by only small amounts of sodium. Table IV shows some of these results. As the transmittance decreases the sensitivity decreases but, by choosing a more appropriate wave band for the redder colors, this could be improved.

TABLE IV	. SENSITIVITY	OF COLORIMETRIC METHOD
	Sodium	Transmittance
	Mg.	%
	0.308	63.2
	0.316	67.8
Difference	0.008	4.6
	0.675	47.2
	0.686	48.3
Difference	0:011	1.1
	1.24	23.2
	1,25	23.8
Difference	0.01	0.6

Figure 2 shows the logarithm of the transmittance and Table V shows the data from which this curve was obtained.

The few samples on which this method was tried out gave excellent results, as shown by Table VI.



	TABLE V. TR	ANSMITTANCH	6			
Sødium Mg.	Transmittance %	Sodium Mg.	Transmittance %			
$\begin{array}{c} 0.223 \\ 0.308 \\ 0.548 \\ 0.879 \\ 1.02 \end{array}$	$\begin{array}{c} 75.2 \\ 63.2 \\ 51.2 \\ 35.8 \\ 30.9 \end{array}$	$1.30 \\ 1.40 \\ 1.66 \\ 1.90 \\ 2.09$	23.2 21.2 17.2 15.1 12.3			
TA	TABLE VI. EXPERIMENTAL RESULTS					
Sample		Na:0 Present %	Na:O Found %			
B. S. flint cla B. S. feldspa B. S. opal gla	y 97 r 70 ss 91	0.33 2.38 8.48	0.33 2.36 8.47			

A few experiments showed that the triple magnesium acetate gave similar results, but no particular advantages were noted.

#### Summary

A colorimetric method for sodium has been developed which depends on treating a solution of the triple acetate,

precipitated by the method of Barber and Kolthoff or of Caley and Foulk, with an excess of ammonium carbonate and hydrogen peroxide which develops an orange to red colored solution. When using a narrow wave band this color is proportional to the concentration of sodium ion in solution. The transmittance-concentration curve for these solutions has been run over the spectral range from 3700 Å. to 7700 Å. A wave band of 5200 Å. was chosen for this comparison. Various factors affecting the stability of the color were investigated and are reported.

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### A Molecular Still Designed for Small Charges

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THE active principle of marihuana is contained in a viscous, high-boiling oily mixture, the active components of which have not as yet been obtained in crystalline form (except cannin, 1).

In working with material of this character, it is frequently desirable to distill small amounts of it under high vacuum, either for the purpose of fractionating or simply to separate it from nonvolatile matter.

The still described herein was devised to afford a convenient means for carrying out this operation. With the dimensions indicated, it has proved satisfactory for distilling from 0.25 to 5 grams of oil. Two fractions of distillate may be collected and the still residue need not exceed 0.15 gram. Transfer losses are avoided, since the distillate is collected directly in tubes in which it may be retained until used in subsequent operations. It does not pass through any ground joints, thus avoiding the possibility of contamination with lubricant.

No provision has been made for determination of the distillation temperature. In distillations of this type, ebullition

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does not take place. The temperature is not a constant, but a variable related to the pressure and the rate of distillation; hence it is more satisfactory to characterize products by such properties as refractive index, rotation, and the like.

#### Apparatus

Apparatus The apparatus is illustrated in the accompanying figure. It consists of a 35-mm. tube, A, 175 mm. in length, through which a 14-mm. tube, B, is sealed so that its axis lies about 6 mm. above that of the outer tube, A. The still pot, C, is formed by two transverse creases, D, in the outer tube, 45 mm. from each end, extending to within 3 mm. of the central tube. To the end chambers formed by the creases are sealed 24/40 § ground joints, E, in which the receivers, F, are supported as indicated, by suitable lengths of glass tubing. To the central tube are sealed, as illustrated, lengths of glass rod, G, leading from a point outside the transverse creases, but as near them as possible, to a point from which distillate will drip directly into the receivers. Filling and cleaning are provided for by a tube, H, bearing a 24/40 § joint sealed to the top of the still. From the closure of this tube a length of 8-mm. tubing, I, leads to the vacuum system. Construction of the device involves considerable strains in the glass and the annealing accordingly must be thorough. The

glass and the annealing accordingly must be thorough. The authors have found an ordinary muffle furnace convenient for the purpose.

#### Operation

In operation a suitable charge is placed in the still pot, and the apparatus is set level and gradually evacuated while the charge is gently warmed. After thorough degassing, the still is tipped (2) a little toward one end, full vacuum is applied, and the charge is heated until distillation proceeds at a suitable rate. Distillate accumulates on the condenser and follows it to the sealed-on glass rod, whence it is diverted to the receiver. The condenser is maintained at such a temperature that distillate flows along it smoothly and does not tend to form large drops which might fall off outside the still pot but before reaching the tip which carries off outside the still pot but before reaching the tip which carries it to the receiver. After one fraction has been collected, the still is tipped toward the other end and the second fraction collected in the same way. The still has been successfully heated by means of a small flame

placed some distance below it. A properly designed electric heater might prove more satisfactory.

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## **Determining Magnesium in Plants and Soils**

#### Adaptation of the 8-Hydroxyquinolate Micromethod

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THE use of 8-hydroxyquinoline in the precipitation and determination of magnesium has received considerable attention, particularly since several micromethods for the estimation of hydroxyquinolate have been found satisfactory (1, 4, 5, 9). The general methods of estimation include oxidation with hexanitrato-cerate in perchloric acid solution and color reactions involving the use of ferric salts or the Folin phenol reagent. A comparison of certain of these methods of estimation has recently been reported by Gerber *et al.* (1). Magnesium hydroxyquinolate has a constant composition and is very sensitive if interfering ions are eliminated.

The determination of magnesium as the phosphate proved entirely unsatisfactory in a system of soil and plant analysis involving use of the more rapid and sensitive micromethods and for this reason several of the hydroxyquinolate procedures were studied (8). Preliminary studies using plant ash and synthetic solutions indicated that the hydroxyquinolate method is sensitive at low magnesium concentrations, even in the presence of considerable amounts of ammonium salts. However, great care is necessary for best results, and certain precautions must be rigidly observed. Consequently the procedure adopted is given in considerable detail and reasons for certain precautions are indicated.

#### **Preparation of Solution**

PLANT MATERIAL. Oxidize 2 grams of the air-dry material, ground to pass a No. 20 A. S. T. M. screen, in a 100-ml. beaker by the method of Gieseking *et al.* (3). For ordinary plant material it is not necessary to treat with nitric acid before adding the mixed nitric and perchloric acid solutions. Oily seeds, such as corn grain may be safely oxidized with perchloric acid if the following procedure is used.

Dry 20 grams of the material at 100° C. and extract several times with anhydrous ether to remove fatty substances that would react too violently with perchloric acid. Treat the extracted material in a 600-ml. beaker on a steam hot plate with 20 ml. of concentrated nitric acid. If considerable frothing occurs, stir vigorously a few times with a stirring rod. After a minute or two when reaction subsides somewhat, cover with a watch glass to prevent too rapid evaporation and allow the mixture to evaporate to a thick yellow paste. Add 30 to 40 ml. more of nitric acid and leave on the steam plate several hours or overnight. Take up the residue with 20 ml. of a mixture of 2 parts of nitric acid and 1 part of perchloric acid, transfer to a gas or electric hot plate, and heat carefully at 140° to 160° C. until the solution becomes clear. If the material becomes dark brown or black during this heating, add more nitric acid, a few milliliters at a time. Usually, however, the solution boils down gently and clears up without trouble.

After the solution clears, remove the watch glass and allow most of the excess perchloric acid to evaporate. Take up the residue in 10 ml. of 1 to 1 hydrochloric acid, heat on the steam hot plate for 20 minutes, and filter through a close-textured filter paper. Wash the filter six times with hot 10 per cent hydrochloric acid and three or four times with water. Transfer the filtrate to a 50-ml. volumetric flask, dilute to volume, and mix thoroughly. Take measured portions of this solution for analysis.

Sor.. Several common methods employed in soil analysis for obtaining solutions of total and replaceable bases have been used and will not be described in detail. After the solution is taken to dryness to destroy organic matter or dehydrate silica, the residue is taken up with 10 ml. of 1 to 1 hydrochloric acid in the same way as described for plant materials, filtered, and transferred to a 50-ml. volumetric flask.

#### **Reagents and Solutions**

QUINOLATE REAGENT. Dissolve 1 gram of 8-hydroxyquinoline in 50 ml. of 95 per cent alcohol. Prepare fresh every 2 or 3 days. One milliliter of this solution will precipitate approximately 1.5 mg. of magnesium.

FERRIC CHLORIDE-ACETIC ACID REAGENT. Dissolve exactly 10 grams of ferric chloride hexahydrate in 2 liters of water containing 10 ml, of glacial acetic acid.

WASH SOLUTION. Mix 1 part of 95 per cent alcohol and 1 part of 10 per cent ammonium hydroxide. Keep in a well-stoppered bottle.

STANDARD MAGNESIUM SULFATE SOLUTION. Dissolve in distilled water 12.038 grams of magnesium sulfate that have been recrystallized from A. C. S. grade magnesium sulfate heptahydrate and dehydrated at a temperature above  $200^{\circ}$  C., and dilute to 2 liters. This solution after mixing is 0.1 N. A 0.01 N solution is prepared by diluting 50 ml. of the standard solution to 500 ml.

#### **Precipitation of Magnesium**

Transfer a measured portion of the solution to be analyzed containing 0.1 to 0.7 mg. of magnesium to a 15-ml. conical centrifuge tube, add 5 drops of glacial acetic acid and 1 drop of methyl red indicator, and mix thoroughly. If the tube is not over half full, mixing can be effected most rapidly by holding the tube near the top firmly between the thumb and forefinger of one hand while the fingers of the other hand are flipped rapidly against the bottom of the tube. Add 1 to 1 ammonium hydroxide carefully from a buret with frequent mixing until the solution turns from red to a very faint red or pink (not yellow) corresponding to about pH 6.0. Add 2 or 3 drops of dilute 1 to 4 acetic acid to give a more distinct red. The solution should finally be between pH 5.0 and 5.3. Add 3 drops of hydroxyquinolate reagent, mix, and place the tube in a beaker of hot water for 10 to 15 minutes to precipitate iron and aluminum. Centrifuge while still hot at 2000 r. p. m. for 10 minutes and pour the supernatant liquid carefully into a second 15-ml. centrifuge tube. Wash the sides of the first tube carefully with a thin stream of warm water from a 2-ml. pipet, stir up the precipitate by the method described above, centrifuge, and transfer the washings to the second tube.

To precipitate calcium add 1 ml. of a saturated solution of ammonium oxalate to the second tube and mix thoroughly. Place the tube upright in a beaker of hot water and heat on a steam hot plate for 30 minutes. Remove the tube from the beaker and place it in a rack to stand 2 to 4 hours. Add 5 or 6 drops of 95 per cent alcohol to the tube to break up any film of calcium oxalate that might have formed at the liquid surface and centrifuge for 10 minutes at 2000 r. p. m. Transfer the supernatant liquid containing magnesium to a third 15-ml. conical centrifuge tube by carefully pouring it over. Wash the calcium oxalate precipitate twice with 2-ml. portions of the alcohol-ammonia wash solution, using the same procedure as for the iron and aluminum precipitate. Centrifuge and add the washings to the tube containing the magnesium solution. If desired, calcium may be determined in the usual way.

To the solution in the third tube, add 0.5 ml. of hydroxyquinolate reagent, or if more than 0.7 mg. of magnesium is present, use 1 ml. Stir thoroughly, this time with a stirring rod, since the tube is too nearly full to mix in the usual way. Add 2 ml. of concentrated ammonia, stir thoroughly, remove the stirring rod, and wash it with a fine stream of water. When precipitation starts, usually within a minute or two, cover the surface of the liquid with a layer of alcohol 1 cm. thick. Put the tube in a beaker of hot water and place on the steam hot plate for 20 minutes. Remove the tube from the hot water bath, stopper with a No. 1 rubber stopper, and place in a rack to stand 1 to 2 hours or overnight if convenient. Be sure the layer of alcohol does not evaporate entirely; this is important because the magnesium hydroxyquinolate precipitate has a strong tendency to creep up the sides of the glass and form a film at the surface of the liquid that will not centrifuge down.





Centrifuge at 2000 r. p. m. for 10 minutes and draw off the liquid with gentle suction, using a tube with the tip drawn out to a capillary and turned up about 1 to 2 mm., so that the liquid can be drawn off without disturbing the precipitate. Wash the can be drawn off without disturbing the precipitate. Wash the precipitate twice with 2-ml. portions of the alcohol-ammonia wash solution, covering the suspension each time with a layer of alcohol. Centrifuge and draw off the supernatant liquid as described above. Dry the precipitate carefully for a few minutes by placing the tube in a beaker of hot water on a steam hot plate, but do not leave so long that the precipitate becomes hard and dissolves too slowly. Remove from the steam bath, add 10 ml. of the ferric chloride-acetic acid reagent to the tube, and break up the precipitate with a small glass stirring rod to hasten solution, or stopper and shake vigorously. Solution is ordinarily complete and full color developed in about 0.5 hour.

Transfer an appropriate portion, usually 2 ml., of the colored solution, to a test tube, dilute with 10 ml. of the ferric chlorideacetic acid reagent, mix, and determine the light transmission by means of a photoelectric colorimeter or spectrophotometer (a Cenco-Sheard spectrophotelometer was used in this study). From the transmission value determine the magnesium content by a standard curve prepared by precipitating 1- to 10-ml. portions of a 0.01 N magnesium sulfate solution by the method described above.

A standard curve at a wave length of 650 millimicrons is shown in Figure 1. The percentage of magnesium in an unknown sample is calculated by picking the amount of magnesium in micrograms from the curve corresponding to the per cent transmission and applying the following formula:

 $Micrograms \times dilution$ Weight of sample  $\times$  1,000,000  $\times$  100 = per cent magnesium

Figure 2 shows a light-absorption curve for the color developed by magnesium hydroxyquinolate in ferric chlorideacetic acid solution. In this curve values for specific extinction are plotted against wave length in millimicrons. The following application of the Beer-Lambert law was used (2, page 75):

$$\log_{10} \left( \frac{I_0}{I} \right) = kcl$$

$$k = \frac{\log_{10} \left( \frac{I_0}{I} \right)}{cl}$$

$$K = \frac{\log_{10} \left( \frac{I_0}{I} \right)}{l}$$

where

 $I_0$  and I = intensity of light at a given wave length transmitted by solvent and solution, respectively k

specific extinction

С concentration of magnesium in mg. per ml.

length of cell in cm. K extinction coefficient ----

This curve shows maximum light absorption at a wave length of 660 millimicrons with a secondary maximum at 460 millimicrons. These maxima have been found to hold at widely different concentrations. Agreement with Beer's law is indicated in Figure 1, where extinction coefficients or Kvalues are plotted against concentration. In this case a line passing through the origin falls on or very near to all points from 1 to 10 micrograms per milliliter.

The values for maximum absorption obtained in this study do not agree exactly with those reported by Gerber et al. (1), who found maxima at 650 and 425 millimicrons. The discrepancies in these values may be due to one or all of the following reasons: differences in the width of the wave band used, calibration of the instrument to proper wave lengths, or differences in the concentration of iron chloride. In the "spectrophotelometer" used in this study, a 1-mm. entrance slit and 2.5-millimicron exit slit was used. At this setting, owing to the side bands of light from the entrance slit, the total wave band isolated is 6.5 millimicrons in width (6). The instrument was calibrated from time to time with a fluorescent lamp at a wave length of 546 millimicrons. It was found in early work with this method that the concen-

TABLE	I.	EFFECT OF MAGNESIU	PHOSPHATE M BY 8-HYDE	ION	ON	PRECIPITATION TOLINE	OF
		Light T	ranamission. W	ave L	engtl	h and form the second second	

	650 Mill	limicrons	
0.01 N	No	0.6 mg. of	Difference
MgSO4	phosphorus	phosphorus	
Ml.	%	%	%
1	78.5	77.0	$-1.9 \\ -0.3 \\ +0.6$
2	59.7	59.5	
3	46.5	46.8	
5	28.5	28.0	-1.8 -1.1
7	18.2	18.0	



FIGURE 2. LIGHT ABSORPTION CURVE FOR MAGNESIUM QUINOLATE

1-cm. cell with 1-mm. entrance slit and 2.5 mµ exit slit

ANALYTICAL EDITION

tration of iron chloride in the reagent has a great effect on the color produced. This effect is of sufficient importance to necessitate some care in preparing the ferric chloride-acetic acid reagent. Each lot of ferric chloride should be checked and kept tightly covered when not in use to prevent change in moisture content.

The concentration curves used in this work were drawn at 650 and 560 millimicrons. At these wave lengths it was unnecessary to use the red filter to prevent stray light in the instrument, and reference readings,  $I_0$  values, of 100 per cent were more easily obtained.

#### **Interfering Substances**

The important cations interfering in the precipitation of magnesium hydroxyquinolate are iron, aluminum, and calcium. Iron and aluminum are usually separated by ammonium hydroxide or ammonium acetate at about pH 6.2. It was found, however, that these ions could be separated most easily and completely by precipitation with 8-hydroxyquinoline in acetic acid solution at about pH 5.3. Calcium is completely separated as the oxalate and thus eliminated. Since the procedure does not remove the phosphate ion, an experiment was set up to find out whether this ion interferes in the precipitation. Two sets of standard magnesium solutions were prepared: one with and one without the addition of 0.6 mg. of phosphorus, corresponding to the maximum amounts present in ordinary analysis. Magnesium was precipitated in both sets. The results shown in Table I indicate that the phosphate ion has little if any effect on the quantitative precipitation of magnesium quinolate. In all but one instance (values for 1 ml. of 0.01 N magnesium sulfate) differences were considered within the limit of error at the time the experiment was conducted. The effect of the 0.6 mg. of phosphorus on the precipitation of magnesium at low concentrations was rechecked at a wave length of 560 millimicrons, so values are not strictly comparable with those given in Table I, but at this wave length the values agreed within 0.5 per cent. It is true, however, that where 1.2 mg. of phosphorus were added, the precipitation of magnesium in amounts below 0.1 mg. was retarded. This is not considered particularly important since 0.1 mg, is at the lowest magnesium level for the accuracy of the method and the phosphorus level is higher than is normally encountered in ordinary analysis.

TABLE II.	RECOVERY OF	Added	MAGNESIUM	IN	WHEAT	TOPS
	(0 103 mg	of mag	(babba muisan			

Sample No.	Found in Sample Ma.	Theoreti- cally Present Ma.	Actually Determined Ma.	Recove Added Ma Ma.	ery of agnesium %
74 75 76 77 78 79 80 81 81 82 83	$\begin{array}{c} 0.433\\ 0.406\\ 0.413\\ 0.459\\ 0.459\\ 0.434\\ 0.400\\ 0.469\\ 0.462\\ 0.429\end{array}$	$\begin{array}{c} 0.536\\ 0.509\\ 0.516\\ 0.562\\ 0.562\\ 0.537\\ 0.503\\ 0.572\\ 0.565\\ 0.532\end{array}$	$\begin{array}{c} 0.537\\ 0.514\\ 0.510\\ 0.554\\ 0.562\\ 0.535\\ 0.513\\ 0.570\\ 0.564\\ 0.533\\ \end{array}$	$\begin{array}{c} 0.104\\ 0.108\\ 0.097\\ 0.095\\ 0.103\\ 0.101\\ 0.113\\ 0.101\\ 0.102\\ 0.104 \end{array}$	101 105 94 92 100 98 110 98 99 101

#### Accuracy of the Method

The method was checked for accuracy in three ways.

Known amounts of magnesium sulfate were added to one of duplicate portions of solution from ten ashed samples of wheat tops grown in a greenhouse experiment, and after determining magnesium in these aliquots, the percentage recovery was cal-culated. The recovery averaged 99.7 per cent for the ten samples. The data are presented in Table II.

Seventeen samples of corn grain were analyzed for magnesium by the above method and by a phosphate method similar to that described by Wall (7). A comparison of the results by the two methods indicates that the 8-hydroxyquinoline method gave an average magnesium content for all samples slightly higher than the phosphate method. The averages for the two methods were 0.113 and 0.111 per cent, respectively. The maximum dif-ference between the methods for any one sample was 12 per cent and four of the seventeen samples gave differences greater than 3.8 per cent. These results are based on single determinations.

3. The base-exchange capacities of two soils were determined by saturating them with magnesium and measuring the amount of this ion taken up by the exchange complex after replacing with ammonium acetate and determining magnesium in the extracts by both the quinolate and phosphate methods. The base-exchange capacities of these soils had previously been determined by the calcium absorption method.

The results obtained by the three methods are shown in Table III. Good agreement was obtained in all cases, with the possible exception of the value 8.6 obtained by the magnesium phosphate method, and this value is within 5 per cent. All values are an average of duplicate determinations.

The method has been used by two analysts in determining the magnesium content of several hundred samples of plant material and soil extracts. In most of these a difference of 6 per cent between duplicate determinations was allowed. It was found necessary on the average to rerun one sample in twenty. The average difference between duplicates was within 2.5 per cent.

TABLE III. BASE-E	XCHANGE (	Capacities of T	WO SOILS DE-
TERMINED BY CALCIU		gnesium Absorp	TION METHODS
	E	Base-Exchange Capa	city
Soil Type	Calcium	Magnesium	Magnesium
	determined	determined	determined
	as oxalate	as quinolate	as phosphate
	А	I. e. per 100 grams o	f soil
Maury silt loam	17.6	17.7	17.5
Unclassified silt loam <sup>a</sup>	8.2	8.2	8.6
<sup>a</sup> From Berea Soil Exp	eriment Field	L.	

#### Summary

A micromethod for magnesium based on precipitation with S-hydroxyquinoline was studied and adapted to the determination of this element in soils and plant materials. Precipitation and determination were found to be most satisfactory and reproducible when the amount of magnesium present in the test solution ranged between 0.1 and 0.7 mg. Magnesium was accurately estimated by the green color of iron hydroxyquinolate in acetic acid solution. The method is capable of a high degree of accuracy and reproducibility.

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## **Microextraction and Microtitration** of Fatty Acids

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HE difficulties inherent in the titration of minute amounts of the higher fatty acids with alkali arise from two main sources: The end point, on the alkaline side of neutrality, is affected by absorbed carbon dioxide; this is particularly manifest when dilute reagents are used. The tint of the indicator at the end point is dependent upon the composition of the solvent, which is usually an alcohol-water mixture.

TABLE I	. DUPLICATE STAN GAINST STEARIC ACI	DARDIZATIONS OF AL	COHOLIC ALKALI
	Stearic Acid Mg.	Displacement Mm.	Normality
A	16.543	10.80	0.1699
	10.056	6.56	0.1700
В	13.679	9.34	0.1625
	13.999	9.54	0.1628
С	13.131	9.06	0.1608
	13.092	8.99	0.1615

In an attempt to minimize these difficulties, samples of fatty In an attempt to minimize these difficulties, samples of fatty acids weighing 8 to 20 mg, have been satisfactorily titrated, using relatively small volumes of fairly concentrated alkali (0.16 N). Both the acid and alkali were dissolved in 90 per cent methanol, to obviate any variation in the composition of the solvent.  $\alpha$ -Naphtholphthalein (3), 0.5 per cent solution in methanol, has proved a satisfactory indicator, and a micrometer-driven microburet of the type described by Scholander (2) has been used to deliver the alkali. The titration mixture was stirred by means of a long statisfactory long at a the black of by means of a long stainless steel wire fastened to the blade of an electric buzzer.

an electric buzzer. Alkali, approximately 0.16 N, was prepared by dissolving ap-propriate amounts of solid sodium hydroxide in freshly boiled 90 per cent methanol. This solution was well mixed and then allowed to stand, to permit settling of the sediment. Solvent for the acid to be titrated was made up by addbe titrated was made up by add-ing 10 drops of indicator solution to 10 ml. of 90 per cent methanol, boiling for a minute or so, and then adding sufficient alkali from the microburet to produce an olive green color. Two to 4 ml. of this solvent mixture were used to dis-solve each sample of fatty acid, and the titration was carried out as rapidly as practicable. The end point taken was the match of the original solvent mixture.

Fading of the indicator on standing, due to absorption of carbon dioxide, was noted. After a half hour the change in the color of the solvent was so marked as to warrant its being discarded. However, it was felt that only small errors would be introduced if each titration was carried out to the same tint as the solvent mixture at that time. There was obviously no necessity for a blank titration.

> FIGURE 1. LIQUID MICROEXTRACTOR



The authors' buret, calibrated according to Scholander, delivered 3.171  $\times$  10<sup>-2</sup> ml. per mm. displacement.

For purposes of standardization, samples of pure stearic acid were weighed on the microbalance into ordinary 15-ml. centri-fuge tubes. Duplicate standardizations of alkali on successive days showed a decrease in normality, indicating the necessity of daily standardization (Table I). In view of the fact that this technique was investigated for the

purpose of determining the total (free plus esterified) fatty acids in plasma, a liquid microextractor was employed (Figure 1). in plasma, a liquid microextractor was employed (Figure 1). Into the lower chamber, A, which had a capacity of about 5 ml., 13.314 mg. of stearic acid were transferred in 1 ml. of ethanol and 1 ml. of 3 N alcoholic hydrochloric acid was added. In tube B were placed 10 ml. of petroleum ether, previously distilled from alkali, a reflux condenser was attached, and the whole assembly was set on the steam bath to extract for one hour. Tube B was then disconnected, and after evaporation of the petroleum ether, was kept overnight in vacuo over solid alkali, to remove traces of volatile acids. The residue was dissolved in neutralized alcohol and titrated precisely as described above. Standardization of alkali: 15.490 mg. of stearic acid required 10.66-mm. displace-ment, N = 0.1613. Titration of extract: acid required 9.16-mm. displacement

#### $9.16 \times 3.171 \times 10^{-2} \times 0.1613 \times 284.3 =$

13.32 mg. stearic acid recovered, corresponding to 100.1 per cent

In the analysis of plasma samples, lipides were extracted from 5-ml. samples of plasma by the alcohol-ether method of Bloor (1). The clear alcohol-ether filtrate was taken to dryness under a bell jar in a stream of nitrogen and the residue redissolved in ether. The solution was filtered into a small centrifuge tube and evap-The solution was intered into a small centrifuge tube and evap-orated to dryness. The residue, in 1 to 2 ml. of ethanol, was trans-ferred to chamber A, of the extractor with the aid of a long slender pipet; 0.2 ml. of 2 N sodium hydroxide in methanol was added and the mixture was gently heated on the steam bath until all the solvent had boiled away. Then 0.4 ml. of 2 N aqueous hy-drochloric acid and 1 ml. of ethanol were added, tube B containing 10 ml. of petroleum ether was fitted on, and extraction under reflux was carried out on the steam bath. The extract in tube B, was dried and titrated as described. Duplicate analyses on three different samples of plasma are given in Table II.

TABLE II. DUPLICATE ANALYSES OF PLASMA FATTY ACIDS IN THREE DIFFERENT SAMPLES

Sample	Fatty Acids Microequivalents per ml.	
A	8.31	8.30
B	6.46	6.38
C	7.77	7.66

#### Summary

A method for the titration of 8- to 20-mg. samples of fatty acids has been described. The microestimation of plasma fatty acids is feasible by this method, in conjunction with a suitable extraction procedure.

#### Acknowledgment

This work was carried out with the aid of a grant from the Josiah Macy, Jr., Foundation.

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Vol. 15, No. 4



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