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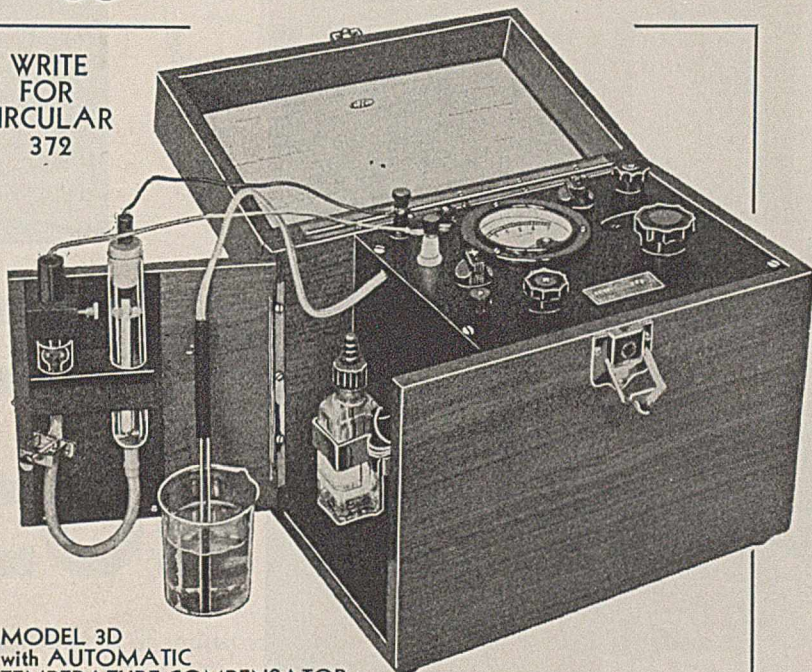


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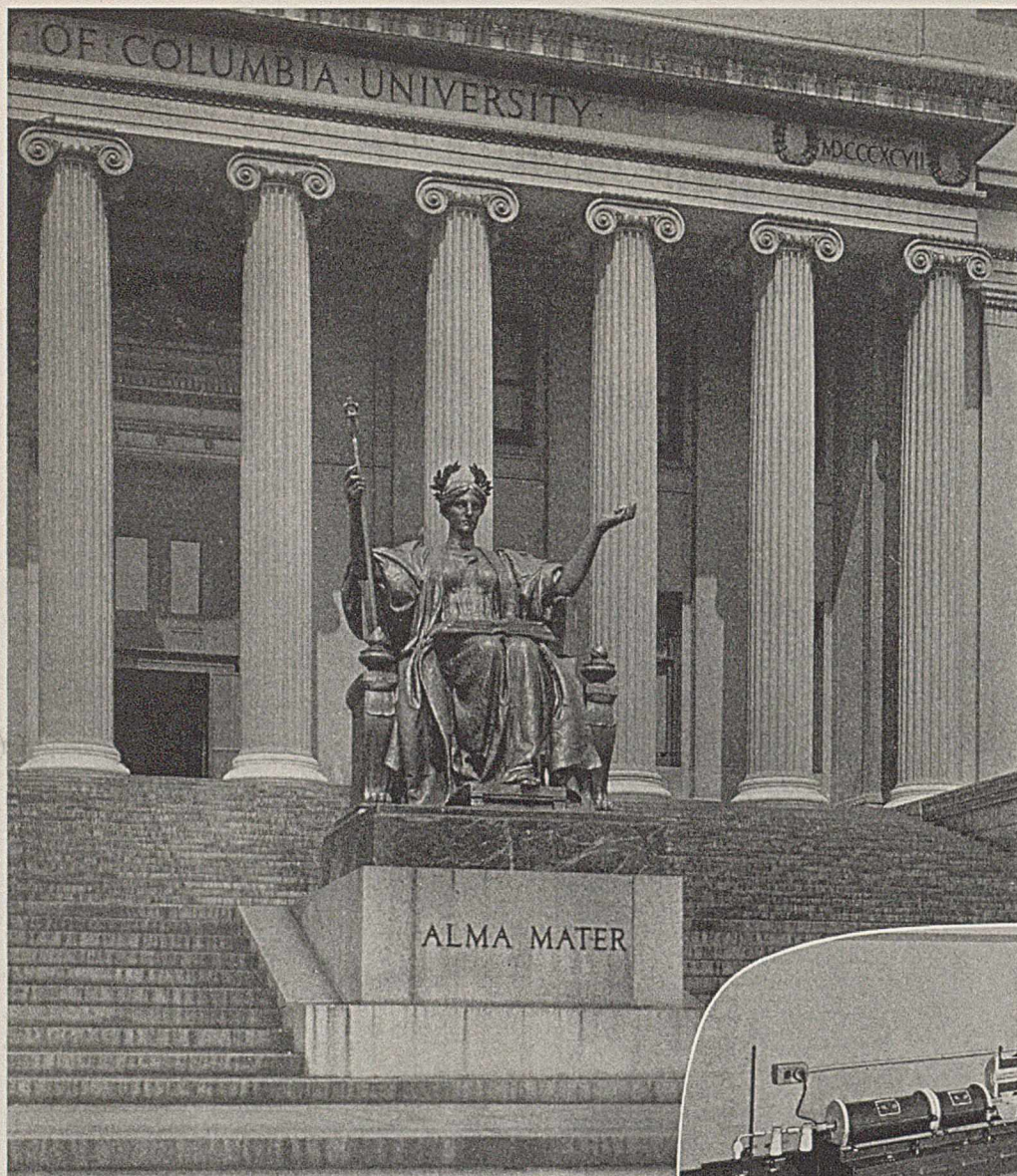
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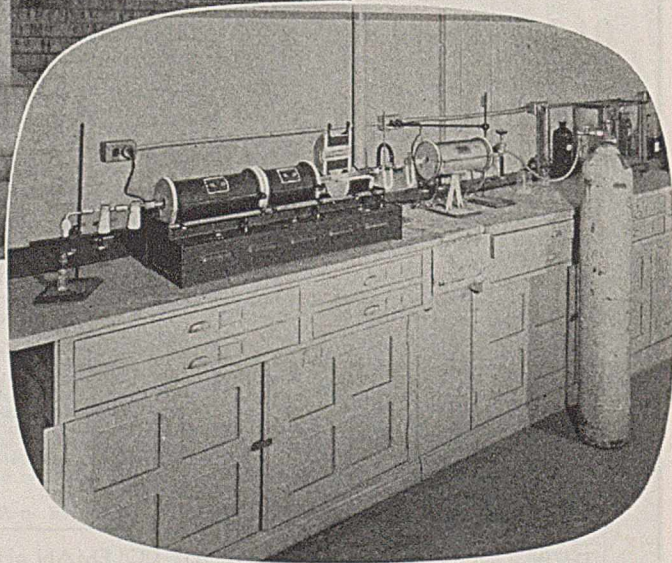
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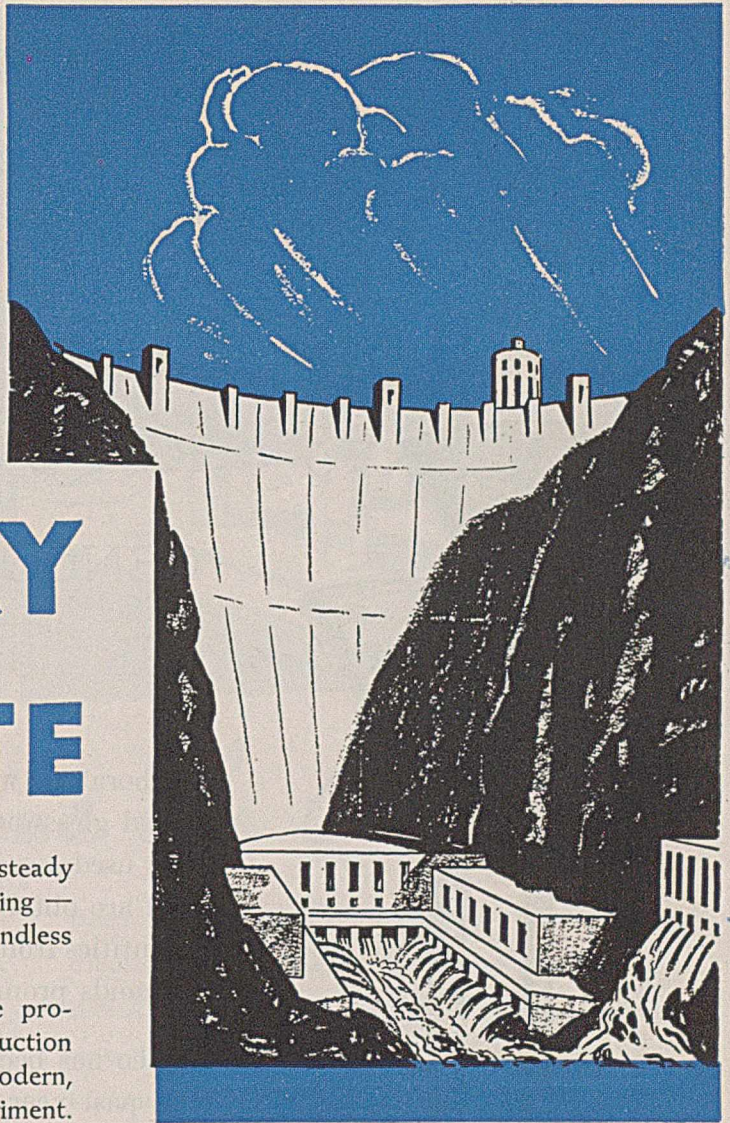
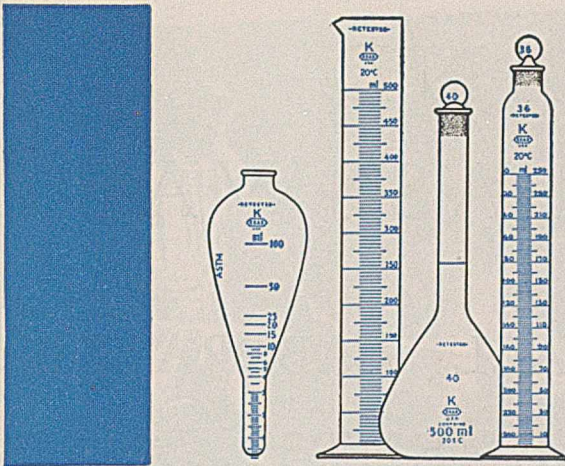


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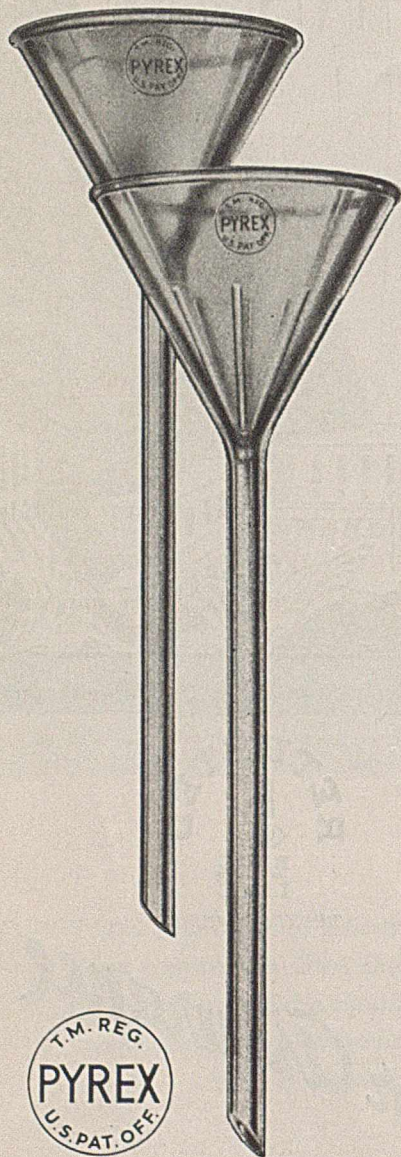
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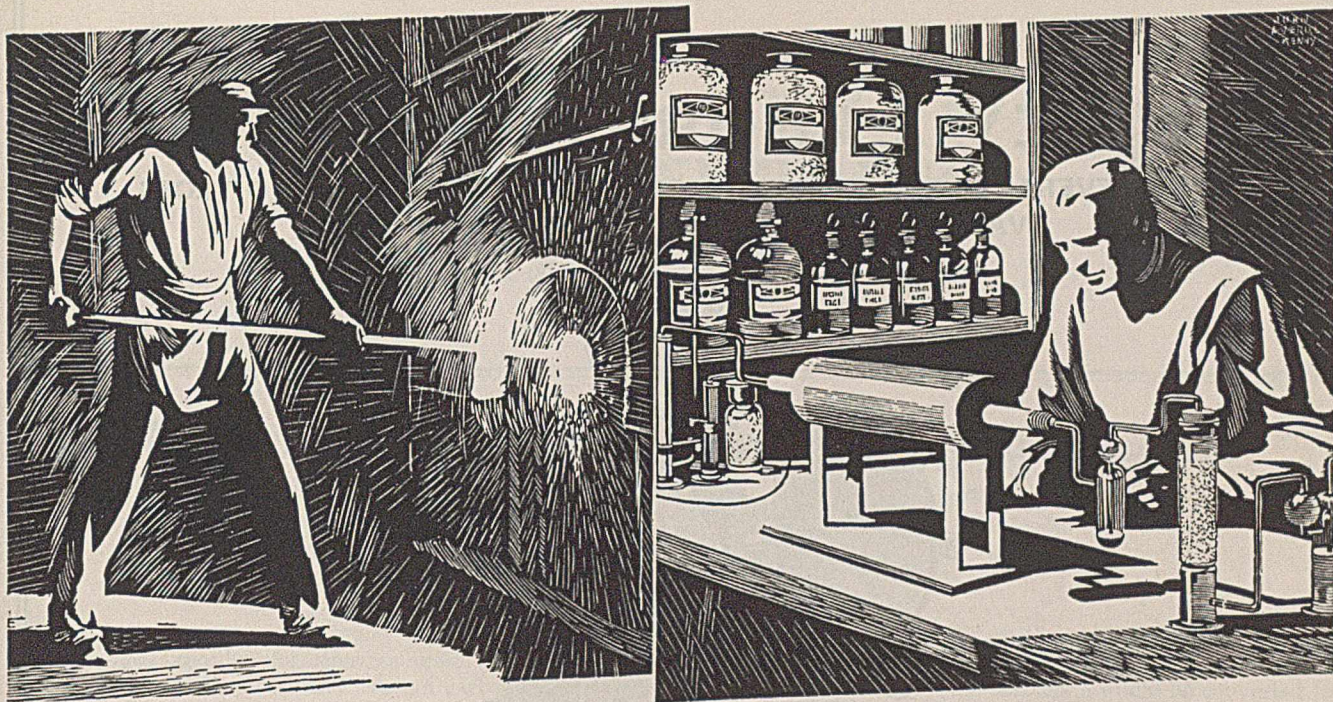
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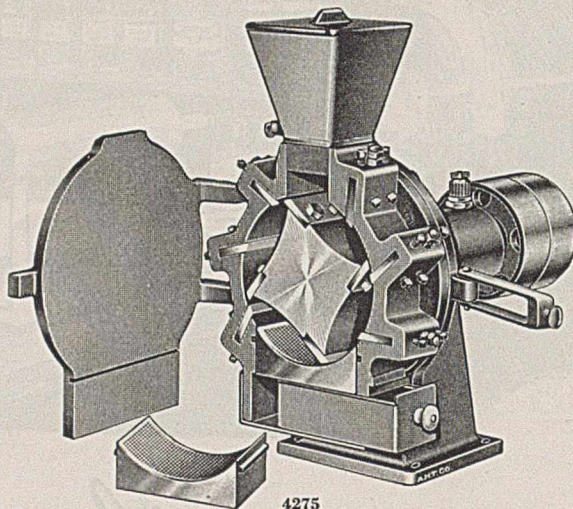
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Determining Ash in High-Carbonate Coals A Study of the Modified Method

O. W. REES, Illinois State Geological Survey, Urbana, Ill.

THIS paper presents the results of an investigation of a modified procedure for determining ash and mineral matter in coals high in pyrite and calcium carbonate, first proposed by S. W. Parr. This investigation was carried on to determine the causes of difficulties encountered in attempting to use this method as described, and, if possible, to find a way of eliminating them. Since the method has received widespread distribution in textbooks (2) and as a recommended optional procedure of the American Society for Testing Materials for determining the mineral matter content of high-sulfur, high-carbonate coals for classification purposes (1), it was deemed desirable to call the attention of the coal analyst to the fallacies involved in the procedure outlined and to recommended changes which would make it more reliable.

Samples which contain comparatively large amounts of both pyrite and carbonate are frequently encountered in coal analysis. These two minerals may undergo various reactions in the course of the regular determination of ash. Pyrite is mainly burned to ferric oxide and sulfur dioxide, but some may be oxidized to ferric sulfate, which on further heating will be decomposed to give ferric oxide with the loss of sulfur trioxide. Calcium carbonate may decompose to some extent to give calcium oxide and carbon dioxide and may react with pyrite to give calcium sulfide and ferric oxide with loss of carbon dioxide. The calcium sulfide so formed may be partially oxidized to calcium sulfate, while the calcium carbonate and oxide may react with sulfur dioxide and oxygen or with sulfur trioxide to form calcium sulfate. It is apparent that no definite composition will be reached by the usual ashing procedure and that some special procedure is necessary for samples containing high amounts of pyrite and carbonate.

As early as 1916 Parr (3), realizing these facts, published a special method for use in such cases. His method was based on

the idea that if the sample was first ashed as usual and then treated with a few drops of sulfuric acid all calcium sulfide, calcium oxide, and calcium carbonate would be converted to calcium sulfate and could be weighed as such, after careful removal of the excess sulfuric acid by heating at a definite temperature for a definite time. If the mineral carbon dioxide content of the sample was determined and if it was assumed that all mineral carbon dioxide was present as calcium carbonate, an assumption for which there is proof, it would be possible to calculate back to the calcium carbonate basis by subtracting three times the equivalent of carbon present as carbon dioxide from the ash as weighed. Parr (3) described his method as follows:

For coals whose mineral carbon dioxide values are large enough to call for correction, say up to 1 per cent or greater, the ash, after the preliminary burning off of the carbon and cooling, is moistened with a few drops of sulfuric acid (diluted 1 to 1) and again after drying brought up to 750° C. and retained at that temperature for 3 to 5 minutes. The capsule is cooled in a desiccator and weighed.

In the course of regular coal analysis in this laboratory the author encountered a series of samples having large amounts of both carbonate and pyrite. As it was evident that a special procedure was necessary, he attempted to use Parr's special method. Disconcerting discrepancies were found in the results obtained. In some cases these unit coal values by Parr's modified method differed to an unexpected degree from those calculated using regular ash values as bases for calculated mineral matter values. Furthermore, a comparison of these values with appropriate county average unit coal values showed them to be entirely too high.

Table I shows that the mineral matter values obtained by calculation (1.08 ash + 0.55 sulfur) from regularly determined ash values vary considerably from the values obtained by

TABLE I. COMPARATIVE VALUES

Lab. No.	Ash	Sulfur	CO ₂	Mineral Matter		Unit Coal Value		County Average Unit Coal Values
				Calculated from routine ash determination	Determined by Parr method	From calculated mineral matter value ^{a, b}	From Parr mineral matter determination ^b	
C-993	19.4	2.24	1.63	22.18	22.76	14744	14854	14690
C-994	11.0	1.68	0.48	12.80	13.22	14742	14814	14690
C-995	14.3	1.77	0.59	16.42	16.60	14786	14818	14690
C-996	19.7	1.97	1.81	22.36	23.19	14443	14599	14690
C-997	30.5	2.87	4.49	34.52	36.02	14515	14855	14690
C-998	36.5	3.95	3.93	41.59	41.79	14957	15008	14690

^a Routine ash to mineral matter. ^b CO₂ correction.

TABLE II. COMPARISON OF VALUES OBTAINED BY TWO DIFFERENT ANALYSTS

Lab. No.	Mineral Matter Values		Unit Coal Values (CO ₂ Correction)	
	1st analyst	2nd analyst	1st analyst	2nd analyst
C-993	22.76	21.94	14854	14700
C-994	13.22	12.71	14814	14727
C-995	16.60	17.13	14818	14912
C-996	23.19	22.30	14599	14431
C-997	36.02	36.68	14855	15010
C-998	41.79	42.19	15008	15112
Further Results on Samples C-997 and C-998				
C-997	36.21	36.29	14899	14918
C-998	41.98	42.01	15057	15065

Parr's modified method. This is especially true in sample C-997 and to a lesser extent in sample C-998, both of which are high in sulfur and carbon dioxide. Unit coal values calculated from the mineral matter values differ considerably. By use of the regular A. S. T. M. ash method, widely varying results were obtained on duplicate portions of the same samples.

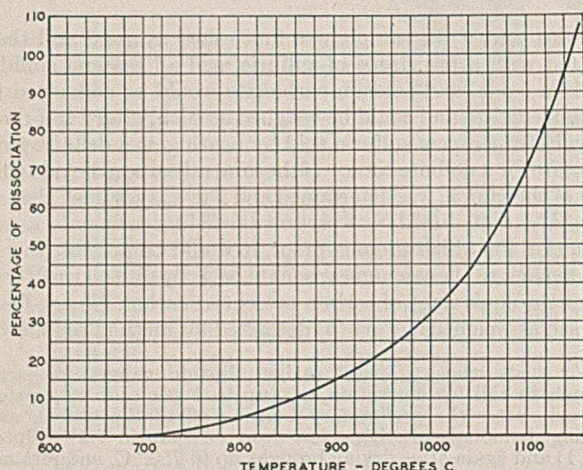


FIGURE 1. DISSOCIATION CURVE FOR CALCIUM SULFATE

Because of these discrepancies a second analyst was asked to check these determinations, using the modified ash determination method. Table II shows a comparison of these two sets of values, together with a comparison of unit coal values in whose calculation these two sets of mineral matter values were used. Deviations which are greater than desirable are noted in this table.

Because of these discrepancies it seemed advisable to study further the method recommended by Parr. Samples C-997 and C-998, which have the highest amounts of sulfur and mineral carbon dioxide, seemed to be best suited to such study.

In making unit coal calculations

$$[\text{Parr formula: } \frac{\text{B. t. u.} - 50S}{100 - (1.08 \text{ ash} + 0.55 \text{ sulfur})} \times 100]$$

three values are used—namely, calorific, sulfur, and mineral matter values. The mineral matter value is obtained either by calculation from the usual ash value (A. S. T. M. standard method) and sulfur value or by Parr's modified method of ash determination described above. The unit coal values in whose calculation mineral matter values obtained by the modified method had been used appeared to be too high. Since the determination of calorific and sulfur values is well standardized, the author suspected that this modified method of ash determination was giving high results.

In Parr's method as described above, the sulfuric acid which is added converts any calcium oxide or calcium sulfide to calcium sulfate, in which form it is weighed, and also con-

verts iron and aluminum oxides at least partially to sulfates. However, these should be quantitatively decomposed upon ignition to the oxides if the method is to give dependable results. Therefore, at the time of weighing the sample after the ignition following the acid treatment, the sulfate present should be exactly equivalent to the calcium present.

In order to see if the above condition held, two 1-gram samples of coal C-997 were treated by the Parr modified procedure and weighed. The ash was then extracted with hot 1 to 1 hydrochloric acid and determinations of calcium oxide and sulfate were made. The quantity of sulfate present was far in excess of that required for calcium sulfate by the calcium oxide found present.

This fact suggested that the heating period of 3 to 5 minutes was not sufficient to expel the excess sulfuric acid or to convert any iron and aluminum sulfates completely to the oxides. A longer heating period at 750° C. or a higher temperature should be used. However, in order to use either of these safely it is necessary to know their effect on the decomposition of calcium sulfate. If the procedure is to be usable at all, calcium sulfate must not be decomposed during the actual procedure and all other sulfates must be quantitatively decomposed. In this connection Parr (3) published some data on the decomposition of calcium sulfate at different temperatures, according to which the decomposition of calcium sulfate begins at about 700° C. and increases rapidly from 900° to 1100° C. He shows that calcium sulfate is decomposed to the extent of about 3.5 per cent at 750° C., while at 1050° C. the decomposition is about 48 per cent. Parr states that there were no values available on the vapor pressures at different temperatures for the decomposition of calcium sulfate, and that "from the decrease in the weight of ash and the corresponding decrease in sulfur trioxide a dissociation curve may be constructed" which he assumes to be the dissociation curve for calcium sulfate (Figure 1). From these data and the decomposition data for calcium carbonate Parr concluded that the sulfated ash should be heated above 700° C. but that

TABLE III. EFFECT OF HEATING CALCIUM SULFATE AT DIFFERENT TEMPERATURES FOR 4- AND 60-MINUTE PERIODS

Temperature ° C.	Loss in Weight						CaSO ₄ Decomposed ^a	
	4-Minute Periods			60-Minute Periods			4 min.	60 min.
	Sample 1	Sample 2	Av.	Sample 1	Sample 2	Av.	%	%
550	0.00	0.14	0.07	0.10	0.10	0.10	0.12	0.17
600	0.00	0.00	0.00	0.25	0.41	0.33	0.00	0.56
650	0.43	0.19	0.31	0.22	0.45	0.34	0.53	0.58
700	0.16	0.14	0.15	0.28	0.22	0.25	0.26	0.43
750	0.46	0.37	0.42	0.37	0.37	0.37	0.71	0.63
800	0.25	0.32	0.29	0.33	0.41	0.37	0.49	0.63
850	0.42	0.37	0.40	0.35	0.40	0.38	0.68	0.65
900	0.37	0.37	0.37	0.37	0.38	0.38	0.63	0.65
950	0.42	0.37	0.40	0.33	0.46	0.40	0.68	0.68
1000	0.38	0.37	0.38	0.37	0.54	0.46	0.65	0.78
1050	0.19	0.28	0.24	0.58	0.53	0.56	0.41	0.95
1100	0.89	0.85	0.87	1.32	1.41	1.37	1.48	2.33

^a Assuming losses in weight by heating due to loss of SO₂ from CaSO₄. Conversion factor 1.7005.

TABLE IV. EFFECT OF HEATING CALCIUM SULFATE AT 750° C. FOR DIFFERENT PERIODS OF TIME

Time of Heating Min.	Loss in Weight			CaSO ₄ Decomposed, Average ^a %
	Sample 1 %	Sample 2 %	Av. %	
4	0.33	0.43	0.38	0.65
8	0.57	0.43	0.50	0.85
12	0.51	0.47	0.49	0.83
16	0.52	0.42	0.47	0.80
20	0.52	0.42	0.47	0.80
24	0.37	0.38	0.38	0.65
28	0.42	0.37	0.40	0.68
32	0.47	0.38	0.42	0.71
36	0.47	0.42	0.45	0.77
60	0.47	0.37	0.42	0.71
80	0.69	0.57	0.63	1.07
110	0.36	0.43	0.40	0.68

^a Assuming losses in weight by heating due to loss of SO₂ from CaSO₄. Conversion factor 1.7005.

TABLE V. EFFECT OF HEAT (750° C.) ON SULFATED ASH

Time Heated Min.	Per Cent Sulfated Ash—Duplicate			Per Cent SO ₃ —Duplicate			Per Cent CaO—Duplicate			SO ₃ , Mole %	CaO, Mole %	SO ₃ /CaO Mole Ratio	Mineral Matter	Unit Coal
	determinations	Difference		determinations	Difference		determinations	Difference						
4	48.06, 43.72	4.34		20.45, 21.20	0.75		5.35, 5.32	0.03		0.2602	0.0952	2.7332	47.26	17,872
8	Av. 45.89 36.34, 37.17	0.83		20.83 8.49, 8.99	0.50		5.34 5.64, 5.54	0.10		0.1092	0.0997	1.0953	37.40	15,057
12	Av. 36.76 36.40, 36.30	0.10		8.74 8.34, 8.29	0.05		5.59 5.72, 5.70	0.02		0.1039	0.1018	1.0206	36.96	14,951
16	Av. 36.35 36.21, 36.46	0.25		8.32 8.29, 8.34	0.05		5.71 5.28, 5.84	0.56		0.1039	0.0991	1.0484	36.95	14,949
20	Av. 36.34 36.19, 35.43	0.76		8.32 8.19, 7.64	0.55		5.56 5.30, 6.00	0.70		0.0989	0.1007	0.9821	36.37	14,813
30	Av. 35.81 36.27, 36.25	0.02		7.92 7.84, 7.99	0.15		5.65 5.50, 4.98	0.52		0.0989	0.0934	1.0589	36.86	14,928
40	Av. 36.26		7.92 7.74,		5.24 5.40,		0.0967	0.0963	1.0042
60	Av. 36.11, 36.34 36.23	0.23		7.84, 7.84 7.84	0.00		5.36, 5.20 5.28	0.16		0.0979	0.0941	1.0404	36.83	14,921

it should not be heated too hot or too long because of the possibility of decomposing calcium sulfate. Therefore, he chose the arbitrary temperature of 750° C. and a heating period of 3 to 5 minutes.

This short heating period is evidently not sufficient to effect removal of excess sulfur trioxide. Before using a longer heating period it seemed best to check the effect of heat on calcium sulfate, varying the temperature and time of heating.

In Table III are given data for the decomposition of calcium sulfate from 550° to 1100° C., heating for 4- and 60-minute periods at each temperature. The calcium sulfate used in these experiments was Mallinckrodt reagent quality CaSO₄·2H₂O which had been heated to 500° C. in platinum to remove the water of crystallization.

In Table IV will be found data on the effect of heating pure calcium sulfate at 750° C. for increasing periods of time.

Table III indicates that calcium sulfate is decomposed only slightly even at temperatures up to 1100° C. and with heating periods of 4 or 60 minutes. When the differences obtained in duplicate determinations as shown in Table III are taken into account, the decomposition is small indeed. According to Parr's curve, data for which were obtained by heating samples of sulfated ash, calcium sulfate is dissociated to the extent of about 34 per cent at 1000° C. On the basis of the evidence obtained from the experiments on calcium sulfate and a knowledge of the composition of coal ash, the author believes that Parr's curve is not a dissociation curve for calcium sulfate but rather indicates the decomposition of iron and aluminum sulfates present in the ash after treatment with sulfuric acid. This curve is in accordance with the known dissociation data for iron sulfate.

In Table IV it will be noted that increasing the time of heating calcium sulfate does not result in material increase of decomposition. From these data it appears that increasing the temperature or the time of heating the sulfated ash would be perfectly safe and desirable. This is in accordance with the findings of Valdez and Camps-Campins (4), who studied the restandardization of the sulfated ash method for determining ash in sugar products.

In view of the above facts, the effect of increased heating periods at 750° C. on the sulfated ash of sample C-997 was studied. This coal had a moisture-free total sulfur value of 2.87 per cent, a moisture-free mineral-matter carbon dioxide value of 4.49 per cent, and a moisture-free calorific value of 9569 B. t. u. Eight 1-gram portions of this sample were ashed and treated with sulfuric acid in accordance with the procedure described by Parr. The first portion was heated 4 minutes, the second 8 minutes, and so on, up to 60 minutes. The samples so heated were first cooled and weighed to give sulfated ash values and then dissolved and analyzed for sulfur trioxide and calcium oxide. The molar ratios of these two constituents were calculated, as well as mineral matter values and unit coal values, using the mineral matter values so obtained.

In Table V the duplicates of the portion heated for 4 minutes show a large deviation, the molar ratio of sulfur trioxide

to calcium oxide is almost 3 to 1 (2.7332) whereas it should be 1 to 1, and the unit coal value calculated from the mineral matter so obtained is unreasonably high. The portion heated for 8 minutes shows a much smaller deviation between duplicates in per cent of sulfated ash, the molar ratio of sulfur trioxide to calcium oxide is only slightly greater than one (1.0953), and the calculated unit coal value is much more reasonable although possibly a little high yet. The portions which were heated 12 minutes and more in general show small deviations between duplicates in per cent of sulfated ash, the ratios of sulfur trioxide to calcium oxide are very close to one, and calculated unit coal values compare much more favorably with the county average value of 14,690 B. t. u. for this coal.

Conclusions

The following facts have been brought out by this investigation:

1. A heating period of 3 to 5 minutes at 750° as described by Parr is not sufficient to expel all sulfur trioxide in excess of that in calcium sulfate.
2. The so-called "dissociation curve for calcium sulfate" as published by Parr is not a dissociation curve for calcium sulfate. The loss may very probably be due to decomposition of iron and aluminum sulfates.
3. The dissociation of calcium sulfate is not materially increased by increased temperature from 750° to 1000° C. or by increased heating periods up to 110 minutes.
4. In making modified ash determinations on coal samples high in carbonate, Parr's procedure may be followed as far as the place where he directs that the sulfated ash be heated 3 to 5 minutes. Instead of heating as directed, the sulfated samples should be heated to constant weight, which should be reached in 15 to 20 minutes. This will ensure complete expulsion of excess sulfur trioxide.

Acknowledgment

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Scattering in the Near Infrared

A Measure of Particle Size and Size Distribution

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SINCE the reinforcing characteristics of pigments in rubber depend to a large extent upon their degree of fineness, there has been considerable interest in the measurement of the particle size of these materials. The principal methods which have been employed are: (1) the direct microscopic measurement, (2) the "count" method using the microscope with "dark field" illumination, (3) the indirect turbidimetric methods, and (4) the sedimentation rate and equilibrium sedimentation methods.

Present Methods of Measuring Particle Diameters

In the first of these methods, a minute amount of the material to be examined is dispersed in some mounting medium such as a melted gum or resin, on a microscope slide. A photograph may be made of the field and the actual diameter of each particle measured on an enlargement, or projection of the negative, or on a directly projected image. The principal advantage in this direct method of particle measurement is that it yields a size distribution curve and, therefore, is not restricted to a single average diameter. There are several objections to the method:

1. To obtain a satisfactory field for projection or photography, the mount should not be more than a few particles thick. This requires pressure on the cover glass or some other method of rubbing out the sample to a very thin layer and on such small amounts of material the procedure may result in a greater degree of deaggregation than it is possible to attain by the usual methods of commercial dispersion. According to the procedure of the individual investigator, all the aggregates in a sample may be broken up or only part of them. In most cases, the particle size as observed microscopically will be at considerable variance with the effective particle sizes in an oil or rubber dispersion. The fume products such as zinc oxide which are relatively free of aggregation will show this difference to a lesser degree than precipitated materials.

2. In the case of nonuniform materials, difficulty is experienced in bringing both coarse and fine particles into focus at the same time. The lack of uniformity experienced in many pigments makes the method extremely laborious because of the necessity of measuring a large number of particles in order to obtain truly representative data.

The dark-field count measurement of particle size as exemplified in the Goodyear method (2) gets away from the variations in grinding between the microscopic mount and actual application, since a rubber compound is used in making the counting suspension. However, this method gives only the diameter of the particle of average volume, D , from which the number of particles per gram may be calculated, but since no information as to size uniformity is obtained, the specific surface cannot be calculated. Its application is restricted to relatively fine and uniform pigments. In the case of samples which are relatively nonuniform, it has been shown (4) that the D diameter is of less significance in indicating the properties of a pigment in rubber than the diameter from which specific surface may be calculated, d_3 , or the diameter of the particle of average weight, d_4 . This is because the first

named fails to evaluate the coarse particles in the degree to which they affect the behavior of paint or rubber. The significance of the several average diameters has been covered extensively by Green (3).

The present methods of measuring the particle size and size distribution of powders are reviewed and the need of a new method is shown. Such a method, based upon the transmission of suspensions at various wave lengths in the visible and near infrared regions, is described. From the shape of the spectral transmission curve obtained, the relative average size and size distribution characteristics of powders can be estimated.

Wells (9) has given a résumé of the turbidimetric methods. The particle sizes of many of the pigments which are of interest in rubber and in paint are in the range where the turbidity or opacity of the suspension to visible radiation is due to both ordinary reflection and scattering phenomena. Since the two phenomena are affected by particle size in different ways, it is difficult to apply these methods to materials lying in the pigment range because of the complexities involved. Their

application is restricted because of the marked influence of size distribution characteristics, and the particle size information obtainable is limited. In the writers' laboratory, for example, one of these methods (7) has been used extensively on relatively fine zinc oxide but it has been possible to correlate the results only with the d_1 or arithmetical mean diameter, which is probably the least significant average diameter as far as rubber properties are concerned. Others working with coarser particles (1 micron or larger in average diameter), where the turbidity is due to simple reflection and depends on the projected area of the particles, have been successful in correlating with specific surface. The methods are indirect in that one of the direct methods must be used for standardization, and are limited to samples which are similar to the standards in their uniformity of particle size distribution. Unless a practical dispersion is used in preparing the suspension, it is open to the same objections as the microscopic method in that the degree of dispersion of the test suspension is not necessarily the same as obtained in actual compounding.

Ultracentrifugal methods as developed by Svedberg (8) and others (1) are at present the best of the sedimentation schemes, but the necessary equipment is so expensive that it may be enjoyed by only a very few laboratories. However, recent work by Hauser and Reed (5) using a cylindrical bowl supercentrifuge appears to be very promising.

From the above discussion it is obvious that a fairly rapid method of attaining size distribution characteristics of pigments in a state comparable with that prevailing in actual use is highly desirable.

Pfund (6) has proposed the adaptation of infrared scattering to this purpose and the present paper merely represents the application and extension of his work on scattering in the near infrared region.

Rayleigh's Law of Scattering and Interpretation of Experimental Data

The extent to which radiation incident upon a suspension of particles in a transparent medium is transmitted is determined by the optical constants of the particulate material and the medium, the size of the suspended particles, and the wave

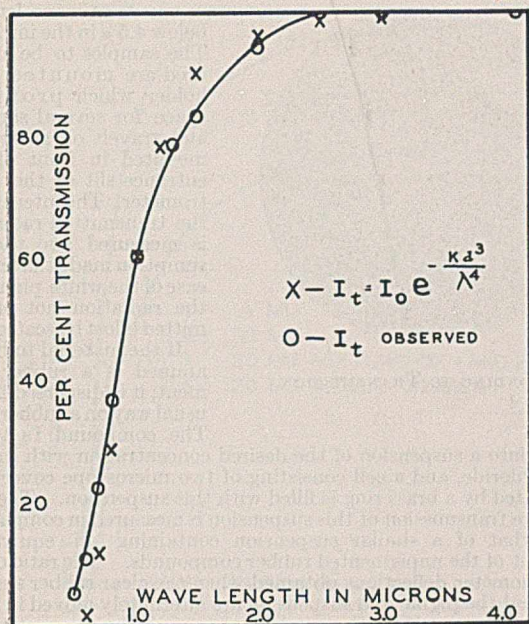


FIGURE 1. AGREEMENT BETWEEN CALCULATED AND OBSERVED TRANSMISSION

length of the radiation. The transparency of the suspension at various wave lengths and the degree to which transparency varies with the wave length yield information as to the average size and size distribution characteristics of the material. Rayleigh has worked out the form of the wave length-transmission curve for the case in which all particles present are small in comparison with the short wave length limit of the spectral range employed. This curve may be calculated from the well-known Rayleigh scattering law. The Rayleigh formula for the transmission of radiation through a scattering medium according to Wien-Harms (10) is:

$$I = I_0 \exp. - \left[\frac{8\pi^3}{3} \left(\frac{n^2 - n_0^2}{n_0^2} \right) \left(\frac{3n_0^2}{n^2 + 2n_0^2} \right) \frac{NV^2}{\lambda^4} \right]$$

where

- I = intensity of the transmitted radiation
- I_0 = intensity of the incident radiation
- n = refractive index of particle
- n_0 = refractive index of medium
- N = number of particles per cc.
- V = volume of each particle
- λ = wave length

By assuming the refractive index terms in the above equation as constant, and since the mass per unit volume or concentration, c , is equal to $N \cdot V \cdot \rho$ where ρ is the specific gravity of the particles, we may substitute $N \cdot V = \frac{C}{\rho}$ in the simplified exponent, $\frac{NV^2}{\lambda^4} K$, and obtain $\frac{CV}{\lambda^4} K$. At a constant concentration of one single pigment and considering the volume V as proportional to d^3 , where d is the diameter of an equivalent spherical particle, the equation becomes $I = I_0 \exp. - \left[\frac{Kd^3}{\lambda^4} \right]$. Thus the intensity of the transmitted radiation varies directly as the fourth power of the wave length and inversely as the third power of the particle diameter.

Figure 1 shows the experimental wave length-transmission curve for a uniform, fine particle size zinc oxide (0.3 micron) compared with that calculated from the above equation. Good agreement is obtained over the region in which the particle size-wave length relationships fulfill Rayleigh's assump-

tions. In calculating this curve, the value for the particle diameter was taken from a direct microscopic determination using the D diameter which is theoretically the diameter involved in the Rayleigh law. The constant K was calculated from the observed transmission at a wave length of 1.0 micron, a point at which the Rayleigh conditions should be fulfilled. It should be borne in mind that in extending the curve into the near infrared no corrections have been made for possible changes in the optical constants of the pigment and medium, and that the Rayleigh law should hold rigidly only when the ratio of the indices of refraction of the particle and medium approaches one.

When the Rayleigh conditions are not fulfilled and the particle size more closely approaches the wave length of the radiation, the transmission becomes less and less dependent upon the wave length, and when the particle becomes equal to or larger than the wave length it is no longer selective in its transmission characteristics and its opacity depends only upon the optical constants and the projected area of the particle.

The method employed here consists in merely measuring the spectral transmission of the pigment suspended in either oil or rubber from the visible blue to a wave length of about 4.0μ in the infrared. From the shape of this spectral transmission curve, the relative average size and size distribution characteristics can be estimated.

Typical transmission curves are shown in Figure 2. Low transmission in the short wave length region is indicative of small particle size and the greater the selectivity (slope of the transmission curve towards longer wave lengths) accompanying the low transmission the finer is the particle size. High transmission in the short wave length region without selectivity is indicative of coarse particle size. Low transmission in the long wave length region is also indicative of a large particle size. The average particle size of the pigment is roughly indicated by the point in the spectral transmission curve at which selectivity begins to develop. This occurs at a point where the particle size approaches the magnitude of the wave length.

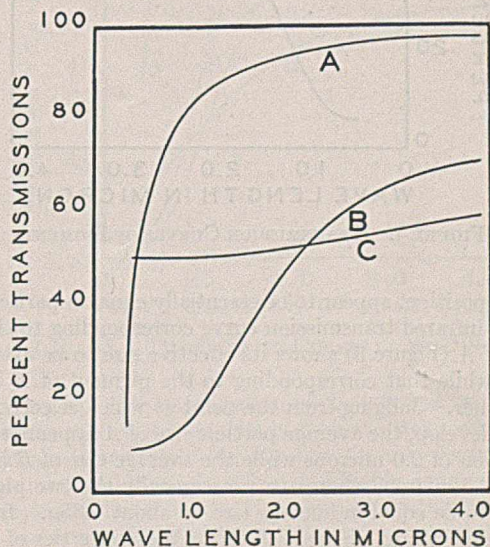


FIGURE 2. TYPICAL INFRARED TRANSMISSION CURVES

Curve A of Figure 2 represents a uniform material of extremely fine size, as indicated by the marked selectivity, high transmission at the long wave lengths, and low transmission at the extremely short wave lengths, the maximum opacity occurring at wave lengths shorter than those included in the illustration. Curve B represents a material of fairly small

average size, as indicated by low transmission and appreciable selectivity in the fairly short wave length region but containing a very appreciable portion of coarse material as indicated by the relatively low transmission in the long wave length region. Curve *C* represents a uniformly coarse material, as indicated by relatively high transmission in the short wave length region, nonselectivity in this same region, and relatively low transmission at long wave lengths.

An example of the differences which may exist between the particle size exhibited in a microscopic mount and that indicated by an infrared examination of the pigment in a practical grind is shown in the photomicrographs of Figure 3 and the corresponding infrared transmission curves of Figure 4. Microscopically, the two pigments, which have the same chemi-

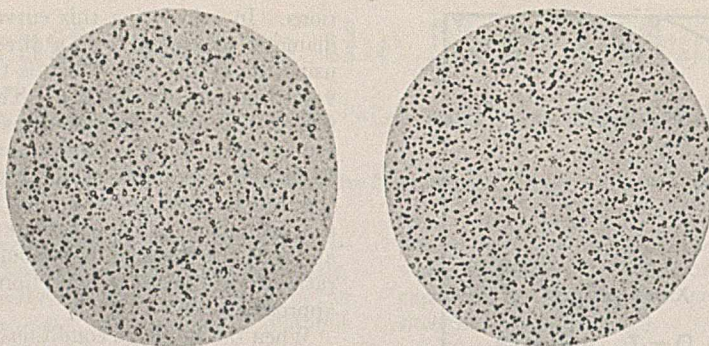


FIGURE 3. PHOTOMICROGRAPHS CORRESPONDING TO TRANSMISSION CURVES OF FIGURE 4

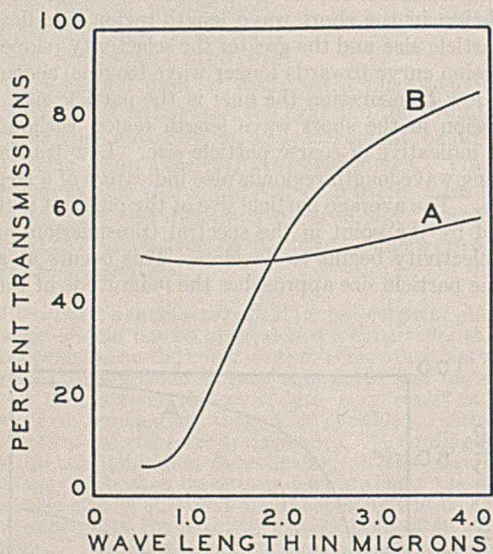


FIGURE 4. TRANSMISSION CURVES OF PIGMENTS

cal composition, appear to be essentially equal in particle size, yet the infrared transmission curve corresponding to the pigment of *A* (Figure 3) shows its effective size to be extremely coarse while that corresponding to the pigment of *B* is very much finer. Judging from the point at which selectivity began to develop, the average particle size of *A* appears to be in the region of 2.0 microns while the average size of *B* is more nearly 0.5 micron, whereas microscopically the two pigments appear to be equal in average size at about 0.35μ . In practical paint grinds, pigment *A* shows the properties of an extremely coarse pigment and *B* those of a much finer material. For example, *A* has a tinting strength of 70 per cent of a given standard and *B*, 120 per cent of the same standard.

Apparatus and Procedure

The usual type of rock salt prism spectrometer was employed in conjunction with a vacuum thermopile and suitable galvanometer for recording the energy transmitted. An ordinary single-filament automobile lamp is used as a source of radiation for meas-

urements at wave lengths below 4.5μ in the infrared. The samples to be measured are mounted in a holder which provides space for several samples and travels on a carriage mounted in front of the entrance slit of the spectrometer. The intensity of the transmitted radiation is measured and the assumption made that in the case of the white pigments the radiation not transmitted is lost by scattering.

If the material to be examined is a rubber pigment, it is dispersed in the usual way on a rubber mill. The compound is then

made into a suspension of the desired concentration with carbon tetrachloride, and a cell consisting of two microscope cover slips separated by a brass ring is filled with this suspension. The percentage transmission of this suspension is measured in comparison with that of a similar suspension containing an equivalent amount of the unpigmented rubber compounds. The ratio of the galvanometer deflections obtained when the clear rubber suspension and the pigmented suspension are alternately moved in front of the entrance slit of the spectrometer gives the per cent transmission. It is obvious that the thickness of the cover slips and of the separating rings must be controlled accurately. If the pigment to be measured is principally of interest in paint, it is made into a paint which is diluted with the particular vehicle to the appropriate concentration, depending largely on the refractive index of the pigment. The measurements are made in comparison with a cell filled with the clear vehicle as the standard. Films of dry powders may be studied by mulling in butyl alcohol, and spreading on plates of glass or rock salt in thin uniform layers, and many other variations in the preparation of the sample are possible.

Experimental Application

Figure 5 shows the infrared transmission curves for a series of zinc oxides of varying particle size. The curves are labeled with the particle size of the zinc oxides which were determined by the dark field count method on rubber suspensions. The transmission curves were measured on similar suspensions. The coarser oxides in this series were made by reheating the finest one. As the particle size increases, the opacity of the pigments in the visible spectrum increases and then decreases in accordance with the results of Stutz and

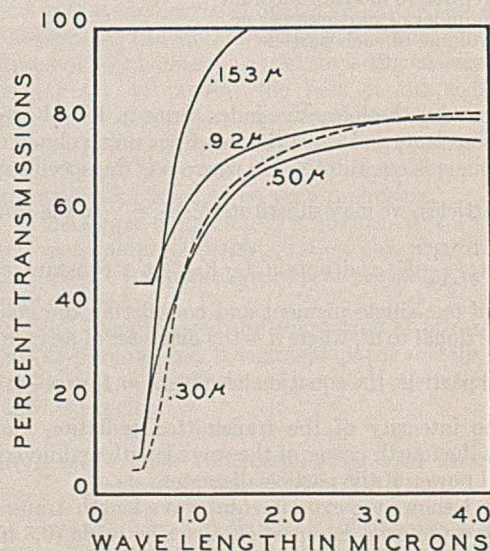


FIGURE 5. TRANSMISSION CURVES OF ZINC OXIDES

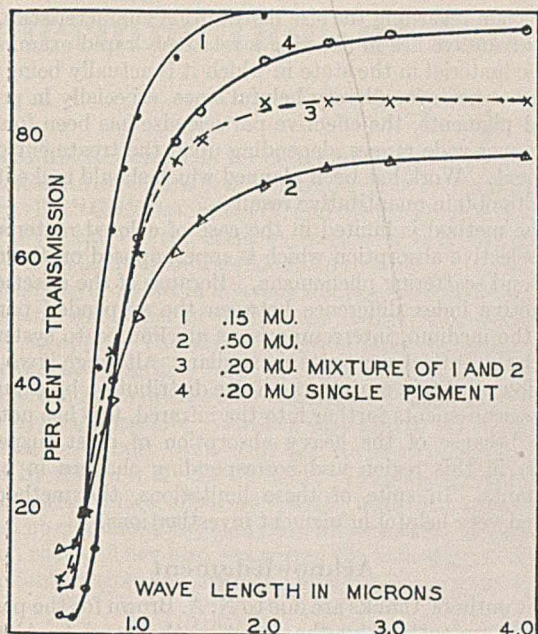


FIGURE 6. EFFECT OF MIXING MATERIALS OF DIFFERENT PARTICLE SIZE

Pfund (7). In the long wave length region, the three reheated oxides have approximately the same transmissions, indicating that there is a definite size limit beyond which the particles will not grow at a given temperature. All these curves show an unusually sharp break at the point where the transmissive characteristics of the pigment change from selective scattering to simple, nonselective reflection. The distinctiveness of this transition point is largely determined by the uniformity of particle size of the pigment and in this case the original zinc oxide was of a high degree of uniformity and was actually improved in this respect by the heat treatment.

Figure 6 shows the effect of mixing equal proportions of the oxides of 0.15 μ and 0.50 μ average diameters. By actual measurement the average particle size of this mixture in a rubber suspension was determined at 0.20 μ . This is in excellent agreement with the value of 0.19 μ , calculated from the

average diameters of the components of the mixture. However, this average diameter fails to indicate the presence of the coarse particles in the mixture which are clearly shown by the infrared transmission curve, particularly by the transmissions at the longer wave lengths. In fact, the radiation transmitted by the mixture is an approximate average of that transmitted by the separate components over the entire range of the curves. The transmission curve for a zinc oxide of the same average diameter as that of the mixture, but with a size distribution corresponding to that of the finest oxide, is included in Figure 6 for comparison. This curve parallels that for the zinc oxide of 0.15 μ average diameter but is slightly displaced towards longer wave lengths. That the coarse particles have a marked effect on the physical properties of rubber compounds is shown by the following data obtained in a formula containing 3 per cent of Hexa, 4 per cent of sulfur, 1 per cent of stearic acid, and 18.5 volumes of zinc oxide in addition to the rubber:

	Particle Size of Zinc Oxide μ	Tensile Strength Lb./sq. in.	Energy to Break Ft. lb./cu. in.	Tear Resistance	Abrasion Index
1	0.15	3750	898	325	162
2	0.50	1850	282	149	68
3	0.20 (mixture)	2415	349	262	94
4	0.20 (single pigment)	3800	579	331	150

Although the average diameter of the mixed oxide is close to that of the finest pigment in the series, the physical properties are not far from those of the coarse component and are very much poorer than those of the zinc oxide having the same average diameter but a much more uniform size distribution.

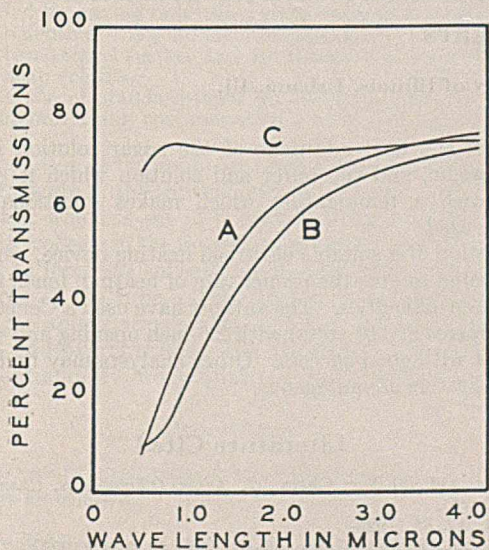


FIGURE 7. TRANSMISSION CURVES OF CARBON BLACK

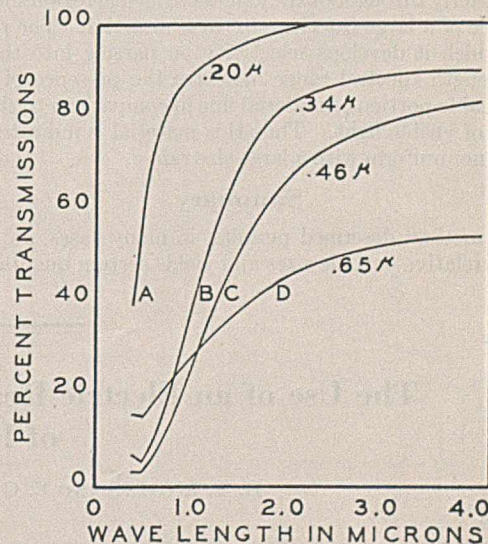


FIGURE 8. TRANSMISSION CURVES OF WHITINGS

Figure 7 shows the application of the infrared transmission method to rubber suspensions of carbon black. Curve A is for a channel process black, B a fine thermal decomposition black, and C an extremely coarse and highly aggregated thermal decomposition black. The physical properties of these three carbon blacks in rubber are in good agreement with the particle size characteristics as indicated by the infrared transmission curves. In a formula accelerated with diphenylguanidine and containing 25 volumes of each of the pigments, the following results were obtained at the optimum cures:

	Tensile Strength Lb./sq. in.	Work of Extension Ft. lb./cu. in.	Tear Resistance	Abrasion Resistance
A	4200	710	797	330
B	3070	565	338	95
C	2610	330	150	50

According to the above physical properties, pigments *A* and *B* are definitely reinforcing, while *C* has comparatively little reinforcing value. In the curves of Figure 7, *A* exhibits a high opacity in the visible spectrum, marked selectivity in this region, and a fairly high transmission in the infrared, all characteristics of a fine material. *B* is similar to *A* but with less opacity and less selectivity through the visible spectrum and slightly lower transmission in the long wave length region, while the selective portion of the curve is shifted slightly towards longer wave lengths. All these characteristics show that *B* has a larger effective average particle size and contains a greater proportion of very coarse particles than *A*. The curve for *C* shows a high transmission throughout the entire spectrum with no selectivity, indicating an extremely large effective particle size. The slope of curve *C* in the visible spectrum is due to superimposed selective absorption of light by the black.

In Figure 8 are given transmission curves for several whittings in rubber. The average diameters shown were determined by the count method on the same rubber suspensions from which the curves were obtained. The high transmission in the near infrared and the lack of opacity accompanied by marked selectivity in the shorter wave length region indicate *A* to be a fine material of high uniformity. *B* and *C* are coarser materials. Both exhibit very similar selectivity in the short wave length region but the appreciably greater opacity of *C* in the near infrared indicates that it differs from *B* in containing a larger fraction of coarse particles, which accounts for its somewhat larger average diameter. *D* is indicated to be a very nonuniform material. Its unusually high opacity throughout the long wave length region shows the presence of a large fraction of coarse material. The rapidity with which it develops selectivity on passing into the short wave length spectral range indicates the presence of a very appreciable portion of material fine in comparison to the wave length of visible light. Thus this material is indicated to be highly nonuniform with a large size range.

Summary

The method described permits, in many cases, an estimation of relative particle sizes and yields certain qualitative in-

formation regarding the size distribution characteristics. Its big advantage lies in allowing a relatively rapid examination of the material in the state in which it is actually being used. This has been found very helpful since, especially in precipitated pigments, the effective particle size has been found to vary over wide ranges, depending upon the treatment of the pigment. Work has been planned which should make it possible to obtain quantitative results.

The method is limited in the case of colored materials by the selective absorption which is superimposed on the reflection and scattering phenomena. Because of the effect of the refractive index difference between the suspended particles and the medium, intercomparisons are limited to systems in which the optical constants are similar. Although it would be possible to obtain more data on size distribution by extending the measurements further into the infrared, this has not been done because of the heavy absorption of most suspension media in this region and corresponding changes in optical constants. In spite of these limitations, the method has proved very helpful in pigment investigations.

Acknowledgment

The authors' thanks are due to N. A. Brown for the particle size determinations by the count method and to Albert J. Smith, R. J. Boyer, and John Fleming for assistance with the infrared transmission measurements.

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The Use of an Electric Heater for the Lane and Eynon Titration of Reducing Sugars

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SEVERAL years ago Lane and Eynon (3) proposed a method for the determination of reducing sugars, involving a complete reduction of a definite amount of Fehling's solution by a titrated volume of sugar solution, which can vary within certain limits. The end point is detected by means of methylene blue as the inside indicator. The method has been carefully studied (1, 2) and amplified, and on account of its rapidity is becoming widely used.

The solution is brought to a boil under carefully regulated temperature conditions and the final small quantity of sugar solution is added to the boiling reaction mixture. This makes necessary holding or supporting the buret over the reaction flask, which must be kept boiling gently to prevent atmospheric oxidation of the indicator after the end point is reached. When the flask is heated over a gas burner, as is ordinarily specified, the analyst must turn the flame high in order to maintain the desired temperature. Because of the stray heat coming up around the outside of the flask, manipulation of the

buret in the final additions of the sugar solution is often troublesome, and the buret and solution which it contains may reach a temperature which makes questionable the volume used.

Adoption of a suitable electrical heating device, which can be adjusted to give the proper rate of heating, tends to minimize these difficulties. The authors have used a Cenco heater (2.3 amperes at 110 volts) with 2.5-inch opening and variable rheostat with good success. Other analysts may find this or similar heaters advantageous.

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Determination of Unsaponifiable Matter in Rosin

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PUBLISHED methods for determining the unsaponifiable matter in rosin are few in number and of doubtful accuracy. Both Griffin's method (2) and the proposed A. S. T. M. method (1) call for the ether extraction of a dilute (2.5 to 5.0 per cent) solution of the saponified rosin soap. Rosin soap is strongly hydrolyzed in aqueous solution, and ether extracts appreciable quantities of resin acids and/or rosin soap from such a solution. The above methods make no attempt to remove these impurities from the ether solution. Moreover, the final residue is dried under conditions which cause serious losses by volatilization. Matlack and Palkin (3) recognized the presence of both resin acids and soaps in the residue obtained by the A. S. T. M. method. They washed the ether solution with dilute alkali and water until the wash water showed no cloudiness on acidifying, thus ensuring the absence of rosin soap. They also recognized the volatility of the unsaponifiable matter and dried the final residue in a vacuum at 70° C.

In the present study it has been found that even with the procedure of Matlack and Palkin the final residue contains an appreciable quantity of titratable acidity. On an average rosin this is equivalent to from 0.3 to 0.6 per cent of resin acids (calculated as abietic acid). In the method described below, the final residue, after weighing, is dissolved in neutral alcohol and titrated with standard alcoholic caustic alkali. The equivalent quantity of resin acid, calculated as abietic acid, is then deducted from the final residue to yield the net unsaponifiable matter in the rosin. This correction is similar to that recommended in the determination of the unsaponifiable matter in soap (5).

In order to ensure complete extraction of the unsaponifiable matter a continuous extractor was designed as shown in Figure 1. (This special piece was constructed from Pyrex glass by the Scientific Glass Apparatus Co., Bloomfield, N. J. The Erlenmeyer flask and reflux condenser, shown in Figure 2, each with a standard-taper ground-glass connection, were stock items obtained from the same company.) This is similar to the apparatus described by Palkin, Murray, and Watkins (4), with the following modifications:

1. The construction of the inner tube or solvent distributor is simplified by having only three small holes in the bulb.
2. The depth of the soap layer is increased so that the droplets of solvent travel further and are therefore in longer contact with the soap solution.
3. The use of standard-taper ground-glass joints is advantageous in preventing contamination and loss of solvent.

The operation of the extractor needs little explanation. As shown in Figure 2, the solvent (ether) is placed in the Erlenmeyer flask which is set in a beaker of warm water. The condensate collects in the inner tube until the "head" becomes sufficient to force the solvent out through the small holes at the bottom of the tube. The droplets of solvent then rise through the aqueous rosin soap solution, collect in a layer above it, and overflow back into the flask. Thus the rosin soap is continuously brought into contact with fresh solvent.

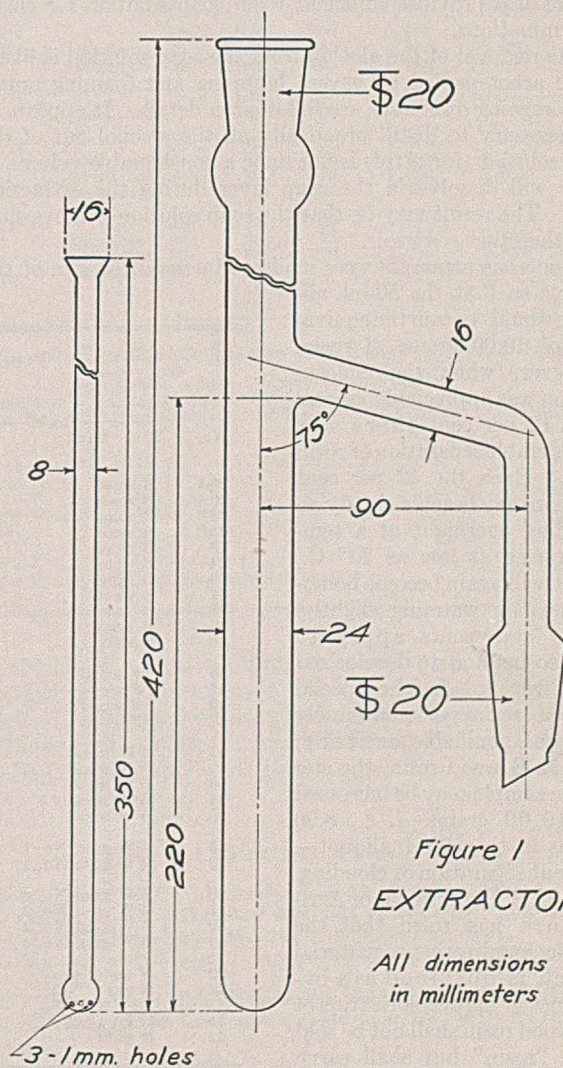
Procedure

The necessary preliminary saponification of the rosin is conducted as follows:

Dissolve 30.00 grams of rosin in 200 ml. of anhydrous alcohol in a 500-ml. round-bottomed flask, and to the slightly cooled

solution add 6.0 ml. of 50 per cent sodium hydroxide solution (sp. gr. 1.52). Boil gently under a reflux condenser for 1.5 hours and then add 150 ml. of water together with an ebullition tube. Set the flask in an oil or glycerol bath and connect it to a condenser. Hold the temperature in the bath at 120° to 130° C. until the total volume of the distillate amounts to 210 ml. Transfer the rosin soap solution quantitatively to a 250-ml. volumetric flask, cool, and dilute to the mark with distilled water.

To obtain the unsaponifiable matter, pipet a 50-ml. aliquot into the extractor. Place 100 ml. of ethyl ether in the Erlenmeyer flask, connect it to the extractor, and set it in a water bath which is maintained at 50° to 55° C. by an electric hot plate. Continue the extraction for 6 hours with the reflux rate approximately 3 drops per second. Pour the ether solution into a 500-ml. Squibb separatory funnel and rinse out the flask with two 15-ml. portions of fresh ether. Shake thoroughly with 50 ml. of 1 per cent sodium hydroxide solution. Draw off the aqueous layer into a second separatory funnel and to it add 30 ml. of fresh ether; shake thoroughly and discard the aqueous layer. Run the ether back into the first separatory funnel and wash the combined ether solutions three times with 50-ml. portions of distilled water. Run the washed ether solution into a carefully tared 250-ml. flask, rinsing the separatory funnel with 15 ml. of fresh ether. Immerse the flask in a water bath and distill off the ether. Then raise the temperature of the water to 67° to 70° C. and maintain a vacuum of 20 to 25 mm. of mercury for 30 minutes. Remove the flask, cool, and weigh. The material recovered is the "net washed extract." Dissolve



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TABLE I. EFFECT OF WASHING THE ETHER EXTRACT

No.	Rosin		Apparatus	Solvent	Gross Extract		Net Washed Extract		Loss on Washing
	Kind	Grams			Grams	%	Grams	%	%
1902	B wood	10.00	Funnels 6X	Ethyl ether	2.303	23.03	1.817	18.17	4.86
4910	B wood	10.00	Continuous	Ethyl ether	2.569	25.69	2.030	20.30	5.39
4911	B wood	10.00	Continuous	Ethyl ether	2.652	26.52	2.066	20.66	5.86
5915	B wood	10.00	Continuous	Petroleum ether	1.295	12.95	1.165	11.65	1.30
1904	B wood	10.00	Continuous	Toluene	2.230	22.30	1.871	18.71	3.59

it in about 40 ml. of neutral alcohol and titrate with standard alcoholic potassium hydroxide (preferably 0.1 N), to a phenolphthalein end point.

$$\frac{(\text{Weight of net washed extract}) \times 100}{\text{Weight of rosin in aliquot} (= 6.00)} = \% \text{ of extract, } E$$

$$\frac{(\text{Ml. of standard alkali}) \times \text{normality} \times 30.2}{\text{Weight of rosin in aliquot} (= 6.00)} = \% \text{ of abietic acid, } A$$

Then

$$E - A = \% \text{ of unsaponifiable matter}$$

Discussion

It was very difficult to obtain satisfactory results when individual samples were saponified and extracted, chiefly because of the difficulty of transferring the rosin soap solution into the extractor quantitatively without using too large a volume of water. The procedure was greatly simplified by saponifying a large sample and transferring aliquot portions of the soap solution to the extractor by means of a pipet. This procedure also provides sufficient rosin soap solution for check determinations.

The removal of the alcohol from the soap solution is likely to be accompanied by severe bumping and foaming unless the foregoing directions are followed in detail. It appears to be necessary to distill practically all the alcohol out of the soap solution, for if this is not done a considerable volume of ether will dissolve in the soap layer during the extraction step. The result may be that the soap solution will overflow into the ether reservoir.

Numerous attempts were made to increase the size of the sample so that the 50-ml. aliquots would contain the equivalent of 10.00 grams of rosin. However, when the concentration was appreciably greater than 12 per cent there was considerable separation of rosin soap. Even the 12 per cent solution may become cloudy on standing overnight at a temperature as low as 20° C., but it will again become homogeneous on warming slightly. These statements apply to gum rosins and to decolorized wood rosins. In the special case of rosins of abnormally high unsaponifiable content, such as B wood resin, the size of the sample may be increased to 40.00 grams—i. e., 8.00 grams in the 50-ml. aliquot—without separation or clouding. (The U. S. Department of Agriculture has ruled that the dark-colored resinous material which is obtained as a by-product in the decolorization of FF wood rosin shall not be sold as a "rosin" but shall carry

the special designation "B wood resin.")

The time required for complete extraction varies somewhat with the kind of rosin. Tests made with WW gum and WW wood rosins showed practically complete extraction in 3 hours; continued extraction with fresh ether for an additional 8 hours showed only 0.10 to 0.15 per cent net extract. But with B wood resin this additional extraction time yielded more than 1.0 per cent net extract. With this special resin the extraction should be run for at least 10 hours.

As to the choice of solvent, Tables I and II show unmistakably that ethyl ether is superior to petroleum ether. While petroleum ether does not extract as large a proportion of resin acids and/or soaps as does ethyl ether, it does not extract all of the unsaponifiable matter, especially from the lower grades of rosin such as FF rosin and B wood resin. Ethyl ether appears to be generally applicable to all kinds of rosin. A few extractions were made with benzene. This solvent appears to be satisfactory on dark rosin, but on the pale grades it yields low results and produces troublesome emulsions.

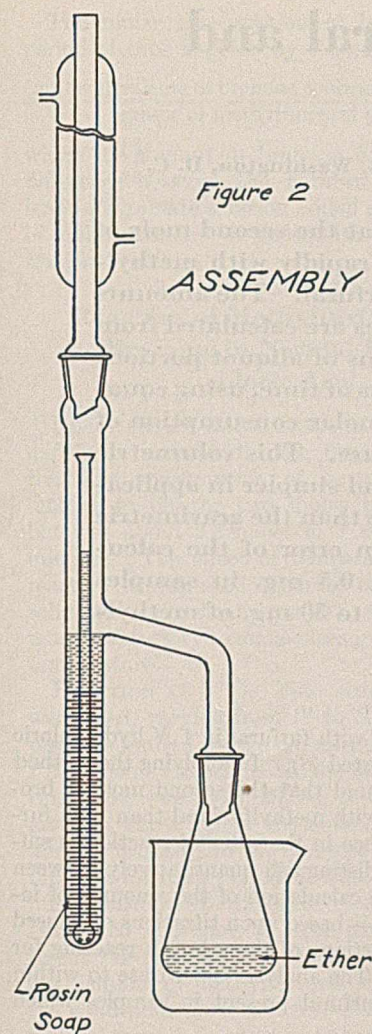
The necessity for washing the ether extract to remove resin acids and/or soaps is shown by Table I. In these runs the ether solution was evaporated directly and weighed to give the gross extract (column 5). This was then redissolved in ether and the solution was washed with dilute alkali and water (as described above) and again evaporated and dried to give the net washed extract (column 6). It is evident from these results that the omission of the washing yields extremely high results.

Very little trouble has been experienced with emulsions in the washing of these ether solutions. In those few cases where an emulsion was formed, the addition of a few cubic centimeters of 1 per cent sodium hydroxide solution caused the emulsion to break quickly and completely.

The data show that the separatory-funnel method does not ex-

TABLE II. UNSAPONIFIABLE MATTER IN VARIOUS ROSINS

No.	Rosin		Apparatus	Solvent	Net Washed Extract		Titratable Acids (Calcd. as Abietic)	Net Unsaponifiable Matter
	Kind	Grams			Grams	%		
28A	B wood	8.00	Funnels 3X	Ethyl ether	1.488	18.60
29A	B wood	8.00	Funnels 3X	Ethyl ether	1.568	19.60
28B	B wood	8.00	Funnels 6X	Ethyl ether	1.718	21.47	0.67	20.80
29B	B wood	8.00	Funnels 6X	Ethyl ether	1.725	21.56	0.67	20.89
19	B wood	8.00	Continuous	Ethyl ether	1.808	22.60	1.00	21.60
24	B wood	8.00	Continuous	Ethyl ether	1.800	22.50	0.79	21.71
30	B wood	8.00	Continuous	Ethyl ether	1.840	22.62	0.88	21.74
37	B wood	8.00	Continuous	Petroleum ether	1.330	16.62	0.50	16.12
38	B wood	8.00	Continuous	Petroleum ether	1.332	15.65	0.40	16.25
35	B wood	8.00	Continuous	Benzene	1.784	22.30	0.70	21.60
36	B wood	8.00	Continuous	Benzene	1.777	22.46	0.80	21.66
14	FF wood	8.00	Continuous	Ethyl ether	1.100	13.75	0.75	13.00
15	FF wood	8.00	Continuous	Ethyl ether	1.094	13.67	0.67	13.00
16	FF wood	8.00	Continuous	Petroleum ether	0.836	10.45	0.11	10.34
17	FF wood	8.00	Continuous	Petroleum ether	0.845	10.56	0.06	10.50
01	WW wood	6.00	Continuous	Ethyl ether	0.555	9.25	0.27	8.98
02	WW wood	6.00	Continuous	Ethyl ether	0.540	9.00	0.18	8.82
03	WW wood	6.00	Continuous	Petroleum ether	0.536	8.93	0.10	8.83
04	WW wood	6.00	Continuous	Petroleum ether	0.526	8.77	0.09	8.68
05	WW wood	6.00	Continuous	Benzene	0.491	8.18	0.09	8.09
06	WW gum No. 1	7.50	Continuous	Ethyl ether	0.888	11.84	0.31	11.53
13	WW gum No. 1	7.50	Continuous	Ethyl ether	0.888	11.84	0.34	11.50
26	WW gum No. 2	6.00	Continuous	Ethyl ether	0.657	10.95	0.31	10.64
27	WW gum No. 2	6.00	Continuous	Ethyl ether	0.675	11.25	0.45	10.80
39	WW gum No. 2	6.00	Continuous	Benzene	0.520	8.67	0.15	8.52
40	WW gum No. 2	6.00	Continuous	Benzene	0.504	8.40	0.10	8.30
20	N gum	6.00	Continuous	Ethyl ether	0.609	10.15	0.36	9.79
22	N gum	6.00	Continuous	Ethyl ether	0.612	10.20	0.52	9.68
31	H gum	6.00	Continuous	Ethyl ether	0.685	11.42	0.89	10.53
32	H gum	6.00	Continuous	Ethyl ether	0.675	11.25	0.59	10.66



tract all the unsaponifiable matter. Even when the rosin soap solution is shaken out with ether six times, instead of the customary three times, the quantity of neutral material extracted (Nos. 28B and 29B in Table II) is distinctly lower than that obtained by the continuous extractor (No. 30) on an aliquot of the same soap solution.

The unsaponifiable matter in rosin is distinctly volatile at 100° C., and special precautions must be taken in drying it. The data in Table III show the losses on drying various samples under different conditions. The loss in the oven at 105° C. (No. 78) is obviously excessive. A moderate vacuum at 100° C. (No. 11) produces a similar loss in weight. A high vacuum at temperatures above 75° C. (No. 14) is also too severe. The best results were obtained with a vacuum of 23 mm. at a tem-

peratures do not appear to be related either to the source or the grade of the rosin. It is possible that in certain rosins the presence of resin acids having a molecular weight lower than that of abietic acid may be partly responsible. This is not the whole explanation, however, for if it were, B wood resin should show the greatest difference; actually it shows the least. Matlack and Palkin (3) found a somewhat similar anomaly which they could not explain.

Acknowledgment

Grateful acknowledgment is made to R. C. Palmer, chief chemist of Newport Industries, Inc., for many helpful suggestions, and also to the management of Newport Industries for permission to publish the results of this investigation.

Summary

In determining the unsaponifiable matter in rosin, data show that the results obtained by previously published methods are not accurate. A method is described which eliminates many of the sources of error in these former methods. The use of a continuous extractor of special design, requiring a

TABLE III. LOSSES ON DRYING UNSAPONIFIABLE MATTER

No.	Drying Time Min.	Temp. ° C.	Pressure Mm. Hg	Net Weight Gram	Loss in Weight	
					During period Gram	Total Gram
78	20	100	300	0.991
	Additional 30	105	762	0.956	0.035	0.035
	Additional 60	105	762	0.919	0.037	0.072
11	20	100	300	0.825
	Additional 30	100	300	0.793	0.032	0.032
14	30	72	23	1.100
	Additional 30	77	23	1.069	0.031	0.031
	Additional 30	76	23	1.056	0.013	0.044
	Additional 30	73	23	1.048	0.008	0.052
15	30	70	23	1.100
	Additional 30	68	23	1.097	0.003	0.003
	Additional 30	68	23	1.095	0.002	0.005
	Additional 30	65	23	1.094	0.001	0.006

TABLE IV. COMPARISON OF FOUND AND CALCULATED VALUES FOR UNSAPONIFIABLE MATTER

Rosin	Acid No.	Saponifica- tion No.	Abietic Acid	Unsaponifiable Matter		Difference %
			Calculated as Saponifiable %	Calculated by difference %	Found ^a %	
B wood	108	144	77.70	22.30	21.68	0.38
FF wood	153	169	91.10	8.90	13.00	4.10
WW wood	168.0	170.5	91.91	8.09	8.90	0.81
WW gum No. 1	159.8	168.4	90.78	9.22	11.51	2.29
WW gum No. 2	157.6	167.0	90.03	9.97	10.72	0.75
N gum	160.3	174.2	93.91	6.09	9.73	3.64
H gum	160.1	168.3	90.68	9.32	10.60	1.28

^a Mean values from Table II obtained with ethyl ether in the continuous extractor.

perature under 70° C. as shown in No. 15, but even under these conditions the residue could not be dried to a constant weight. At lower temperatures (60° C.) there was a tendency for droplets of water to remain under the residue, making it impossible to obtain an accurate result. It was finally decided to dry the residue for 30 minutes under a 20- to 25-mm. vacuum at a temperature of 67° to 70° C. in the water bath. Under these more or less arbitrary conditions satisfactory check determinations were obtained, as shown in Table II.

The saponification number of a rosin is the number of milligrams of potassium hydroxide required to saponify one gram of rosin. This can, of course, be expressed as a percentage of abietic acid (molecular weight 302). It would seem as if the difference between this percentage and 100 might be a rough approximation of the unsaponifiable matter in the rosin, but the data presented in Table IV show that such an assumption is incorrect. The saponification number of each of the rosins used in this study was determined and then the unsaponifiable matter was calculated by difference (column 5). The results show very poor correlation with the percentages actually found by analysis (column 6). The

minimum of attention during the ether extraction, offers a marked improvement over the tedious separatory-funnel method. The method described shows a reproducibility of 0.25 per cent or better on check determinations, and appears to be generally applicable to the commercial grades of both gum and wood rosin.

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Analysis of Mixtures of Furfural and Methylfurfural

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The estimation of pentosans and methylpentosans in natural products is based upon the amount of furfural and methylfurfural which they yield upon distillation with 12 per cent hydrochloric acid. It is difficult to distinguish between these aldehydes because of the similarity of their chemical and physical behaviors. The gravimetric procedure usually employed is not satisfactory. No volumetric procedure which can be applied to mixtures of the two has been reported.

In studying the reaction of bromine with methylfurfural in 1 *N* hydrochloric acid at

0° C., it was found that the second mole of bromine reacts more rapidly with methylfurfural than with furfural. The amounts of individual aldehydes are calculated from the results of titrations of aliquot portions at two different periods of time, using equations expressing the molar consumption of bromine by the mixture. This volumetric method has been found simpler in application and more reliable than the gravimetric procedure. The mean error of the calculated values is about 0.5 mg. in samples which contain from 3 to 50 mg. of methylfurfural.

THE pentosans and methylpentosans, together with some hexose derivatives present in natural products, yield furfural, methylfurfural, and ω -hydroxymethylfurfural upon distillation with mineral acids. It is difficult to distinguish between these distillation products because of the similarity of their chemical and physical behaviors. When pentosans are determined in wood, methylfurfural may be present in the distillate up to about 5 per cent of the furfural. One to 2 per cent of ω -hydroxymethylfurfural may be slowly formed from hexoses, starch, and cellulose, and may be a cause of error in the pentosan determination. This error may be largely avoided if the distillation is stopped when there is no appreciable further evolution of furfural, as indicated by the aniline acetate test. The production of furfural is rapid and is almost completed before much ω -hydroxymethylfurfural is collected in the distillate.

No accurate method for determination of mixtures of furfural and methylfurfural has been reported. Both may be determined gravimetrically by using phloroglucinol (1), thiobarbituric acid (4), or better, 2,4-dinitrophenylhydrazine (10, 15, 18). In working with pure methylfurfural distilled from rhamnose it was found that the methylfurfural phloroglucide was more soluble in hot ethyl alcohol than the furfural phloroglucide (5, 6, 19). The usual method of determination of pentosans includes an extraction of the phloroglucides, using Krober's tables (11) for solubility corrections. The method, which is long and tedious, is not satisfactory as a means of determining these aldehydes in mixtures because investigators are not in agreement on the empirical correction factors (4, 7, 10).

Furfural has been determined volumetrically with such reagents as hydroxylamine, potassium bisulfite, and phenylhydrazine, and more successfully by various modifications of the excess bromine method (8, 12, 13, 14). Attempts which have been made to apply volumetric methods to methylfurfural have been without success (10, 12).

Other investigators have studied colorimetric and volumetric procedures, and the effect of methylfurfural and ω -hydroxymethylfurfural on the pentosan determination (2). Most of the methods are discussed by Dorée (3) and Schorger (17). The large error in the determination of furfural when methylfurfural is present has been considered unavoidable.

The reaction of bromine with furfural in 1 *N* hydrochloric acid at 0° C. has been reported (8). In applying the method to methylfurfural it was found that the second mole of bromine reacts more rapidly with methylfurfural than with furfural, and that the difference in the rates of reaction is sufficiently large at 0° C. to distinguish quantitatively between these two aldehydes. The calculation of the amounts of individual aldehydes present is based upon titrations of unused bromine in two aliquot portions of the solution reacting for different periods of time. The analysis is accurate to within about 0.5 mg. of methylfurfural present in samples which contain from 3 to 50 mg.

Experimental Procedure

Methylfurfural was prepared from sucrose by the method of Rinkes (16). It distilled at 86–7° C. at 21 mm. and gave quantitative precipitation with thiobarbituric acid and 2, 4-dinitrophenylhydrazine.

The procedure was the same as that used in experiments on furfural (8). The freshly distilled methylfurfural was sealed in glass bulbs to prevent oxidation of the aldehyde and loss in weighing. Solutions were prepared by breaking the weighed bulbs under water in a volumetric flask and aliquot portions were withdrawn by means of pipets. The methylfurfural solution was added to 200 ml. of 1 *N* hydrochloric acid in a special side-arm titration flask, a sketch of which was given in an earlier paper (9). One arm of the flask contained 25 ml. of approximately 0.1 *N* potassium bromate-bromide solution and the other arm contained 10 ml. of approximately 10 per cent potassium iodide solution. Several flasks were prepared with reagents for each series of experiments. The titration flasks were modified by attaching to each ground-glass stopper a thermometer well which extended into the solution. By this means the temperature may be observed without opening the flask.

In these experiments an ice bath was used to cool the solutions. About 0.5 hour was required for them to attain a temperature of 0° to 0.5° C., which was maintained throughout the reaction. Shaved ice may be used to cool the solutions more quickly or they may be placed in a refrigerator regulated at 0° C. The reaction was timed with a stop watch which was started when the bromate solution began to flow from the side arm into the methylfurfural and hydrochloric acid solution. At the end of the desired period of time the potassium iodide solution was added from the other side arm and the flask shaken to ensure complete absorption of bromine vapor. The iodine thus liberated was titrated with 0.1 *N* sodium thiosulfate using starch as an indicator. Blanks were run in a similar manner.

The molar consumption of bromine at any period of time is given by the expression

$$\frac{(\text{milliequivalents of bromine consumed}) \times (0.05505)}{\text{grams of methylfurfural present}}$$

where the amount of bromine consumed is the difference between the number of milliequivalents of bromate solution added and the number of milliequivalents of thiosulfate used in the titration.

Reaction of Methylfurfural with Bromine in Normal Hydrochloric Acid

REACTION AT ROOM TEMPERATURE. Preliminary experiments at room temperature showed that the consumption of bromine was not limited to one or two moles per mole of methylfurfural, but was about 2.3 moles in 1 minute and 2.4 moles in 30 minutes. The effect of temperature upon the rate of the reaction necessitated accurate control of temperature of the solution for consistent results. As with furfural, it was found more satisfactory to make measurements at 0° C. than at room temperature.

REACTION AT 0° C. Four sizes of methylfurfural samples were used, varying from 12 to 50 mg. The size of the samples was limited by the amount of bromate added, this being 2.5 milliequivalents in all the experiments. The periods of time used were 5, 10, 20, 30, 40, and 60 minutes. The data given in Table I show the number of milliequivalents of bromine consumed and the corresponding molar consumption of bromine for each period of time. The molar ratio of bromine consumed to aldehyde present as a function of time is illustrated in Figure 1. The curves for methylfurfural represent the reaction of approximately 13-, 26-, 46-, and 51-mg. samples of methylfurfural with bromine at 0° C. under the conditions given above. For comparison, the curve for furfural from data given in an earlier paper (8) is also shown. It is readily seen that methylfurfural reacts rapidly with the first mole of bromine, as does furfural; and that the reaction continues at a fairly rapid rate until over 2.3 moles of bromine are consumed, whereas the reaction of the second mole of bromine with furfural is very slow under the same conditions. The effect of the ratio of the concentration of bromine to that of aldehyde is larger in the reaction with methylfurfural than previously noted with furfural (8). As the amount of methylfurfural used in the solutions is decreased there is available a greater excess of bromine, leading to an increased molar consumption of bromine for a given time period.

TABLE I. REACTION OF METHYLFURFURAL WITH BROMINE AT 0° C. IN NORMAL HYDROCHLORIC ACID

Allowed for Reaction Min.	Bromine Consumed ^a							
	0.05133 gram methylfurfural		0.04570 gram methylfurfural		0.02561 gram methylfurfural		0.01280 gram methylfurfural	
	Milli-equivalents	Moles/mole of aldehyde	Milli-equivalents	Moles/mole of aldehyde	Milli-equivalents	Moles/mole of aldehyde	Milli-equivalents	Moles/mole of aldehyde
5	1.288	1.38	1.141	1.37	0.649	1.39
10	1.538	1.65	1.340	1.61	0.778	1.67	0.304	1.69
20	1.813	1.94	1.601	1.93	0.924	1.99	0.480	2.06
30	1.975	2.11	1.788	2.15	1.029	2.21	0.514	2.21
40	2.065	2.21	1.852	2.23	1.074	2.31
60	2.154	2.31	1.937	2.33	1.108	2.38	0.559	2.40

^a At the start of the reaction there were 2.486 milliequivalents of bromine present. The moles of bromine consumed per mole of methylfurfural are equal to $(\text{milliequivalents of bromine consumed}) \times (0.05505) / \text{weight of methylfurfural in grams}$

The results for 0.05133 and 0.02561 gram are averages of duplicate determinations agreeing within ±0.5%, while those for 0.04570 and 0.01280 gram are single experiments.

This effect may be taken into account by using the three variables, time, size of sample, and milliequivalents of bromine consumed, to express the results in a three-dimensional graph as illustrated in Figure 2. Acknowledgment is made to Baker Wingfield for valuable aid in devising and drafting this graph.

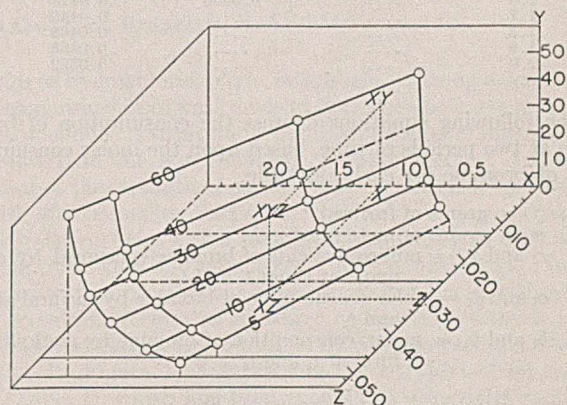


FIGURE 2. REACTION OF METHYLFURFURAL WITH BROMINE AT 0° C. IN NORMAL HYDROCHLORIC ACID

- X. Milliequivalents of bromine consumed
- Y. Minutes of reaction time
- Z. Grams of methylfurfural

On the X axis there is plotted the number of milliequivalents of bromine consumed; on the Y axis, the time allowed for the reaction; and on the Z axis, the weight of methylfurfural in the sample. The curves extending upward into space represent as a function of time the 13-, 26-, 46-, and 51-mg. portions of methylfurfural as they react with bromine under the specified conditions. Although the slopes of the curves are not quite the same, owing to the effect of the concentration of bromine and aldehyde, the points for a given period of time lie on a straight line. Lines have been drawn through these points and designated "time lines."

An illustration of the method of analyzing an unknown is shown in Figure 2. Suppose 1.200 milliequivalents of bromine are consumed by an unknown amount of methylfurfural during a 30-minute period of reaction. As indicated by the small dotted lines, the value for X is then 1.200 and Y is 30, which gives the point XY. In order to find Z, a line is now projected from XY parallel to the Z axis to the 30-minute "time line" on the curved surface; this is the point XYZ. The number of milligrams of methylfurfural, Z, may then be found by dropping down the distance Y from XYZ, obtaining XZ, and finally projecting across to the Z axis for the point Z.

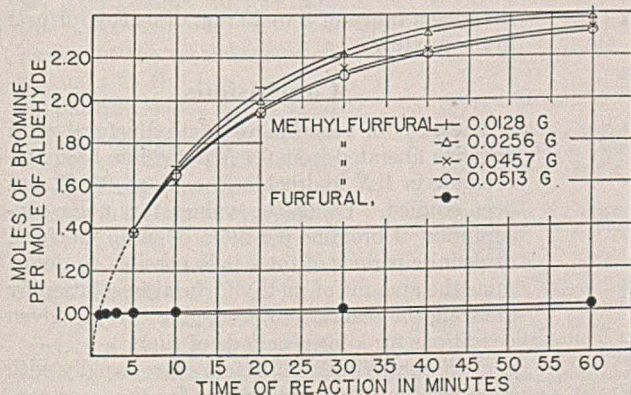


FIGURE 1. REACTION OF METHYLFURFURAL AND FURFURAL WITH BROMINE AT 0° C. IN NORMAL HYDROCHLORIC ACID

Since it is difficult to use the chart on a small scale, values which have been interpolated graphically between the experimental points are given in Table II.

Determination of Methylfurfural and Furfural in Mixtures

Because of the difference in the rates of reaction of the two aldehydes with bromine (Figure 1), it is possible to calculate the amount of each aldehyde present from the results of titrations made on aliquot portions which have been allowed to react for two periods of time.

TABLE II. METHYL-FURFURAL CORRESPONDING TO BROMINE CONSUMED AT DIFFERENT PERIODS OF TIME

Bromine Consumed Milliequivalents	Methylfurfural Found		
	At 5 min. Gram	At 10 min. Gram	At 30 min. Gram
0.4	0.0156	0.0127	0.0112
0.5	0.0198	0.0162	0.0139
0.6	0.0236	0.0197	0.0167
0.7	0.0276	0.0232	0.0195
0.8	0.0316	0.0266	0.0222
0.9	0.0357	0.0300	0.0249
1.0	0.0398	0.0333	0.0276
1.1	0.0438	0.0367	0.0304
1.2	0.0478	0.0401	0.0331
1.3	0.0518	0.0435	0.0358
1.4	0.0468	0.0385
1.5	0.0502	0.0413
1.6	0.0536	0.0440
1.7	0.0468
1.8	0.0495
1.9	0.0522
2.0

The following equations express the consumption of bromine at two periods of time, based upon the molar consumption of bromine for each aldehyde.

Let f = grams of furfural
 m = grams of methylfurfural
 x_1 and x_2 = milliequivalents of bromine consumed by aliquots at times t_1 and t_2
 a_1 and a_2 = molar consumption of bromine by furfural at t_1 and t_2
 b_1 and b_2 = molar consumption of bromine by methylfurfural at t_1 and t_2

$$\text{At } t_1, x_1 = \frac{f}{0.048} (a_1) + \frac{m}{0.055} (b_1) \quad (1)$$

$$\text{At } t_2, x_2 = \frac{f}{0.048} (a_2) + \frac{m}{0.055} (b_2) \quad (2)$$

TABLE III. ANALYSES OF MIXTURES OF FURFURAL AND METHYL-FURFURAL BY REACTION WITH BROMINE AT 0° C. IN NORMAL HYDROCHLORIC ACID

Experimental Time of reaction, t_1 and t_2 , Min.	Bromine consumed, x_1 and x_2 , Milli-equivalents	m^a and f Present in Mixture	m^a and f Determined in Mixture ^b	m Present in Mixture	m Determined in Mixture
		Gram	Gram	%	%
5	1.230	$m = 0.0259$	$m = 0.0255$	48.0	47.4
10	1.346	$f = 0.0281$	$f = 0.0283$		
		0.0540	0.0538		
5	0.873	$m = 0.0115$	$m = 0.0125$	29.0	31.8
10	0.930	$f = 0.0281$	$f = 0.0268$		
		0.0396	0.0393		
10	1.626	$m = 0.0147$	$m = 0.0153$	20.4	21.4
30	1.780	$f = 0.0573$	$f = 0.0563$		
		0.0720	0.0716		
5	1.489	$m = 0.0130$	$m = 0.0123$	18.8	17.9
10	1.545	$f = 0.0560$	$f = 0.0566$		
		0.0690	0.0689		
10	1.373	$m = 0.0060$	$m = 0.0055$	9.5	8.6
30	1.444	$f = 0.0573$	$f = 0.0581$		
		0.0633	0.0636		
10	1.285	$m = 0.0030$	$m = 0.0028$	5.0	4.6
30	1.333	$f = 0.0573$	$f = 0.0577$		
		0.0603	0.0605		
10	1.642	$m = 0.0030$	$m = 0.0025$	3.9	3.2
30	1.695	$f = 0.0744$	$f = 0.0752$		
		0.0774	0.0777		

^a m = methylfurfural, f = furfural.
^b By Equations 3 and 4.

Solving these equations for m and f gives

$$m = (0.055) \frac{a_1 x_2 - a_2 x_1}{a_1 b_2 - a_2 b_1} \quad (3)$$

$$= (0.048) \frac{b_2 x_1 - b_1 x_2}{a_1 b_2 - a_2 b_1} \quad (4)$$

Table III gives the results of titrations made on a number of mixtures. Assuming that the furfural reacted independently of the methylfurfural in the mixtures, the amount of bromine which the furfural would consume was subtracted from the amount which the mixture consumed by experiment, and thus the molar consumption of bromine by the methylfurfural in the mixture was calculated. An average of the values for each period of time was taken, giving 1.38 for 5 minutes, 1.63 for 10 minutes, and 2.10 for 30 minutes. These values are not appreciably different from those given in Table I, and are used in these equations as the factor b . It might appear from the data in Table I that it would be advantageous to apply a variable factor dependent upon the amount of bromine in excess, as has been done in the case of methylfurfural alone (Figure 2 and Table II). However, in the experiments with the mixtures, the variation in the excess of bromine was much less than that for the pure methylfurfural samples; also, the equations used for calculating the mixtures are based upon differences which in some cases are very small, and the above factors simplify the use of the equations and give satisfactory results.

It is obvious from Figure 1 that when short periods of time, 5 and 10 minutes, are used for the reactions, the factor a for furfural is 1.00. At 30 minutes a is 1.02, owing to increased bromine consumption (8). Specifically, for the 5- and 10-minute reaction periods, Equations 3 and 4 become

$$m = (0.055) \frac{(1.00)(x_2) - (1.00)(x_1)}{(1.00)(1.63) - (1.00)(1.38)}$$

$$f = (0.048) \frac{(1.63)(x_1) - (1.38)(x_2)}{(1.00)(1.63) - (1.00)(1.38)}$$

The data in Table III show the varying proportions of furfural and methylfurfural, the number of milliequivalents of bromine consumed by aliquot portions of the mixtures at two different periods of time, and the calculated amounts of the two aldehydes, using Equations 3 and 4 as one would for unknowns. The figures given are the results of single experiments. The higher percentages of methylfurfural in some of the mixtures are rarely encountered in the usual pentosan determinations, but were used to show the application of the method. The lowest weight of methylfurfural used is 3 mg. Below this the error in the titration becomes significant, although it is possible to obtain measurable differences for amounts as low as 1 mg. The average error in these experiments is about 0.5 mg., covering a range of 3 to 25 mg. of methylfurfural in the mixtures.

Conclusions

The rate of reaction of methylfurfural with bromine liberated from 0.1 *N* potassium bromate-bromide in 1 *N* hydrochloric acid at 0° C. has been studied. Using the values for molar consumption of bromine per mole of methylfurfural at definite periods of time, it is possible to determine the amount of methylfurfural in solution by allowing the reaction to proceed under the given conditions for known periods of time.

Since methylfurfural reacts more rapidly with bromine than does furfural under the same conditions, the method has also been applied to mixtures of the two aldehydes. The amounts

of individual aldehydes are calculated from the results of titrations of aliquot portions at two different periods of time, using equations which express the molar consumption of bromine by the mixture.

This volumetric method has been found simpler in application, and more reliable, than the gravimetric procedure. The mean error in the calculated values is about 0.5 mg. in samples containing from 3 to 50 mg. of methylfurfural.

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Small Chemical Changes in an Insulating Oil Associated with Oxidation

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Analytical procedures are given for the determination of strong acid, soluble copper or lead, and saponifiable material in insulating oil. The modification of the procedures consists chiefly in refinement of measurement with especial emphasis on the detection of small changes in composition of the oil. A type of oil oxidation inhibition is illustrated in which a strong acid is the only measurable product of the reaction.

acids as hydrochloric, picric, or sulfuric. Strong acids may be distinguished from weak acids in that when both are present in the nonaqueous titration medium, two points of inflection are obtained in the potentiometric titration curve. Additional proof of the strength of an acid may be obtained by titration with the potassium salt of a weak acid. Thus, potassium stearate will react with a strong acid as readily as does potassium hydroxide but cannot react with a weak acid. In this manner, it is possible to neutralize a strong acid without the concomitant formation of water of neutralization—a result which also may be accomplished by the use of sodium *n*-butylate. In Figure 1, *A* represents the titration of oil sample 8 (Table I), which had been exposed to ultraviolet radiation at room temperature and pressure. It is clear that the entire titration could have been carried out employing potassium hydroxide, in which event the strong-acid point of inflection would have indicated the same quantity of acid. Curve *B* represents the titration of the water extract of oil sample 8, the aqueous layer having been concentrated to a volume of 1 ml. by evaporation before the addition of 100 ml. of *n*-butanol

THE initial chemical changes associated with the oxidation of an insulating oil can be revealed only by analytical procedures which aim towards greater refinement in experimental technic. The formation of strong acid in the first stage of the deterioration is not normally associated with oxidation; nevertheless, by means of improved apparatus for the determination of acidity in oil (1) it is possible to illustrate this point definitely. The behavior of the oil deterioration products in the presence of copper and paper is discussed under conditions which simulate those of the high-voltage oil-filled cable in operation. The oil is a commonly used insulating oil with a viscosity of 100 seconds (Saybolt) at 37.78° C. (100° F.).

The term "strong acid" designates a type of acid which exhibits a comparatively high hydrogen-ion activity for a given concentration of acid in *n*-butanol—for example, such

TABLE I. CHANGES IN CHEMICAL PROPERTIES OF OIL

No.	Sample ^a	Oxygen	Period of Test Months	Neutralization Number, Electrometric		Saponification Number		Soluble Copper, Dithizone Method P. p. m.
				Strong	Weak	Electrometric ^b	Baader ^c	
	As received	0	0	0.005	0.36	0.08	...
1	100 ml. oil	Excess	8.5	0.002	0.006	..	0.13	..
2	100 ml. oil, 10 g. paper	Excess	8.5	0	0.007	..	0	..
3	100 ml. oil, 0.1 g. copper	Excess	8.5	0.009	0.047	..	0.28	7
4	100 ml. oil, 10 g. paper, 0.1 g. copper	1/2 atmosphere	9	0.007	0.063	..	0.09	2.5
5	100 ml. oil	Nil	17	0	0.005	0.38
6	100 ml. oil, 10 g. paper	Nil	19.5	0	0.021	0
7	100 ml. oil, 10 g. paper, 0.1 g. copper	Nil	19.5	0	0.030	0.07	..	4.5
			Hours					
8	100 ml. oil, ultraviolet radiation	1/2 atmosphere	30	0.005
9	25 ml. oil, ultraviolet radiation	Nil	30	0
10	25 ml. oil, 0.1 g. copper, ultraviolet radiation	Nil	30	0

^a Samples 1-7, inclusive, aged at 60° ± 0.05° C.; 8-10, inclusive, at room temperature. Peroxide No. of all aged samples was approximately zero. Peroxide No. of oil as received was 5.
^b Hydrolysis in a mixture of 20 per cent water, 40 per cent ethanol, and 40 per cent benzene.
^c Hydrolysis in a mixture of 40 per cent benzene and 60 per cent methanol, using alkali blue as the titration indicator.

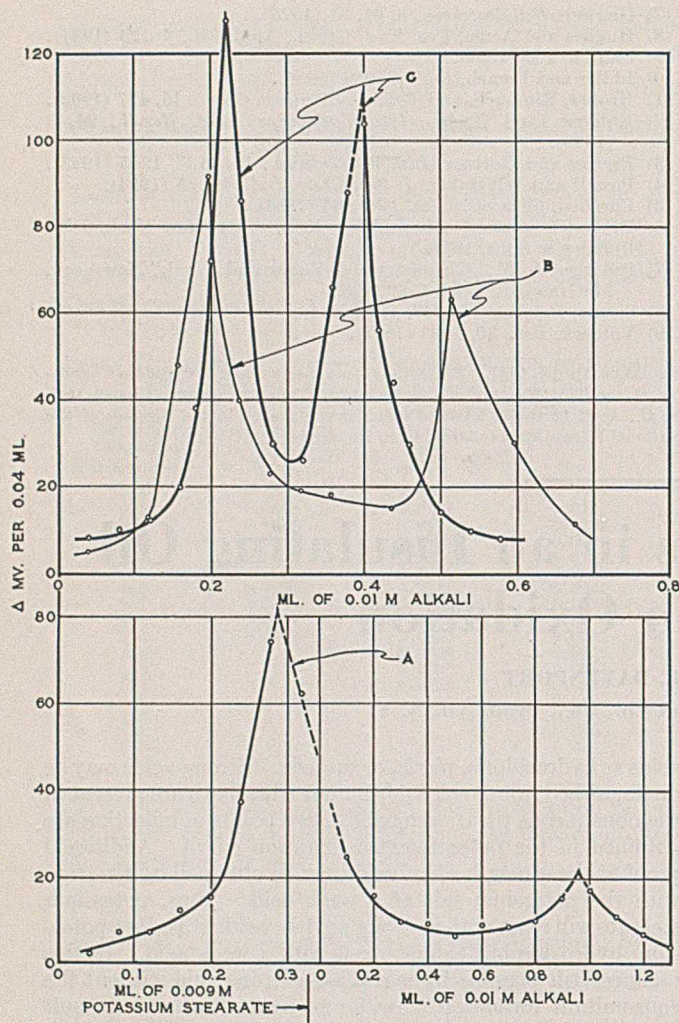


FIGURE 1. TITRATION OF OIL ACIDITY

- A. Acidity determination on 10 grams of oil 8 (Table I)
 B. Acidity determination of water extract of oil 8
 C. Titration of 1 ml. of 0.0025 *N* sulfuric acid

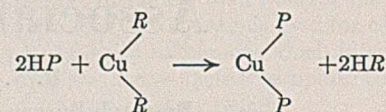
as the titration medium. Curve C is the titration of 1 ml. of 0.0025 *N* sulfuric acid plus an equivalent amount of weak acid.

The chemical behavior of a cable oil may not be considered without some attention to the effect of the presence of paper and copper on oil deterioration. The soluble metal content of the oil—approximately 1 p. p. m. in practice—exerts a marked influence on the rate of chemical change. The use of diphenylthiocarbazon as a test reagent for copper (and lead) in aqueous solutions was reported by Fischer and Leopoldi (2). Later—indeed as the authors' work was in progress—Wichmann et al. (3) published their work on the colorimetric lead determination by means of dithizone. Since the test procedure has been thoroughly presented by previous investigators, only a discussion of the transfer of the soluble metal from oil to water will be included.

Ten grams of oil were diluted with 50 ml. of a mixture of 10 per cent by volume of pyridine in benzene and the solution was centrifuged for 15 minutes. The solvent was then removed in a stream of nitrogen at an elevated temperature and 10 ml. of 10 per cent aqueous nitric acid were added to the oily residue. After refluxing for 15 minutes and cooling, the oil was removed by extraction with ether and the aqueous layer was evaporated repeatedly to dryness in the presence of sulfuric-nitric acid mixture. When the residue was taken up with a definite amount of heavy metal-free water, both copper and lead were determined as originally outlined by Fischer and Leopoldi.

In the course of the development of the method, it was shown synthetically that coarse particles of copper produced no measurable positive error due to solvent action of the pyridine and that the metals were completely removed by obtaining negative results when the oil sample was re-treated employing the procedure described above. Considerable experimental work was carried out endeavoring to differentiate between free copper and copper soap by a mild hydrolytic action of dilute alcoholic sulfuric acid, followed by the more strenuous aqueous nitric acid treatment for free copper. While the method showed some degree of success when working with known compounds, for the type of oil under consideration it was felt that because of the initial formation of strong acid, the presence of soap would not be expected. In a sample of an oil, 0.1 microgram of copper or lead can be detected. Duplicate analyses of samples containing 1 to 5 p. p. m. of soluble metal agree within 10 per cent of the reported value where the matching of colors is accomplished visually.

The state of chemical combination of the copper was further investigated by means of a potentiometric titration method in which strong acid in excess is added to the oil sample in dioxane, whereupon the following reaction takes place:



R = weak acid radical
P = strong acid radical

The increase in titer of the weak-acid point of inflection represents the weak acid liberated from the soap, whereas the difference in titer of the strong acid with and without the oil

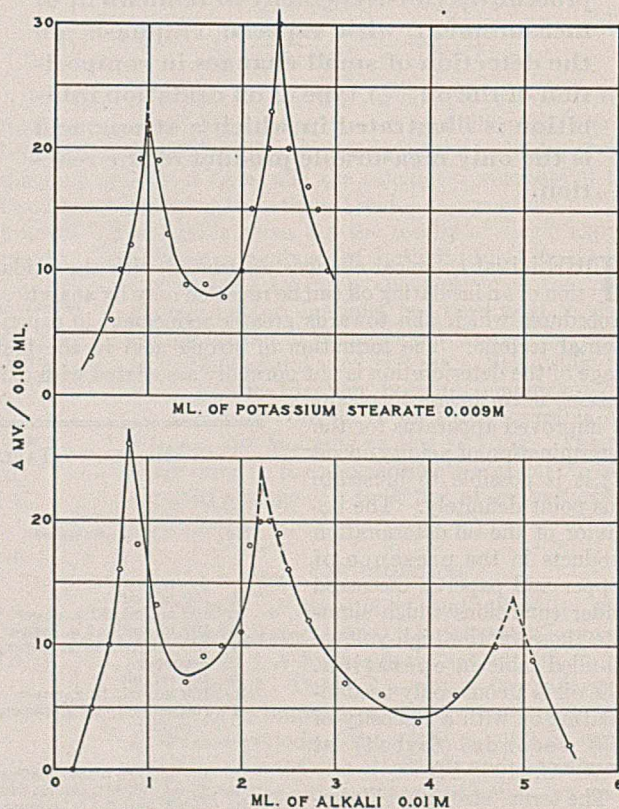


FIGURE 2. ACTION OF PICRIC ACID ON COPPER STEARATE IN DIOXANE

Lower, titration of 5 mg. of copper stearate plus excess picric acid
 Blank, strong acid, 2.25 ml.; weak acid, 1.20 ml.
 Upper, titration of 4.0 mg. of copper stearate plus excess picric acid
 Blank, strong acid, 2.40 ml.

sample measures the amount used up in the above reaction. Originally it was expected that the weak-acid titer increase would serve as a measure of the soap content of the oil sample, but it was later found, as previously reported (1), that many copper soaps are readily neutralized, yielding a point of inflection as distinct as the corresponding acids. Consequently, no increase in weak-acid titer would be expected. A typical curve may be seen in Figure 2, in which the first point of inflection corresponds to the excess picric acid, the second corresponds to the copper picrate, and the third is a measure of the liberated plus the free weak acid. Copper chloride, sulfate, and trichloroacetate behaved in a similar manner—that is, a distinct point of inflection resulted when titrated, due to the alcoholysis or hydrolysis of the salt. There was no difference in result when potassium stearate was substituted for potassium hydroxide. If one assumes that the disappearance of strong acid is a result only of the reaction indicated in the previous equation, then the decrease in titer may serve as a measure of the soap. Because of such a controversial assumption and because for small amounts of copper (1 p. p. m.) the excess strong-acid point of inflection tends to merge with that of the copper salt, limiting the smallness of the amount which may be determined, it was considered unprofitable to continue this phase of the work. However, the appearance of the copper salt point of inflection was believed observed in several titrations of the oil samples aged in the presence of copper (Curve C, Figure 5, 1).

In Table I the change in chemical properties of the oil is listed as a result of exposure to different experimental conditions.

In samples 1, 2, and 3 the three compartments containing oil, oil plus paper, and oil plus copper were interconnected and thus were subjected to the same oxygen pressure. No attempt was made to ascertain the initial inhibitory period of the oil oxidation reaction, since in the present study it was desired to show that oxygen was a necessary requisite for strong-acid formation. Sample 4 was protected from atmospheric contamination by means of an ascarite and dehydrite tube. In samples 5, 6, and 7, the oil was evacuated for a period of 10 days; the last 3 days produced no change in the residual gas pressure (0.1 micron as measured with a MacLeod gage). After sealing off from the vacuum pump, inversion of the flask permitted the oil to run down onto the paper or the copper. Samples 8 and 9 were prepared like samples 4 and 5, respectively, and exposed to ultraviolet radiation through Pyrex glass. Here again yield per unit time was considered unimportant except as it had a bearing on the relative formation of strong acid. In sample 10 the oil was evacuated in contact with the copper particles.

The apparatus for saponification experiments is shown in Figure 3. It was designed to permit saponification in an atmosphere of nitrogen and transference to the titration beaker without absorption of carbon dioxide from the air.

Conclusions

The chief conclusions which may be drawn from the limited data in Table I are: (1) Oxygen must be present to bring about strong-acid formation. (2) Either the strong acid has been absorbed by the paper or its tendency to form has been decreased by substances removed by the oil from the paper. In an attempt to decide whether the alkalinity of the paper or the specific absorption action of the paper was responsible for the decrease in strong-acid formation, experiments with acid-treated paper were inconclusive. Thus, the mere contact of oil and paper, after the strong acid had been formed in the oil, caused a disappearance of strong acid, but acid-treated paper was only slightly less active in this respect than paper which had not been washed with acid. (3) Copper was instrumental in increasing the strong-acid formation, the data in Table I representing the free acid. (4) In the absence of copper, the paper completely removed the saponifiable material from the oxidized oil.

Consideration of the chemical and physical properties of

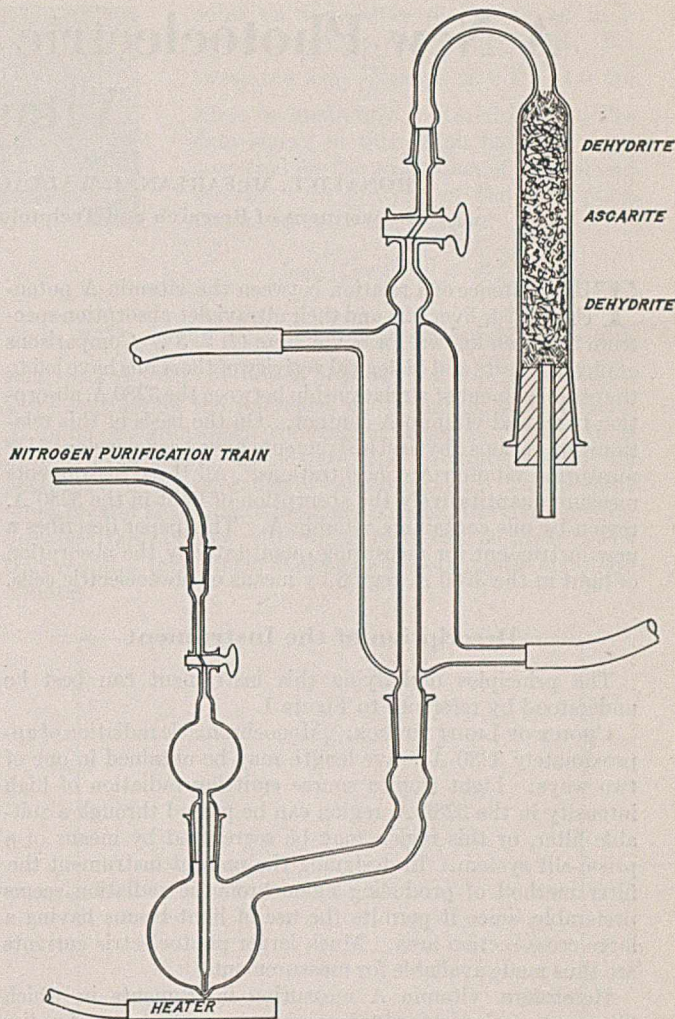


FIGURE 3. APPARATUS FOR DETERMINATION OF SAPONIFICATION NUMBER OF OILS

the strong acid suggested its similarity to sulfuric acid. Extraction of oil sample 8 (Table I) with water and partial evaporation of the water layer, followed by addition of acidified barium chloride, produced a precipitate which was similar in appearance to the precipitate formed when an equal volume of sulfuric acid of the same concentration was treated in like manner. It was concluded that the oil contained a sulfur complex which in its role as an oxidation inhibitor forms a strong acid. The presence of the strong acid precludes the formation of copper soaps and compounds of a peroxide nature. Furthermore, it would appear that the application of a theoretical oxidation mechanism to oil would be, in practice, greatly complicated by side reactions.

Acknowledgment

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A New Photoelectric Method for Measuring Vitamin A

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THE existence of a relation between the vitamin A potencies of fish-liver oils and their ultraviolet absorption spectrum has been known for some time (1, 2, 3). Comparisons of physical tests and biological activity of these oils have led to the establishment of a relationship between the 3280 Å. absorption band and vitamin A content. On the basis of this relationship, various physical instruments have been developed for measuring vitamin A concentrations. All these instruments measure quantitatively the absorption of light in the 3280 Å. region by oils containing vitamin A. This paper describes a new instrument for measuring quantitatively the absorption of light in the 3280 Å. region by means of photoelectric cells.

Description of the Instrument

The principles underlying this instrument can best be understood by reference to Figure 1.

CHOICE OF LIGHT SOURCE. Monochromatic radiation of approximately 3280 Å. wave length may be obtained in one of two ways: Light from a source emitting radiation of high intensity in the 3280 Å. region can be passed through a suitable filter, or this region may be segregated by means of a prism-slit system. In designing the present instrument the filter method of producing monochromatic radiation seems preferable, since it permits the use of light beams having a large cross-section area. Much larger photoelectric currents are thus made available for measurement.

Heretofore, vitamin A measuring instruments in which filters are employed to obtain a monochromatic beam of radiation have used the copper arc as a light source. The spectrum emitted by the copper arc is shown in Figure 2. (These spectra were taken by G. R. Harrison of the Massachusetts Institute of Technology.)

Two very intense lines occur, one at 3274 Å. and the other at 3247 Å. Both lines fall near the peak of the vitamin A absorption curve (1) shown in Figure 3. Consequently their absorption by oils containing vitamin A should give a measure of the vitamin A present. But, as is evident from Figures 2 and 3, the copper spectrum contains many wave lengths of appreciable intensity, which do not lie near the peak of the vitamin A absorption curve, and so are not absorbed in proportion to the vitamin A content of oils through which they may pass. In order to eliminate this extraneous radiation as much as possible, various types of filters have been tried.

One type consists of a half-silvered quartz plate combined with a thin plate of Woods glass. The copper arc radiation transmitted through this filter is shown in Figure 2 in the spectrum marked Cu-silver filter. This spectrum shows considerable radiation intensity not lying in the 3280 Å. region.

The other filter is the Corning No. 597 Red Purple Ultra. Unfortunately, the authors do not have a spectrum of the copper arc taken through this filter, but it is possible to check its efficiency by examining the spectrum marked Cu-Corex filter. This spectrum, which was taken through a 5-mm. thickness of Corning Red Purple Corex, No. 986, shows a large amount of radiation intensity lying outside the vitamin A absorption curve. The transmission curves published by the Corning Glass Company show that the No. 597 filter transmits radiation farther into the visible region than does the No. 986. Consequently, even more radiation lying outside the 3280 Å. region will be transmitted by the No. 597 filter than is shown in the spectrum of the No. 986 filter. It would thus appear that neither of these light source-filter combinations provides a good monochromatic beam of radiation for vitamin A absorption measurements.

In addition, the well-known difficulties of maintaining a steady copper arc of constant intensity help to make this arc an unsatisfactory source. However, it is possible to eliminate all these difficulties by substituting a sodium arc for the copper arc. The spectrum obtained when radiation from the sodium arc is filtered through a 5-mm. thickness of Corning Red Purple Corex No. 986 is shown in Figure 1 in the spectrum marked Na-Corex filter. The resulting radiation is perfectly monochromatic, and has a wave length of 3303 Å., which is only 23 Å. removed from the vitamin A absorption peak, as compared with 6 and 33 Å. for the principal lines of the copper arc. The sodium arc has the further advantage of being glass-enclosed, and is thus free from the variations of the copper arc.

OPTICAL SYSTEM. Radiation from the sodium arc passes through a fused-quartz collimating lens, and is then divided into two beams by two fused-quartz total reflecting prisms. The intensity of each of these beams is controlled by a variable-area slit. One of these slits is connected to a logarithmic scale by a mechanism such that $\log_{10} A_0/A$ may be read directly. A_0 and A represent the full open and variable slit areas, respectively. The light beam controlled by this slit also passes through an absorption cell containing the diluted oil under examination. The two variable-area slits have the same maximum aperture. Both light beams pass through a Corning Red Purple Corex No. 986 filter before reaching the phototubes. The absorption cells are covered with fused-quartz windows, and the cells are

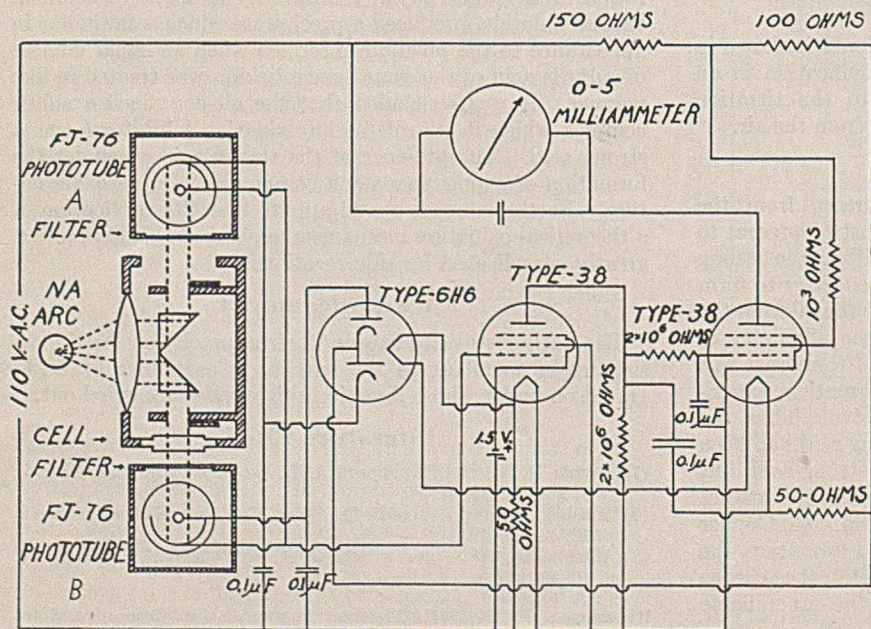


FIGURE 1. DIAGRAM OF INSTRUMENT

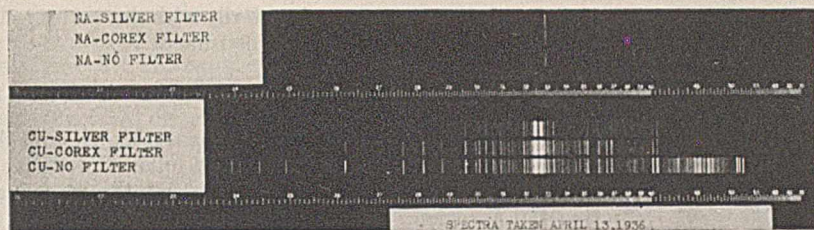


FIGURE 2

so constructed that the thickness of the enclosed liquid sample is exactly 1 cm. Although all optical parts in the present instrument are made of fused quartz, some of the ultraviolet glasses could be substituted without loss of light intensity.

CHOICE OF PHOTOTUBES. The choice of the proper phototubes is governed by two considerations: It is desirable to obtain the maximum possible response to radiation in the 3280 Å. region, and there must be no response to any other radiation which may succeed in getting through the filter system. In Figure 2, the spectrum marked Na-Corex filter shows all the radiation to be concentrated in the 3303 Å. line. However, only radiation of wave length less than 7000 Å. appears in this spectrum, while above 7000 Å. the Corning Red Purple Corex No. 986 filter again begins to transmit appreciable radiation. Since any hot body, including the sodium arc, will emit appreciable black body radiation above 7000 Å., it is essential that there be no phototube response above this wave length. Several commercially available phototubes satisfy these requirements, and in the present instrument the FJ-76 tubes manufactured by the General Electric Company are used.

AMPLIFIER CIRCUIT. The currents produced in the two FJ-76 phototubes are amplified by means of the circuit shown in Figure 1. (This circuit was designed by F. H. Shepard, Jr., of the Research and Development Laboratory, RCA Mfg. Company, Inc. The authors wish to express their appreciation for his many courtesies.) The 6H6 tube provides the direct current potentials for the phototubes. The currents from these phototubes are bucked against each other, and the resultant current is fed on to the grid of the first 38 tube. Successive amplifications by the two 38 tubes permit easy reading of the resultant phototube current on the meter.

Method of Operation

An absorption cell containing a vitamin A oil dissolved in cyclohexane is inserted in the path of the light beam impinging on phototube B (Figure 1). The calibrated variable-area slit controlling this light beam is opened wide. The other variable-area slit, which controls the light intensity falling on phototube A, is then adjusted to give zero resultant phototube current. The absorption cell is next removed from the instrument, and the calibrated variable-area slit is adjusted until zero resultant phototube current is again obtained. The calibrated scale reading corresponding to this balance point indicates the amount of light absorbed. The same procedure is followed for a cell filled with the pure solvent, and the difference between the two observed absorptions gives the actual absorption by the vitamin A oil.

This method of operation eliminates any necessity for matched phototubes, since the use of two variable-area slits automatically compensates for any inequality in current response of the phototubes. Furthermore, this method of operation effectively recalibrates the instrument for each reading. Errors arising from changes in light intensity are automatically eliminated by the use of two phototubes. However, if the ambient temperature of the phototubes is permitted to drop too far below room temperature, say 10° to 20° C., the current response from the phototubes is small, and the instrument becomes sluggish and inaccurate. But if the phototubes are operated at ordinary room temperature, say 18° to 30° C., the above method of operation gives reproducible results.

CALIBRATION. In Figure 4 is shown the experimental relation between concentration and $\log_{10} \frac{I_0}{I}$ as read on the instrument. The curve is that of U. S. P. reference cod liver oil. Each

point on this curve represents an individual reading, and not an average. Between the $\log_{10} \frac{I_0}{I}$ range of 0.1 to 1.0 the curve is accurately a straight line. The data shown in this graph have not been corrected for the absorption of the cell and solvent. An analysis of the absorption factors leads to the relation

$$\log_{10} \frac{I_0}{I} = 0.049 + E_{1 \text{ cm.}}^{p\%}$$

where $E_{1 \text{ cm.}}^{p\%}$ is the extinction coefficient for a p per cent solution. A value of 1.32 is obtained for $E_{1 \text{ cm.}}^{1\%}$ at 3303 Å. and—considering the reference oil to contain 3000 vitamin A units per gram—the conversion factor is 2270. As is evident from Figure 4, constant and accurate results are obtained over a large range of concentrations. This permits much greater flexibility in making dilutions, and consequently increases the rapidity with which tests can be made. The time required for a single reading on a diluted oil is about 1.5 minutes.

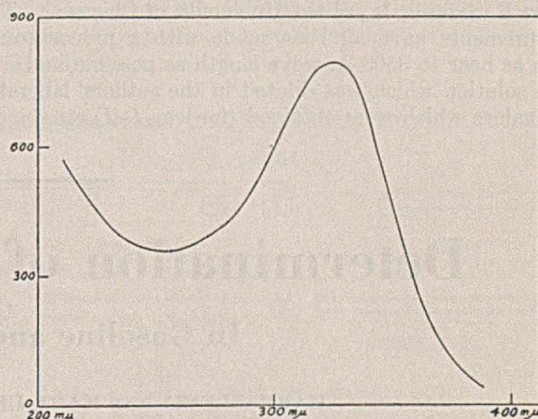


FIGURE 3. VITAMIN A ABSORPTION CURVE

In Table I are given various determinations as made on several oils by the present instrument, and also by a spectrophotometer. (The spectrophotometer readings were very kindly made by the Atlantic Coast Fisheries Corporation of New York.) The oils were received by the authors on July 31, 1936, and the tests were made with the new instrument on December 2, 1936. The values are expressed in vitamin A units. The spectrophotometer readings were made

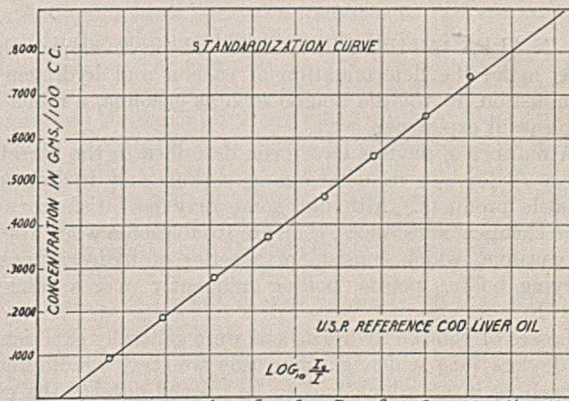


FIGURE 4

TABLE I. DETERMINATIONS ON OILS

Photoelectric Instrument	Spectrophotometer
25,590	25,450
32,230	32,100
78,890	74,040
102,200	98,010
177,800	176,760

TABLE II. COMPARATIVE MEASUREMENTS

Solution I	Solution II
1.14	0.552
1.10	...
1.00	...
1.13	...

at 3280 Å. The agreement between these readings is well within the limits of experimental error.

Comparative absorption measurements have also been made by several laboratories on two potassium bichromate solutions. (For these measurements the authors are indebted to C. S. Leonard of the Health Products Corporation, A. W. Wells of the Atlantic Coast Fisheries Corporation, G. R. Harrison of the Massachusetts Institute of Technology, and Albert E. Sidwell, Jr., of the University of Chicago.) These measurements have all been made with a monochromatic beam as near to 3303 Å. wave length as possible, and on the same solution which was diluted in the authors' laboratory. The values which were obtained (for $\log_{10} I_0/I$) are shown in

Table II, and compare very satisfactorily with the values 1.10 and 0.544, as read on the authors' instrument.

Conclusions

A new photoelectric instrument for measuring vitamin A has been developed which incorporates the following features:

1. A monochromatic beam of light of high intensity, lying in the 3280 Å. region.
2. Accurate measurement of the vitamin A absorption coefficient over the $\log I_0/I$ range of 0.1 to 1.0. With care this range may be extended somewhat.
3. Rapid and easy measurements. The time required for a single measurement on a properly diluted oil is less than 2 minutes.
4. An accuracy of 1 per cent in reading absorption coefficients, which may with care be pushed to less than 0.5 per cent.
5. Reproducible results day after day.
6. Elimination of personal matching errors.

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Determination of Carbon and Hydrogen In Gasoline and Other Volatile Liquids

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An apparatus and procedure are described which enable one to determine the carbon and hydrogen content of gasoline or other volatile liquids by combustion.

A feature of the apparatus is a device by means of which the rate of volatilization can be controlled and combustions conducted to completion in an atmosphere of oxygen without explosion.

AN APPARATUS and technic have been developed which make the determination of carbon and hydrogen by combustion, in volatile liquids such as gasoline, a much less unpleasant experience.

A number of devices have been described in the literature (1, 3-7) for use in determining carbon and hydrogen in volatile products. Although some may be satisfactory for pure chemical substances, they are troublesome when applied to gasoline, which consists of a series of hydrocarbons of varying boiling points, boiling frequently over a range of 300° F.

Losses of volatile hydrocarbons were generally experienced in devices into which gasoline was weighed by difference, as well as in all which had to be opened outside the combustion tube. Incomplete combustion of heavy or oxidized gasoline residues frequently resulted from vaporization out-

side the combustion tube. Control of volatilization rate was rarely possible with those devices which suddenly exposed the entire volatile sample to temperatures above its initial boiling point—for example, breaking a weighing bulb by means of plunger rods. Explosions were common with devices which required that oxygen be passed through or over the entire gasoline sample. The procedure recently described by Bruun and Faulconer (2) has not been tested by the authors.

The apparatus which the authors have developed has the following advantages: (1) It permits weighing of sample in a sealed glass bulb; (2) the bulb is not opened until it is within the combustion tube and the latter is assembled for test; (3) vaporization of the contents of the weighing bulb is at all times under control; (4) vaporization residues are left in the weighing bulb and can be completely burned after crushing the bulb within the combustion tube; and (5) combustion is carried out in an atmosphere of oxygen, ensuring completeness, without explosion hazard. Though hundreds of determinations have been made by this method during the past 6 years, no explosions were experienced.

Apparatus

A multiple-unit type of electric combustion furnace having three heating elements has been found satisfactory when equipped with the usual accessories for combustion analysis. A special combustion tube and a bulb-crusher assembly are needed.

The special combustion tube consists of a long and a short section joined by a shorter capillary section, as illustrated in Figure 1. The capillary section is of heavy-walled 3-mm. inside diameter tubing. This tube, made of Pyrex glass, has been furnished on order by the Emil Greiner Co., New York, N. Y.

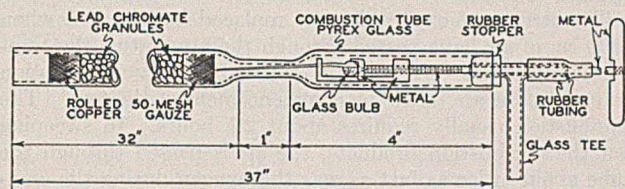


FIGURE 1. BULB-CRUSHER ASSEMBLY WITH SAMPLE IN PLACE
(Connected to prepared combustion tube.)

The metal parts of the bulb-crusher assembly were made of Monel metal in the authors' machine shop, in accordance with Figure 2, which is drawn to scale. It is seen assembled and in position in the combustion tube in Figure 1.

COMBUSTION TUBE. The combustion tube is filled by inserting a roll of copper gauze about 5 cm. (2 inches) long and of such diameter as to fit tightly within the tube. This is forced down as far as it will go and should be within 2.5 cm. (1 inch) of the capillary portion of the tube. Kahlbaum's lead chromate is then poured in to a depth of within 12.5 cm. (5 inches) of the other end of the tube. (The lead chromate was chosen because it retains sulfur and prevents the passage of sulfur dioxide into the carbon dioxide absorber; many incompletely refined gasolines contain appreciable amounts of sulfur.) This is followed by another roll of copper gauze about 8.75 cm. (3.5 inches) long and of similar diameter to the first. Before using this tube for an actual determination it should be burned out by placing it in the combustion furnace, bringing the tube to a dull red heat, and slowly passing 20 liters (5 gallons) of oxygen through it while being so heated.

The combustion tube should not be placed directly upon the metal trough which usually comes with the electric furnace; the tube frequently becomes hot enough to fuse and adhere to the metal, and then upon cooling, the combustion tube may be fractured because of the difference of expansion. To avoid such destruction, a strip of asbestos tape 1.9 cm. (0.75 inch) wide and as long as the tube itself is interposed.

PURIFYING TRAIN. The usual purifying train for the removal of carbon dioxide and moisture from the oxygen and air used in this test is preceded by a Fisher bubble counter of the same size as that used after the absorbers. This bubble counter should contain a small amount of concentrated sulfuric acid, through which the gases pass before entering the purifying train.

BULB-CRUSHER ASSEMBLY. This is prepared as shown in Figures 1 and 2. Before actual use those metal portions of the bulb crusher, which in the final assembly will be within the combustion tube, should be heated in a flame to ensure removal of combustible impurities from its surface.

The bulb-crusher assembly (minus the weighing bulb) consists of (1) the bulb crusher; (2) glass T 0.6-cm. (0.25-inch) outside diameter, one arm of which is 1.9 cm. (0.75 inch) long and the other arm 3.1 cm. (1.25 inches) long. The vertical portion of the T is 5 cm. (2 inches) long; the longer arm carries the rubber stopper; (3) a one-hole rubber stopper that fits into the combustion tube; (4) two pieces of rubber tubing of diameter to make a gas-tight connection between the spindle of the bulb crusher and the glass T through which it passes; the smaller rubber tubing is placed over the spindle and within the T, the larger over the T and the small tubing.

ABSORPTION TRAIN. This consists of one Marchand drying tube filled with Anhydron (anhydrous magnesium perchlorate; absorbs water) and another Marchand drying tube filled with Ascarite (sodium hydroxide asbestos; absorbs carbon dioxide).

Procedure

The combustion tube is brought to a dull red heat, the three heating units being together and as near the outlet end of the furnace as they can be placed. While the furnace is reaching the desired temperature the sample and absorbers are weighed. During all this time a slow stream of oxygen is

kept flowing through the train of scrubbers and the combustion tube, with the bulb-crusher assembly (minus the bulb) in place; the purpose of this is to dry all parts thoroughly and to ensure the presence of oxygen within the tube.

The sample (60 to 100 mg.) is taken in a glass weighing bulb in the following manner:

The outside of the empty bulb is rinsed with ethyl ether, waved dry, placed in a desiccator to come to normal temperature conditions, and very carefully weighed. The bulb is then gently warmed, and the capillary end is promptly immersed in the sample to be tested, which for this purpose is kept in a small crucible. As the bulb cools, the sample is drawn into it, and experience soon teaches when the desired amount of sample has been obtained. The weighing bulb is then removed, held in an upright position, and a few drops of ether are poured on the outside of the bulb in order to chill it sufficiently to cause all the liquids within it to flow from the stem into the bulb proper. Holding the bulb in an upright position, the tip of the stem is sealed by fusing in a flame. The bulb is then again desiccated, and subsequently weighed. Throughout all these operations it is important to handle the bulb so that its contents do not flow into the stem. The bulb is now returned to the desiccator to remain there until introduced into the combustion tube.

The weighed Anhydron and Ascarite absorbers are then connected in the usual manner to the outlet end of the combustion tube, and to the latter absorber is attached a Fisher bubble counter containing a small amount of concentrated sulfuric acid.

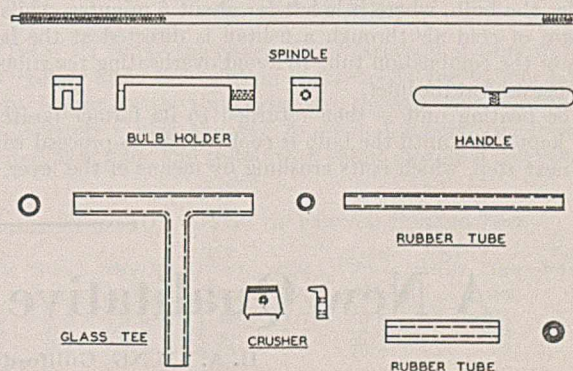


FIGURE 2. BULB-CRUSHER DETAILS

A plate of shatterproof glass 60 cm. (2 feet) square, supported in a suitable manner, is placed between the inlet end of the combustion tube and the operator, where it is kept, for safety, throughout the test. This precaution may appear unnecessary, since with their apparatus and method the authors have never had an explosion, but explosions with other devices recommended for combustion analysis of volatile liquids have been so unpleasant as in their opinion to justify this additional safety precaution.

The bulb-crusher assembly is withdrawn from the tube; in its jaws is immediately placed the bulb containing the sample, and the assembly is promptly returned to its original position. The spindle of the bulb crusher is so adjusted that, when this assembly is returned, the tip of the closed capillary of the bulb is almost in contact with the roll of copper gauze in the combustion tube. Figure 1 shows the bulb-crusher assembly with the sample in place, connected to the combustion tube.

The stream of oxygen is now regulated so that 40 to 60 bubbles per minute emanate from the bubble counter.

A small forward pressure applied by hand to the spindle of the bulb crusher serves to force the capillary stem of the bulb against the roll of copper gauze in the combustion tube, breaking the stem at its point of contact. The contents of

the bulb are now able to escape into the tube in vapor form, and are assisted in this volatilization by the very cautious and gentle application of heat from a Bunsen burner to the section of the combustion tube containing the bulb. This heating must be carried out with extreme caution so as to volatilize the sample slowly. A too rapid volatilization will result in incomplete combustion and erroneous results.

TABLE I. RESULTS ON KNOWN AND UNKNOWN

	Found		Theoretical	
	Carbon %	Hydrogen %	Carbon %	Hydrogen %
Benzene	92.10	7.75	92.25	7.75
Ethyl ether	64.61	13.49	64.80	13.60
Gasoline 1				
Run 1	86.29	13.57
Run 2	86.22	13.57
Gasoline 2				
Run 1	86.23	13.41
Run 2	86.44	13.23
Gasoline 3				
Run 1	85.31	14.54
Run 2	85.45	14.48
Gasoline 4				
Run 1	85.49	14.64
Run 2	85.28	14.68
Gasoline 5				
Run 1	84.64	15.27
Run 2	84.43	15.37
Run 3	84.56	15.37
Run 4	84.61	15.22

When all visible liquid has left the bulb proper, the nearest heating unit of the furnace is gradually moved until it encircles the bulb, where it is left for about 5 minutes, while a stream of cold air through a fishtail is directed at the last inch of the combustion tube to avoid overheating the rubber stopper used at the inlet.

The heating unit is then returned to its former position and kept there until the bulb is cool enough to proceed with the next step, which is its crushing by means of the lever of

the bulb crusher. The bulb is crushed by advancing the movable jaw of the bulb crusher by means of the spindle handle without opening the tube, after which the heating unit is again moved to cover the bulb area and kept there until the broken glass parts are absolutely clean—that is, until all carbon has been burnt—when it is returned to its original position.

The stream of oxygen is now replaced by air, and when 1500 cc. of air have passed through the apparatus, the combustion products are usually removed and the absorption train contains air, as at the commencement of the test. The combustion usually requires about 2.5 hours. In sweeping out the combustion products, the air is passed through the tube about twice as fast as was the oxygen during the combustion.

The absorption train is removed, properly stoppered, and allowed to cool and remain near the balance for 30 minutes. The stoppers are then removed and the absorbers are weighed against a counterpoise in the usual manner. From the increase in weight of the Anhydrone tube (water) the hydrogen is calculated, and from the increase of the weight of the Ascarite tube (carbon dioxide) the carbon is computed.

Table I indicates the accuracy and reproducibility of this method when applied to known and unknown volatile liquids.

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RECEIVED April 21, 1937.

A New Qualitative Test for Selenium. I.

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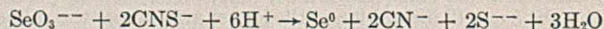
SINCE the advent of the use of selenium in steels, and since its poisoning effect on plants and animals through its presence in soils have become known, much work has been done on its qualitative detection and quantitative determination. Recently published papers give details for the determination of selenium in plants (6), in animal tissue, milk, and urine (3), and in steels (2, 5). Knight (4) has recently spoken on the selenium problem with regard to agriculture in the midwest and west.

The present work on selenium was undertaken with a view to finding and developing a new method for quantitative determination, in which a stable reducing agent might be used. Common reducing agents, such as potassium iodide and sulfur dioxide, are objectionable because of their instability as standard solutions. The use of the thiocyanate ion as a reducing agent in other analytical reactions has suggested it as a possible reducing agent for selenious acid. The literature contains no reference to such application, however, and no theoretical data are available.

It has been found in this laboratory that the thiocyanate ion is capable of reducing the selenite ion in solutions made acid with hydrochloric acid. It was thought, since the alkali and ammonium thiocyanates are stable reagents and can be conveniently standardized, that this reaction might be used as a basis for the quantitative volumetric determination of selenium. In this work it was necessary to begin with a study

of the concentration of reducing agent, the hydrogen-ion concentration, the time of completion of the reaction, the temperature at which the reaction takes place, the sensitivity of the reaction, and the interfering elements. Work is now in progress on the applications of the reaction.

Since hydrogen sulfide is evolved during the reaction and red metallic selenium is precipitated, the following equation may be written to represent the reaction between these two ions:



However, the volumetric relationships indicate that a whole molecular weight of thiocyanate is required by the selenite ion. Preliminary determinations of the equivalent weight of the thiocyanate ion indicate this to be true; hence another equation must be written to represent the exact quantitative relationship between the ions. This is now under investigation. Solutions were made up, however, in accordance with the above equation and experiments were carried out to determine the properties of the reaction before the above volumetric relationship was known.

The selenite and the thiocyanate ions react in solutions acid with sulfuric acid, forming a yellow-orange precipitate. The results obtained thus far seem to indicate that the reaction is slow to start, but takes place rather rapidly.

Reagents

A standard solution of selenious acid was prepared by weighing out resublimed selenium dioxide, previously dried for 1 hour at 150° C., and dissolving in water to make a solution containing approximately 1 mg. of selenium per cc. This solution was subsequently standardized by reducing the selenious acid with sulfur dioxide in acid solution, filtering on a Gooch crucible, drying, and weighing. The results agreed satisfactorily with the weighed amount of selenium dioxide. This solution contained 1.0473 mg. of selenium per cc. (0.05289 *N*).

TABLE I. EFFECT OF VARYING THIOCYANATE-ION CONCENTRATION

No.	H ₂ SeO ₃ Cc.	NH ₄ CNS Cc.	HCl (12 <i>N</i>) Cc.	H ₂ O Cc.	Total Volume Cc.	Nor- mality	Fil- trate
1	0.5	0.5	5.0	4.0	10.0	6	+
2	0.5	1.0	5.0	3.5	10.0	6	+
3	0.5	1.5	5.0	3.0	10.0	6	+
4	0.5	2.0	5.0	2.5	10.0	6	—
5	0.5	2.5	5.0	2.0	10.0	6	—
6	0.5	3.0	5.0	1.5	10.0	6	—
7	0.5	3.5	5.0	1.0	10.0	6	—
8	0.5	4.0	5.0	0.5	10.0	6	—
9	0.5	4.5	5.0	0.0	10.0	6	—
10	0.5	5.0	5.0	0.0	10.0	5.88	—

A solution of ammonium thiocyanate was prepared, approximately 0.025 *N*, in accordance with Equation 1, and was standardized against a standard solution of potassium iodate according to the method suggested by Andrews (1).

A solution of potassium iodate was prepared by weighing out sufficient pure salts, previously dried at 110° C. for 1 hour, to make a solution approximately 0.1 *N*.

Ordinary concentrated c. p. hydrochloric acid was used, of B & A grade.

General Procedure

The sample of selenious acid was measured out, and water was added, followed by the hydrochloric acid and the thiocyanate solution, calculating the volumes so that the total volume of the mixture would be 10.0 cc. The solution was then heated to boiling and boiled for 1 minute except where otherwise noted, and the observations were made. All tests were carried out in 15-cm. (6-inch) test tubes.

Variation of Reducing Agent

Table I shows the effect of the variation of the thiocyanate-ion concentration. The acid concentration was held at 6 *N* because the reduction of selenious acid with sulfur dioxide proceeds better in a high hydrogen-ion concentration. Upon completion of each test the solutions were filtered, if necessary, and tested for complete precipitation, using sulfur dioxide. A qualitative color comparison test was used here, as the small amount of selenium remained suspended in solution for at least an hour. The color imparted to the solution depends upon the amount of selenium precipitated. The color of the precipitate varied from red to green to greenish yellow to almost white by reflected light. With large amounts of selenium, the color imparted to the solution is reddish blue by transmitted light. Observations made by transmitted light are not as delicate as those made by reflected light. In each case the solution gave a positive test with the thiocyanate ion. In the last column of Table I a plus or minus sign indicates the type of test obtained.

Table I shows that the selenium is completely precipitated at the thiocyanate-ion concentration shown, which is twice that indicated by Equation 1. The amounts of selenium obtained in the filtrates using sulfur dioxide showed a decrease from No. 1 through No. 3. The reaction proceeds much faster as the concentration of the thiocyanate ion increases. The selenium began to show up within 10 seconds after reaching the boiling point.

Variation of Acid Concentration

Table II shows the effect of the variation of the hydrogen-ion concentration. In addition to the thiocyanate test, the

solutions were tested with sulfur dioxide. In each case the solution gave a positive test with the thiocyanate ion.

TABLE II. EFFECT OF VARYING HYDROGEN-ION CONCENTRATION

No.	H ₂ SeO ₃ Cc.	NH ₄ CNS Cc.	HCl Cc.	H ₂ O Cc.	Total Volume Cc.	Nor- mality	Fil- trate
1	0.5	2.0	2.0 (<i>N</i>)	5.5	10.0	0.2	+
2	0.5	2.0	4.0 (<i>N</i>)	3.5	10.0	0.4	+
3	0.5	2.0	6.0 (<i>N</i>)	1.5	10.0	0.6	+
4	0.5	2.0	2.0 (4 <i>N</i>)	5.5	10.0	0.8	+
5	0.5	2.0	2.5 (4 <i>N</i>)	5.0	10.0	1.0	+
6	0.5	2.0	5.0 (4 <i>N</i>)	2.5	10.0	2.0	+
7	0.5	2.0	3.4 (12 <i>N</i>)	4.1	10.0	4.08	—
8	0.5	2.0	5.0 (12 <i>N</i>)	2.5	10.0	6.0	—
9	0.5	2.0	6.7 (12 <i>N</i>)	0.8	10.0	8.04	—
10	0.5	2.0	7.5 (12 <i>N</i>)	0.0	10.0	9.0	—

The reduction of the selenite ion is complete in 6 *N* acid solutions. The reaction proceeds more rapidly as the hydrogen-ion concentration increases, as shown by the time required for the appearance of the selenium precipitate; in the case of No. 10, the precipitate began to appear within 2 to 3 seconds after reaching the boiling point. Table II indicates that the thiocyanate ion requires a higher hydrogen-ion concentration to effect the reduction of the selenite ion than is commonly employed when sulfur dioxide is the reducing agent. The tests obtained in Nos. 1 to 5 were poor, but increasingly better in the same order.

Variation of Time

Table III shows the effect of the variation of time allowed for boiling after the solution had reached the boiling point. After boiling for the time indicated, the solutions were cooled immediately under the tap to room temperature, filtered, heated to boiling, and tested with sulfur dioxide if necessary.

TABLE III. EFFECT OF VARYING BOILING TIME

No.	H ₂ SeO ₃ Cc.	NH ₄ CNS Cc.	HCl (12 <i>N</i>) Cc.	H ₂ O Cc.	Total Volume Cc.	Nor- mality	Time Sec.	Fil- trate
1	0.5	2.0	5.85	1.7	10.0	7	10	+
2	0.5	2.0	5.85	1.7	10.0	7	20	—
3	0.5	2.0	5.85	1.7	10.0	7	30	—

At this concentration the reduction is complete within 20 to 30 seconds. Filtrates 1 and 2 gave a faint coloration upon reboiling, fainter in No. 2; filtrate 3 showed no coloration. Filtrate 1 gave an exceedingly faint test with sulfur dioxide. As the heating period became longer, the precipitate became more compact and less finely divided.

Sensitivity

Table IV shows the effect of reducing the amount of selenium in each test solution.

As little as 1 part of selenium in 20,040,000 parts of solution can be detected by this reaction. The tests became increasingly faint, beginning to give a greenish color with No. 7 and fading off to almost white with Nos. 12, 13, and 14. Tests 13 and 14 showed up only after standing for 48 hours. An excess of thiocyanate was added to the tests in the latter part of the series, it being noted that the tests showed up very slowly. In the presence of an excess of thiocyanate the reduction proceeds much more rapidly. In the cases of Nos. 12, 13, and 14 the selenious acid solution and thiocyanate solutions were diluted so that readable volumes could be used. This dilution is not indicated, but the volumes are read in terms of the original solutions for this series, obtained by diluting the first solution of selenious acid to ten times its volume and diluting the first solution of thiocyanate to twice its volume.

TABLE IV. EFFECT OF REDUCING AMOUNT OF SELENIUM

No.	H ₂ SeO ₃ Cc.	NH ₄ CNS Cc.	HCl (12 N) Cc.	H ₂ O Cc.	Total Volume Cc.	Normality Solution	
1	1.00	0.80	5.85	2.35	10.0	7	Good
2	0.80	0.65	5.85	2.70	10.0	7	Good
3	0.60	0.50	5.85	3.05	10.0	7	Good
4	0.40	0.35	5.85	3.40	10.0	7	Good
5	0.20	0.20	5.85	3.75	10.0	7	Good
6	0.10	0.10	5.85	3.95	10.0	7	Good
7	0.05	0.05	5.85	4.05	10.0	7	Faint
8	0.04	0.04	5.85	4.07	10.0	7	+
9	0.03	0.03	5.85	4.09	10.0	7	+
10	0.02	0.02	5.85	4.11	10.0	7	+
11	0.01	0.01	5.85	4.13	10.0	7	+
12	0.005	0.01	5.85	4.13	10.0	7	+
13	0.00375	0.01	5.85	4.14	10.0	7	+
14	0.0025	0.01	5.85	4.14	10.0	7	+

Temperature-Time Variation

In order to find the lowest temperature at which the reaction begins, a series of experiments was conducted by mixing the proportions of solutions indicated, placing them in a Thiele melting-point tube, heating slowly to the temperature indicated $\pm 1^\circ \text{C}$., and holding at this temperature for the time indicated. The solution was then cooled to room temperature and filtered, and a portion of the filtrate was heated to boiling prior to testing for complete precipitation.

TABLE V. TEMPERATURE-TIME VARIATION

No.	H ₂ SeO ₃ Cc.	NH ₄ CNS Cc.	HCl (12 N) Cc.	H ₂ O Cc.	Total Volume Cc.	Normality	Temperature ° C. Min.	Time	Filtrate
1	2.5	10.0	29.35	8.5	50.0	7	40	30	No reaction
2	2.5	10.0	29.35	8.5	50.0	7	55	15	+
3	2.5	10.0	29.35	8.5	50.0	7	55	30	+ < No. 2
4	2.5	10.0	29.35	8.5	50.0	7	60	15	+ > No. 3
5	2.5	10.0	29.35	8.5	50.0	7	60	30	-
6	2.5	10.0	29.35	8.5	50.0	7	65	15	+ Faint
7	2.5	10.0	29.35	8.5	50.0	7	70	15	-

From Table V it is seen that the reaction is complete at this concentration within 30 minutes at a temperature of 60°C .; that with an increase in temperature the time required for completion becomes less; and that the reaction is complete within 15 minutes at 70°C . The reaction begins rapidly at 60°C .

A similar experiment showed that the reaction takes place at room temperature, but is not complete within 30 hours.

Interferences

In order to determine the interfering ions, experiments similar to those previously conducted were carried out in the presence of approximately 100 mg. of each ion shown in Table VI, in the cases of the noninterfering ions the precipitates were filtered off, dissolved in nitric acid, and tested for the metal. In no case was a positive test for the metal obtained.

TABLE VI. INTERFERENCES

Interfering Ions	Fe ⁺⁺ , Sb ⁺⁺⁺ , Sn ⁺⁺
Noninterfering Ions	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Pb ⁺⁺ , Cu ⁺⁺ , Bi ⁺⁺⁺ , Cd ⁺⁺ , Hg ⁺⁺

Summary

A new reaction has been used in the development of a test for the selenite ion, and is sensitive to 1 part of selenium in 20,040,000 parts of solution. The sensitivity is much greater (1 part of selenium in 38,168,000 parts of solution) if the solution is allowed to stand for at least 48 hours.

The reduction of the selenite ion is complete in solutions 6 N with respect to hydrochloric acid.

There is an exact stoichiometric relationship between the reacting ions.

The reaction takes place only slowly at room temperature, much more rapidly at elevated temperatures, and for small quantities of selenium is complete within 20 to 30 seconds at the boiling point.

Acknowledgment

The problem of selenium determinations was first suggested to the author by G. Frederick Smith, Department of Chemistry, University of Illinois. The author wishes to express his appreciation to J. T. Dobbins, Department of Chemistry, University of North Carolina, for his interest in the writing of this paper.

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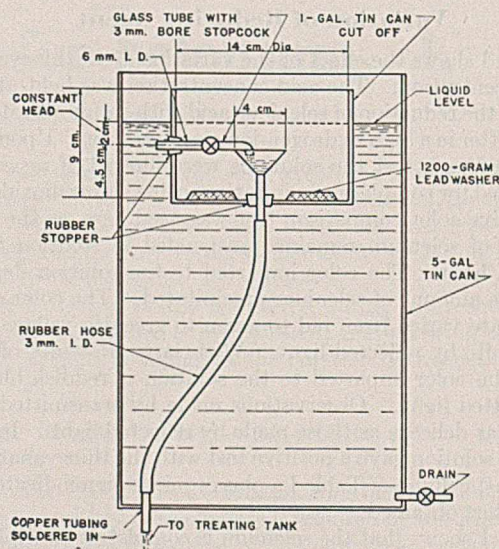
RECEIVED April 22, 1937.

Feeding Device for Boiler Compound

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THE feeding device illustrated is in use at this plant for adding boiler compound at steady rates to boiler feed water. It maintains a constant head and constant rate by floating the intake end of the delivery tube. It is simple in construction and the necessary materials should be found in any laboratory.



A 20-liter (5-gallon) and a 4-liter (1-gallon) tin can, a small glass funnel, copper tubing, a glass stopcock, rubber stoppers, scrap lead, small-bore rubber tubing, and a piece of glass tubing are all the materials needed. The device as illustrated will deliver from 20 to 180 ml. per minute at constant rate. Higher or lower rates may be obtained by varying the ballast in the float to vary the head, or by using tubing and stopcock of larger or smaller bore.

RECEIVED May 14, 1937

Determination of Barium, Sulfur, and Sulfates

A Rapid and Accurate Volumetric Method

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THE approved standard gravimetric sulfate determination has the inherent disadvantages of being tedious and of giving low or high results depending upon whether precipitation is made after removal or in the presence of undesirable ions. Many investigators therefore have been searching for a time- and labor-saving method, having reasonable accuracy and wide application. The ever-increasing number of papers appearing in the literature is sufficient proof that the analytical chemist of today is still in need of a satisfactory and practical procedure.

Much significant and valuable work has been done in recent years to achieve this purpose. Of all the various means of approach, the most promising were the volumetric methods using oxyquinone derivative solutions to determine the end point. Elaborate literature references are given by Streibinger, Zombory, and Pollak (3) and by Schroeder (2).

Over a thousand volumetric sulfate determinations were made by the writer, following proposed methods in which oxyquinone derivative solutions to determine the end point are used. In more than 20 per cent of these determinations, he was unable to obtain check or acceptable figures, as the gradual color change made the end-point observation very difficult.

He therefore started an elaborate investigation to determine the causes or factors that were responsible for obtaining accurate results in some instances and not in others. At the very beginning, experimental evidence showed that it was not sufficient to accept the fact that oxyquinone compounds form red-colored barium salts, and that the presence of interfering ions is the cause of the discrepancies in the results. He therefore attempted to clear up the mechanism of the end-point reaction and studied the very interesting behavior of these compounds in solution. This investigation is not yet completed, and its results will be the subject of a separate paper.

The method described herein is the first practical achievement of this investigational work. It has been tried out on a large number of coal samples and on samples of various industrial products, yielding satisfactory check results in every case.

In the present method the author coordinates well-known analytical procedures. For the end-point determination he takes advantage of the fact that with a spot test on filter paper, using oxyquinone compound solutions as reagents, the presence of less than 1 γ of Ba^{++} ion may be positively detected. As a reagent either tetrahydroxyquinone or dioxidiquinone (rhodizonic acid) salt solutions can be used. The preparation of these reagents is described by Homolka (1). The author prefers to call these compounds reagents instead of indicators, for the reason that they do not follow Wilhelm Ostwald's theory, accepted for organic indicators.

The following solutions are necessary for the determination:

Standard barium chloride solution. The normality may vary according to the amount of SO_4^{--} ion to be determined and the degree of accuracy desired.

The present method coordinates various well-known analytical procedures. It is based on the fact that the presence of a few ten-millionths of a gram of Ba^{++} ion can be definitely detected by means of a spot reaction on filter paper with a solution of oxybenzoquinone derivatives. By using standard solutions of varying normalities a desired accuracy can be very easily obtained in all practical determinations.

Standard sodium or potassium sulfate solution. The normality should correspond to that of the barium chloride solution.

Oxyquinone compound solution, prepared in the laboratory or secured on the market.

General Procedure

Introduce the solution containing the sulfate into a 250-cc. beaker, render acid with hydrochloric acid, evaporate to a volume of about 25 cc., and treat with an excess of ammonia. If the

presence of phosphates is suspected, precipitate with ferric chloride. Without filtering, evaporate the mixture to about 10 cc. and introduce barium chloride solution until a drop produces a definite red coloration on filter paper previously treated with the reagent solution. It is advisable to mark a strip, 10 to 12.5 cm. (4 to 5 inches) long and 0.6 cm. (0.25 inch) wide, with the reagent solution, so that successive tests can be made on the same paper, thus facilitating comparison with the reaction previously obtained. To make the spot test, the solution containing all precipitated matter must be ammoniacal in reaction.

Evaporate again to a volume of 10 cc., add approximately 0.5 gram of sodium acetate as a buffer, and test to see whether Ba^{++} is still in excess; render alkaline with ammonia and retitrate with the sodium sulfate solution until the presence of Ba^{++} is no longer shown. The addition of 0.1 cc. of standard barium chloride or sodium sulfate solution is sufficient (10 cc. volume) to bring about the reappearance or the disappearance of the red coloration on the test paper. The discharge of the red color is taken as the end point. The difference in readings of the two burets gives the exact result. Where great accuracy is not the chief requirement, the time of evaporation can be saved, but corrections should be made for volume differences previously ascertained on blank determinations.

STANDARDIZING SODIUM SULFATE SOLUTION AGAINST BARIUM CHLORIDE. (1 cc. = 1 mg. of S = 2.5 mg. of SO_3 = 3 mg. of SO_4 .) To 29 cc. of barium chloride add 30 cc. of the sodium sulfate solution, and evaporate to a volume of about 10 cc. Render it alkaline with 3 drops of strong ammonia and add about 0.5 gram of sodium acetate. If the spot test is negative introduce 1.5 cc. more of the barium chloride solution when a definite rose-red border line develops on the test paper. For back-titration 0.5 cc. of the sodium sulfate is used. Addition of 0.1 cc. of either solution is sufficient to make the red color appear or disappear on the test paper.

Three gravimetric checks are made. Each time 30 cc. of sodium sulfate solution are drawn from the same buret and the average weight of barium sulfate equals 0.2172 gram or 29.85 mg. of sulfur.

DETERMINATION OF SULFUR IN COAL. Neutralize the collected washings of the calorimetric bomb, after the B. t. u. determination, with the usual sodium carbonate solution, using methyl orange as an indicator. In most cases the volume of sodium carbonate solution used gives an indication of the approximate amount of sulfur present. First neutralize the solution with hydrochloric acid, add 8 to 10 drops in excess, and then oxidize with 5 to 6 cc. of saturated bromine water. Evaporate the solution to 20 to 25 cc., then render it ammoniacal, and evaporate further to about 10 cc.

Add barium chloride solution in excess (spot test positive) and follow the general procedure. Filtration now is not necessary, as by making the spot test on the prepared filter paper, the precipitates present in the drop will remain fixed in the center. In the case of bituminous coals, which contain 12 to 25 mg. of sulfur per gram, standard barium chloride solution having a value of 1 mg. of sulfur per cc. is used. For hard coals, in which more than 1 per cent of sulfur is rarely found, the use of a 0.025 *N* barium chloride solution is advisable (1 cc. = 0.4 mg. S = 1 mg. SO_3 = 1.2 mg. SO_4).

TABLE I. TOTAL SULFUR DETERMINATION

Analysis	Sulfur Found in Rubber	
	Gravimetric Mg.	Spot test Mg.
1	18.12	17.5
2	16.93	17.9
3	17.5 ^a	18.3
4 ^b	15.8	15.7

^a Gravimetric determination made after the bulk of zinc had been removed from the solution with sodium hydroxide.

^b Two 1-gram samples were burned. After oxidation and precipitation of the bulk of zinc from the united bomb washings, the filtrate was brought to 200 cc. volume. The colloidal zinc hydroxide precipitate was washed 8 times with cold water, 6 to 8 cc. at a time. A volume of 100 cc. was used for each determination.

The zinc hydroxide precipitate was redissolved in hydrochloric acid, treated according to the general procedure, and titrated with a 0.025 *N* barium chloride solution. In the zinc hydroxide precipitate 3.0 mg. of sulfur were found.

The following is a tabulation of sulfur results, on a gram basis, obtained in several types of coal, by both the gravimetric and the present volumetric methods:

	Gravimetric Mg.	Spot Test Mg.
Barley	10.2	10.3
Semibituminous slack	36.4	36.9
Bituminous nut	21.6	21.6
Bituminous R/M.	24.8	24.8

In a series of 30 determinations a 0.5-mg. deviation was the largest found. In 18 cases there were no differences in the results found by the two methods. On the remaining samples the checks were between 0.1 and 0.3 mg.

A B. t. u. and volumetric determination can be finished conveniently in 2 hours. In routine work 6 sulfur determinations may be made in 3.5 to 4 hours' time by one operator with two oxygen bombs at his disposal.

TOTAL SULFUR DETERMINATION IN RUBBER. Burn a 1-gram sample with oxygen (25 atmospheres) in the calorimetric bomb. After oxidizing the collected washings with bromine water, follow the general procedure. In spite of the presence of amphoteric zinc, exceeding 10 to 20 times the amount of sulfur, the end point determination is definite and accurate to at least 0.2 cc. of the standard solution used.

Four volumetric determinations and gravimetric checks were made on the same rubber sample, each time using 1 gram of the sample (Table I). The gravimetric determination was made in the presence of zinc. The determinations when the author's procedure was pursued were finished in 1 to 1.25 hours, including the weighing time.

DETERMINATION OF SULFATE IN PLASTER OF PARIS. Weigh preferably 5 grams of the sample, dissolve, and make up to 500 cc. volume, to assure a fair representation of the material. Take a 10-cc. aliquot for a determination, or transfer a 0.1-gram sample into a 250-cc. beaker and dissolve in hydrochloric acid and water, according to standard methods. The total volume should not exceed 20 to 25 cc. Introduce into the hot solution standard barium chloride solution (1 cc. = 1 mg. S) in excess and then follow the general procedure described above.

In 10 cc. of solution representing 0.1 gram of plaster of Paris, the gravimeter method gave 82.5 per cent of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, and the spot test 82.8 per cent. The total time consumed in making this type of analysis, using a 0.1-gram sample, was between 0.5 and 0.75 hour.

DETERMINATION OF SO_4^{--} IN CEMENT. Transfer a 1-gram sample into a 250-cc. beaker, bring it into solution according to approved methods, and dilute with hot water to 20 to 25 cc. Introduce into the hot acid solution 0.025 *N* barium chloride solution in excess, heat to boiling, and follow the general procedure for an end-point determination.

An analysis of a cement gave the following results: by the gravimetric method, 18.3 mg.; by the proposed spot test,

18.7 mg. The time consumed for the volumetric analysis, including the weighing, was 0.75 hour.

DETERMINATION OF SO_4^{--} IN ZINC SULFATE. After solution, follow the general procedure.

In 10 cc. of zinc sulfate solution analyzed by both methods the following quantities of SO_4^{--} ions were found: gravimetric, 49.5 mg.; volumetric, 49.8 mg. The volumetric analysis was performed in 0.5 hour.

DETERMINATION OF SO_4^{--} IN ALUM OR ALUMINUM SULFATE. To an aliquot of the sample, introduce the standardized barium chloride solution in excess. Heat to boiling, neutralize, add an excess of ammonia, then follow the general procedure.

Using both methods, in 10 cc. of solution the following quantities of SO_4^{--} ions were found: gravimetric, 46.14 mg.; present volumetric method, 45.6 mg. The volumetric analysis took 15 to 20 minutes.

The barium sulfate precipitate after weighing was extracted with dilute hydrochloric acid. The filtrate was evaporated to a volume of 2 to 3 cc. and then made alkaline with ammonia in excess. A white flocculent precipitate soluble in sodium hydroxide was produced, showing the presence of occluded alumina in the barium sulfate and thus accounting for the higher value obtained by the gravimetric method.

DETERMINATION OF SULFUR IN IRON AND STEEL. Dissolve the iron or steel in an evolution flask in the usual way and collect the hydrogen sulfide in 25 cc. of water containing 1 gram of sodium hydroxide. Acidify with hydrochloric acid, oxidize with bromine water, and evaporate to 3 to 5 cc. volume. Then add ammonia, and follow the general procedure, using the 0.025 *N* solutions of barium chloride and sodium sulfate.

Analysis of two 5-gram samples gave by the cadmium sulfide method 2.45 and 1.70 mg., by the volumetric method 2.32 and 1.52 mg. of sulfur.

DETERMINATION OF GELATIN-ASH SULFATE CONTENT. Ash 5 grams of gelatin by the standard method in a platinum dish. Dissolve the ash in 5 to 10 cc. of hot water and 2 to 3 cc. of strong hydrochloric acid. Add 2 to 3 drops of ferric chloride solution, neutralize, and render it ammoniacal with ammonia, after which introduce 0.025 *N* barium chloride solution in excess and follow the general procedures.

Analysis of a 5-gram gelatin sample gave by the gravimetric method 11.5 mg., and by the volumetric method 11.28 mg. of sulfur. After ashing was completed, the determination by the author's method was finished in 15 to 20 minutes.

DETERMINATION OF SULFUR IN INSECTICIDE SOLUTIONS. Two samples of insecticides were analyzed by the gravimetric and volumetric methods. For the gravimetric determination in each instance two 2.5-gram samples were burned with oxygen at 30 atmospheres' pressure in the calorimetric bomb; for the volumetric determination a 2.5-gram sample was used. The SO_4^{--} ions resulting from the combustion were determined in the gravimetric determinations according to the standard procedure, and in the volumetric determination by the present method. The time consumed for the volumetric determination, including weighing the sample, was 1.25 hours.

	Mg. ^a
Sample 1	
Gravimetric	4.2
Volumetric	4.4
Sample 2	
Gravimetric	3.88
Volumetric	3.88

^a Results calculated to a 2.5-gram sample.

Discussion

The examples were selected at random. All the volumetric determinations (except check determinations of sulfur in steel) were made by the writer. All the gravimetric analyses and their checks (except coal analysis) were made by workers with

15 to 25 years of analytical laboratory experience. In every instance the results by the volumetric method were completed in the specified time, but those by gravimetric methods were not complete until the following day. A great number of precise gravimetric tests in triplicate were made on coal and no result was higher than any obtained by the proposed method. In all tests performed by the author's present method, there was no instance when a definite end point could not easily be secured within a range of 0.1 to 0.2 cc.

No interference was experienced when common ions were present. The strontium ion if present may interfere with obtaining the true end point, as it gives a red-colored precipitate with oxyquinone compounds; however, this precipitate is soluble in dilute acetic acid.

From the qualitative experimental evidences presented, it appears that the method can be applied not only for the accurate determination of sulfur or sulfate in inorganic technical products, but also in biochemical laboratories (urine analysis, etc.), and in the organic chemical industries—for instance, for the rapid determination of free sulfuric acid and sulfonated components in phenol and naphthalene sulfonation mixtures.

Acknowledgment

As the analytical part of this work was carried out in the Central Testing Laboratory of the City of New York, the author wishes to express appreciation to Stroud Jordan and the entire staff of the laboratory for their coöperation. He is indebted to Stanley Mayer for many encouraging suggestions, and to Martin Lang and Harry Dash for their assistance and performance of a great number of gravimetric checks.

At the same time the author feels it his duty to express his sincere thanks to the Ba-Re Company, 185 Madison Ave., New York, N. Y., for the liberal supply of stable solution of oxyquinone compounds, which courtesy enabled him to achieve the foregoing work of research.

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RECEIVED February 3, 1937. Part of a paper presented first at the regular meeting of the chemists of the Central Testing Laboratory of the City of New York, January 9, 1937.

A Simple Gas Thermoregulator

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THERE are occasions in many laboratories when, if for any reason an electric thermoregulator is not convenient or available, a gas regulator could be used. In most gas regulators now in use, the flow of gas is controlled by a column of mercury which is adjusted to close a small inlet at the temperature desired. A common fault of these regulators is that the current of incoming gas causes small globules of mercury

to rise and adhere to the sides of the tube, thereby causing a rise in temperature above that which is desired.

The accompanying sketch illustrates a gas regulator in which the flow of gas is controlled by a glass valve, 2, which closes or opens the inlet opening as the mercury column rises or falls because of changes of temperature. Thus, any splashing of mercury and consequent change of temperature are prevented. The regulator can be adjusted to the desired temperature by turning the thumbscrew, 7, as in other gas regulators.

The principal dimensions are indicated on the sketch. Tubes 1, 4, 6, and 9 are of 5-mm. inside diameter, the mercury bulb, 5, and the valve chamber, 3, are of 15- and 8-mm. inside diameter, respectively, and the valve, 2, is of 4-mm. outside diameter.

The opening in the inlet tube which acts as a valve seat is prepared before sealing by cutting the tube off square and filing, if necessary, to make it perfectly flat. A small notch about 0.25 mm. deep is made across one edge, and the end is then uniformly polished in a flame. The valve is made by drawing out a thin-walled tube to a diameter of 1 or 2 mm. and sealing it so as to leave a prong about 1 cm. long. The tube is heated carefully and a slight bulb is blown at the point where the tube starts to taper. The opposite end is then drawn out and sealed about 3 cm. from the bulb. The valve is then inserted and the inlet tube is sealed in place.

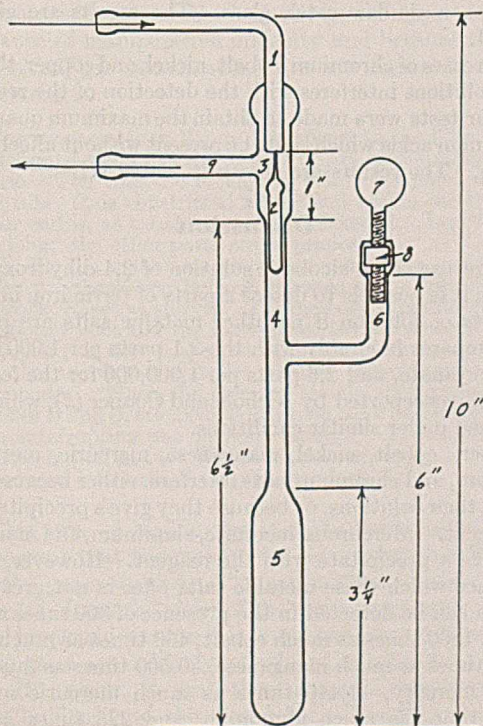
Any thumbscrew taken from a small ringstand clamp can be used for an adjusting screw. A small nut, selected to fit the screw, is filed down to about 6 or 7 mm. in diameter and cemented into the enlarged opening in the side arm, 6, with a thick litharge and glycerol cement.

In order to permit accurate adjustment for all temperatures, the top of the mercury in the adjusting arm should be about 5 mm. below the level of the mercury in the main column when at room temperature.

Other details of construction are evident from the sketch.

A regulator of this type has been in use for more than a year, and controls the temperature of a 12-liter water bath within a range of 50° to 100° C., with a variation of about $\pm 0.5^\circ$ C.

RECEIVED May 3, 1937



2,4-Dihydroxyacetophenone as a Qualitative Reagent for Ferric Iron

S. R. COOPER, Howard University, Washington, D. C.

SEVERAL methods have been proposed for the qualitative detection of ferric iron, but the ferrocyanide and thiocyanate methods of Wagner (3) are commonly employed in systematic analysis. Necki and Sieber (1) prepared 2,4-dihydroxyacetophenone and observed that it gave a red color with a solution of ferric chloride.

The purpose of this investigation was to ascertain if this color reaction could be used as the basis for a sensitive qualitative detection of ferric iron.

Preparation of Reagents

The 2,4-dihydroxyacetophenone was prepared and purified according to the method given by Necki and Sieber (1). One and five-tenths parts by weight of anhydrous zinc chloride were dissolved in 1.5 parts by weight of glacial acetic acid, through the application of heat, and to the solution one part by weight of resorcinol was added. The mixture was heated on a sand bath until it had started to boil (145° to 150° C.). Then the flame was removed and the reaction allowed to complete itself while the mixture remained on the sand bath. The temperature was kept below 150° C. in order to prevent the formation of resinous products. Upon diluting the reaction mixture with cold water, the crystalline compound separated. These crystals were washed with a cold dilute solution of hydrochloric acid to remove the zinc chloride. The substance was further purified by mixing it with dilute hydrochloric acid solution and animal charcoal, and boiling for a few minutes. The hot solution was filtered, and upon cooling the compound precipitated. This procedure was repeated several times, giving a final product which consisted of white needles. The melting point of the compound was 142° C. A solution consisting of 10 grams of the compound dissolved in 100 ml. of 95 per cent ethyl alcohol was made.

The following solutions were prepared and standardized: (1) a solution of ferric chloride containing approximately 2 mg. of iron per ml. and 5 ml. of 6 *M* hydrochloric acid per liter; (2) solutions of copper nitrate, mercurous nitrate, mercuric nitrate, chromic nitrate, cobalt nitrate, nickel nitrate, manganese chlo-

ride, and aluminum chloride containing approximately 100 mg. of metal ion per ml.; (3) approximately 2 *N* solutions of hydrochloric, nitric, and sulfuric acids.

Sensitiveness of Test for Iron

One milliliter of the iron solution to be tested was placed on a colorless watch glass, and 2 drops of the reagent were added. The coloration produced was compared with 1 ml. of the same solution to which 2 drops of alcohol had been added. All the solutions of ferric iron were made from the stock solution by proper dilution with distilled water. The results are given in Table I.

The limit of detection was 0.002 mg. of iron in 1 ml. of solution, or 2 parts of iron in 1,000,000 parts of solution.

Action of Foreign Salts and Acids on Color Test

Solutions of salts of silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, divalent iron, aluminum, chromium, cobalt, nickel, manganese, zinc, barium, strontium, calcium, sodium, potassium, magnesium, and the ammonium radical were tested with the reagent to observe if any reactions occurred. No reactions were noted except in the following cases: mercurous nitrate gave a light yellow precipitate upon standing, mercuric nitrate gave a white precipitate upon standing, and aluminum and manganese chlorides gave white precipitates.

Tests were next made to ascertain the maximum quantity of the interfering metal salts, which could be present without interfering with the detection of the iron. For these tests 1 ml. of a mixture of the ferric iron solution and the interfering substance was placed on a watch glass, and 3 drops of the reagent were added. The colors produced were compared with 1 ml. of the mixture containing 3 drops of alcohol and placed on a similar watch glass. The results are given in Table II.

In the cases of chromium, cobalt, nickel, and copper, the color of the solutions interferes with the detection of the red color.

Similar tests were made to obtain the maximum quantity of the common acids which could be present without affecting the reaction. The results are shown in Table III.

Discussion

By the use of an alcoholic solution of 2,4-dihydroxyacetophenone it is possible to detect 2 parts of ferric iron in 1,000,000 parts of solution if no other metallic salts are present. This compares favorably with the 2.1 parts per 1,000,000 for the thiocyanate, and 2.6 parts per 1,000,000 for the ferrocyanide tests as reported by Nichols and Cooper (2), which were performed under similar conditions.

Copper, cobalt, nickel, manganese, mercuric, mercurous, aluminum, and chromium salts interfere, either because of the color of their solutions, or because they give a precipitate with the reagent. Mercurous, mercuric, aluminum, and manganese salts give a precipitate with the reagent. However, the interference which these metallic salts offer is not great, since the iron can be detected in the presence of 300 times as much copper, 1800 times as much cobalt, 400 times as much nickel, 25,000 times as much manganese, 30,500 times as much mercurous mercury, 11,440 times as much mercuric mercury, 32,500 times as much aluminum, and 225 times as much

TABLE I. SENSITIVENESS OF TEST FOR IRON WITH 2,4-DI-HYDROXYACETOPHENONE

Volume of Solution ml.	Weight of Iron Mg.	Observation
1	0.0040	Light red color
1	0.0033	Light red color
1	0.0025	Light red color
1	0.0022	Very light red color
1	0.0020	Faint red color
1	0.0018	No visible color

TABLE II. SENSITIVENESS OF TEST IN PRESENCE OF INTERFERING METAL IONS

Salt	Limit of Detection for Iron Mg./ml.	Weight of Interfering Metal Present Mg./ml.	Ratio of Iron Metal to Iron
Cu(NO ₃) ₂	0.2857	86.71	300
Co(NO ₃) ₂	0.0571	102.34	1,800
Ni(NO ₃) ₂	0.2000	88.11	440
MnCl ₂	0.0041	101.49	25,000
Hg ₂ (NO ₃) ₂	0.0034	103.65	30,500
Hg(NO ₃) ₂	0.0097	110.94	11,440
AlCl ₃	0.0031	100.59	32,500
Cr(NO ₃) ₃	0.5000	112.53	225

TABLE III. LIMITING CONCENTRATIONS OF COMMON ACIDS

Acid	Limiting Concentration N	Weight of Iron Mg.
HCl	0.0606	1.000
HNO ₃	0.0608	1.000
H ₂ SO ₄	0.0314	1.000

chromium. It is possible in solutions of ordinary analytical strength (10 mg. of metal ion per ml.) to detect the ferric iron in the original solution, since aluminum, mercurous mercury, mercuric mercury, and manganese salts do not precipitate before the red color has appeared.

The solution can be approximately 0.06 *N* in hydrochloric acid, 0.06 *N* in nitric acid, or 0.03 *N* in sulfuric acid without affecting the sensitiveness of the test. However, if the solution is strongly acid, it can be neutralized to the point of incipient precipitation with ammonium hydroxide or sodium hydroxide solution and then the test applied.

Oxalates, tartrates, and citrates are not usually present in a solution which is to be examined qualitatively, but if they are present they interfere with the detection. From the very

nature of the test, phosphates must be absent since they precipitate the ferric iron. Sugar and glycerol have no effect upon the reaction.

In short, the test compares favorably with the common methods which are employed for the detection of ferric iron. Above all, the compound is not difficult to prepare and is not costly.

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A Sloping Manometer

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NEITHER the McLeod nor the Dubrovin gages are suitable for the measurement of pressures of the order of 1 mm. when the pressure is subject to constant variation and must be continuously followed. In a previous article (1) reference was made to a sloping manometer used for rapid and accurate measurement of such pressures; because of its convenience, some curiosity has been expressed as to its design and the method of filling. The complete manometer, together with the filling equipment, is shown in Figure 1. Although the method of filling is fully as rapid as that of Doja (2), there is an advantage in that the mercury is boiled out within the apparatus and that the mercury which passes into the manometer does not come into contact with stopcocks or the grease there present. The rapidity and convenience of this method are an advantage over Cameron's distillation method (3). Ordinary boiling out is, of course, an unsatisfactory method of filling this type of manometer because of manipulative difficulty and because even a trace of residual gas becomes an important factor in sloping manometers.

The manometer in Figure 1 is affixed to the filler at A, and is so designed that the legs, B and C, are in the same plane when in use. The trap, D, is slightly below the plane when in use. The tube, C, is constricted at the end within the trap, and the upper end is, as usual, somewhat thickened. Leg C is about 30 cm. long; the other parts are in proportion.

To fill, the manometer is baked out under vacuum and the mercury in the 250-cc. bulb, E, is boiled at the same time with the stopcock, F, set as shown. The mercury is permitted to become completely cool and the manometer is then rebaked and cooled. Stopcock F is then turned so as to admit air slowly into tube G, and the mercury is thus forced over through tube H into the manometer. When the mercury stands approximately halfway in tubes B and C, stopcock F is turned back to the position shown, thus interrupting the mercury stream. The manometer may then be cut off at A. Whenever desired, more mercury may be introduced into bulb E through stopcock F.

This type of manometer is particularly useful when it is important that the manometer liquid shall not be a solvent for the gases studied. The constriction at the open end of tube C reduces the effect of the mercury hammer. The trap, D, is employed because it is found as a matter of practice that, when gases are suddenly introduced into a sloping manometer (as often occurs in use), there is a tendency toward pulling over bubbles into the closed leg. The trap prevents this.

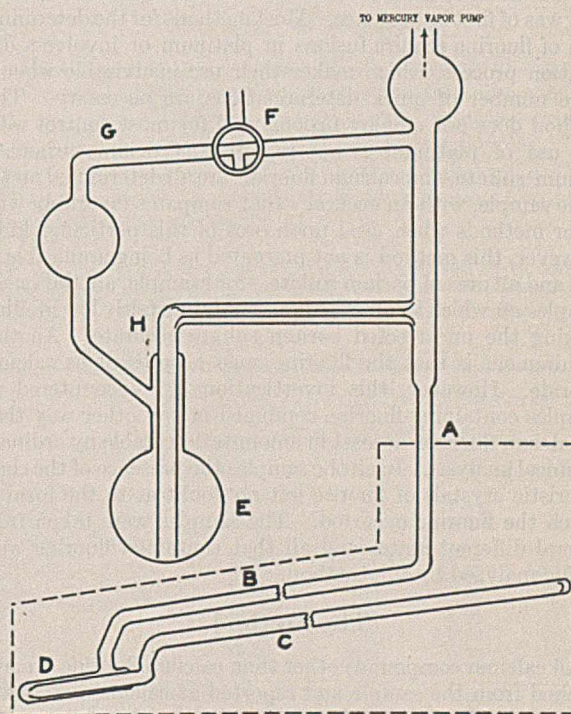


FIGURE 1

Any bubbles pulled over collect just below the inner seal and have no effect on the pressure reading.

If subsequent sticking is to be avoided, the gage should be thoroughly cleaned before any attempt is made to fill it.

The author has used the manometer successfully at a slope ratio of 25 to 1. The method of filling is, of course, equally satisfactory for the ordinary vertical U-tube manometer.

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Rapid Analysis of Barite Ores Containing Calcium Fluoride

Without the Use of Fusions

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THE analysis of barite ores that contain a considerable amount of calcium fluoride presents a number of unusual difficulties, especially if a large number of samples must be analyzed in a short time. The books on quantitative analysis give methods suitable for the determination of barium sulfate in a high-grade barite ore, and methods for fluorine in fluor-spar, but these methods were not intended for samples in which barium sulfate and calcium fluoride occur in combination.

The following method was designed for use in the control work on a series of concentration tests made on barite ores at the Southern Experiment Station of the U. S. Bureau of Mines. One of the main purposes of these tests was the elimination of calcium fluoride from the ores and for this reason its estimation was of first importance. Most methods for the determination of fluorine require fusions in platinum or involve a distillation process, which makes their use inadvisable when a large number of quick determinations are necessary. This method does not employ fusions, and for most control work the use of platinum is not required. Calcium carbonate, barium sulfate, and calcium fluoride are all determined on the same sample, with an accuracy that compares favorably with other methods when used upon ores of this particular kind. However, this method is not presented as being applicable to any and all ores of barium sulfate—for example, all the barite samples on which this method was used were fairly low in silica, making the uncorrected barium sulfate accurate. Another requirement is that the fluorine must be present as calcium fluoride. However, this investigation has encountered no samples containing fluorine combined in any other way than as calcium fluoride, at least in amounts detectable by ordinary chemical analysis. In all the samples the presence of the characteristic crystals of fluorite left no doubt as to the form in which the fluorine occurred. The samples were taken from several different states and all that contained fluorine were easily analyzed by this method.

The Method

All calcium compounds other than calcium fluoride are first leached from the sample and reported as calcium carbonate. Then the calcium fluoride, together with other acid-soluble compounds, is decomposed by a new wet method, leaving the barium sulfate and a small amount of silica behind as a residue. The amount of calcium oxide obtained from the decomposition of the calcium fluoride is then determined, and from this the fluorine or calcium fluoride is calculated.

PROCEDURE 1. DETERMINATION OF CALCIUM CARBONATE. Weigh out a 1-gram sample of <100-mesh ore into a 100-cc. lipless beaker, add 10 cc. of 10 per cent acetic acid, and give the beaker a rotary motion until the sample is thoroughly wetted by the solution. Cover with a watch glass and digest on hot plate for 1 hour. Keep at a temperature considerably below boiling, by placing the beaker at a distance from the part heated by direct flame. Give the beaker a rotary motion from time to time to bring the sample into contact with fresh liquid. Filter through a retentive type of filter, such as C. S. & S. 589 blue-label paper, and wash six times with cold water. If the sample contains gypsum more washings will be necessary. However, none of the samples encountered in this investigation contained more than a trace of gypsum, if indeed they contained any at all.

Ignite the filter and residue at a temperature of about 537.77° C. (1000° F.) for 30 minutes, weigh the residue, and report the loss in weight as calcium carbonate. If the loss on ignition at 537.77° C. (1000° F.) for 30 minutes is obtained from an unleached sample and subtracted from the above calcium carbonate, a more nearly correct figure will be obtained. This treatment is assumed to remove all calcium except that combined as calcium fluoride from the sample. No compounds that would render this assumption incorrect have been found in any samples tested.

PROCEDURE 2. DETERMINATION OF BARIUM SULFATE. Return the ignited insoluble to the 100-cc. beaker and add 20 cc. of concentrated hydrochloric acid and then approximately 0.5 gram of crystalline boric acid. The purpose of the boric acid is to speed up and make complete the decomposition of the fluor-spar. Boil gently for 15 minutes and then add 1 cc. of concentrated nitric acid. Continue just below boiling for 45 minutes longer. The volume of the solution should be down to about 7 or 8 cc.; if it tends to get below this volume before the time is up, add a little concentrated hydrochloric acid as needed. When the time is up, remove from the hot plate and add concentrated hydrochloric acid till the volume is approximately 10 cc. This may be gaged with sufficient accuracy by comparing with a similar beaker containing 10 cc. of water. Return to the hot plate and boil gently for about 5 minutes, then wash the contents into a 250-cc. beaker, and dilute to about 75 cc. with distilled water. Add 2 drops of methyl red indicator and make alkaline, using concentrated ammonium hydroxide. Add concentrated hydrochloric acid, drop by drop, till acid and then add 2 cc. in excess. If, as sometimes happens, the methyl red is decolorized before the neutralization can be completed, litmus paper may be used as the indicator.

Dilute to 100 cc. using distilled water, and allow to stand for 1 hour. Heat quickly on a hot plate, and when near boiling add 2 cc. of dilute sulfuric acid (1 part of concentrated sulfuric acid to 39 parts of water), boil 5 minutes, and filter while hot. After the filter has drained, fill with hot water, drain completely, and repeat, then give four ordinary washings with cold water. Ignite the filter and residue at 815.5° C. (1500° F.). Weigh and report as barium sulfate. If the barium sulfate is fairly high (95.0 per cent or over), this figure will be fully as accurate as any of the usual fusion determinations. If the ore contains very little quartz, it will be accurate at much lower percentages of barium sulfate. If desired, this barium sulfate may be corrected for any silica it contains by treating it according to Procedure 2S.

PROCEDURE 2S. CORRECTION OF BARIUM SULFATE FOR SILICA. Transfer the barium sulfate residue to a platinum crucible, ignite for a minute, cool, and weigh crucible and contents. Add 5 cc. of concentrated hydrofluoric acid and 4 or 5 drops of concentrated sulfuric acid, evaporate to dryness, fume off the remaining sulfuric acid, and ignite 15 minutes at about 815.5° C. (1500° F.). Report the weight of the residue as barium sulfate after adding 0.002 gram to the weight of this residue to allow for its solubility in the hydrochloric acid from which it was filtered. This correction is not recommended unless the barium sulfate has been purified from silica as above, as the two sources of error tend to balance each other.

PROCEDURE 3. DETERMINATION OF CALCIUM FLUORIDE. Heat the filtrate from Procedure 2 to about 60° C., add 2 drops of methyl red indicator, and then add concentrated ammonium hydroxide till alkaline. Make just acid with 10 per cent oxalic acid solution and then add 12 cc. in excess. Bring quickly to a boil and continue for about 2 minutes, remove from the hot plate, and add 100 cc. of a saturated solution of ammonium oxalate. Allow to stand 1 hour and filter cold. Wash 6 times with a hot 2 per cent solution of ammonium nitrate, to which has been added a little ammonium oxalate. Ignite filter paper and precipitate at 870° to 925° C. (1600° to 1700° F.) for an hour. Cool in a desiccator and weigh promptly. The weight of the calcium oxide times 1.3923 equals the weight of calcium fluoride.

The filtrate from Procedure 2 contains all the calcium derived from the decomposition of the fluor-spar, the other calcium compounds having been removed by the acetic acid extraction. It is only necessary to determine the calcium in this solution and then

TABLE I. INTERFERENCE PRODUCED BY DEFINITE AMOUNTS OF CERTAIN MINERALS

(One gram of barite sample X used in each case. Procedure 3L to eliminate lead not used in these tests.)

Mineral Added	Gram	Interfering Compound	Analyses by Procedures 1, 2, and 3		
			CaCO ₂ %	BaSO ₄ %	CaF ₂ %
...	..	None	1.92	96.19	1.03
...	..	None	2.03	96.07	1.00
Sphalerite	0.05	5% ZnS	1.91	96.22	1.06
C. P. Fe ₂ O ₃	0.05	5% Fe ₂ O ₃	1.86	95.90	1.06
Galena	0.01	1% PbS	1.91	96.09	1.00
Galena	0.05	5% PbS	1.75	96.23	1.18
Celestite	0.01	1% SrSO ₄	2.08	96.37	1.35
Celestite	0.05	5% SrSO ₄	2.42	97.41	2.53
Phosphate rock	0.01	1% Ca ₃ (PO ₄) ₂	2.25	96.24	1.42

to calculate the amount of calcium fluoride from which it was derived. However, procedures commonly recommended for calcium cannot be used here. In the first place, iron and aluminum cannot be separated from calcium by the use of ammonium hydroxide, because calcium fluoride is precipitated along with the iron and aluminum as soon as the solution becomes alkaline. Therefore, the calcium is precipitated as oxalate in an acid solution. At this point, if there is much lead in the sample it will be partially precipitated along with the calcium, and so the method splits into two variations. If the sample contains not over 1 per cent of galena or lead sulfide the interference of the lead is very slight and may be neglected. If more than this amount of lead is present, use Procedure 3L.

PROCEDURE 3L. DETERMINATION OF CALCIUM FLUORIDE IN THE PRESENCE OF MORE THAN 1 PER CENT OF GALENA. Pass hydrogen sulfide into the filtrate from Procedure 2 for 5 minutes. A black precipitate will form if lead is present. Then add 2 cc. of 1 to 1 ammonium hydroxide and pass in hydrogen sulfide for about 3 minutes longer. Filter off the lead sulfide and wash several times with hydrogen sulfide water. The filtrate should still be acid. Boil the filtrate for about 1 hour to drive off the hydrogen sulfide, then make alkaline with ammonium hydroxide. If a black precipitate forms, make the solution acid with hydrochloric acid and boil longer to drive off all the hydrogen sulfide. Then on making alkaline the iron will come down as a reddish brown precipitate of ferric hydroxide, rather than a black one of iron sulfide. Now make acid with hydrochloric acid, adding 2 cc. in excess, and treat the solution by Procedure 3.

Interference of Other Minerals

This method is intended to give the amount of calcium carbonate, barium sulfate, and calcium fluoride present in the barite ores. If an appreciable amount of silica is present an approximate idea of its amount can also be obtained by correcting the barium sulfate for silica. Other constituents may be present in relatively small amounts. Those occurring in the ores tested in this work, named in order of importance, were ferric oxide, galena, and sphalerite. The sphalerite was present in only one sample, and then in very small amount.

Some data which will give an idea of the amount of interference caused by various minerals are reviewed in Table I. In every analysis, a 1-gram sample of the same high-grade barite was used, and a given amount of the mineral to be tested was added—for example, if 5 per cent of galena is mentioned it means that 0.05 gram of galena was added to the 1-gram sample of barite. This was not strictly a 5 per cent sample, but it did contain an amount of galena equal to 5 per cent of a 1-gram sample. By using 1 gram of barite in every case, the same analysis would always be expected from the barite and any deviation (outside of the limits of experimental error) was due to the mineral whose effect was being studied. Table I shows that 5 per cent of ferric oxide, 5 per cent of sphalerite, and 1 per cent of galena cause practically no interference in the analysis. Higher percentages of galena are cared for by using Procedure 3L. Any considerable percentage of strontium sulfate interferes with the accuracy of the method; it appears in the analysis as calcium carbonate, barium sulfate, and calcium fluoride, and some is not recorded at all. None of the samples

encountered in these tests contained strontium either as sulfate or carbonate. Strontium carbonate if present would interfere only with the calcium carbonate analysis. If any strontium sulfate is present, a portion of it will positively appear in the calcium oxide obtained from Procedure 3. As this calcium oxide contains only traces of barium and is comparatively free from other metals, it can easily be tested qualitatively for strontium. A heavy precipitate of strontium qualitatively be obtained from this calcium oxide if as little as 1 per cent of celestite (strontium sulfate) had been added to any of the barite samples. On the other hand, if the sample was fused to get into solution and then separated according to the usual scheme of qualitative analysis, 1 part of strontium sulfate in 95 parts of barium sulfate was very hard to detect.

Calcium phosphate is another constituent that should not be present if great accuracy is desired in the calcium fluoride determination. However, judging from the small amount of phosphorus present (Table II) in all the samples tested, it is not likely to cause trouble.

Table II gives data on four of the original untreated ores, each from a different locality. These analyses show that the minerals causing serious interference either were not present in the ores or else were there in such small amounts that their effect was negligible. The effects of the various correction procedures are also shown.

Accuracy of Method

The results obtained by this method, especially in regard to the calcium fluoride determination, were carefully checked. The calcium fluoride was run on several samples, using a method that depended on entirely different principles. This method, referred to in Table III as the distillation method, was modified from one used by the Krebs Chemical Company, and, briefly, was as follows:

A 10-gram sample was placed in a flask, and 100 cc. of concentrated phosphoric acid were added. Then water was added until the total volume was 125 cc. This mixture was distilled at con-

TABLE II. DETAILED ANALYSIS OF FOUR OF THE ORIGINAL ORES

Constituent	Constituent Present			
	Sample A %	Sample B %	Sample C %	Sample D %
CaCO ₂ (uncorrected for ignition loss)	8.78	2.26	1.41	0.52
Loss on ignition*	0.85	0.45	0.69	0.18
CaCO ₂ (corrected for ignition loss)*	7.93	1.81	0.72	0.34
BaSO ₄ by Procedure 2	81.89	34.51	87.57	94.23
BaSO ₄ by Procedure 2S*	81.98	34.20	87.42	94.02
SiO ₂ by Procedure 2S*	0.11	0.51	0.35	0.41
CaF ₂ *	7.89	56.42	4.87	4.48
Fe ₂ O ₃ *	0.44	0.29	5.42	0.15
PbS*	None	5.30	None	None
P*	0.01	0.02	0.01	0.01
Gypsum, maximum per cent*	0.13	0.11	0.09	0.07
BaCO ₃ , maximum per cent*	0.01	0.00	0.01	0.01
SrSO ₄	None	None	None	None
SrCO ₃	None	None	None	None
Total of constituents marked with asterisks	99.35	99.11	99.58	99.67

TABLE III. CALCIUM FLUORIDE ANALYSES BY TWO UNRELATED METHODS

Sample No.	Calcium Fluoride	
	Distillation method %	Method described in this paper %
1	16.56	16.71
2	2.59	2.74
3	7.75	7.89
4	1.32	1.38
5	26.40	26.31
6	4.81	4.87
7	11.16	11.26
8	4.49	4.48

TABLE IV. COMPARISON OF ORIGINAL ORE ANALYSES WITH CUMULATIVE ANALYSES FROM CONCENTRATION TESTS

Product	Analyses		
	CaCO ₃ %	BaSO ₄ %	CaF ₂ %
Fraction A-1	2.88	95.39	1.28
Fraction A-2	7.29	86.36	5.26
Fraction A-3	21.17	53.21	22.72
^a Composite, all fractions	8.76	82.00	8.00
Original ore A	8.78	81.89	7.89
Fraction B-1	0.42	97.40	1.95
Fraction B-2	1.07	83.96	12.56
Fraction B-3	1.62	71.00	22.30
^a Composite, all fractions	0.56	94.43	4.25
Original ore B	0.52	94.23	4.48

^a Cumulated on basis of individual weights and analyses.

stant volume through a condenser into a small quantity of ammonia water. After 400 cc. had been distilled over, all the fluorine was in the distillate. This distillate was then purified and the fluorine was precipitated by calcium acetate. It was then filtered off, washed, ignited, and weighed. This method appears to be reliable and closely checks the method described in this paper, as is shown in Table III.

Perhaps the best test of the accuracy of the method was given by analysis of the products in the various concentration tests. In the first place, an analysis of the original ore was

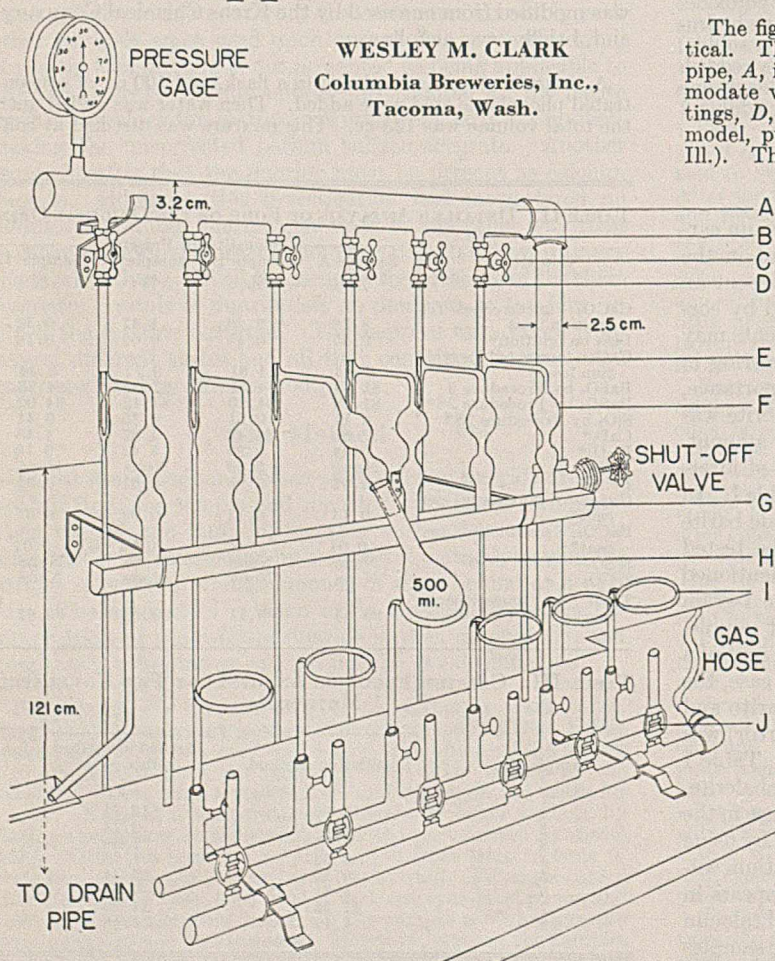
made and then the ore was put through the concentration process which separated it into several fractions of widely different chemical composition. These new fractions were then analyzed separately and were composited, each in proportion to its weight percentage, to determine the cumulative analyses. In other words, the cumulative analysis is the result that would have been obtained if all the fractions had been thoroughly mixed into one sample and this single sample analyzed.

Theoretically the cumulative analysis should be exactly the same as that of the original ore. Small losses during the concentration operations and experimental errors in the analyses themselves are responsible for slight departures from the ideal. However, when the analyses of the original ore and the calculated cumulative analyses are reasonably close together over a large number of tests, there is good reason to believe that the method is reliable. Table IV contains detailed analyses obtained from the samples of two concentration tests. It gives a general idea of what may be expected of this method, and shows that the method is not confined to samples whose analysis is limited to a certain narrow range.

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A Kjeldahl Digestion Apparatus

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THE easily constructed Kjeldahl digestion apparatus described below may be effectively used without a fume hood. It has no costly fittings, is economical of space, and each unit may be run independently of all the others, thus reducing operating expenses to a minimum.

The figure shows a six-unit set, but larger ones are also practical. The apparatus consists of a horizontal water reservoir pipe, *A*, into which are welded couplings, *B*, threaded to accommodate valves, *C*. Connected to the valves by short pipe fittings, *D*, are glass suction pumps, *E* (University of Minnesota model, purchased from E. H. Sargent and Company, Chicago, Ill.). These, like all the glass parts, are joined together by tapping over the ordinary rubber-tube connection. This type of union allows for sufficient flexibility of the parts to make the danger of breaking negligible.

The lower bulbs of the two-bulb stoppers, *F*, fit snugly against the lips of the Kjeldahl flasks, while the ends, projecting into the flasks, fit loosely. This facilitates use, and avoids breakage when removing the flasks for shaking, yet serves adequately to suck out the vapors during digestion. When not in use, the ends of the bulb-stoppers rest in a half section of acid-proofed pipe or shallow lead trough, *G*, by means of which a small amount of sulfuric acid drip is drained into the sink. Connecting the suction pumps to the drain pipe (below the table and not shown in the diagram) are pieces of glass tubing, *H*, of the same diameter as the lower arm of the pumps. These fit into holes in the drain pipe by means of rubber stoppers, which are then sealed with pitch and taped. The ring supports, *I*, for the flasks are adjustable, and for convenience are attached rigidly by two clamps to the heating unit. The burners, *J*, are the Fletcher adjustable type, with threads in the base for screwing into the gas line. The shutoff valve, while not necessary, is convenient in case it is desired to drain *A* or repair one of the valves, *C*.

As for the corrosive action of the hot vapors and strong acid on the rubber-tube connections, the union between the bulb-stopper and the pump would be the only one seriously affected, the other two being on the water line and continually flushed out by the flowing water. However, because of the

large volumes of air drawn through this connection when the suction is on, which keep the upper end of the flask and the bulb-stopper cool, any action on the rubber is very greatly minimized. Furthermore, the operator can manipulate his flasks with perfect comfort and safety.

If a larger number of units is desired, it is only necessary to increase the size of the water supply and drainage pipes. For the six-unit set a 3.75-cm. (1.5-inch) supply and a 7.5-cm. (3-inch) drainage pipe serve adequately when the pressure is 2.8 kg. per sq. cm. (40 pounds) or more. For a 12-unit set a 6.25-cm. (2.5-inch) supply and a 10-cm. (4-inch) drain pipe would suffice.

Diphenylguanidine as a Standard in Neutralization Processes

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SOME 14 years ago Carlton (7) proposed the use of symmetrical diphenylguanidine as a reference substance in acidimetry and alkalimetry. His test determinations are excellent; hence, in view of the obvious advantages to be gained through the employment of a soluble and sufficiently strong (18) organic base, it is rather surprising that the method has not attracted more widespread attention. Several other authorities (6, 9, 14, 15), presumably on the basis of experience, have commented upon the material in question with great lack of agreement. Accordingly, the somewhat controversial state in which the subject seems to exist led to the present re-examination.

Experimental

In putting the matter to the test, reliance was placed upon constant-boiling hydrochloric acid; for the composition of aqueous hydrogen chloride, when distilling at a fixed temperature under the existing pressure, appears to have been exhaustively studied (1-5, 8, 10, 11, 13, 16, 17, 19, 21-27). Having prepared a considerable quantity of such acid, an approximately 0.1 *N* solution was obtained by diluting an appropriate amount of it to the requisite volume. The normality factor of the resulting liquid was calculated and found to be either 0.10057 (13) or 0.10059 (10). For greater surety, the value of the solution was established gravimetrically by precipitating the chloride ion with silver nitrate, taking the usual precautions that make for accuracy (12, 20). Two such experiments showed the hydrochloric acid to be 0.10054 *N* and 0.10049 *N*.

In the purification of diphenylguanidine the instructions of Carlton (7) were conscientiously followed, using a supposedly high-grade specimen of the base, which had been purchased from a reputable supply house. Moreover, in carrying out titrations with the above-described hydrochloric acid, Carlton's "double indicator" (bromophenol blue and methyl red) was introduced into the alcoholic solution of the recrystallized diphenylguanidine to reveal the point of complete reaction. Four experiments yielded the following concordant results: 0.10114 *N*, 0.10117 *N*, 0.10114 *N*, and 0.10111 *N*, the average of which is 0.10114 *N*.

Conclusions

This discrepancy between the normality deduced from constant-boiling hydrochloric acid (0.10058 *N*) and obtained by titrating the basic substance, amounting to nearly 0.56

The material for the apparatus, including pressure gage and shutoff valve, costs only \$25. The set has been in constant use for more than 2 years, during which time hundreds of digestions have been made without any breakage or replacement of a single connection.

Acknowledgment

The writer wishes to express his thanks to Edward Ehmke for the construction of the diagram.

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per cent of the lower value, leads to the conclusion that diphenylguanidine, as procured in the open market, may not yield a reliable product under Carlton's treatment (7). On the other hand, could it be readily purified, such an organic base would be an eminently convenient volumetric standard. In fact, diphenylguanidine itself seems to react definitely with a strong acid, and the end point is sharp and easily discerned.

The present authors are planning to pursue the investigation further in the hope of either preparing really pure diphenylguanidine in a way that will not be too difficult or, acting upon the suggestion of Callan and Strafford (6), obtaining triphenylguanidine of the correct composition.

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RECEIVED March 1, 1937.

A Modification of the Berl-Kullmann Melting Point Block

Electrically Heated Glass Melting Point Apparatus

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TO AVOID the use of liquid baths for the determination of melting points, Thiele (7) constructed a copper block, which proved to be satisfactory only in the modified form described by Berl and Kullmann (1; cf. 3, 5, 6, 8). This block is of considerable value when one is concerned with substances of high melting point, but it suffers from the disadvantage that the capillary is observed against an illuminated background, so that the contents appear almost black and it is very hard to observe color changes or sweating prior to melting. It is felt that these difficulties have been overcome in the present modification, since the capillary is illuminated by light directed from above at an angle, the contents appearing therefore as in the customary liquid bath.

An electrically heated glass melting point apparatus designed for use with an ordinary 250° or 360° thermometer without stem correction is also described.

The copper block, *FGHI*, together with the lamp used for the illumination of the melting point specimen and its housing, *ABCDE*, is shown in Figure 1. The block itself is 5 cm. in diameter by 7 cm. in length (the dimensions in Figure 1 are given in inches) and it is pierced by a hole, *IJ*, parallel to the bottom and intersecting the vertical axis. A small hole, *G*, is drilled along the axis of the block to enter *IJ*, while a second hole, *KP*, is drilled from above to intersect *IJ* at the center. The angle ϕ which this hole makes with the vertical is 45–50°, and the angle θ between the intersecting planes determined by *GI-PK* and *GP-PJ* is 45–55°. If ϕ is 90°, it is difficult to observe the specimen in the capillary because of reflections from the surface of the glass. The thermometer is placed in *H*, which is drilled slightly below the bottom of *PJ* so that the melting point specimen in the capillary will be approximately on a level with the center of the thermometer. A little glass wool or copper powder is placed in the bottom of *H* to lessen the danger of breaking the thermometer.

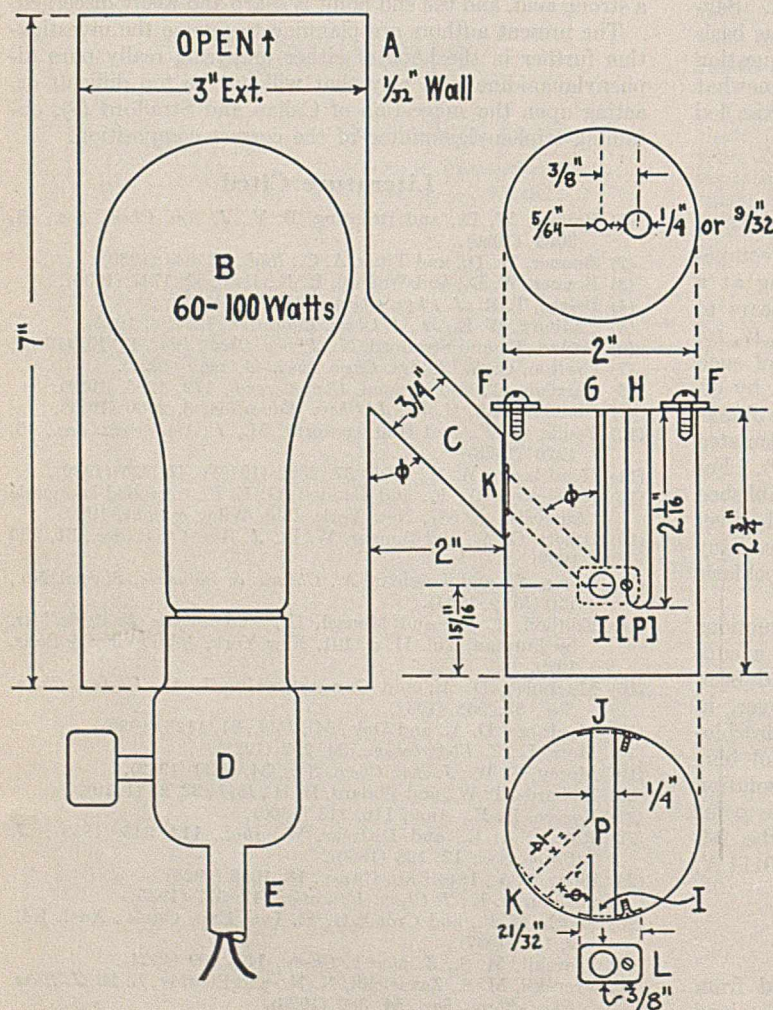


FIGURE 1

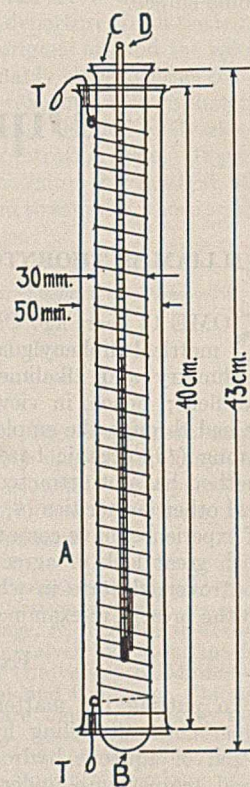


FIGURE 2

The bottom of the capillary is illuminated through the slanting hole, *KP*, by means of the electric lamp, *B*, which is surrounded by a housing, *A*, made of brass tubing 0.8 mm. (0.03 inch) in thickness. The open end of *C*, which fits snugly against the melting point block, should be ground concavely to the same radius of curvature. The holes, *I*, *J*, and *K*, are covered with small mica windows held in place by means of Monel metal or stainless steel frames (see *L*) with a radius of curvature equal to that of the block. (The author is indebted to the department mechanic, Mr. Grebmeier, for the design of these window frames, and for the actual construction of the block.) The window, *K*, closing the slanting hole, *KP*, is 12 mm. (0.5 inch) wide, instead of the 10 mm. (0.375 inch) shown in Figure 1 at *L*. Small mica windows, such as are described, show less tendency than larger ones to split in use.

Four small metal washers, *FF*, held on the top of the block by set screws, serve to support the block in a ring of 5-cm. (2-inch) internal diameter (it may be necessary to cut away a portion of the ring to accommodate *C*). An alternate support is afforded by four set screws (with large heads) around the side of the block near the top.

Heat is supplied by a Bunsen burner shielded from drafts by a thin brass or steel cylinder or pipe, but the portion of the block below *I* can be wound with asbestos-covered Nichrome wire and heated electrically in the manner described by Monsch (6).

It is recommended that the block be heated rapidly to a temperature 10° or 15° below the melting point of the specimen, and then at a rate gradually diminishing to 1° or 1.5° a minute within 3° to 5° of the melting point. If the block is heated too rapidly, the thermometer lags, and the observed melting point is low. The results, with proper operation, are as reliable as those obtained with a liquid bath.

For observation of the capillary and its contents (through window I), it is best to use one eye only, the other being kept open and directed against a dark background to avoid strain. One or two cheap magnifying glasses are placed in front of I and a square of metal (painted black) or black paper is placed behind window I, unless the substance in the capillary is dark colored or gives a dark-colored melt, in which case a dully illuminated white asbestos or transite board background is generally more satisfactory.

Glass Melting Point Apparatus

The electrically heated glass melting point apparatus shown in Figure 2 is a modification of that described by Dowzard and Russo (2).

The heating element of Nichrome wire (No. 24, 1.63 ohms per foot) is wound on a long Pyrex tube, B, whose dimensions vary with the thermometers available. The spacing of the windings is uniformly 1.5 or 2.0 cm. To provide some insulation, an outer tube, A, is placed around B, being held in place by two asbestos

"stoppers" made by wrapping slightly moistened asbestos paper (2.5 cm. or 1 inch, in width) several times around B. The terminals of the heating element are tied to two small glass rings at the ends of B, and are brought through the asbestos stoppers to the outside. The melting point tube is fastened to the thermometer by means of fine copper wire or asbestos string. The thermometer passes through a cork stopper closing the top of tube B, the cork having a small V-groove cut on the side parallel to the axis. Heat regulation is provided by a rheostat (capacity 6 amperes) or by a bank of lamps. The rate of heating near the melting point should not exceed 1° a minute.

The melting point apparatus just described may be made with a Dewar seal at the top, as in the heater described by Franklin (4).

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Quantitative Determination of Oil in Fish Flesh

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Fish oils, being unusually susceptible to oxidation and polymerization, are difficult to extract quantitatively from fish flesh except after drying the flesh in a vacuum desiccator for a period of a week or more. A method is described in which the drying and oil-extraction processes are combined by extracting the fish with acetone. The crude oil thus obtained is purified by treatment with ethyl ether. A rapid semi-

quantitative method is also described in which the oil is extracted by agitating the moist fish flesh with anhydrous sodium sulfate and ethyl ether.

Data are presented to show that the widely quoted value of 7.1 per cent for the oil content of the common mackerel is in error, a value of 12 to 15 per cent being closer to the average oil content of this species.

ORDINARY methods of determining oil in flesh products such as meat are not entirely satisfactory for fish, because of the tendency of fish oil to decompose very readily when heated with the flesh. Such decomposition prevents a complete extraction of the oil from the fish. In the methods ordinarily used for such products the substance is first dried thoroughly, in order to prevent the extraction of water soluble material and to ensure a complete recovery of the oil. The dried material is then extracted for about 15 hours in a continuous extractor, using ethyl ether or petroleum ether, more frequently the former. The solvent is then removed by evaporation and the oil is dried and weighed.

In fish flesh, the greatest decomposition of the oil usually occurs during the drying process; in order to minimize these changes, it is customary to employ a vacuum desiccator for this step, drying the fish over sulfuric acid. Since fish contains large quantities of glue-like substances, it has a tendency to dry to a hornlike mass, enclosing moisture which is very difficult to remove. By mixing the fish flesh with sand or cotton, this difficulty is lessened, and a fairly thorough dry-

ing is attained in from 10 days to 2 weeks. This procedure may result in a loss of oil either during the mixing of the flesh with the sand or during the subsequent transfer of the dried material to the extraction apparatus. Moreover, such a lengthy procedure is undesirable and in endeavoring to avoid it, the following methods were developed. The first method described is a rapid semiquantitative one. The second method is believed to give at least as great precision as any existing method and with a considerable saving in time. This method, in conformance with general usage, assumes that the oil content of a substance is equivalent to the content of substances extracted by ethyl ether from the dried material.

Semiquantitative Method

A brief description by Sebelin (4) has been given of a method, devised by Bull, for determining the oil content of fish. This method consists of mixing a weighed portion of finely ground fish with anhydrous sodium sulfate and then shaking with a measured quantity of benzene. An aliquot

TABLE I. FACTORS AFFECTING EXTRACTION OF OIL BY COLD METHOD

Effect of Solvent (Na ₂ SO ₄ Used as Dehydrant)		Effect of Dehydrant (Ether Used as Solvent)		Effect of Mixing Dehydrant with Fish						
Solvent	Oil recovered %	Dehydrant	Shaking time Min.	Oil found %	Method	Solvent	Oil found %	Av. %	Oil found %	Av. %
									Fish 1	Fish 2
Benzene	17.8	CaCl ₂	10	2.3, 2.1	Well mixed	Benzene	8.4, 7.8	8.1	5.5, 5.4	5.45
Ether	17.7	Na ₂ SO ₄	10	4.4, 4.6	Well mixed	Ether	8.3, 7.4	7.9	5.35, 5.55	5.45
Chloroform	17.5	CaCl ₂	30	6.4, 8.9	Not well mixed	Benzene	5.2, 5.1	5.15		
Acetone	14.3	Na ₂ SO ₄	30	8.3, 8.4	Not well mixed	Ether	8.6, 7.6	8.1	5.45, 5.75	5.6
		CaCl ₂	60	10.2, 9.9						
		Na ₂ SO ₄	60	10.1, 10.7						

portion of the benzene solution is then pipetted into one pan of a special balance equipped with a heating unit. The benzene is evaporated, and the balance then indicates directly the percentage of oil in the fish. The principle of this method, the extraction of oil by shaking with an oil solvent and dehydrating agent, has been used as a basis for the present method. A number of solvents and dehydrants were tried. It was observed that when benzene was used, as in the original Bull method, a very thorough mixing of the dehydrant with the fish flesh was required, a process involving the risk of loss of oil. When ether was used this difficulty was eliminated, similar results being obtained with or without mixing. Data regarding these experiments are shown in Table I. From a consideration of these data, it was decided that ethyl ether and sodium sulfate gave the best combination to be used.

TABLE II. EFFECT OF TIME OF SHAKING ON OIL RECOVERED

Sample I		Sample II	
Shaking time Min.	Oil found %	Shaking time Min.	Oil found %
10	8.3, 8.4	5	9.6, 3.7
30	10.1, 9.8	15	11.3, 10.8
60	10.7, 10.1	30	12.1, 11.7
		60	12.3
		120	12.7
		240	12.8

For shaking the samples a machine was used which had a 12.5-cm. (5-inch) horizontal stroke repeated 228 times per minute. Using this machine, the effect of the time of shaking upon the oil content found was determined as shown in Table II. It was concluded that a 1-hour shaking period was most suitable from the standpoint of obtaining most of the oil in the shortest possible time. While glass-stoppered bottles are most suitable, in the present work they could not be used, since the shaking machine required a special type of bottle. Cork stoppers gave the best results, neither dissolving in the ether nor allowing an appreciable escape of liquid; rubber stoppers are unsuitable. The following procedure was adopted:

Twenty grams of the finely ground flesh, free of skin and bones, are weighed into a shaking bottle. Twenty-five grams of anhydrous sodium sulfate and exactly 100 ml. of ethyl ether are added, and the bottle and contents are shaken for 60 minutes. After allowing most of the fine solid particles to settle out, a 20-ml. aliquot of the solution is pipetted through a filter and into a weighed beaker. The filter is washed with three 3- to 5-ml. portions of ether. The ether is evaporated off on a water bath or in front of an electric fan and the oil dried for 1 hour at 100° C. and then weighed.

Results using this method compared with other methods are shown in Table IV. This method is especially valuable in cases where subsequent tests are to be made on the oil where it is essential that no decomposition can have taken place. In such cases, a further aliquot of the ether solution is used for these tests.

When less than about 10 per cent of oil is present in the fish flesh this method is not at all accurate and a more thorough extraction using fresh solvent is required. In such cases the following modified procedure is used:

Twenty grams of the ground fish flesh and 25 grams of anhydrous sodium sulfate are stirred electrically for 5 minutes in a 250-ml. centrifuge bottle with about 50 ml. of ethyl ether. The bottle is centrifuged and the solution decanted through a sintered-glass crucible. This process is then repeated five times and the filter washed. The combined filtrates are then transferred to a weighed dish, the ether is evaporated, and the oil is dried and weighed as in the previous method.

This method is more accurate than the shaking method, but it is not suitable for running many samples at once, and hence is often of less value. For fish of low oil content, however, it is the only available rapid method. This modification is also suitable for the determination of the oil content of fish livers.

Quantitative Method

Where a higher degree of accuracy is required, the following method has proved to be satisfactory:

A 15- to 20-gram sample of finely ground fish flesh is placed in a continuous extractor and heated for 16 hours, replacing the solvent with fresh acetone after 2 hours. The solutions are then heated on a steam bath until all of the acetone and most of the water is removed. They are then put in a vacuum desiccator over freshly boiled sulfuric acid and the desiccator is evacuated. When practically all of the water has been removed, as indicated by the cessation of foaming and bubbling or after about 3 hours, the oils are removed, and 35 ml. of ethyl ether are added. After thorough shaking, the solution is poured through a filter, preferably one of the sintered-glass type. The residue is washed with several small portions of ether until the wash liquid is colorless, pouring the solution in each case through the filter. The oil solution is washed into a weighed beaker and the ether removed in front of an electric fan. When the odor of ether is no longer apparent, the beaker is placed in an oven at from 100° to 105° C. for 45 minutes. The beaker and oil are then cooled and weighed.

TABLE III. EFFECT OF TIME OF ACETONE EXTRACTION ON PER CENT OF OIL FOUND

Extraction Time Hours	Oil Obtained %
6	12.32, 11.82
12	13.10, 13.25
16	14.03, 14.14
16 more with ether	14.33, 14.39
A. O. A. C. method	14.01, 14.11

TABLE IV. COMPARISON OF RESULTS OBTAINED BY THE DIFFERENT METHODS

Sample No.	A. O. A. C. Method %	Acetone Method %	Cold-Centrifuge Method %	Cold-Shaking Method %
I	18.81	18.74	18.62	18.0
	18.79	18.69	18.54	17.6
	Av. 18.80	18.71	18.58	17.8
II	12.59	12.71	12.59	12.3
	12.70	12.65	12.54	11.9
	Av. 12.64	12.68	12.56	12.1
III	6.11	6.14	6.11	5.3
	6.18	6.19	6.15	4.7
	Av. 6.14	6.16	6.13	5.0
IV	2.49	2.54	2.59	1.14
	2.54	2.58	2.63	1.75
	Av. 2.51	2.54	2.61	1.45

Using this method a number of precautions must be observed in order to obtain the best results.

SAMPLING. If the oil content of the edible portion of the fish is desired, it is necessary to remove skin and bones. In removing the skin care must be taken to avoid loss of oil, since in many species of fish a considerable portion of the oil occurs next to the skin. It is better to leave some of the skin adhering to the flesh, if necessary, rather than to lose considerable oil. Fish flesh loses water by evaporation very readily, and for this reason it is important to complete the initial steps, to the point where the flesh has been weighed out, as rapidly as possible.

EXTRACTION. For this work the Fire Underwriters model extraction apparatus was used, although undoubtedly any type of continuous extractor would be suitable. Extractions longer than 16 hours give very little additional oil. A few experiments were run in which the fish which had been extracted for 16 hours with acetone was then reextracted for 16 hours with ethyl ether. The second extraction gave a small amount of oil, sufficient to change the results by only a few tenths of a per cent. On the other hand, a minimum of nearly 16 hours of extraction is required, as was shown by lower values obtained with shorter extraction periods. Some of these results are shown in Table III.

The fact that a 16-hour heating with acetone does not decrease the solubility of oil in ether was established by refluxing a pure sample of fish oil with acetone for this period, removing the acetone, and dissolving in ether. The oil was then completely soluble.

REMOVAL OF ACETONE AND WATER. Most of the water as well as the acetone should be removed on a steam bath, since otherwise a considerable period of time will be required to remove water in the desiccator. On the other hand, it was believed to be safer to remove the last portion of water in a desiccator rather than to risk any oxidation which might occur upon prolonged heating. Probably a small trace of the water is not removed by the desiccator at all, but this amount is not large enough to interfere with the method. The acetone-water solution containing a little oil obtained from the first 2 hours' extraction should be kept in a separate container from the main bulk of oil and acetone throughout the drying process, since this greatly aids in removing the water.

PURIFICATION OF CRUDE OIL. After removal of acetone and water, oil and other extractives remain in the flask. These extractives are of a somewhat gummy consistency, insoluble in ether and soluble in water. There is often present also some fine protein material that has passed through the thimble. The oil can be very easily separated from these substances by a short shaking period with ether. If the oil solution is filtered through paper, considerable difficulty is encountered in washing the oil from the paper. This can be avoided by the use of a fine grade of sintered-glass crucibles. The residue remaining after treatment with ether should be completely soluble in water.

DRYING OF OIL. This step is one of the most unsatisfactory of any, since even a short heating tends to decompose the oil. However, a certain amount of heating is required to remove water. Experience has shown that when a 45-minute period is used, the error will be small unless considerable water is present; this may occur if the preceding steps were not carried out properly. In order to make certain that the oil is dry, it is well to heat for a second 45-minute period, and then reweigh.

FROZEN AND SALTED FISH. Frozen and salted fish which have been kept in storage for a considerable period will give very poor results when the oil content is determined by any method employing ether or any of the other well-known oil solvents. This is due to the decreased solubility of decom-

posed fish oils in the various solvents. Instances have been encountered in which there was an apparent drop in oil content of nearly 50 per cent for fish kept in storage for several months. This difficulty cannot be overcome until some other solvents are found which will dissolve both fresh and decomposed fish oils. These considerations apply to fish meal to an even greater extent.

Results

The method of the Association of Official Agricultural Chemists (1) for oil determination in meats which allows a number of variations in drying procedure was used as a standard to compare the methods developed in this paper. The method used involved drying the fish flesh mixed with sand in a vacuum desiccator over sulfuric acid. Results in Table IV compare these methods. The acetone-extraction method compares very well with the ordinary ether-extraction method. The cold-shaking method gives approximate results on fairly oily fish. On samples having a low oil content, the cold-centrifuge method gives much better results.

TABLE V. VARIATION IN OIL CONTENT OF MACKEREL (*Scomber scombrus*)

Month Fish Caught	Average Oil Content %
April	4.3
May	8.5
June	9.0
July	10.6
August	18.3
October	10.1
November	8.2

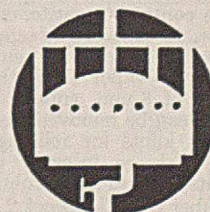
The acetone method has been applied to the determination of oil in the common mackerel (*Scomber scombrus*), which is listed in a number of charts and reference works (2, 3, 5) as having an oil content of 7.1 per cent. The authors' studies indicate a wide variation in the oil content of this fish, with an average value of about 12 to 15 per cent. Aside from a few fish caught in the spring, or late fall, a value of 7 per cent is rarely encountered. Table V shows the seasonal variation in the oil content of mackerel. It should be pointed out that over 70 per cent of the mackerel are caught from July through September.

While these methods have not been applied to any substances other than fish or fish products, it appears probable that they would be of value for oil determinations in other food materials.

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The Determination of Dissolved Nitrogen in Water

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IN THE COURSE of the study of sea water it became necessary to make determinations of its nitrogen content. Earlier measurements were not explicit on the separation of the argon and other inert gases, and a method was accordingly sought which would yield values for nitrogen directly, rather than by difference. It was essential that the analysis be fairly rapid, to permit the routine determination of as many samples as possible, and accurate to about 1 per cent of the nitrogen present, and that it require not more than about 100 ml. of water.

The procedure to be described consists of two definite parts: removal of the total gas from the water sample, and its analysis for nitrogen. The first step is accomplished by repeatedly spraying the water into an evacuated chamber, removing the extracted gas after each injection. The quantity of extracted gas is measured manometrically in a constant volume, and its content of oxygen and nitrogen, respectively, measured in the same way after reaction with phosphorus and with lithium. Calcium, magnesium, and lithium have all been used as reagents for combination with free nitrogen, but preliminary work showed that lithium was the most suitable under the conditions necessary for this work.

Description of Apparatus

Figure 1 shows the necessary working parts of the apparatus, with a slight exaggeration of scale for the smaller parts.

It is constructed entirely of Pyrex glass, although soft glass may of course be substituted for the long manometer arms. All connections are made of 7-mm. tubing, and the section in which the analysis is carried out, between *a*, *b*, *d*, and *f*, is of 7-mm. capillary, to reduce the volume.

The mercury reservoir, *D*, which serves as a pump, has a volume of 250 ml. The evacuation chamber, *E*, in which the gas is extracted, has a volume of 300 ml. and connects with a large mercury leveling bulb, as shown. Chamber *F*, in which the water sample is measured and stored, has a capacity of 100 ml. Ground-glass joints occur at *a*, *f*, *g*, and *b*, and the latter, which is not lubricated, is protected with a mercury seal held in place by a short piece of rubber tubing.

The phosphorus chamber, *A*, has a volume of between 2 and 3 ml. with a small plug of glass wool. The lithium chamber, *B*, has a similar volume and contains a deep steel crucible made by drilling out a steel rod. The chamber is surrounded with an asbestos shield.

The tip of the jet, *h*, where it enters *E*, is drawn down to about 0.5 mm. This orifice should be as small as possible, without danger of clogging. The water enters *E* through this orifice, at high velocity.

The inverted U-tube contains ascarite, calcium chloride, and dehydrite, in that order, separated by plugs of cotton, for the purpose of removing carbon dioxide and water vapor from the extracted gas. It is made of 8-mm. tubing, about 20 cm. from *f* to *g*. It can be removed from the line at the ground-glass joints for refilling, and short lengths of glass rod are inserted in the male parts of these joints, to reduce the volume.

The volumes of chamber *C* and stopcock 2 are de-

termined before sealing them into the line, and should lie between 1.5 and 2 ml., approximately the volume of the sample to be analyzed.

The analytical part of the apparatus as far as stopcock 5 is evacuated by means of a Hy-vac pump, and the suction line contains a 3-way stopcock (not shown) through which dry air can be admitted to the system through calcium chloride and soda lime.

The mercury used in *D* should be dried in an oven occasionally, and the manometer evacuated to remove moisture.

Manipulation

PREPARATION OF PHOSPHORUS. After filling the phosphorus chamber with pieces cut under water, and plugging the end with glass wool, the moisture must be removed by heating and evacuation, being careful that bubbles do not carry phosphorus out of the tube. The removal of water is complete when the pressure in the system is constant on heating and cooling.

PREPARATION OF LITHIUM. Bright pieces of lithium are cut under dry carbon tetrachloride and placed in the steel crucible and the chamber is closed and evacuated as rapidly as possible. After evacuation the lithium is melted to drive off all volatile matter. It was found that the first heating of fresh lithium liberated some volatile products, most of which recombined with the metal on continued heating. The noncombined residue is then pumped off, after which repeated heating and cooling pro-

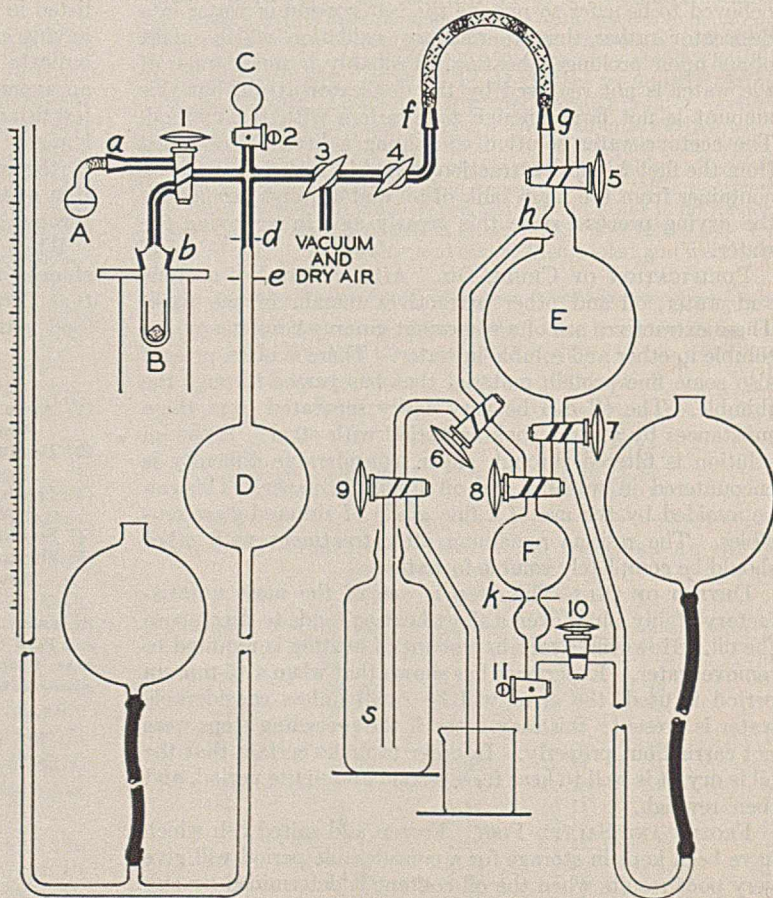


FIGURE 1. DIAGRAM OF APPARATUS

duce no further changes in pressure. The nature of this phenomenon was not further investigated, but it was observed that subsequent reaction of the lithium and nitrogen proceeded more rapidly if only the noncombining residue was pumped off. Lithium from which all the volatile substances were removed during heating was very slow to react with nitrogen the first two or three times, but its reactivity increased thereafter.

The lithium prepared in this way can be used for as many as ten analyses.

CALIBRATION OF VOLUME. A reference mark is established at *e*, about 1 cm. below the end of the capillary tubing, and all pressure and volume measurements are made with the mercury at this mark. The gas being measured is in every case contained in *C* and in the rest of the system between 1, 3, and *e*. The volume of *C* being known accurately, this quantity of dry air can be introduced into the system and the pressure read on the manometer. The difference between this reading and that of the evacuated system calibrates the manometer for subsequent readings, subject, of course, to changes in atmospheric conditions.

MEASUREMENT OF WATER SAMPLE. The water sample is measured in *F*, between stopcock 6 and a reference mark, *k*. Chamber *F* and the inlet connections around to the end of tube *s* are first filled with mercury and the sample is sucked in slowly from the original bottle. The volume contained in this chamber is calibrated by the weight of water removed from a sample. For this particular apparatus it was 101 ml.

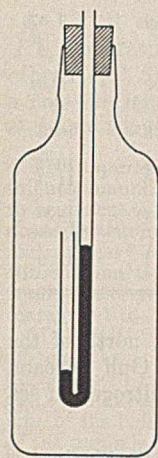


FIGURE 2

tained in this chamber is calibrated by the weight of water removed from a sample. For this particular apparatus it was 101 ml.

Gas Extraction

It is convenient to arrange three supports for the main mercury leveling bulb: one at the level of 5, another at the level of 10, and another about 80 cm. below 10.

The water sample is sucked into *F* as described above. Chamber *E* is evacuated by filling with mercury and lowering. Raising the mercury bulb, the water is forced from *F* into *E*, by both suction and pressure. This is continued until mercury comes through *h*. As the water issues from the orifice at high velocity and strikes the neck of the flask, the greater portion of the dissolved gas is removed from solution. The water sample is run down into *F* again, through 7 and 8. Mercury is then run up into *E*, through 7, and the extracted gas is forced into the drying tube, which in the meantime has been evacuated by the oil pump, along with the remainder of the analytical line. There will always be a few drops of water on the surface of the mercury and a little of this must be run up into the stopcock and later removed very carefully by suction.

Chamber *E* is then evacuated by lowering the mercury and the water sample again injected through 8, 6, and *h*. The small amount of gas extracted in this stage is also forced into the drying tube. Four such circulations of the water, or at most five, will remove all but insignificant amounts of dissolved gas. The first stage is always somewhat slower than the subsequent ones, because of air bubbles.

Analysis of Gas

After reading the manometer with the analytical line evacuated, stopcock 1 is closed, 3 and 4 are opened, and the mercury is lowered in *D*, whereby most of the extracted gas is removed from the drying tube. Stopcocks 3 and 4 are closed and the gas is forced into *C*. Stopcock 2 is then closed and the remaining gas in the drying tube is pumped into *D* by lowering the mercury again. This is also forced into *C*, leaving only an insignificant residue in the drying tube. Opening 2, the volume of total gas is measured manometrically between 1, 3, and *e*.

By means of the mercury in *D* the gas is pumped out of *C* into *A*. The phosphorus is melted by gentle heating and allowed to react for 5 minutes, after which the remaining gas is pumped out of *A* into *D* and then back again, where it is allowed to react with the melted phosphorus for a few minutes longer.

The deoxygenated gas is pumped back again into *C*, in two stages as before, and its volume measured manometrically. In the same way, it is then pumped in two stages into the lithium chamber, *B*. The lithium is heated above its melting point. This can be done electrically, but it was found more convenient to use a Bunsen burner. As combination of the nitrogen with the lithium goes on it is necessary to lower the mercury level con-

tinually, to keep the inside level approximately at *d*. The reaction is generally completed in 5 minutes.

After cooling, the residue is pumped into *C* again and its volume is measured by the manometer. From the four pressure readings and the laboratory temperature and pressure it is possible to calculate the total volume of gas dissolved per liter of water and the relative and absolute amounts of oxygen and nitrogen in the gas.

The entire process of extraction and analysis requires about an hour and a quarter, but the actual time may be considerably shortened by carrying out the analysis of one sample and the extraction of the next simultaneously. The drying tube may be evacuated and closed off ready for the next sample as soon as the preceding one has been pumped out of it.

Accuracy of the Method

Attempts were made to check the accuracy of the method by comparing the volumes of gas extracted from air-saturated distilled water with accepted values. Water was shaken with air in a flask for 15 minutes and then allowed to stand open in the laboratory for several days. The volumes of air extracted from such water samples and the accepted values for the solubility of air are given in Table I. Uncertainty as to the degree of saturation of the water may partially account for the fact that the observed results were about 1 per cent below the theoretical. Nevertheless, this percentage of error is not considered unreasonable.

The completeness with which oxygen is removed by this method was checked by comparing the values obtained for oxygen in samples of sea water against the results obtained simultaneously by the standard Winkler method. Table II shows this comparison. Only in the last case is the discrepancy significantly beyond the limits of error of the two methods.

Samples of air were analyzed for oxygen and nitrogen, further to check the accuracy of the method. This was done by filling chamber *C* with air passed through calcium chloride and soda lime. The volume of this sample, 1.52 ml., is approximately that obtained from 100 ml. of sea water. Table III shows the results, compared with values from International Critical Tables.

TABLE I. DETERMINATION OF DISSOLVED AIR

Temp. ° C.	Dissolved Air	
	Observed	Theoretical
	Ml./l.	
24.3	17.3	17.5
22.0	18.0	18.0
22.0	17.8	18.0
22.0	17.8	18.0
23.0	17.3	17.7
Av.	17.6	17.8

TABLE II. REMOVAL OF OXYGEN

O ₂ by Extraction	O ₂ by Winkler	O ₂ by Extraction	O ₂ by Winkler
Ml./l.	Ml./l.	Ml./l.	Ml./l.
4.45	4.46	4.31	4.28
4.85	4.89	5.12	5.12
5.01	4.94	5.15	5.20
4.60	4.52	5.42	5.54
4.76	4.71	Av. 4.85	4.85

TABLE III. ANALYSIS OF AIR

O ₂	N ₂	O ₂	N ₂
%	%	%	%
20.7	77.7	20.9	...
20.7	78.1	20.8	78.1
20.9	77.8	21.1	78.1
21.1	77.1	Av.	20.8
20.6	...	Theoretical	20.99
20.6	78.3		78.03 (Critical Tables)

Storage of Water Samples

Since the apparatus was not adapted for use on board ship, it was necessary to store the water samples taken at sea in such a way as to prevent interchange of gas between the water and the atmosphere. It is impossible to keep samples in the ordinary type of citrate bottle, tightly clamped with no cushion of air over the water, without a large percentage of breakage. This difficulty was completely overcome by the device shown in Figure 2, which consists of a U-tube partially filled with mercury and inserted in a citrate bottle completely filled with water. Expansion and contraction merely move the mercury column, and although water may escape outward past the mercury none passes the other way. When inserting the tube care must be taken that water completely fills the short arm and that no air is trapped by the stopper. Samples are stored in a refrigerator until analyzed, especially the deeper, colder samples, which may become supersaturated at higher temperatures.

Analyses

To show the results of the application of the method to actual sea water some analyses are given in Table IV. These samples are from various depths at two different stations in

TABLE IV. ANALYSES OF SEA WATER

Station 2666			Station 2667		
Depth Meters	Temp. ° C.	Nitrogen Ml./l.	Depth Meters	Temp. ° C.	Nitrogen Ml./l.
0	25	9.72	10	26.0	8.83
10	22.5	9.50	60	20.9	9.67
40	14.3	11.0	200	18.2	9.64
60	12.5	11.0	500	17.3	10.3
80	12.0	10.8	800	14.8	10.4
100	12.3	11.1	1000	11.5	11.3
150	7.9	11.4	1500	5.2	12.6
200	9.6	11.7	4000	3.1	13.9
300	7.7	12.4			
400	5.2	12.6			
500	4.7	12.7			
600	4.7	12.5			
800	5.2	12.6			
1000	4.0	12.5			
1200	4.1	12.8			
1500	3.6	12.8			
2000	3.5	13.0			
3000	2.6	13.3			
....			

the Atlantic south of Cape Cod: No. 2666, north of the Gulf Stream; and No. 2667, south of the Gulf Stream. Further studies on the content of dissolved nitrogen in sea water will be reported in a subsequent paper.

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An Improved Salt Bridge for Electrometric Measurements

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IN THE course of making electrometric measurements, it was found that available salt bridges were not entirely satisfactory. At the present time the bridges most recommended are those developed by Irving and Smith (3) by a modification of an earlier type described by La Mer and Baker (4, 5), or of the type devised by Stern (8). Other apparatus of this nature has been introduced by Clark (1), Müller (7), and Michaelis (6).

The chief disadvantage of such siphon bridges has been the necessity of maintaining the same liquid level throughout the system, or using a bridge containing an aqueous gel such as agar saturated with potassium chloride. The former method is inconvenient and the gels are unsatisfactory, as the presence of a foreign porous material at a junction may be a cause of error (2). Also, it is advantageous to use a free liquid junction in order to ensure a rapid attainment of equilibrium conditions.

The bridge shown in the figure is entirely constructed of hard-glass tubing with 0.5-cm. bore, except for reservoir B which is

made from the bottom of a 250-mm. Pyrex test tube. The ground-glass plug shown at D, which is used to maintain the liquid column in the tube below it, may be replaced by a short rubber tube and a clamp.

In preparing the bridge for use, the reservoir is filled with the chosen salt solution. After closing the stopcock at A, which is part of the reference electrode vessel, the reservoir is forced on rubber stopper C. This will fill the bridge to E, with any excess being drawn off through the lower stopcock. The vertical tube is then filled by drawing the salt solution up into it with the stopcock at F open, then closing F while the plug at D is fitted into the tube. An extension tube may be fastened to G to allow any convenient height arrangement of the apparatus as is usual in titrations or pH determinations.

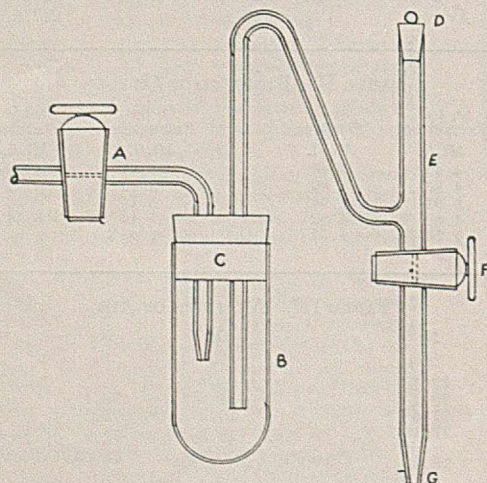
This bridge has been used in a number of other ways. The tip of a single electrode vessel may be introduced at D in place of the plug while the stopcock in the vertical tube is closed, for determination of cell potential. Measurement of concentration cells has also been accomplished with this apparatus.

This salt bridge may be left connected in a circuit for a long time, as it provides a very long path for diffusion. It gives a free liquid junction, and may be used at any height in reference to the liquid levels in the rest of the system. The only precaution to be observed is that connections must be air-tight to prevent siphoning.

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RECEIVED May 7, 1937.



A Pressure Regulator for Vacuum Distillation

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AFTER considerable experience with various forms of apparatus similar to those described by Bertrand and others (1, 2, 3) for regulating pressure in vacuum distillation, a pressure regulator was developed which is more compact and better adapted for practical usage, as shown in Figure 1.

The apparatus is mounted by a buret clamp on the stem, *L*, in such manner that it may be rotated clockwise. The system to be evacuated is attached at *A* and the pump at *B*. When the desired vacuum is approached, the stopcock, *D*, is opened slightly and mercury is allowed to rise almost to the inlet, *H*. When the vacuum is within 1 or 2 mm. of that desired, the mercury is allowed to rise further to close off inlet *H* so that a globule of mercury, 1 to 2 mm. high, circulates in the system *KL*.

If there is no bleed or introduction of gas into the distilling system, the circulation of the mercury will soon cease and the pressure will remain constant. If there is an intentional bleed, the circulation of the mercury in *KL* is dependent on the volume of the bleed and the capacity of the pump. If the capacity of the pump is far in excess of the gas entering as a bleed, a gradual reduction in pressure may develop when the distillation is continued over several hours. This can be prevented by the addition of a side tube on the inlet tube, *A*, above the junction, *H*, which is controlled by a pinchcock and a piece of pressure tubing. This is opened sufficiently to balance approximately the pump capacity and bleed. The circulation of the mercury in *KL* is thus maintained constant, and the mercury does not tend to rise in inlet tube *A*. At the close of the distillation and

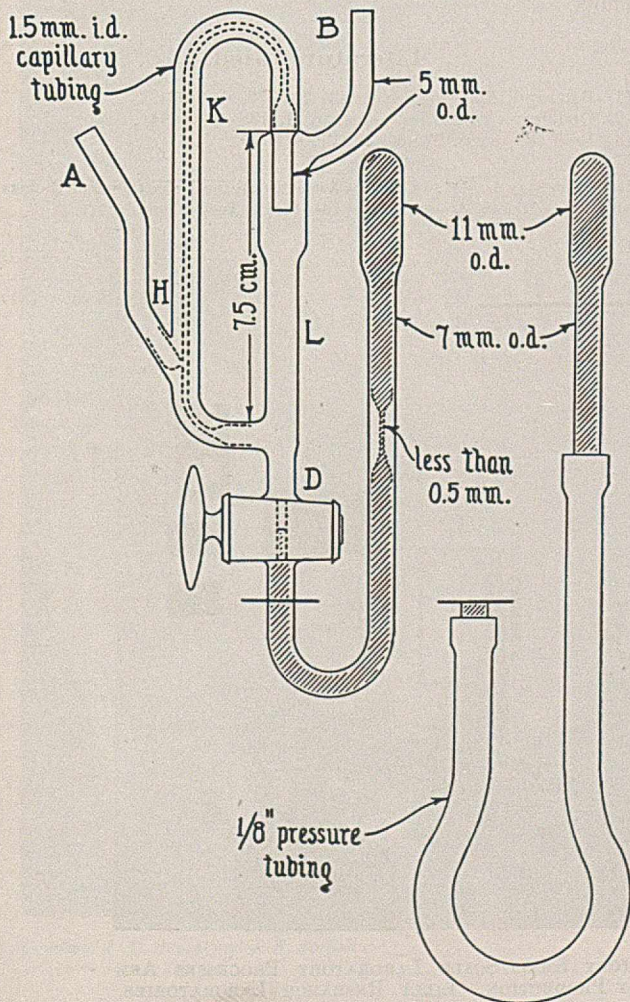


FIGURE 1

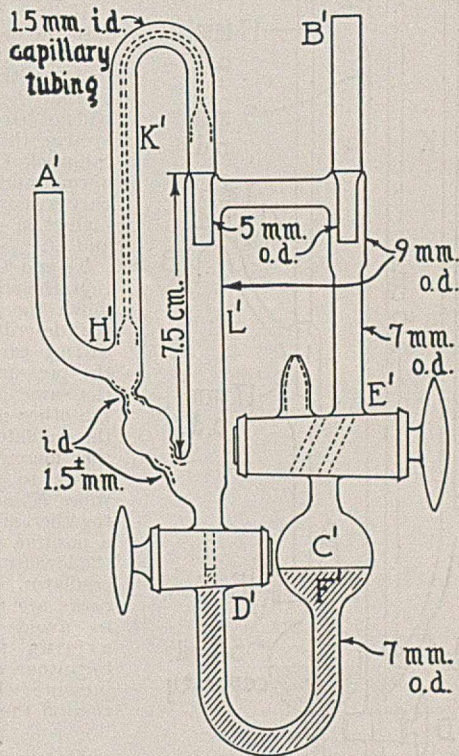


FIGURE 2

before the pump is shut off, the apparatus is rotated clockwise, stopcock *D* is opened, and the mercury is allowed to flow back into the manometer.

The apparatus can be constructed without a stopcock and the regulation controlled by the rotation of the apparatus held in the buret clamp. In this case it is best to evacuate with the regulator rotated to a nearly horizontal position. When the desired vacuum is approached, the apparatus is rotated anticlockwise to form the 1- to 2-mm. mercury seal circulating in *KL*.

A flexible manometer head, attached just below stopcock *D*, as shown, obviates the use of a rotating clamp and can be used when a rigid apparatus is desired. The flexible manometer head is simply lowered at the close of the operation, the stopcock is opened, and the mercury is allowed to return to the bulb before shutting off the pump. The stopcock can also be omitted in this form, if desired, but the circulation of the mercury in *KL* is not so uniform.

Another modification is shown in Figure 2.

The manometer is replaced by a bulb, *C'* which is controllable by the oblique three-way stopcock, *E'*. The circulation of mercury in *K'L'* is the same as above described, but the manipulation of the mercury in *C'* requires considerable care. The regulator is connected as described above, with both stopcocks open and the air in *C'* at atmospheric pressure. Before starting the pump, both stopcocks are closed. When the desired vacuum is approached, stopcock *D'* is opened and mercury is allowed to approach *H'* as before.

To lower the pressure, the air in reservoir *C'* must be evacuated by the careful manipulation of stopcock *E'*. Unless considerable caution is exercised, the momentary increase in pressure in the regulator arms, *K'* and *L'*, will force mercury through *A'* into the system. When the pressure in *C'* is the same as that throughout the regulator, stopcock *D'* is carefully opened. When

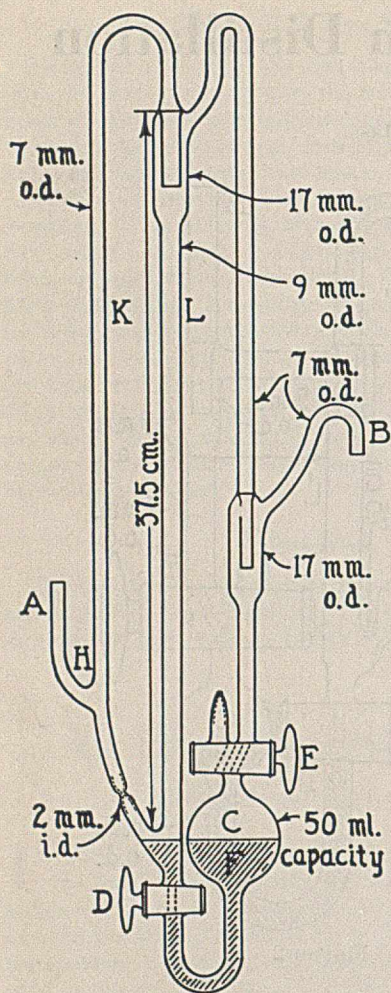


FIGURE 3

the level in K' and L' has fallen sufficiently, D' is again closed, and the air is withdrawn from the system until equalization takes place at a lower pressure.

If it is desired to raise the pressure, air must first be allowed to enter the system so that the mercury will not back into the system through A' . Stopcock D' is then opened and the mercury is allowed to rise higher in tubes K' and L' .

To end the operation, the procedure is much the same as that described above, being careful that the pressure in C' is the same as that of the other portion of the regulator. Then the mercury is allowed to fall from tubes K' and L' altogether, and assume a position of rest in the lower part of the regulator. The stopcocks are now shut, to avoid splashing arising from any fortuitous change in pressure when shutting off the pump.

If it is desired to regulate the pressure within narrow limits, especially in

the range of 1 to 10 mm., a larger size (Figure 3) can be used which is filled with *n*-butyl phthalate instead of mercury. The phthalate may be colored with Sudan III if desired. In the phthalate type the inlet tube in the trap above E has a vent close to the ring seal. This allows the regulator to function, even though phthalate may have been carried over accidentally from the upper trap on L .

Butyl phthalate may also be used in place of mercury in the types described above having one stopcock. In these the dimensions shown to the left in Figure 3 may be used and a suitable manometer, either fixed or flexible, attached just below stopcock D . The type with the flexible manometer is much easier to operate than that shown in Figure 3 with two stopcocks.

The proper functioning is dependent on a more or less constant exhaust system. Nitrobenzene was distilled at variously reduced pressures and the resulting curve agreed with that derived from data in the International Critical Tables.

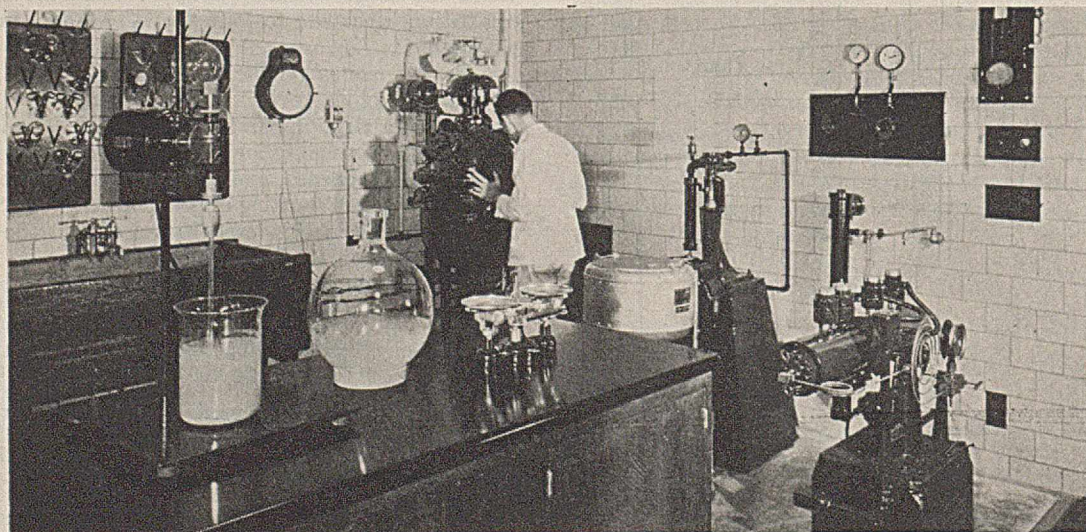
Of the three forms shown, the second and third can be fused to other glass parts of the complete apparatus, if all-glass construction is desired, while the first must be connected by pressure tubing to allow for the rotation of the regulator. All forms function satisfactorily, but in the third style the control of the mercury by the pressure in the bulb C' requires some care and experience.

Of the two sizes, the mercury one is more compact, the total range is higher, and the manometer fluid is not susceptible to the casual entrance of vapors, while in the phthalate type the adjustment can be regulated within narrower limits.

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RECEIVED May 6, 1937. Contribution 98 from the Department of Biology and Public Health, Massachusetts Institute of Technology.



IN THIS ORGANIC RESEARCH DEVELOPMENT LABORATORY SMALL-SCALE LABORATORY PROCESSES ARE STUDIED BEFORE A PRODUCT IS RELEASED FOR FACTORY PRODUCTION. LILLY RESEARCH LABORATORIES, INDIANAPOLIS, IND.

A black and white micrograph showing a complex, branching, dendritic structure. The structure consists of numerous dark, interconnected lines that form a dense, web-like pattern. The lines vary in thickness and orientation, creating a highly textured appearance. The background is a light, uniform gray. The word "MICROCHEMISTRY" is printed in a bold, white, sans-serif font across the center of the image.

MICROCHEMISTRY

Courtesy, J. T. Bryant and J. R. Rachele

**Quinhydrone by Oxidation
of Hydroquinone**

Separation and Determination of Impurities in Lead

I. Tin

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THE accurate determination of commonly occurring impurities in lead has been difficult because of the problems involved in effecting a quantitative separation of the impurities from the lead. Certain impurities, such as bismuth, copper, and silver, can be rapidly and efficiently separated by "internal" electrolysis (1), but metals less noble than lead are not susceptible to this method of attack. The separation of lead as sulfate cannot be employed for accurate work because of the notably strong tendency of lead sulfate to adsorb other metal ions. Moreover, the nitric acid solution of the sample, which is usually employed for lead, is entirely unsuitable when the objective is the determination of small quantities of tin, arsenic, and antimony.

In the first part of this paper an apparatus is described in which the solution of a lead sample in hydrochloric acid and the separation of the lead from the impurities are accomplished simultaneously. The second part of the paper describes the application of the method to the separation and determination of small quantities of tin in lead.

Lead-Solution Apparatus

The apparatus described below was designed to take advantage of the very large difference in solubility of lead chloride in hot and cold hydrochloric acid solution (2, 4). All impurities that form soluble chlorides are thus separated from the lead, which is precipitated as lead chloride in pure crystalline form as rapidly as dissolved. The advantages gained by solution in hydrochloric acid by the method described are: the high purity of the lead chloride precipitate obtained; and the favorable conditions afforded by a hydrochloric acid solution for the subsequent determination of such impurities as tin, arsenic, and antimony.

The apparatus, details of which are shown in Figures 1 and 2, consists of the following parts:

The solution flask, *A*, in which the solution of the sample is effected.

The lead chloride trap, *B*, in which precipitation of the lead chloride occurs, thereby separating the lead from the other metals present in the solution. The trap is equipped with a sealed-in cooling coil through which ice-cold water is continuously circulated. The solution from flask *A*, nearly saturated with lead chloride at approximately 100° C., is thus cooled or entering the trap, with the result that lead chloride crystallizes out. A filter pad, carried by a perforated glass plate sealed inside the trap, retains the lead chloride crystals in the trap but permits the liquid to pass through.

Air lift and connecting crosspiece, *C*. The air lift is connected to the low-pressure air supply and a slow, regular stream of air is admitted at *D*. By means of this air, the solution passing through the lead chloride trap, *B*, is pumped back into the solution flask, *A*, and is thus made available for effecting further solution of the sample.

Condenser and trap, *E*. The hot vapors from the solution flask *A* are condensed by the condenser and returned to the flask, thus keeping the volume of the solution constant. Any volatile chlorides not returned by the condenser are caught in the trap which contains dilute hydrochloric acid.

Heater. Since the temperature of the solution in flask *A* must be maintained at 90° to 100° C., it is essential to use a heater equipped with a heat-output control. Cenco electric flask heaters

with rheostat control have been found very satisfactory for this purpose.

The apparatus is made of "E. J." Pyrex glass. All connections are made by means of standard interchangeable ground-glass joints.

PROCEDURE FOR SOLUTION OF THE SAMPLE. The lead sample should be reduced to coarse filings or turnings of a particle size of approximately 10 mesh or larger. Material of a smaller particle size, owing to the larger surface area presented, will cause a more rapid rate of solution. As a consequence the solution in the flask, *A*, may become saturated with lead chloride; if this occurs the tube leading from *A* to *B* (Figure 1) may become clogged with crystals of lead chloride. Within limits, this difficulty can be obviated by increasing the rate of circulation proportionately to the increase in rate of solution of the sample. The reagents used are hydrochloric acid, 1 to 3; hydrochloric acid, 5 per cent by volume; concentrated nitric acid, and paper-pulp suspension.

1. In effecting the solution of the sample, the apparatus is assembled as shown in Figure 1 and is supported by clamps and stands.

2. Form a thin filter pad in the lead chloride trap by pouring in some paper-pulp suspension and allowing the water to drain off. Connect the trap to the air lift, and then fill the trap with sufficient 1 to 3 hydrochloric acid to cover the cooling coil. Connect the solution flask to the trap and then place in the flask 50 grams of the sample being analyzed for impurities. Add 1 to 3 hydrochloric acid until the level of the solution is slightly above that of the siphoning arm; then add 10 ml. of nitric acid. Fit the flask with the condenser and trap which should be half-filled with 5 per cent hydrochloric acid. Connect the air lift and flask by means of the crosspiece; to prevent the crosspiece from being lifted by the air pressure, it should be fastened by means of rubber bands to the air lift and also to the flask.

3. When the apparatus has been thus assembled, pass a stream of cold water through the cooling coil in the trap and through the condenser. To obtain as low a temperature as possible in the trap, the water before entering the coil should be passed through a

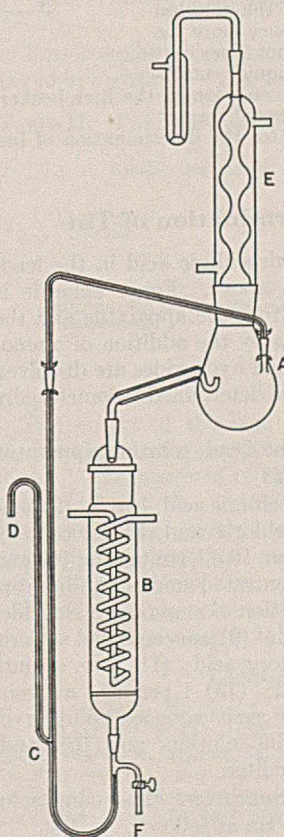


FIGURE 1. DIAGRAM OF LEAD-SOLUTION APPARATUS

copper coil placed in an ice bath. To facilitate ease of operation, the water passing from the trap can be used as the cooling water in the condenser. Connect the air lift to the low-pressure air supply and pass in a slow stream of air. This air breaks the solution from the trap into droplets and carries them over into the solution flask. Regulate the air pressure so as to give a steady flow. (The rate of circulation must be so adjusted that the solution in flask *A* never reaches saturation with respect to lead chloride.) As the solution in the trap is carried into the flask, that in the flask is siphoned over into the trap, thus effecting a continuous circulation of the solution.

4. Place the heater in position and heat the solution in the flask to between 90° and 100° C. Maintain this temperature throughout the process of solution and do not at any time allow the solution to boil. The solution of the alloy requires from 12 to 24 hours and is most conveniently effected by allowing the apparatus to run overnight. By morning, solution of the alloy will have been completed.

5. When the alloy is dissolved, remove the source of heat and continue the circulatory process for at least 1 hour, by which time the temperature of the solution in the flask should not be over 10° C. Remove the trap from the condenser and then shut off the air supply. Wash down the walls of the condenser, open stopcock *F*, and allow the solution in the trap to run into a 1-liter beaker. Remove the flask, *A*, and transfer the solution in it to the same beaker, washing out the flask with water. Close stopcock *F*, and fill the trap to above the cooling coil with hot 5 per cent hydrochloric acid.

Break up the mass of lead chloride crystals by means of a glass rod to permit more efficient washing of the crystals. Continue passing ice-cold water through the coil. When the solution in the trap is cooled to at least 10° C., run it into the beaker containing the solution from the trap and flask. Repeat once more the washing of the lead chloride with hot 5 per cent hydrochloric acid. Wash out any liquid remaining in the air lift and add it to the solution in the liter beaker. Add also the solution in the condensed trap.

Reserve the combined solutions for the determination of impurities.

Separation and Determination of Tin

The sample is dissolved in hydrochloric acid in the lead-solution apparatus as described above. Ferric chloride is added to the solution obtained from the apparatus and the tin is co-precipitated with the iron by the addition of ammonium hydroxide. The precipitated hydroxides are dissolved in hydrochloric acid and the tin is determined iodometrically after reduction with lead (3).

The apparatus consists of the lead solution apparatus and the tin-reduction apparatus (3).

The reagents used are (1) hydrochloric acid, 1 to 3; (2) concentrated nitric acid; (3) hydrochloric acid, 10 per cent by volume; (4) ferric chloride solution, 10 ml. containing 100 mg. of iron; (5) superoxol; (6) concentrated ammonium hydroxide; (7) 1 per cent aqueous solution of ammonium chloride; (8) ammonium hydroxide, 1 to 3; (9) concentrated sulfuric acid; (10) concentrated hydrochloric acid; (11) c. p. sodium chloride; (12) granular test lead; (13) 1 per cent aqueous solution of starch; (14) 10 per cent aqueous solution of potassium iodide; (15) 0.01 *N* iodine solution; and (16) standard tin solution, 0.4000 gram per liter.

STANDARDIZATION OF IODINE SOLUTION. The iodine solution is standardized against pure tin as follows:

Transfer a volume of a standard tin solution equivalent to 10 mg. of tin to a 500-ml. wide-mouthed Erlenmeyer flask. Add 75

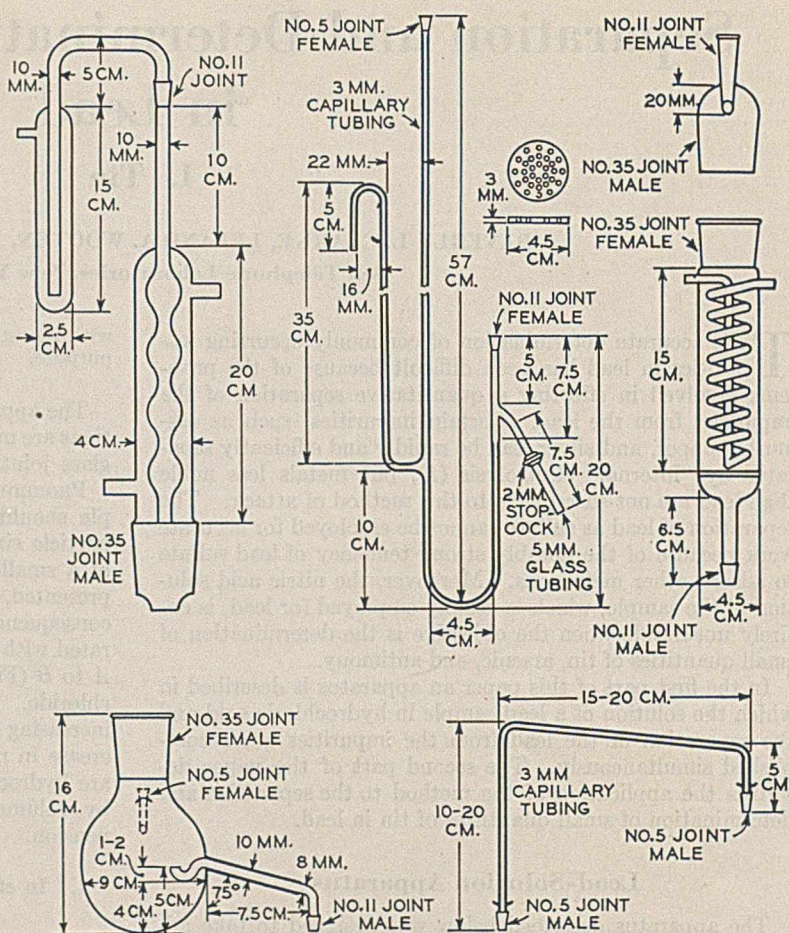


FIGURE 2. DETAILS OF LEAD-SOLUTION APPARATUS

ml. of hydrochloric acid and dilute to 300 ml. with water. Add 5 grams of test lead and 20 grams of sodium chloride. Place the flask on the hot plate. Insert the stopper carrying the air condenser, etc., and pass a stream of carbon dioxide through the apparatus.

Heat to boiling and boil gently for 1 hour. Cool in ice water, regulating the current of carbon dioxide so as to prevent back pressure. When the solution has cooled to at least 10° C., remove the glass plug in the stopper and immediately add, by means of a pipet, 5 ml. of potassium iodide solution and 5 ml. of starch solution. Insert the tip of the buret containing the iodine solution and titrate to the first permanent shade of blue.

Deduct the volume of iodine solution required for a blank determination on the reagents.

$$\text{Tin equivalent per ml.} = \frac{\text{weight of tin taken}}{\text{ml. of iodine solution}}$$

PROCEDURE. 1. Dissolve 50 grams of the lead sample in the lead-solution apparatus as described above. Transfer the solution and washings to a 1-liter beaker.

2. To the solution in the beaker add 20 ml. of ferric chloride solution and a few drops of superoxol to ensure oxidation of the iron. Boil gently for a few minutes to remove the excess superoxol. Cool to between 70° and 80° C. Add ammonium hydroxide until the precipitate of ferric hydroxide no longer redissolves on stirring, and then add 10 ml. in excess. Boil for 1 or 2 minutes, allow to settle, and then filter on a No. 41 Whatman paper. Wash with hot ammonium chloride solution.

3. Dissolve the precipitate on the filter paper in 1 to 3 hydrochloric acid, collecting the solution in the beaker in which the first precipitation was made. Dilute to 150 to 200 ml. Add 1 to 3 ammonium hydroxide dropwise until all of the ferric hydroxide but little or none of the lead hydroxide is precipitated. (The beginning of the precipitation of lead hydroxide is shown by the appearance of a white cloudiness in the solution. The addition of ammonium hydroxide should be stopped before this point is reached.) Boil for 1 minute, filter on the paper used to collec-

the first precipitate, and wash with hot ammonium chloride solution.

4. Dissolve the precipitate in a small quantity of 1 to 3 hydrochloric acid, collecting the solution in the beaker in which the precipitation was made. Reserve the solution. Transfer the filter paper to a 500-ml. wide-mouthed Erlenmeyer flask, and add 5 ml. of sulfuric acid and sufficient nitric acid to destroy all organic matter. Evaporate to fumes of sulfur trioxide, and continue heating until a clear solution is obtained, adding more nitric acid if necessary. Cool. Add 10 ml. of water and again evaporate to fumes. Cool.

5. Transfer the hydrochloric acid solution obtained in Paragraph 4 to the residue in the 500-ml. Erlenmeyer flask. Add 75 ml. of hydrochloric acid and dilute to 300 ml. with water. Add 20 grams of sodium chloride and 5 grams of test lead. Insert the stopper carrying the air condenser, etc., and proceed with the reduction and titration of the tin exactly as described above under "Standardization of Iodine Solution."

Deduct the volume of iodine solution required for a blank determination on the reagents.

$$\frac{\text{Ml. of I}_2 \text{ solution} \times \text{Sn equivalent} \times 100}{\text{sample weight}} = \% \text{ tin}$$

EXPERIMENTAL DATA. Fifty-gram samples of a commercial lead were placed in the solution flask. Known amounts of tin in hydrochloric acid solution were added and the sample was then treated as recorded in the procedure. The lead used in these experiments had the following approximate percentage composition:

Copper	0.06	Antimony	0.002
Bismuth	0.015	Arsenic	<0.001
Silver	0.006	Tin	0.0002
Iron	<0.001		

The tin solutions were prepared from Kahlbaum's "for analysis" tin. The results obtained are shown in Table I.

TABLE I. DETERMINATION OF TIN IN THE PRESENCE OF LEAD AND COMMON IMPURITIES OF LEAD

Lead Present Grams	Tin Present Mg.	Tin ^a Found Mg.	Error Mg.	Average Deviation from Mean Mg.
50	1.00	0.94	-0.06	
50	1.00	0.97	-0.03	
50	1.00	0.96	-0.04	±0.03
50	1.00	0.98	-0.02	
50	1.00	1.02	+0.02	
50	1.00	1.02	+0.02	
		Av. 0.98	-0.02	
50	4.00	4.00	0.00	
50	4.00	4.00	0.00	±0.02
50	4.00	4.05	+0.05	
		Av. 4.02	+0.02	
50	5.00	4.95	-0.05	
50	5.00	4.96	-0.04	
50	5.00	5.00	0.00	
50	5.00	5.06	+0.06	
50	5.00	5.00	0.00	±0.03
50	5.00	5.03	+0.03	
50	5.00	4.94	-0.06	
50	5.00	5.02	+0.02	
50	5.00	4.97	-0.03	
		Av. 4.99	-0.01	
50	10.00	9.79	-0.21	
50	10.00	9.85	-0.15	
50	10.00	9.84	-0.16	
50	10.00	10.12	+0.12	±0.13
50	10.00	10.12	+0.12	
50	10.00	10.06	+0.06	
50	10.00	10.10	+0.10	
		Av. 9.98	-0.02	
20	20.00	20.00	0.00	
20	20.00	20.11	+0.11	±0.05
20	20.00	20.02	+0.02	
20	20.00	20.09	+0.09	
		Av. 20.05	+0.05	

^a Results corrected for blank run on lead used.

Two samples of lead containing tin were also analyzed by the above method. The results are shown in Table II.

TABLE II. PRECISION OF METHOD APPLIED TO TYPICAL SAMPLES

Sample Designation	Tin %	Deviation from Mean %
Commercial lead containing tin, Sample A	0.0026	0.0000
	0.0026	0.0000
	0.0025	-0.0001
	0.0026	0.0000
Av.	0.0026	0.0000
Commercial lead containing tin, Sample B	0.0056	+0.0001
	0.0056	+0.0001
	0.0053	-0.0002
	0.0054	-0.0001
Av.	0.0055	±0.0001

The purity of the lead chloride precipitate obtained in these experiments was determined by means of the spectrograph. The presence of tin was not detected in any of the samples analyzed. Traces of copper and iron were found, but neither was present in a significant quantity. Silver also was found present, as would be expected from the insolubility of its chloride.

In a future paper quantitative data on the separation of arsenic and antimony from lead will be presented.

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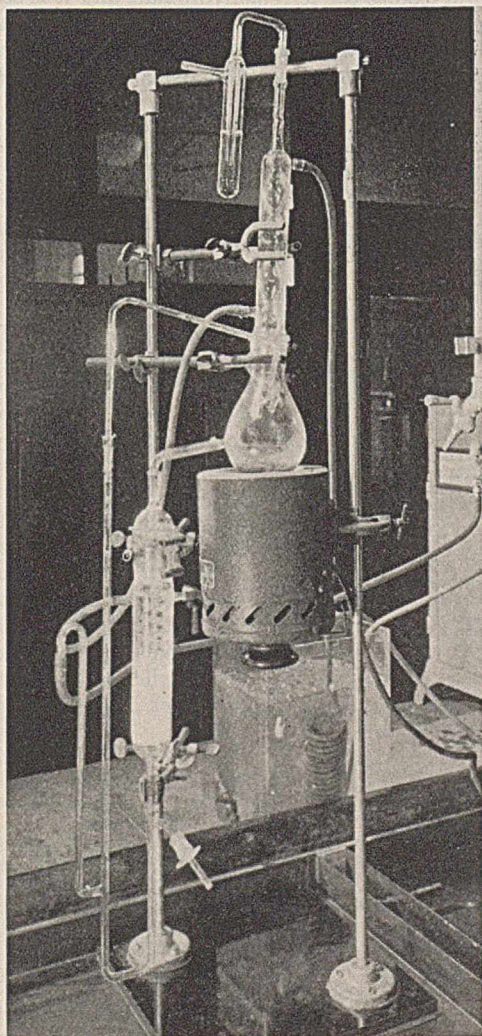


FIGURE 3. LEAD-SOLUTION APPARATUS IN OPERATION

RECEIVED April 27, 1937. Presented before the Division of Physical and Inorganic Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.

A Semimicro Qualitative Test for the Nitro Group in Organic Compounds

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SEVERAL qualitative tests for the nitro group have been reported.

Vortmann (18) suggests three: reduction to amino group and subsequent identification, formation of chloropierin which may be recognized by its odor, and the red or yellow coloration produced by boiling solutions of alkaline hydroxides. Mulliken and Barker (13) have shown these to be inadequate and present two additional tests. The first involves the reduction with zinc and alcohol to a substituted hydroxylamine which in turn is identified by its reducing action on ammoniacal silver nitrate. The second test utilizes the oxidizing power of the nitro group to change "aniline oil" (equal parts of *o*- and *p*-toluidine, and aniline) to the highly colored magenta red. Mulliken does not quote this last test in his "Identification of Pure Organic Compounds" (12).

Janovsky (9) found that aromatic dinitro compounds in acetone gave colorations with aqueous potassium hydroxide. This work was extended and its limitations observed by Bitto (3), Reitzenstein and Stamm (15), and Rudolph (17). Bost and Nicholson (5) have confirmed this test and find that, in general, mononitro aromatic compounds give no colorations, dinitro compounds give a purple, and trinitro compounds produce a blood red coloration. The presence of amino or hydroxyl groups in the nucleus, however, interfere. Konowalow (11) tested for primary and secondary nitro groups by treating their sodium salts with ferric chloride and extracting the colors in suitable organic solvents. Dimethylaniline (19) gives colors with many nitro compounds. Anhydrous aluminum bromide in benzene (14) has also been reported to give a red color with aromatic nitro compounds. Rosenthaler (16) states that nitromethane when treated with ammonium hydroxide and vanillin and heated gives a red color which disappears on cooling. If sodium nitroprusside is used in place of vanillin, he states that an indigo blue coloring appears, which gradually changes to green and then to yellow.

The higher homologs were found to give a brick red coloration. Bose (4) has found that all except mononitro aromatic compounds will split off potassium nitrite with strong potassium hydroxide which in turn is identified with Griess-Ilosvay's reagent. Kamm (10) has described a test which involves the reduction of the group to various colored compounds by means of sodium amalgam and alcohol.

The presented test is dependent upon the oxidation of a suspension of ferrous hydroxide by the nitro compound. Ferrous hydroxide has been used many times in the past for preparing amino compounds from nitro compounds. For example, (*m*-aminophenyl)-glyoxylic acid (6), *o*-aminophenylpropionic acid (1), *o*-aminobenzaldehyde (2), and *o*-aminocinnamic acid (7) have been prepared by the reduction of the corresponding nitro compounds by means of ferrous hydroxide. Jacobs and Heidelberger (8) have prepared a number of amino acids, amides, and ureas by reducing the nitro compound with ferrous hydroxide and ammonia. The authors have been unable, however, to find any reference to the use of this reagent in a qualitative test.

Procedure

Two solutions are required.

1. IRON SOLUTION. A 500-ml. portion of distilled water is boiled for 15 minutes to remove any dissolved air. After cooling, 25 grams of ferrous ammonium sulfate and 2 ml. of concentrated sulfuric acid are added. An iron nail may be added to retard oxidation by the air.

2. BASE SOLUTION. 30 grams of stick potassium hydroxide are dissolved in 30 ml. of distilled water and then added to 200 ml. of 95 per cent ethyl alcohol.

A 0.7-ml. portion of the iron solution is pipetted into a 4-ml. test tube, and a small quantity (10 mg.) of the finely powdered un-

known is added. Then 0.5 ml. of the base solution is added and a stream of natural gas (or any inert gas) is passed through the tube to remove any air. The tube is quickly stoppered and shaken. A positive test is indicated by the formation of a red-brown to brown precipitate of ferric hydroxide. Negative tests in many cases gave a very light green precipitate. However, in some cases the precipitate became dark due to slight oxidation.

Discussion and Conclusion

In the aromatic series, forty-five nitro compounds were tested and all gave a positive test in less than 30 seconds. Unfortunately nitromethane was the only representative of the aliphatic series available, and it gave a positive test only after a minute. The speed with which the iron is oxidized was seen to be a function of the solubility of the nitro compound. Thus *p*-nitrobenzoic acid gave a positive result almost immediately, while nitronaphthalene required 25 seconds. Obviously any organic oxidizing agent powerful enough will oxidize the ferrous hydroxide, and it is seen that nitroso compounds, aliphatic nitrates and nitrites, quinones, and hydroxylamine will also show a positive test. As in any color test, highly colored compounds cannot be successfully

TABLE I. RESULTS OF TESTS

Compound	Color of Ppt.	Time Sec.
Compounds Containing the Nitro Group		
Nitromethane	Brown	60
Mononitrobenzene	Brown	2
<i>m</i> -Dinitrobenzene	Brown	10
Nitronaphthalene	Brown	25
<i>p</i> -Nitrobenzoic acid	Brown	2
<i>p</i> -Nitrophenylacetic acid	Brown	2
<i>p</i> -Nitroacetanilide	Brown	10
2,4-Dinitrophenol	Brown	3
<i>m</i> -Nitroaniline	Brown	3
<i>o</i> -Nitroanisole	Brown	2
<i>m</i> -Nitrobenzaldehyde	Brown	1
<i>p</i> -Nitrobenzoyl cyanide	Brown	5
<i>m</i> -Nitrobenzhydrazide	Brown	5
<i>m</i> -Nitrophenylhydrazine	Brown	2
2,4,6-Trinitro-1,3-dimethyl-5- <i>tert</i> -butylbenzene	Brown	25
Compounds Not Containing the Nitro Group		
Ethyl alcohol	Light green	5
<i>n</i> -Amyl alcohol	Light green	5
Benzaldehyde	Light green	5
Acetone	Light green	5
Benzoic acid	Light green	5
Benzoin	Dark green	5
Benzyl	Dark green	5
Benzidine	Gray green	5
Dimethylaniline	Light green	5
Benzaldehyde-phenylhydrazone	Light green	5
Glucosazone	Yellow green	5
Acetamide	Light green	5
		Sec.
Ethyl nitrite	Brown	5
Ethyl nitrate	Brown	30
1,4-Naphthoquinone	Dark brown	30
Benzoquinone	Brown	5
		Min.
Benzoyl peroxide	Light green	5
		Sec.
<i>o</i> -Nitroso- <i>m</i> -cresol	Brown	3
Tetrachloroquinone	Brown	7
		Min.
Anthraquinone	Red solution	5
Dimethyl sulfate	Light green	5
Resorcinol	Light green	5
Diphenyl sulfone	Light green	5
Sodium benzene sulfonate	Light green	5
Triphenyl phosphate	Light green	5
		Sec.
Hydroxylamine hydrochloride	Brown	2
		Min.
Benzophenone	Light green	5

tested. Seventy-five compounds not containing the nitro group were tested and were all found to be negative with the exceptions noted above.

The test as outlined, when used in correlation with other accepted tests, will be a decided aid in the detection of the nitro group in organic compounds.

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An Improved Reaction Microapparatus

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NUMEROUS micromethods involve the evolution and quantitative absorption of various gases and vapors. The usual setup for this type of analysis is frequently cumbersome and inefficient because of the use of rubber stoppers and connections. The all-glass apparatus described here obviates these difficulties, is very compact, and titrations may be carried out directly in the apparatus. It was originally designed for the microdetermination of bromine by evolution and absorption in potassium iodide solution, but may be employed without modification for a wide range of analyses.

Details of construction are shown in Figure 1, Pyrex glass and standard taper ground joints being used throughout. The use of the apparatus is illustrated by the technic employed in carrying out bromine determinations by a modification of the Yates (2) method developed in this laboratory.

The sample, equivalent to not more than 500 gamma of bromine, is transferred to the reaction flask with 7 cc. of water, and 2.5 cc. of concentrated sulfuric acid are added through the tap funnel over a period of 10 minutes, cooling the flask in ice water during this addition. This is followed by 4 cc. of chromic acid solution (20 grams of CrO_3 , 40 cc. of concentrated sulfuric acid, and 120 cc. of water). The inlet to the tap funnel is then connected to a wash bottle containing 20 per cent potassium hydroxide solu-

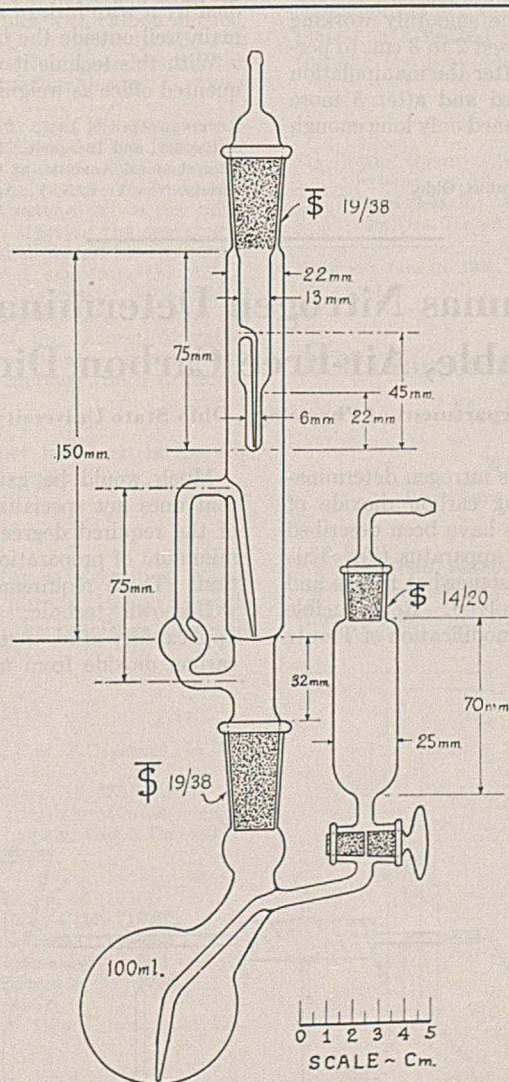


FIGURE 1. DIAGRAM OF APPARATUS

tion. The main absorber is charged with 3 cc. of 10 per cent potassium iodide solution containing 3 to 4 drops of 0.5 per cent starch solution prepared according to the method of Nichols (1) and the secondary absorbing trap with 1 cc. of the above potassium iodide solution. Air is then aspirated through the system at a rate of approximately one bubble per second, for 5 hours. At the end of this period the absorption unit is disconnected, the upper stopper is loosened, and the contents of the trap are blown into the main absorber which is then washed with two successive 1-cc. portions of the 10 per cent potassium iodide solution. Titration is carried out in the main absorber with 0.001 *N* sodium thiosulfate.

Prior to the development of this reaction vessel, the percentage recovery of bromine was in the order of 95 to 96 per cent, while with its use the recovery ranges between 98 and 100 per cent with greatly reduced variability between replicates.

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RECEIVED April 14, 1937. Contribution from the Grain Research Laboratory, Board of Grain Commissioners, Winnipeg, Manitoba, with financial assistance from the National Research Council of Canada. Published as paper No. 119 of the Associate Committee on Grain Research, National Research Council of Canada and Dominion Department of Agriculture.

Operation of Analytical Microbalances Highly Sensitive to Temperature Changes

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THE high degree of sensitivity attained by most analytical microbalances is not infrequently impaired by their great temperature sensitivity. Some instruments are more sensitive toward temperature fluctuations than others of the same manufacture, and according to information from an experienced maker of microbalances the causes of this different behavior have not yet been traced definitely.

The precautions which were found necessary to make practical weighings to ± 1 gamma with an extremely temperature-sensitive instrument of the long-beam type are reported in this note. They should be of general value if microanalytical weighings have to be carried out under handicap.

Protection of the Balance

PROTECTION FROM OUTSIDE DISTURBANCES. A protective case shields the balance against drafts and heat radiating from the operator. Between weighings the side windows of the balance case are kept open and the smoothly working sash window of the protective case is raised 2 to 3 cm. to permit "acclimatization." Five minutes after the manipulation of weights, etc., all windows are closed and after 5 more minutes the outer (protective) case is opened only long enough

to permit starting the balance to swing. During the weighing proper this case is kept closed.

PROTECTION FROM EFFECTS OF MANIPULATIONS IN THE BALANCE CASE. An aluminum sheet separating the beam from the lower part of the balance (pans) was kindly installed by Christian Becker, Inc., New York, and the balance floor was covered with sheet copper to dissipate local heating of the balance floor. By lengthening the rider carrier and release handles for 20 cm., the inconvenience of counterbalancing the heat radiation of the hand can be omitted.

Manipulation of Weights and Objects to Be Weighed

Ordinary crucible tongs 24 cm. long to which the ivory-tipped forceps of the set of analytical weights are attached, and another pair of these tongs for boats, weighing flasks, etc., minimize heat radiations from the hands of the operator. Pregl's carbon dioxide- and water-absorption tubes are handled by a wire fork of such length that the hands always remain well outside the balance case.

With this technic it was even possible to use an often-frequented office as weighing room.

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Modified Micro-Dumas Nitrogen Determination with Readily Available, Air-Free Carbon Dioxide

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THE success of Pregl's micro-Dumas nitrogen determination depends mainly on procuring carbon dioxide of exceptional purity. Various generators have been described (1, 2, 4, 7, 8, 10), among them Poth's apparatus (8). This has proved very satisfactory, but it is somewhat fragile and the starting operations are rather involved. Reproducible blanks have been made possible by the modification of Trautz and Niederl (11).

Much would be gained, particularly for the laboratory that does not specialize in microanalysis, if carbon dioxide of the required degree of purity could be provided with a minimum of preparation in an apparatus of simple construction. These requirements are fulfilled in Dumas' original well-known technic. Pregl (9), intent upon the general applicability of his methods, discarded the idea of generating carbon dioxide from magnesite or sodium bicarbonate, be-

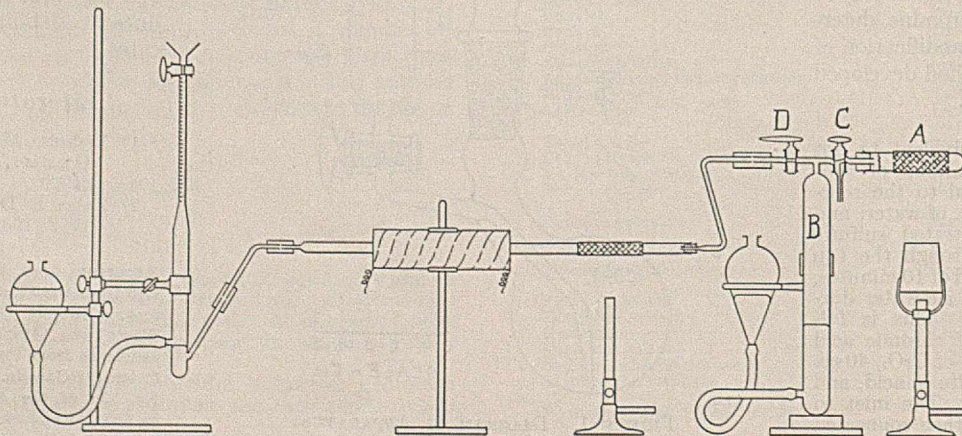


FIGURE 1

cause of the danger of volatilizing part of the sample by the hot carrier gas in the initial scavenging of the tube. Moreover, the highly important rate of gas flow could be secured more safely with the Kipp generator. Dubsy (3), Govaert (5), and Ide (6) have successfully applied magnesite to the micro-Dumas analysis of less volatile material.

The apparatus shown in Figure 1 supplies a well-controlled flow of carbon dioxide at room temperature. Its construction requires little skill in glass blowing.

A Pyrex test tube, preferably heavy-walled (bomb tubing), *A*, 10 to 15 cm. long is attached by means of a rubber stopper to a gasometer, such as *B*, of 250- to 300-cc. capacity. A two-way stopcock, *C*, permits removal of air from *A*. Cock *D* takes over the functions of regulating the gas flow, the customary stopcock between microazotometer and combustion tube thereby being eliminated. Sodium bicarbonate (analytical grade), being generally available in the laboratory, is used instead of magnesite, of which a special grade (Kahlbaum's) is required. Mercury serves as confining liquid in the gasometer. One charge of sodium bicarbonate, packed tightly, will serve for seven to eight analyses (one day's work).

By gently heating for 2 to 3 minutes the portion of test tube *A* covered with wire gauze, air is expelled through *C*. Gasometer *B* is then filled with carbon dioxide. Water formed in the liberation of carbon dioxide condenses on the mercury surface and does not interfere with the determination. It is removed through *C* when recharging test tube *A*. When first assembling the apparatus and after it has been unused for some time, it is necessary to flush the storage vessel two to three times with carbon dioxide, to remove air adsorbed on the walls. Care should be taken to eliminate air pockets from the pressure tubing connecting the gasometer and leveling bulb. By evacuation through *C*, traces of air can also be removed.

The combustion proper and the measuring of the nitrogen volume are carried out according to Pregl's directions (9). Since the gases in the combustion tube are at a pressure close to atmospheric, the mercury level confining the potassium hydroxide solution in the microazotometer should extend only a few millimeters over the gas inlet tube. When starting the scavenging operation, the flame of the movable burner should hit the empty portion of the combustion tube about 1 cm. from the filling. After gas evolution in the nitrometer has ceased, stopcock *D* should be manipulated slowly and with great care. Results are well within 0.1 per cent (absolute) of the theoretical value. Ordinarily, no blank determination is necessary. When not in use, the gasometer remains filled with mercury, both stopcocks being closed.

The method described in this paper has been in use for some time in this and in another laboratory.

Summary

A simple carbon dioxide generator is described which promptly supplies gas of the required purity. Pregl's apparatus is further simplified by placing the precision stopcock between combustion tube and generator.

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A Macro- or Micro-Gooch Filter

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A SMALL Gooch funnel can be readily fashioned from two sizes of laboratory glass tubing, as shown, and is particularly convenient for determining halogens by indirect methods (2). Other uses, where small precipitates are handled quantitatively, will suggest themselves. It combines the essential features of the usual Gooch crucible, supporting funnel, and connecting rubber tubing, and is prepared and used like any typical Gooch filter.

The smaller size of tubing should be about 6 or 8 mm., to enter readily the openings of ordinary rubber stoppers, and the larger size will depend upon the probable uses of the funnel. A solid, round glass bead will serve as a loose support for the asbestos fibers, which are added in the usual manner.

The prepared funnel can be most conveniently heated in an electric oven or electric or gas micromuffle (1). After the combined silver halides are weighed, the funnel may be placed in a heated tube. A slow stream of chlorine passed through the tube displaces the bromine or iodine present.



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RECEIVED June 10, 1937.

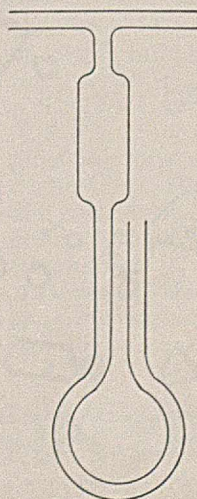
A Manometer for Carbon and Hydrogen Pressure Regulation

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THE maintenance of correct pressure relations in the micro-determination of carbon and hydrogen is facilitated by the introduction of a simple water manometer between the carbon dioxide absorption tube and the Mariotte flask. The addition of a drop of ink to the water assists in reading; a small bulb precludes the possibility of sucking water into the gas line.

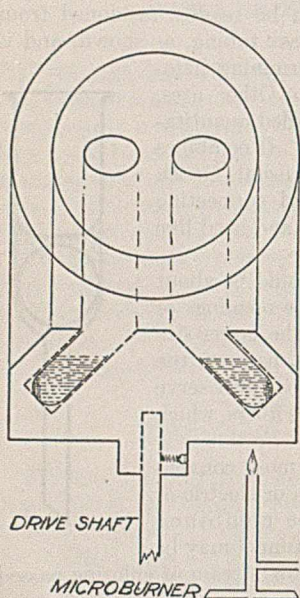
The rate of gas flow may be adjusted in the usual manner or with the temporary assistance of a second manometer at the junction of the combustion tube and the water absorption tube, the pressure regulator and the Mariotte flask being so adjusted as to maintain atmospheric pressure at this junction. The proper difference in water levels is marked on the first manometer and this difference is maintained during subsequent runs.



RECEIVED May 19, 1937.

A Microcentrifuge

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THE advantages of centrifugation over filtration in micro and semimicro operations are well recognized among microchemists. In using the ordinary bucket type of head for centrifuging in semimicro qualitative analysis, the author has found it difficult to keep solutions hot during the operation. The head described below can be kept hot and has other advantages over the bucket type.

The head is similar to that on the so-called "angle" centrifuge (1) and consists of a cylindrical aluminum block (diameter, 7.5 cm.) with two or more holes for holding

centrifuge tubes, drilled opposite each other and at an angle of about 45° to the horizontal. The head is fastened to a drive shaft operated by electric, hand, or air power. A Cenco stirring motor fastened in an inverted position is convenient for this purpose.

In the hot-water extraction of lead chloride from silver and mercurous chlorides, it is necessary to keep the centrifuge tube and contents hot during the centrifuging process. For

this purpose a microburner is suspended just below the aluminum block, which can then be heated to 100°C . in 1 to 2 minutes. It can likewise be cooled rapidly for subsequent use at room temperature. The draft produced by the rotating head does not extinguish the burner.

The maximum speed necessary to throw down quickly any precipitates encountered in the usual schemes of qualitative analysis does not exceed 1200 r. p. m. From experience in this laboratory with aluminum centrifuge heads of the size used here, it is estimated that the maximum rotational speed attainable with the Cenco stirring motor is not more than one-tenth that required to split the block. For this reason it is not necessary to use a device for the protection of the worker.

For heads designed to carry microcentrifuge tubes only, the author has found a large cork sufficiently strong and light enough to be driven at the required speed by the air pressures usually available in a laboratory.

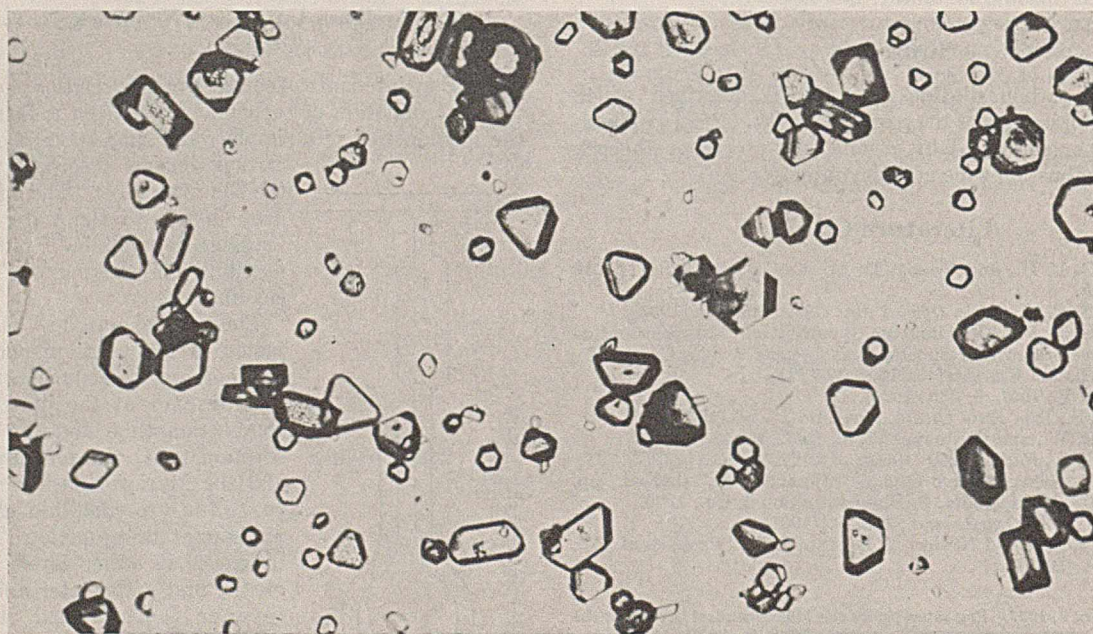
Acknowledgment

Thanks are due to R. P. Schneider of the Department of Industrial Engineering, Ohio State University, for casting the aluminum blocks used and to John Betz, technical assistant to the Department of Chemistry, Ohio State University, for the excellence of his mechanical work in the construction of the apparatus.

Literature Cited

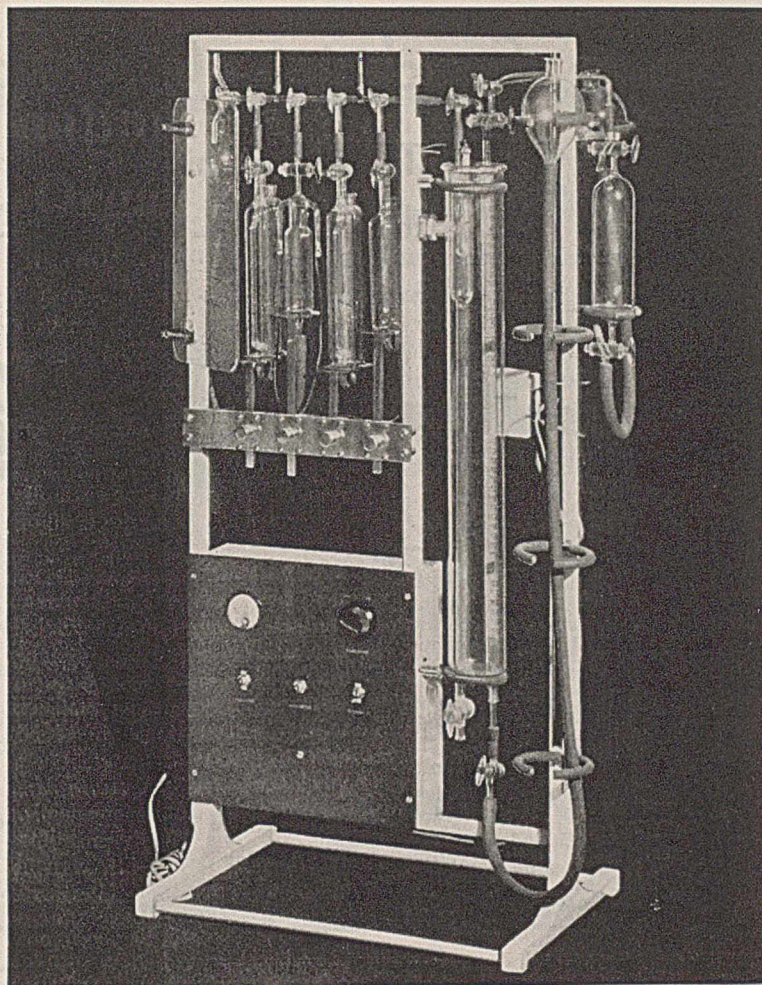
- (1) Lundgren, K. T. R., U. S. Patent 1,730,776 (October 8, 1929). Ivan Sorvall, 4141 46th St., Long Island City, N. Y., U. S. representative.

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Silver Chloride

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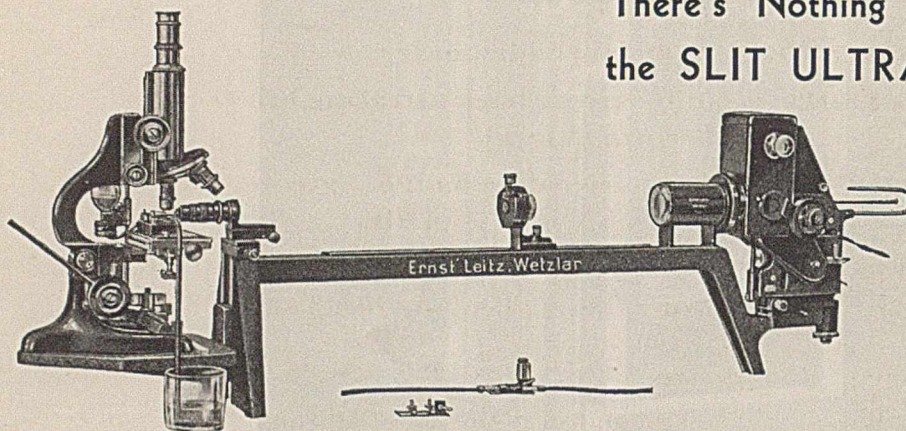
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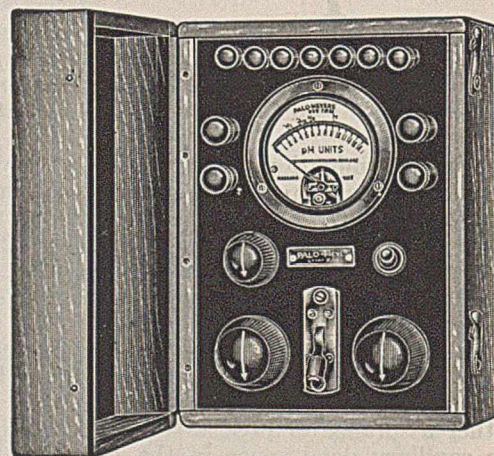
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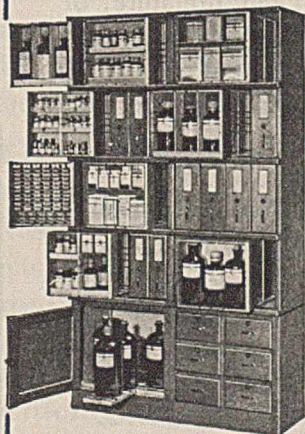
REFERENCE—Mutschin and Pollak, *Zeitschrift für analytische Chemie* 108, 8 and 309 (1937)

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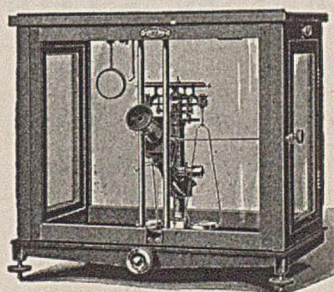
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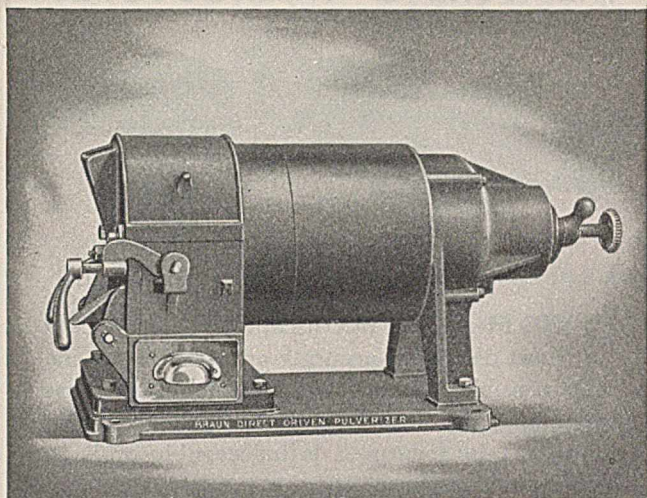
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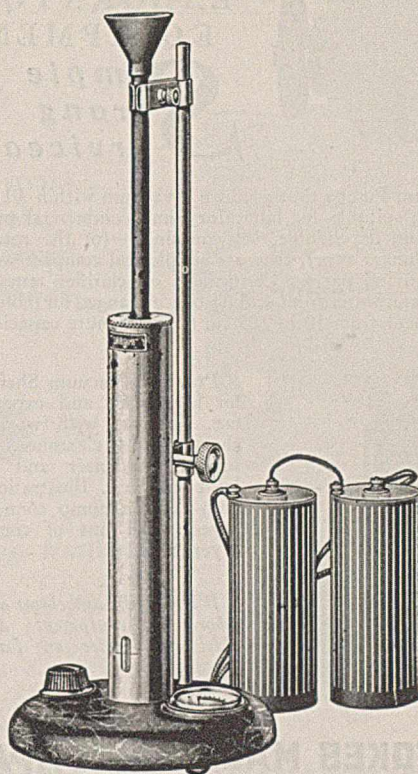
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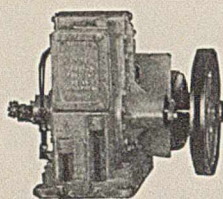
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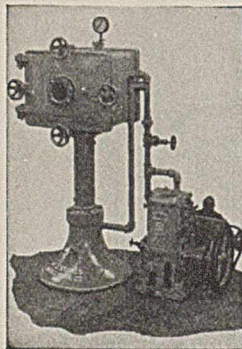
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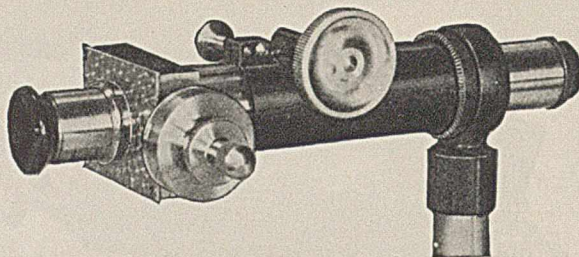
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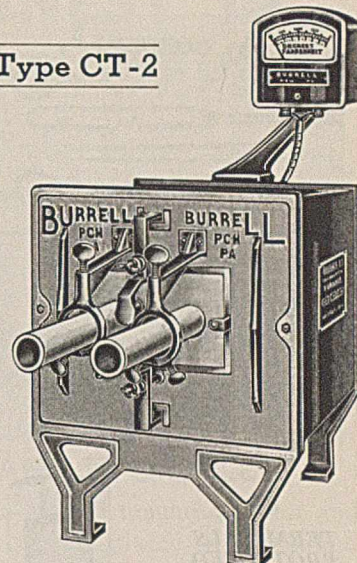
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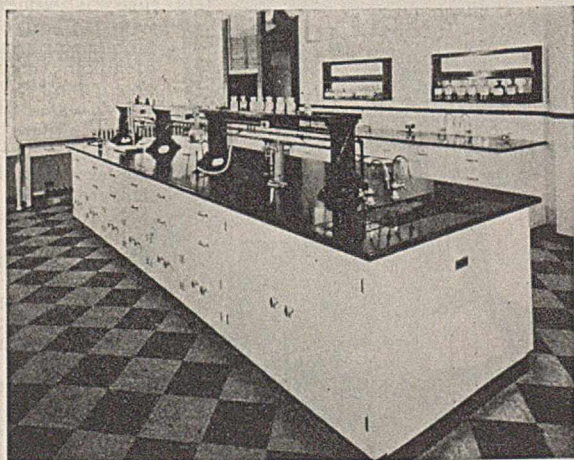
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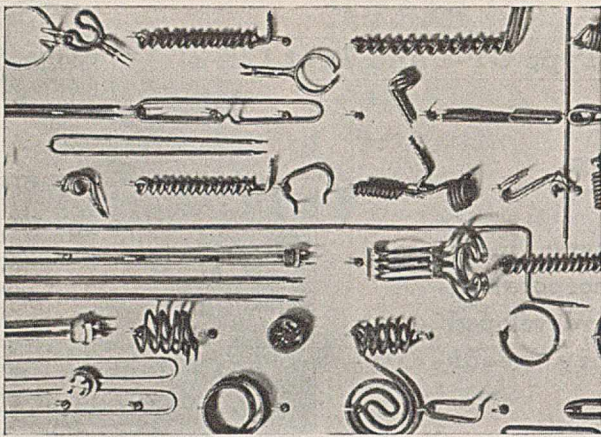
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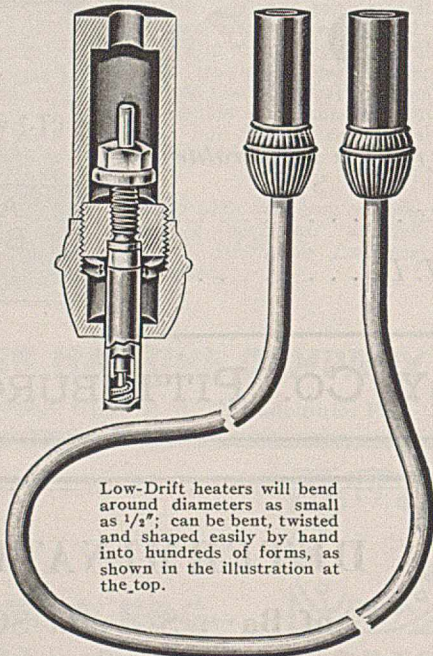
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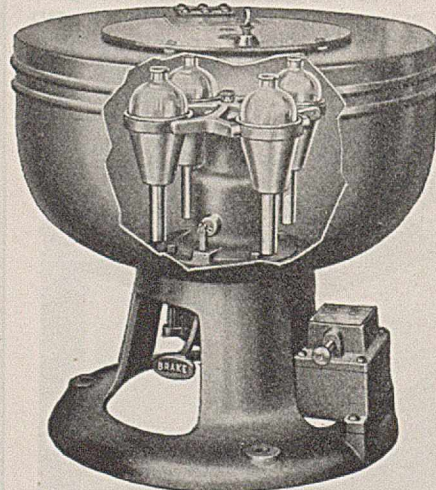
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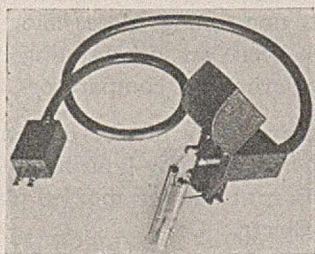
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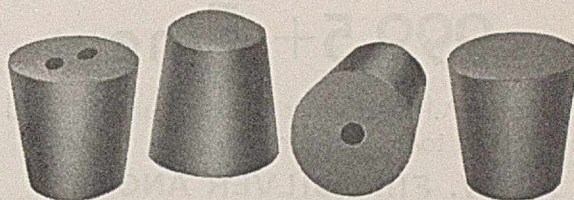
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