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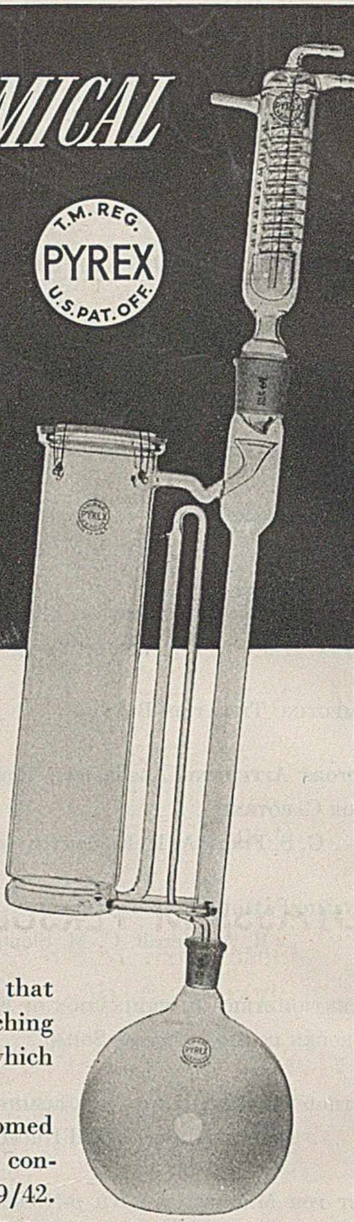

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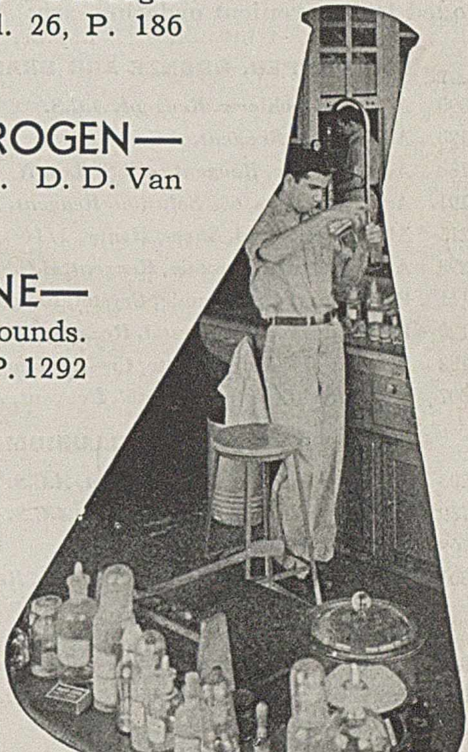

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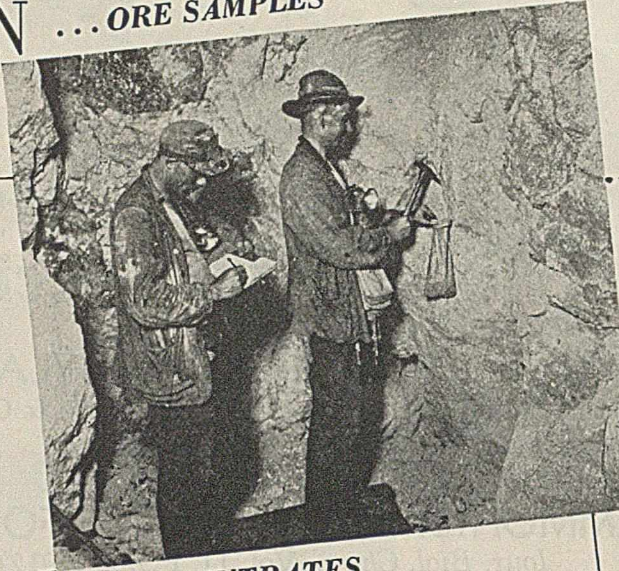

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2120	Potassium Iodide, *Crystal, Reagent, A.C.S.*
2128	Potassium Permanganate, *Crystal, Reagent, A.C.S.*
2307	Sodium Thiosulfate, *Crystal, Reagent, A.C.S.*
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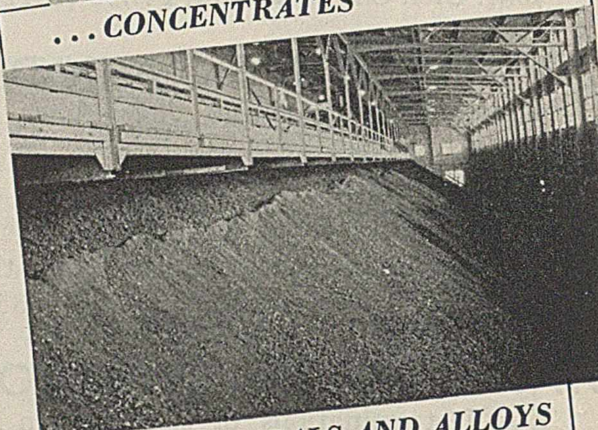

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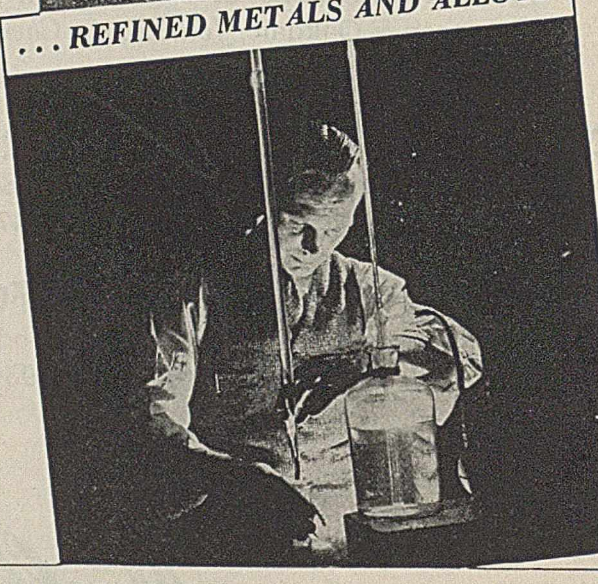

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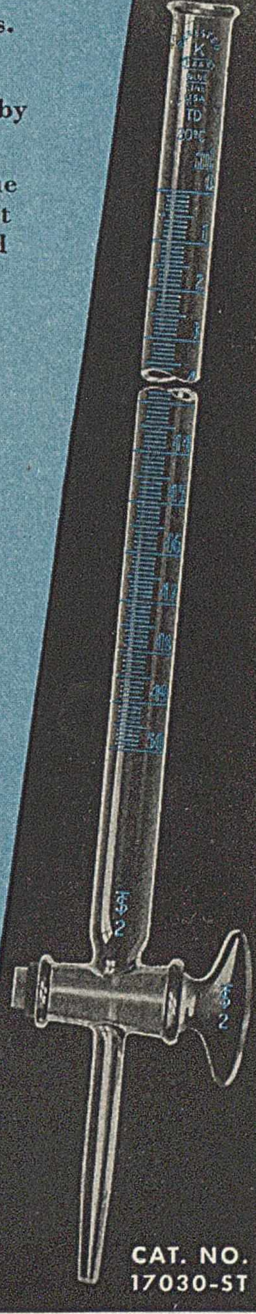

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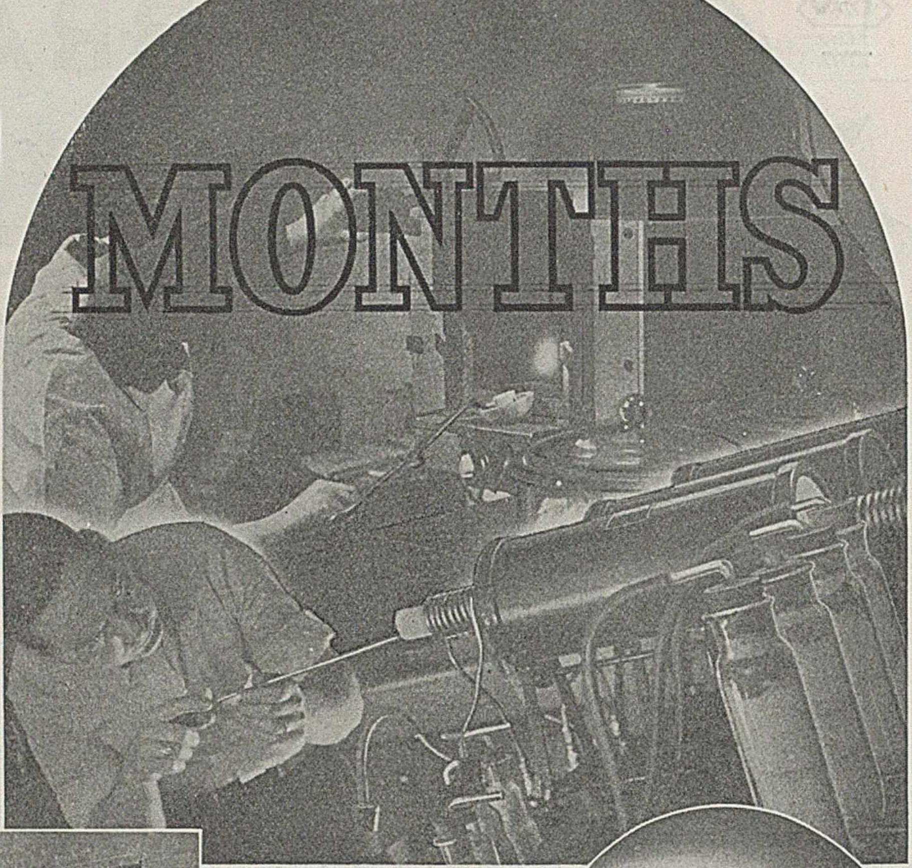

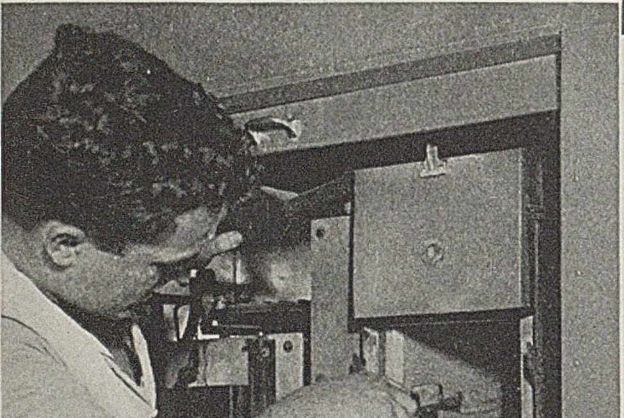

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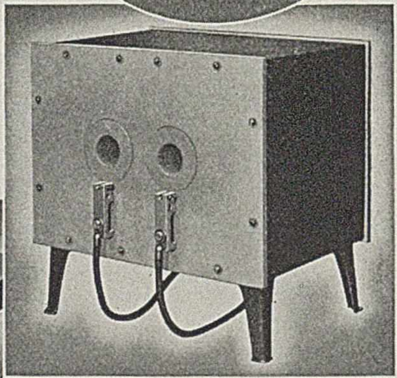

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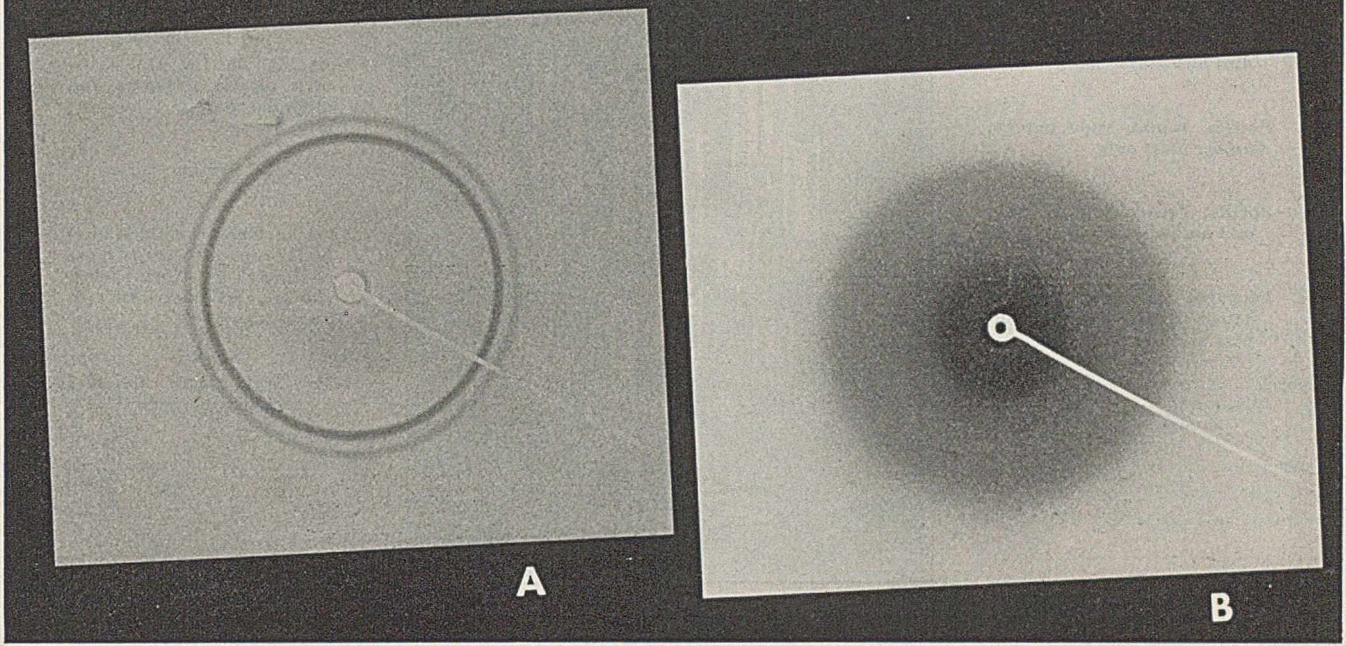
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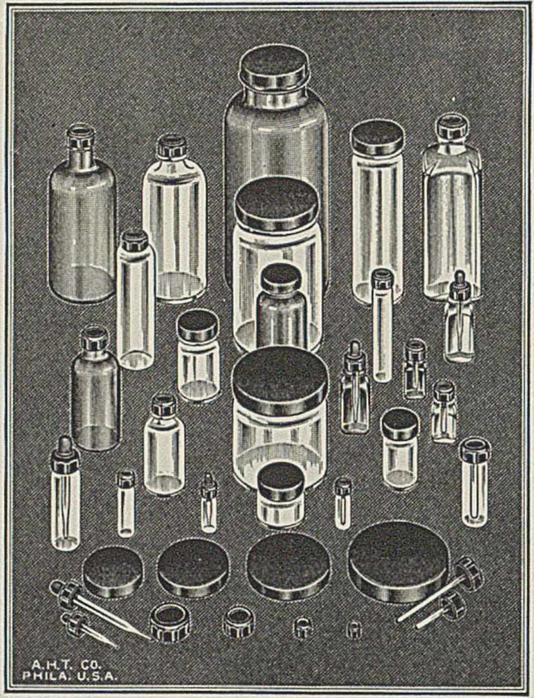

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PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY ● HARRISON E. HOWE, EDITOR

Effect of Sulfur and Sulfur Compounds in Naphtha upon Certain Corrosion Tests

Sensitivity of the Doctor Test

L. M. HENDERSON, M. S. AGRUSS, AND GEORGE W. AYERS, JR.
The Pure Oil Company, Chicago, Ill.

IN THE manufacture of special naphthas it is desirable to know the effect of dissolved free sulfur or sulfur compounds upon the distillation-corrosion test, the copper-strip corrosion tests at 50° C. (122° F.) and 100° C. (212° F.), and the doctor test of the naphthas. Since there are few data on this subject in the literature, the authors have determined the effects of a number of mercaptans, sulfides, and disulfides, and of free sulfur, *n*-dibutyl sulfone, and thiophene, dissolved in Stoddard solvent, varnish makers' and painters' (V. M. & P.) naphtha, and rubber solvent upon the distillation-corrosion test, the copper-strip corrosion test at 50° C. (122° F.), and the doctor test.

Table I. Tests on Naphtha Samples

(From Michigan crude oil)

	Stoddard Solvent	V. M. & P. Naphtha	Rubber Solvent
A. P. I. Gravity at 60° F.	54.3	60.7	71.4
	° *F.*	° *F.*	° *F.*
A.S.T.M. distillation			
Initial boiling point	308	220	118
5% recovered	318	233	139
10% recovered	321	237	147
20% recovered	325	240	158
30% recovered	329	243	169
40% recovered	333	246	176
50% recovered	338	250	186
60% recovered	344	253	196
70% recovered	351	257	206
80% recovered	360	260	217
90% recovered	374	268	234
95% recovered	389	276	254
End point	400	291	264
Recovered, %	98.0	99.0	97.3
Residue, %	1.0	0.7	0.7
Loss, %	1.0	0.3	2.0
Total sulfur, %	0.025	0.034	0.010
Kauri butanol value	31.1	34.1	32.7

Tests on three of the four naphtha samples used in this work are shown in Table I. The fourth sample (Stoddard solvent from Texas crude oil) was used for the purpose of showing that the results obtained were not specific for Michigan naphthas; hence complete tests were not obtained on this sample. None of the naphtha samples contained free sulfur (mercury test) or mercaptans (doctor and silver nitrate titration, 7, tests). They were all sweet to the doctor test and did not tarnish copper in the distillation-corrosion test or in the copper-strip corrosion test at 122° F. (3 hours).

Since 0.05 per cent of sulfur possibly represents a maximum for any one type of sulfur compound that could be present in commercial naphthas and since the most severe conditions of test were desired, free sulfur or various organic sulfur compounds were dissolved in the naphthas in such amount that 0.05 per cent by weight of sulfur was added. All mercaptans used were Eastman materials which were redistilled and the middle fractions used immediately for making the naphtha solutions.

Distillation-Corrosion Test

For a number of years there have been several types of copper-strip corrosion tests involving temperatures in the vicinity of the boiling point of the naphtha. Many are simple adaptations of the ordinary copper-strip corrosion test.

The Philadelphia Production Club (*6*) stipulates a polished strip of 28-gage copper, 0.62 × 4.25 cm. (0.25 × 1.5 inches), in the distillation flask and notes the discoloration during the distillation test. Birch and Norris (*2*) added a polished copper strip of unmentioned size to the distillation flask and then distilled the naphtha to dryness. The latter workers added various mercaptans, sulfides, disulfides, diisoamyl sulfone, diethyl sulfate, and thiophene to a specially prepared V. M. & P. naphtha in proportions ranging from 0.29 to 0.42 per cent of "combined" sulfur, but found no action on the copper strips in their corrosion tests. However, they did obtain pronounced blackening of the copper strips when solutions of sulfoxides in the specially prepared V. M. & P. naphtha were used.

About 10 years ago a more severe test of this type made its appearance and has been very widely used in the manufacture and sale of special naphthas. This test, called the distillation-corrosion test in the present report, consists of the addition of a highly polished copper strip (7.6 × 1.27 cm., 3 × 0.5 inches) to the A. S. T. M. distillation flask containing 100 cc. of the naphtha. Before the distillation is started the strip is placed in a position as nearly vertical as possible, so that one end of the strip will dip into the residue at the end of the distillation. The distillation is conducted exactly as specified in A. S. T. M. Designation D86-38 for distillation of gasoline, naphtha, kerosene, and similar petroleum products, except for the presence of the copper strip. The directions must be followed with extreme care in the vicinity of the end point of the naphtha. Heating of the flask is stopped as soon as the temperature, as noted on the distillation thermometer, falls slightly (usually after a temperature drop of about 2.2° C., 4° F.). The flask containing the copper strip is allowed to cool to room temperature before it is taken from the apparatus and the strip removed. If the strip is removed too soon, it will be colored brilliant green, purple, or red and interpretation of the test may be erroneous.

The results obtained from distillation-corrosion tests on naphtha solutions of free sulfur or organic sulfur compounds are shown in Table II. A careful examination shows that there are two determining factors pertaining to distillation-corrosion tests on sulfur compounds in naphtha solution: (1) the boiling point of the sulfur compound with reference to the boiling range and end point of the solvent, and (2) the stability of the sulfur compound at moderately high temperatures. The quantity of sulfur compound present will, of course, also affect the distillation-corrosion test in many instances.

Table II. Effect of Sulfur Compounds upon Distillation-Corrosion Test of Naphthas

(0.05% by weight of free or combined sulfur added in each case. 0.0001% free sulfur in Michigan Stoddard solvent gives a fair test; 0.001% gives a bad* test)

Sulfur Compound Present	Boiling Point of Sulfur Compound, ° F.	Distillation-Corrosion Test Results[a]			
		Michigan Stoddard solvent	Texas Stoddard solvent	Michigan V. M. & P. naphtha	Michigan rubber solvent
		End Point of Naphtha			
		400	394	291	264
None	...	Good	Good	Good	Good
Free sulfur	...	Bad	...	...	...
Ethyl mercaptan	94	Good	...	Good	Good
n-Propyl mercaptan	154	Fair	...	Good	Good
n-Butyl mercaptan	210	Fair	...	Fair	Good
n-Amyl mercaptan	260	Poor	...	Fair	Fair
Isoamyl mercaptan	243	Poor	...	Fair	Fair
n-Heptyl mercaptan	349	Poor	...	Poor	Fair-poor
Phenyl mercaptan	337	Good	...	Good	Good
Ethyl sulfide	196	Good	...	Good	Good
n-Propyl sulfide	287	Good	...	Good	Good
Isopropyl sulfide	246	Fair-good	...	Fair	Fair
n-Butyl sulfide	368	Fair	Fair	Fair-poor	Fair
Isobutyl sulfide	335	Fair	...	Fair-poor	Fair
n-Amyl sulfide	441	Fair-poor	Poor	Fair-poor	Fair-poor
Isoamyl sulfide	418	Fair-poor	...	Fair-poor	Fair-poor
Ethyl disulfide	307	Good	Fair	Poor	Bad*
n-Propyl disulfide	377	Fair	Poor	Bad*	Bad*
n-Butyl disulfide	442	Fair-poor	Bad	Bad*	Bad*
n-Amyl disulfide	518	Bad*	Bad*	Bad*	Bad*
Thiophene	183	Good	...	Good	Good
n-Butyl sulfone, m. p.	44	Good	...	...	...

[a] Good, no coating on strip.
Fair, slight discoloration of strip.
Poor, more or less corrosion of strip.
Bad, gray or black coating on strip.
Bad*, black-scaly.

Mercaptans are rather unstable substances (*8*) at moderately high temperatures, breaking down into olefins, hydrogen sulfide, and other products. The effect of heat on the breakdown of mercaptans is strikingly illustrated by the distillation-corrosion results on mercaptans in Stoddard solvent, V. M. & P. naphtha, and rubber solvent. The Stoddard solvent has the higher distillation range; hence the mercaptans which have not already distilled over are subjected to a much higher temperature than when rubber solvent is used. In general, the distillation-corrosion test gives a more corroded strip with the higher-boiling naphthas than with the lower-boiling ones. Phenyl mercaptan is more stable than the aliphatic mercaptans and hence has no noticeable effect upon the copper strip either in Stoddard solvent solution or in rubber solvent solution. If the mercaptan has a sufficiently low boiling point, it distills over completely with the naphtha and the distillation-corrosion test is good.

Aliphatic sulfides are somewhat more stable to heat (*2*, *9*) than are the corresponding mercaptans. This fact is shown in Table II, where the results for aliphatic sulfides are slightly better than those for the aliphatic mercaptans of corresponding boiling points. Though many of these sulfides have boiling points above the end point of the particular solvent used, there is insufficient decomposition of the sulfides to give bad distillation-corrosion tests. The results indicate that the slight corrosion of the copper strip is due in each case to the slight breakdown of the sulfide concentrated in the distillation residue.

Disulfides are apparently stable in naphtha solutions at moderate temperatures, but when decomposition does occur (in the distillation residue) very corrosive products are formed. If the disulfide can be distilled over with the naphtha, the distillation-corrosion test will be satisfactory; otherwise copper strips will be obtained which are very badly corroded. The lower-boiling disulfides affect the copper strip less when dissolved in Stoddard solvent than when dissolved in rubber solvent.

Thiophene and *n*-butyl sulfone in naphtha solution do not affect the copper strip in the distillation-corrosion test. Thiophanes were not dealt with, since they are simply cyclic sulfides and react as such.

The authors have found that 0.0001 per cent of free sulfur in Michigan Stoddard solvent is sufficient to affect the distillation-corrosion test. In most cases in which bad distillation-corrosion tests were obtained with solutions of sulfides or disulfides in naphtha, the distillation residue contained both free sulfur (mercury test) and mercaptans (doctor test after hydrogen sulfide removal).

Copper-Strip Corrosion Test

The copper-strip corrosion test at 122° F. (3 hours, *1*) is widely used for all light distillates in the petroleum industry, but there are very few data in the literature concerning the effect of free sulfur or of sulfur compounds upon this test.

Wirth and Strong (*15*) have shown that the smallest amount of free sulfur in mid-continent straight-run gasoline or mid-continent cracked gasoline which affects the copper-strip corrosion test lies between 0.003 and 0.004 per cent. Wood, Sheely, and Trusty (*17*) found that a 0.26 per cent solution of free sulfur in naphtha reacted strongly with copper in the copper-strip corrosion test; they also claimed that a solution of isoamyl mercaptan in naphtha (corresponding to 0.29 per cent of mercaptan sulfur) reacts mildly with copper. *n*-Butyl sulfide in naphtha (corresponding to 0.30 per cent of sulfide sulfur) was unreactive to copper, *n*-propyl disulfide in naphtha (0.36 per cent disulfide sulfur) was practically unreactive, and *n*-butyl sulfone in naphtha (0.08 per cent sulfone sulfur) was unreactive (*17*). In the presence of air, copper powder reacts with mercaptans in hydrocarbon solution at 25° C. to give cuprous mercaptides and disulfides, but it is indifferent to alkyl sulfides and disulfides (*10*).

Table III. Sensitivity of Doctor Test[a] with Solutions of Mercaptans in Naphthas

(Minimum % by weight of mercaptan sulfur in naphtha required to give positive doctor test)

Mercaptan	Michigan Stoddard Solvent	Michigan V. M. & P. Naphtha	Michigan Rubber Solvent	1° Benzene
Ethyl	0.0006	0.0005	0.0006	....
n-Propyl	0.0003	0.0003	0.0003	....
n-Butyl	0.00015	0.0002	0.00015	0.0005
n-Amyl	0.0002	0.0002	0.0002	....
Isoamyl	0.0001	0.0002	0.0001	....
n-Heptyl	0.0001	0.0002	0.0002	....
Phenyl	0.0010	0.0010	0.0008	....

[a] Federal Specifications VV-L-791a.

A 0.05 per cent solution of free sulfur in Michigan Stoddard solvent was prepared in the following manner:

An excess of powdered roll sulfur was weighed into a known amount of the solvent; after standing for 3 or 4 days, with occasional agitation, the suspension was filtered through a weighed Gooch crucible and the filtrate carefully removed and saved. The sulfur on the Gooch crucible was washed with ether and, after drying at 105° C., was weighed. Tests showed that the ether washings contained no detectable amount of sulfur. From the weight of sulfur dissolved by the Stoddard solvent, calculations were made and the sulfur concentration was adjusted to 0.05 per cent by weight of free sulfur by adding the required quantity of fresh Stoddard solvent.

This solution was strongly corrosive to copper in the copper-strip test. It was found that the concentration just affecting a copper strip lay between 0.003 and 0.004 per cent free sulfur in the Stoddard solvent. Because of this agreement with previous work for gasoline (*15*), no further work was done with solutions of free sulfur in V. M. & P. naphtha and rubber solvent.

TABLE IV. EFFECT OF TYPE OF CONTAINER UPON SENSITIVITY OF DOCTOR TEST[a] WITH SOLUTIONS OF MERCAPTANS IN NAPHTHA

(Minimum % by weight of mercaptan sulfur in Michigan Stoddard solvent required to give positive doctor test)

	4-Ounce Oil Test Bottle	5 × 0.75 Inch Test Tube
	Michigan Stoddard Solvent	
Mercaptan		
Ethyl	0.0006	0.0006
n-Propyl	0.0003	0.0002
n-Butyl	0.00015	0.00002
n-Amyl	0.0002	0.0003
Isoamyl	0.0001	0.00004
n-Heptyl	0.0001	0.00003
Phenyl	0.0010	0.0006
	1° Benzene Solvent	
n-Butyl	0.0005	0.00015

[a] Federal Specifications VV-L-791a; Commercial Standard CS3-38.

The authors have found that the following organic sulfur compounds, when dissolved in Michigan Stoddard solvent, Michigan V. M. & P. naphtha, or Michigan rubber solvent, so that 0.05 per cent of combined sulfur was added, had no effect upon the copper-strip corrosion test at 122° F. for 3 hours:

Mercaptans: ethyl, *n*-propyl, *n*-butyl, *n*-amyl, isoamyl, *n*-heptyl, and phenyl
Sulfides: ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, and isoamyl
Disulfides: ethyl, *n*-propyl, *n*-butyl, and *n*-amyl
Thiophene
n-Butyl sulfone

If the copper strips are allowed to stand several days in contact with the test solutions after the duration of the copper-strip corrosion tests, they are changed to a dull copper or gray color and the naphtha solutions become somewhat cloudy in the case of the mercaptans; under the same conditions there is no change in the case of the sulfides, disulfides, and thiophene. This reactivity shown by the mercaptans agrees with the observations of previous workers (*10, 17*).

Sensitivity of the Doctor Test

Since marketable naphthas must be sweet to the doctor test (*5, 13*), a determination of the sensitivity of this test is of importance.

Wendt and Diggs (*14*) showed that a "sour" doctor test is due to the presence of mercaptans and/or hydrogen sulfide. There is relatively little in the literature to show the minimum concentrations of various mercaptans necessary to react positively to the doctor test.

Wood, Lowy, and Faragher (*16*) found that 1 part of isoamyl mercaptan in 100,000 parts of naphtha (0.0003 per cent of mercaptan sulfur) was distinctly positive to the doctor test.

Boyd (*3*) showed that the doctor test (U. S. Bureau of Mines method) would detect methyl, *n*-butyl, and *n*-heptyl mercaptans in naphtha in concentrations amounting to 0.002, 0.0002 and 0.00009 per cent of mercaptan sulfur, respectively, and that the Natural Gasoline Association of America method would detect *n*-butyl mercaptan in naphtha amounting to 0.0003 per cent of mercaptan sulfur. The Bureau of Mines method for the doctor test (*12*) [similar to that of Dow (*4*) and to that specified for Stoddard solvent (*13*)] employs a test tube of unspecified size for the doctor test; the method has now been replaced (except for Stoddard solvent) by that contained in the Federal Stock Catalog (*5*) in which a 118-cc. (4-ounce) oil sample bottle is used. The N. G. A. A. method mentioned by Boyd is contained in specifications effective January 1, 1932, and issued by the Natural Gasoline Association of America; it employs a 4-ounce bottle for the test. The Universal Oil Products Company has stated that a concentration of *n*-butyl mercaptan greater than 0.0025 per cent (0.0009 per cent of mercaptan sulfur) can be detected by the doctor test described (*11*) which employs a test tube as container rather than a 4-ounce sample bottle.

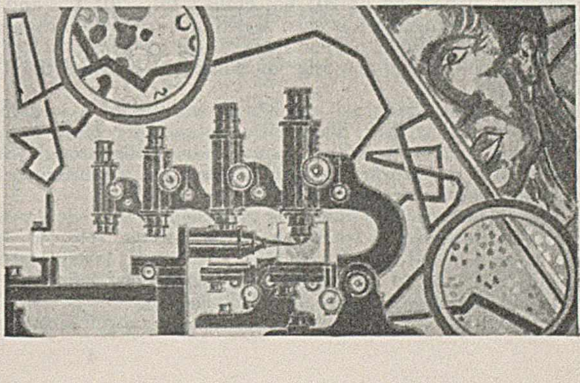
In Table III the sensitivity of the doctor test (*5*) is shown for solutions of various mercaptans in Michigan Stoddard solvent, Michigan V. M. & P. naphtha, and Michigan rubber solvent, and also for *n*-butyl mercaptan in 1° benzene. The interesting conclusion can be drawn that with each mercaptan the sensitivity is practically the same with each of the three naphthas. In benzene, however, the sensitivity is less for *n*-butyl mercaptan, the only mercaptan tried out in this solvent. The doctor test is a very slow reaction in the cases where phenyl mercaptan was used.

Table IV shows the difference in sensitivity of the doctor test resulting from the use of an ordinary (12.7 × 1.9 cm., 5 × 0.75 inch) test tube instead of the specified 4-ounce bottle. The difference is due to variation in the interfacial area. It is easier to note a slightly sour doctor test carried out in a test tube than in a 4-ounce bottle.

Literature Cited

(1) Am. Soc. Testing Materials, "Standard Method of Test for Detection of Free Sulfur and Corrosive Sulfur Compounds in Gasoline", A. S. T. M. Designation D130-30, Triennial Standards, Part II, p. 973, 1936.
(2) Birch, S. F., and Norris, W. S., IND. ENG. CHEM., **21**, 1088 (1929).
(3) Boyd, G. A., *Oil Gas J.*, **32**, No. 8, 16 (1933).
(4) Dow, D. B., Bur. Mines, *Repts. Investigations* **2191** (1920); *Refiner Natural Gasoline Mfr.*, 2, No. 5, 12 (1923); *Natl. Petroleum News*, 15, No. 20, 99 (1923).
(5) Federal Standard Stock Catalog, Method 520.31, "Doctor Test (Sodium Plumbite)", Section IV, Part 5, p. 123 (VV-L-791a), 1934.
(6) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors", 9th ed., p. 313, Washington Institute of Paint and Varnish Research, 1939.
(7) Malisoff, W. M., and Anding, C. E., IND. ENG. CHEM., Anal. Ed., 7, 86 (1935).
(8) Malisoff, W. M., and Marks, E. M., IND. ENG. CHEM., **23**, 1114 (1931).
(9) *Ibid.*, 25, 780 (1933).
(10) Slagle, K. H., and Reid, E. E., *Ibid.*, 24, 448 (1932).
(11) Universal Oil Products Co., Method H-41, "U. O. P. Laboratory Test Methods for Petroleum and Its Products", p. 210, 1937.
(12) U. S. Bureau of Mines, Method 520.3, *Tech. Paper* **323B**, 96 (1927).
(13) U. S. Bureau of Standards, Commercial Standard CS 3-38, "Stoddard Solvent", 2nd ed., pp. 1, 4 (effective February 10, 1938), 1937.
(14) Wendt, G. L., and Diggs, S. H., IND. ENG. CHEM., **16**, 1113 (1924).
(15) Wirth, C., and Strong, J. R., *Ibid.*, Anal. Ed., 8, 345 (1936).
(16) Wood, A. E., Lowy, A., and Faragher, W. F., IND. ENG. CHEM., 16, 1116 (1924).
(17) Wood, A. E., Sheely, C., and Trusty, A. W., *Ibid.*, **17**, 798 (1925).

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



Low-Temperature Set as a Measure of State of Vulcanization

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When rubber is vulcanized with sulfur, its tendency to freeze under tension is altered. A constant-temperature method of evaluating this tendency is described. The method is quantitative and has the advantage of simplicity of equipment and manipulation.

IN HIS various patents on vulcanization, Charles Goodyear made several references to the change produced in the low-temperature behavior of rubber. In his earliest patent (*7*) he stated that vulcanized rubber would not be "injuriously affected by exposure to cold". The reissues of this patent (*8, 9*) stated the problem more clearly. "The leading object of my exertions was to render india-rubber capable of resisting the action of heat and cold within the range of atmospheric temperatures. * * * * When compounded with sulphur, by the application of a high degree of artificial heat, I obtained good results, and when compounded with sulphur and the carbonate of lead I obtained the best results." * * * The new product "is water-proof, permanently and highly elastic under all conditions of its use".

Whether Goodyear was referring to the freezing of rubber under tension or under no tension we do not know, but it is probable that he had experienced both effects without distinguishing between them. It is interesting to find now that one hundred years later, rubber chemists are still looking at this change in low-temperature behavior which he recognized as an effect of vulcanization, and are using the effect as a measure of degree of vulcanization.

In recent years the T-50 (*6*) test has gained considerable popularity as a quantitative measure of the tendency of rubber to freeze under tension. Its popularity is justified, since it can be applied over a broad range of cure and since it measures very precisely a seemingly fundamental property of rubber. It is, however, not the only means of expressing this effect quantitatively. The purpose of the present paper is to demonstrate a simpler method which yields surprisingly precise results in spite of the fact that none of the usual scientific equipment is used, and no measurements other than length measurements are required. Although other papers have approached this subject (*1, 5, 12–15*), none has as yet offered a simple substitute for T-50.

Methods Compared

In the T-50 test a sample of cured rubber is stretched to a predetermined elongation at 20° C., chilled to −70° C., and released. The temperature is then raised at a controlled rate, and the test piece retracts. The temperature at which it has recovered 50 per cent of the original elongation is called the T-50 temperature.

The equipment required consists essentially of a stretching clamp in a Dewar flask filled with acetone, a cooling bath of acetone and solid carbon dioxide surrounding coils through which the acetone of the Dewar flask is circulated, and a suitable heater for raising the temperature at a controlled rate.

In the 0° set test the sample is stretched to a predetermined elongation immersed in ice water for 2 minutes, released, held in ice water 1 minute, and measured. The result is expressed as "per cent set", based on the original unstretched length, or as "fractional set", based on the initial elongation.

The equipment for the 0° set test consists of a stretching clamp and a constant-temperature bath. The temperature of melting ice (0° C.) is the easiest constant temperature to maintain experimentally, and is used for that reason, although within certain limits any other constant temperature would be suitable. All that is required is a copious supply of ice, and a fair degree of forced circulation.

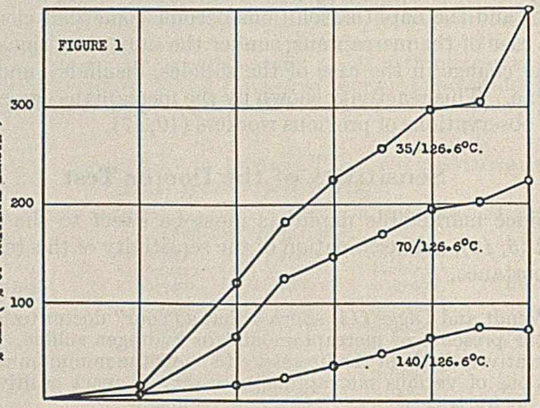
Conditions of Test

In the work reported here, three typical compounds have been used: a tread compound, a high-zinc, and a low-zinc compound.

Table I. Compounds Tested

	Compound A	Compound B	Compound C
Rubber	100	100	100
Channel black	50	...	...
Zinc oxide	5	120	50
Sulfur	3	2.5	4
Mercaptobenzothiazole	1	0.5	0.5
Stearic acid	4	1	1
Pine tar	5	...	...
Phenyl-β-naphthylamine	1	...	...
	169	224.0	155.5

The effects of the variables of testing will be illustrated by data on compound A. In Table II it is apparent that time of freezing between 0.5 and 5 minutes has only a very slight effect. Time of retraction between 0.5 minute and 2 minutes has even less effect. Purely as a matter of standardization,



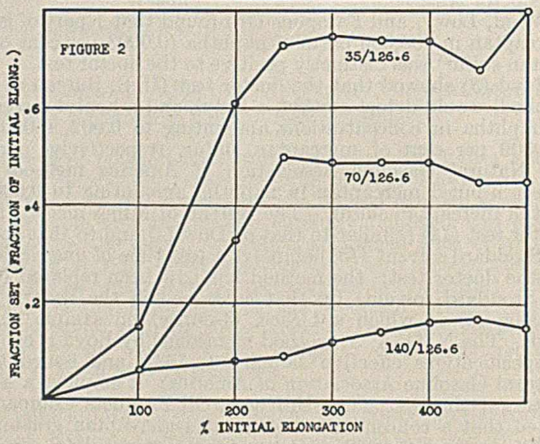


Figure 1. Per Cent Set *vs.* Initial Elongation
Figure 2. Fractional Set *vs.* Initial Elongation

the values of 2 minutes' freezing and 1 minute's retraction have been adopted.

Degree of initial stretch is more important. The data of Table II, if plotted, indicate that at an original stretch of 100 per cent there is practically no set. At 200 per cent, however, a very definite amount of freezing can take place. Thereafter, as the initial stretch is increased, the per cent set increases progressively. If this is expressed as a fraction of the initial stretch, it appears that beyond about 300 per cent the fractional set is not increased by further stretch and might even pass through a maximum.

TABLE II. CONDITIONS OF TEST[a]

Original Stretch	Time of Freezing	Set after Various Retraction Times			
		0.5 min.	1 min.	0.5 min.	2 min.
%	*Min.*	%	%	%	%
300	0.5	136	133	133	133
..	1	136	133	133	133
..	1.5	140	137	137	136
..	2	140	139	138	136
..	3	142	140	139	138
..	5	145	144	142	142
400	2	188	188	186	186
500	2	203	201	198	198
100	2	8	8	8	8
200	2	66	64	64	63

[a] Work done on sheets of compound A cured 70 minutes at 126.6° C. Test strip was 4 × 2 mm. Each figure is an average of three tests. Procedure: Stretch at room temperature, freeze at 0° C., release, and measure. Set expressed as % of initial length.

This work was repeated at three cures (Table III, Figures 1 and 2). There are evidently experimental difficulties in picking the maximum (if any), but it appears that at the best cure and the undercure the fractional set increases up to an initial stretch of 250 to 300 per cent, while at the overcure it increases up to about 400 per cent. At the undercure, moreover, something else happens beyond 450 per cent, which brings about an even higher set. None of the possible explanations for this has been investigated.

TABLE III. EFFECT OF DEGREE OF STRETCH[a]

Elongation, %	35-Minute Cure	70-Minute Cure	140-Minute Cure
	A. Per Cent Set Based on Initial Unstretched Length		
100	15	6	6
200	122	66	16
250	183	125	22
300	226	147	35
350	257	170	48
400	297	195	63
450	305	203	75
500	400	225	73
	B. Retained Fractional Set		
100	0.15	0.06	0.06
200	0.61	0.33	0.08
250	0.73	0.50	0.09
300	0.75	0.49	0.12
350	0.74	0.49	0.12
400	0.74	0.49	0.16
450	0.68	0.45	0.17
500	0.80	0.45	0.15

[a] Each figure is average of four tests. All work done at 0° C. according to procedure of Table II, using 2 minutes' freezing and 1 minute's retraction. All samples are compound A, cured at 126.6° C. as indicated. Retained fractional set is set, as in A, divided by elongation.

As a characteristic measure of state of cure, the fractional set could be considered to be practically independent of elongation between the limits 250 and 400 per cent. However, for everyday use in compounding problems or as a control, it is more convenient merely to standardize on 300 per cent elongation for tread type stocks (550 per cent for most other stocks), and express the result as per cent set, meaning per cent of original length.

The effect of freezing temperature was illustrated by curing a set of sheets of tread stock at ten logarithmically spaced time intervals, and testing at three bath temperatures: 9°, 0°, and −9° C.

It will be noted (Table IV, Figure 3) that at each temperature the set is high at the undercure and low at the overcure, and that the point in cure at which the most rapid transition from high to low set occurs is a function of the freezing temperature. The lower the freezing temperature the higher the set for a given time of cure, and the higher the state of cure at which the rapid transition from high to low set takes place. It is possible to read from the curves a property which is analogous to T-50. The 9° C. curve crosses the 150 per cent set coordinate (0.5 fractional set) at a cure of 42 minutes. To put this in the language of T-50, we may say that the 42-minute cure has a 0.5 fractional set temperature of 9° C.—i. e., it retracts to one half of its initial stretch at 9° C. Regarding the other curves in similar fashion and interpolating a combined sulfur curve, we get the following:

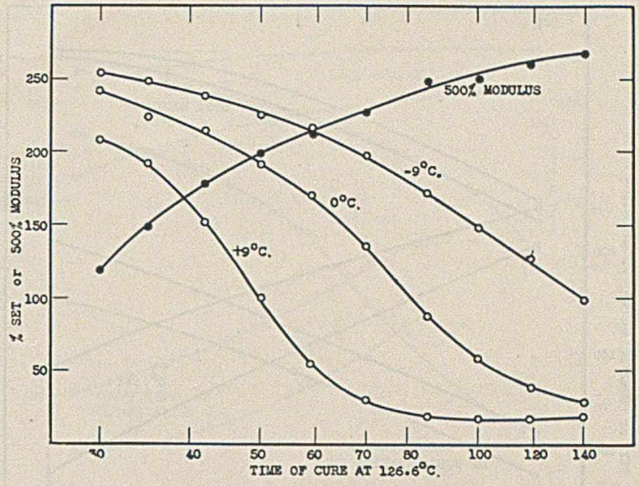


FIGURE 3. SET AT VARIOUS TEMPERATURES *vs.* TIME OF CURE

Time of Cure	Temperature for 0.5 Fractional Set	Coefficient of Vulcanization
Min.	° C.	%
42	9	1.04
65	0	1.66
98	−9	2.32

There is a straight-line relationship between these temperature and combined sulfur data with a slope indicating that 1 per cent combined sulfur is equivalent to 14° C. in bath temperature, which compares well with the published value of 13° C. in T-50. This agreement strengthens the belief that set measurements at constant temperature are governed by the same fundamental properties as T-50, and that from the standpoint of useful results, at least, nothing has been lost by omitting the chilling at −70° C.

Variations in the Formula

Previously published work has shown definitely that T-50 is more closely connected with combined sulfur than with any physical property (*6*, *10*, *16*). This is found true also with the 0° set test, although there is evidence that the correlation is not perfect.

TABLE IV. EFFECT OF BATH TEMPERATURE[a]

Cure at 126.6° C.	Set at +9° C.	Set at 0° C.	Set at −9° C.	500% Modulus
Min.	%	%	%	*Kg./sq. cm.*
30	208	242	253	119
35	192	224	248	148
42	152	214	238	178
50	100	192	225	199
59	55	170	217	212
70	30	136	197	227
85	19	87	172	248
100	17	58	148	250
118	17	39	127	260
140	19	28	99	269

[a] Each set figure is average of three tests, each modulus average of two. Work done at three bath temperatures as indicated according to procedure of Table II, using 2 minutes' freezing and 1 minute's retraction. Initial elongation 300%. Compound A.

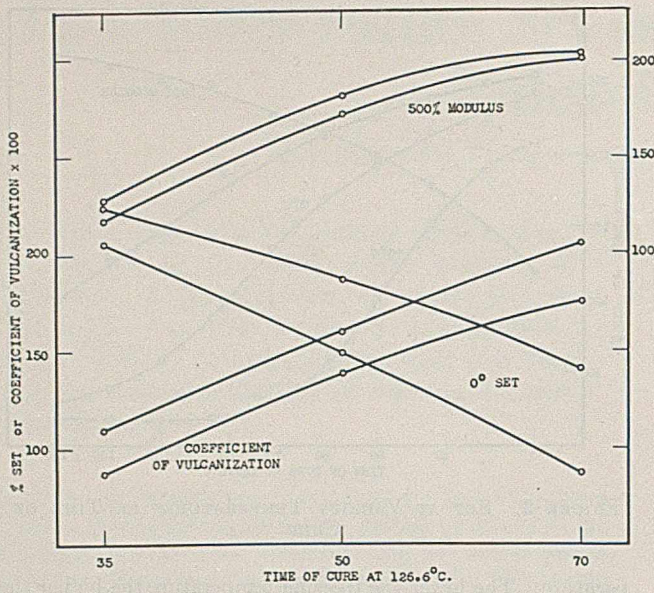


Figure 4. Fast- and Slow-Curing Carbon Black

Table V. Set and Combined Sulfur as Affected by Black[a]

Cure at 126.6° C. *Min.*	Coefficient of Vulcanization	0° Set %	500% Modulus
		Black A	
35	0.86	225	117
50	1.38	186	172
70	1.75	141	201
		Black B	
35	1.09	206	128
50	1.59	149	182
70	2.05	86	203

[a] Compound A with two channel blacks, normal (A) and fast-curing (B). Coefficient of vulcanization is % of combined sulfur based on rubber content

The effect of variability of carbon black on the rate of cure of a Captax stock is often underestimated, because the changes in modulus and tensile that it produces, particularly in the range of the optimum cure, are rather slight. However, the 0° set test penetrates beyond these physical effects, and reveals the true effects on combined sulfur. In Table V is a comparison of a fast- and a slow-curing channel black having widely different set and combined sulfur values at equal times of cure, but very slight differences in modulus (Figure 4). However, when cured to equal set values, they have nearly equal combined sulfur (Figure 5).

Fast- and slow-curing zinc oxides (*3*) also have a comparatively slight effect on modulus, but the effect on 0° set is so marked that sharp divisions in state of cure are easily made (Table VI, Figure 6). Again the agreement of set with combined sulfur is close, but not exact (Figure 7). The same is true of fast- and slow-curing rubber (Table VII, Figure 8), and it is interesting that the slow-curing rubber has other effects on modulus, so that when cured such times that it has the same combined sulfur as the fast-curing rubber, its modulus is lower (*2*)—for example, at the 140-minute cure the slow rubber has a combined sulfur of 1.38. This combined sulfur is reached by the fast rubber in a little less than 100 minutes. The modulus figures are, respectively, 108 and 125. Again combined sulfur and cold set are closely related (Figure 9).

The data of Tables VIII to X and Figures 10 to 12 are included as further evidence that 0° set is unrelated to modulus. Unfortunately, combined sulfur data are not available. It is possible to vary the total sulfur in a tread stock over the range from 1 to 3 of sulfur and still practically duplicate the modulus. It is known by experience that with high ac-

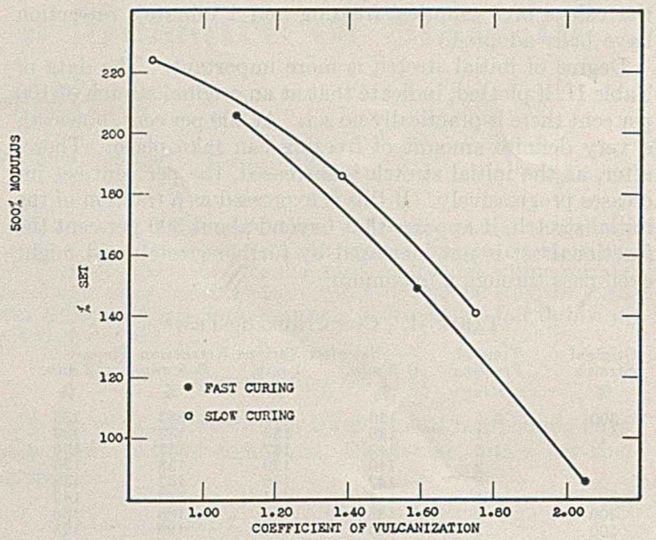


Figure 5. Agreement of Set and Combined Sulfur, Carbon Black

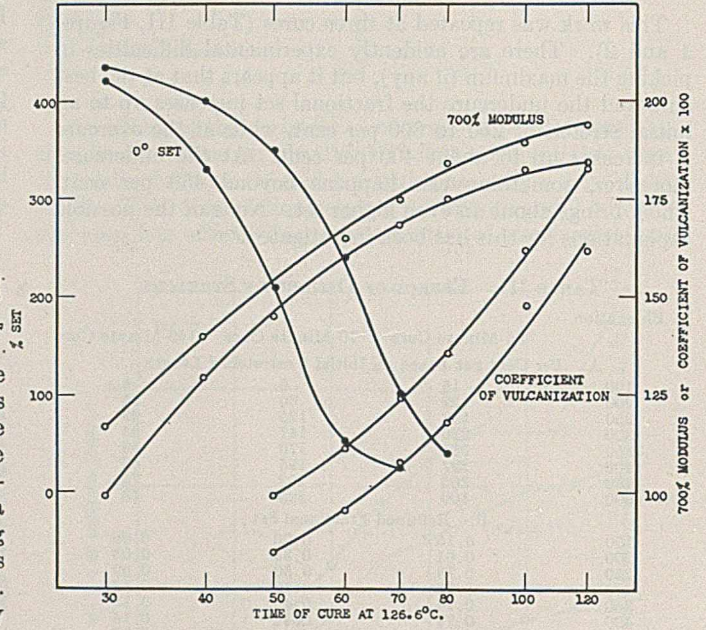


Figure 6. Fast and Slow Zinc Oxides

Table VI. Comparison of Zinc Oxides[a]

Cure at 126.6° C. *Min.*	700% Modulus	Coefficient of Vulcanization	0° C. Set %
	Slow-Curing Zinc Oxide		
30	98	..	435
40	129	..	400
50	145	0.84	350
60	160	0.95	240
70	168	1.07	100
80	175	1.18	40
100	182	1.48	..
120	184	1.62	..
	Fast-Curing Zinc Oxide		
30	117	..	420
40	140	..	330
50	152	0.99	210
60	165	1.11	50
70	175	1.24	25
80	184	1.36	..
100	189	1.62	..
120	195	1.83	..

[a] Two zinc oxides compared in compound C. 0° C. set determined according to procedure of Table III using initial elongation of 550%.

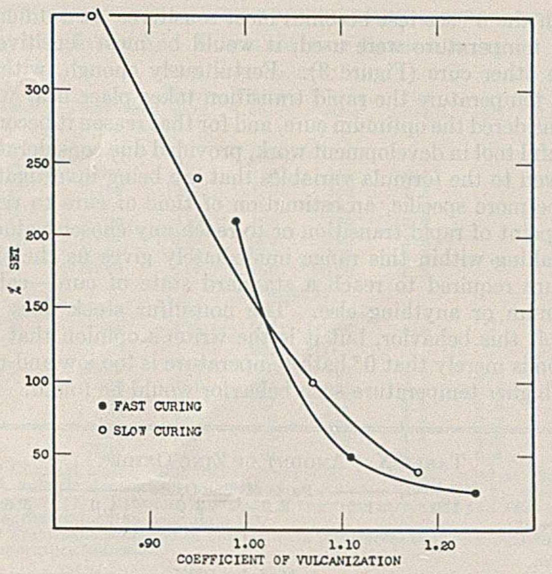


FIGURE 7. AGREEMENT OF SET AND COMBINED SULFUR, ZINC OXIDES

TABLE VII. COMPARISON OF FAST- AND SLOW-CURING RUBBER[a]

Cure at 126.6° C. *Min.*	500% Modulus *Kg./sq. cm.*	Coefficient of Vulcanization	0° C. Set
	Slow-Curing Pale Crepe		
50	62	0.71	431
70	80	0.79	419
80	88	..	405
90	92	..	390
100	95	1.07	378
120	101	1.19	365
140	104	1.46	330
200	108	..	250
	Fast-Curing Pale Crepe		
50	108	1.02	370
70	118	1.21	338
80	123	..	315
90	124	..	290
100	126	1.48	270
120	128	1.70	195
140	130	1.79	150
200	128	..	60

[a] Two types of rubber compared in compound B. 0° C. set determined according to procedure of Table III using initial elongation of 550%.

TABLE VIII. AMOUNT OF SULFUR[a]

Parts of sulfur	0	1.0	1.5	3.0
Parts of Tuads	3.0	0.25	0.1	..
Parts of Captax	..	1.5	1.5	1.0
Cure at 126.6° C. *Min.*				
	Modulus 500%			
35	182	143	148	145
50	195	194	197	198
70	197	223	225	218
100	203	243	243	246
140	215	258	259	255
200	213	..	..	..
	0° C. Set			
35	192	250	225	212
50	187	212	175	125
70	204	150	75	50
100	191	62	43	37
140	188	44	36	40
200	184	..	..	..

[a] Stocks are compound A with sulfur and accelerator varied as indicated.

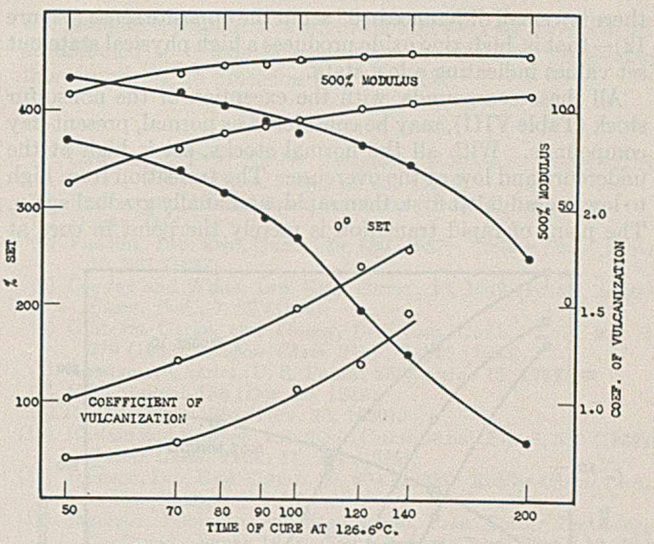


FIGURE 8. FAST AND SLOW RUBBER

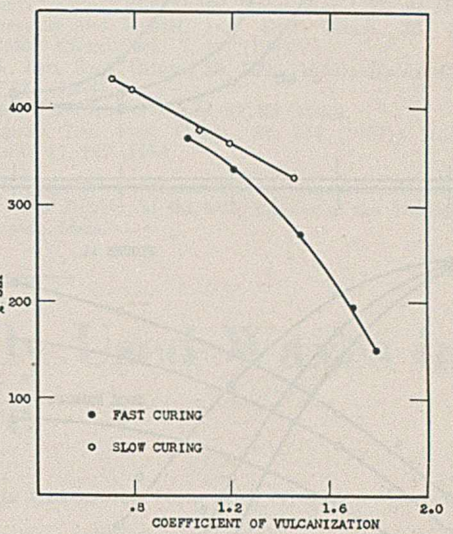


FIGURE 9. AGREEMENT OF SET AND COMBINED SULFUR, RUBBER

TABLE IX. AMOUNT OF FATTY ACID[a]

Cure at 126.6° C. *Min.*	Parts of Stearic Acid 0	2	3	4
	Modulus 500%			
35	80	111	123	134
50	128	170	183	192
70	162	206	222	233
100	183	231	251	262
140	187	243	268	282
	0° C. Set			
35	214	212	211	210
50	196	177	170	161
70	148	101	80	67
100	77	28	25	25
140	28	19	19	19

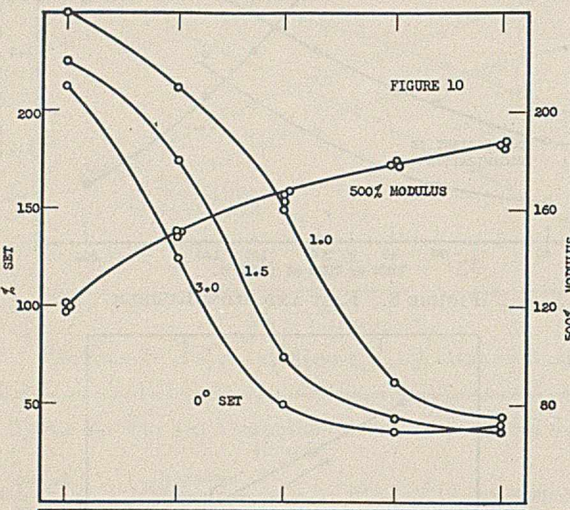
[a] Stocks are compound A with stearic acid varied as indicated.

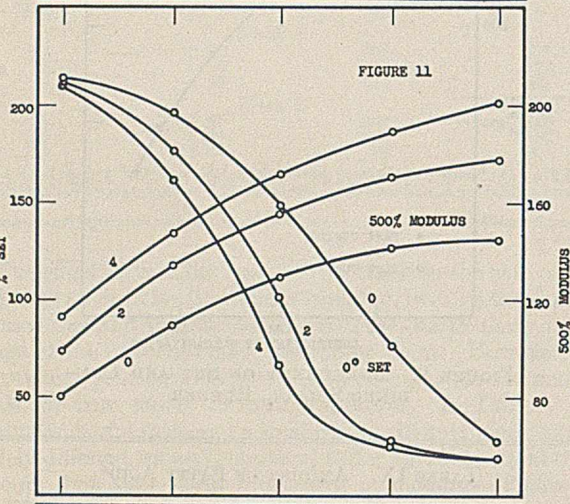
celeration and low sulfur, we produce a given physical effect with less combined sulfur. Zero degree set (Figure 10) varies in the same order as this prediction of combined sulfur. It is affected greatly by the change in formula, while the physical effect is negligible.

As opposed to this, the amount of fatty acid has a very great effect on the physical properties of a tread stock, but its effect on combined sulfur is small. Figure 11 shows some change in 0° set as acid is varied, but a much greater change in modulus, and in fact a development of modulus in the high-acid stock that cannot be attained in the low-acid stock. In other words, this represents a large physical effect, accompanied by a relatively smaller effect on set.

The amount of zinc oxide used for activation in a tread stock has a marked effect on physical properties, the higher zinc oxide developing higher modulus. As opposed to this, there is a small difference in 0° set in the opposite sense (Figure 12)—that is, high zinc oxide produces a high physical state but set values indicating a low state.

All these compounds, with the exception of the nonsulfur stock (Table VIII), may be considered as normal, present-day compounds. With all the normal stocks, set is high at the undercure and low at the overcure. The transition from high to low is gradual at first, then rapid, and finally gradual again. The point of rapid transition is merely the point in cure at which the 0° set test becomes most sensitive. If a different bath temperature were used, it would be most sensitive at some other cure (Figure 3). Fortuitously enough, with 0° bath temperature the rapid transition takes place near what is considered the optimum cure, and for that reason it becomes a useful tool in development work, provided due consideration is given to the formula variables that are being investigated. To be more specific, an estimation of time of cure to reach this point of rapid transition or to reach any chosen value of set falling within this range immediately gives us the time of cure required to reach a standard state of cure—call it optimum or anything else. The nonsulfur stock does not exhibit this behavior, but it is the writer's opinion that the reason is merely that 0° bath temperature is too low and that at a higher temperature such behavior would be found.





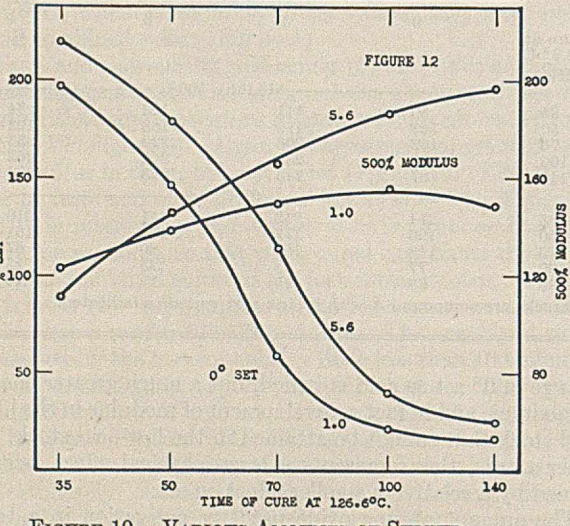


Figure 10. Various Amounts of Sulfur
Figure 11. Various Amounts of Stearic Acid
Figure 12. Various Amounts of Zinc Oxide

Table X. Amount of Zinc Oxide[a]

Cure at 126.6° C. *Min.*	Parts of Zinc Oxide 1.0	1.5	2.0	3.0	4.0	5.6
	Modulus 500%					
35	151	140	146	134	133	132
50	177	186	191	196	188	190
70	196	212	227	232	230	223
100	206	229	252	263	263	257
140	194	232	269	280	283	274
	0° C. Set					
35	197	213	214	216	219	220
50	147	168	173	167	180	179
70	59	69	85	83	98	114
100	22	25	27	31	41	40
140	17	19	19	23	25	25

[a] Stocks are compound A with zinc oxide varied as indicated.

Use as a Control

In control problems we are interested more in the sensitivity of a test to variations in the raw material than in the numerical significance of the results. Carbon black, particularly when the oxygen content of its surface varies, has a considerable effect on rate of cure. One means of estimating this effect is the volatile loss of 950° C. This is a purely arbitrary test, but we know that when the volatile loss is high the oxygen content is high and the rate of cure will be low.

It has been shown above that there is no necessary connection between the numerical values of set and modulus. This is because modulus is affected by so many other things besides combined sulfur. In the case of carbon black it is affected considerably by the reinforcing action of the black in the range of the optimum cure and beyond. As a result, changes due to the retarding effects of different types of black are masked and a certain numerical value of modulus does not indicate any definite state of cure. However, at a distinct undercure the reverse is true, and in compound A the modulus at the 35-minute cure is sensitive to variation in rate of cure in carbon black. It can be used as a practical indication of rate of cure even though the compound is to be used at much higher states of cure.

Zero degree set as a control test should be used at the cure at which it is most sensitive and for compound A this is in the neighborhood of 70 minutes. In Table XI is shown a series of channel blacks having varying effects on rate of cure as well as a variation in other properties. Inspection of the table reveals good agreement between these three measures of rate of cure. Zero degree set at 70 minutes and modulus at 35 minutes are well in line, low set and high modulus going together in indicating a high rate of cure. There is likewise a parallelism between set and net volatile, low set and low volatile going together. As a matter of interest correlation coefficients (Pearson's) for these two comparisons are: for set of modulus −0.90 ±0.03 and for set and volatile 0.87 ±0.04. Both figures indicate a high degree of correlation.

Table XI. Comparison of Carbon Blacks[a]

Black	Treatment ° C.	500% Modulus, 0° C. Set 35-min. cure	70-min. cure	70-min. cure	Net Volatile	pH	Rebound
			Series I				
C	None	94	180	159	8.1	..	67.8
D	None	107	190	153	7.3	..	64.4
E	None	111	186	142	5.3	..	59.2
F	None	110	186	133	6.7	..	66.0
G	None	128	204	125	5.6	..	64.8
H	None	122	200	123	5.8	..	68.6
I	None	114	189	120	5.5	..	59.1
			Series II				
J	None	117	201	141	6.1	..	64.9
K	None	128	203	86	4.9	..	63.2
			Series III[b]				
L	None	129	200	94	5.3	4.5	63.9
	350	121	201	122	6.2	3.8	..
	500	105	187	153	6.2	3.8	..
	700	135	210	122	5.8	4.2	..
	900	178	225	69	4.1	4.9	..
	1000	175	230	66	3.5	6.4	..

[a] Channel blacks compared in compound A. Stocks cured at 126.6° C. Net volatile determined by method of Johnson (*11*). pH by method of Wiegand (*17*). Rebound is average of two tests each at 85 and 140 minutes' cure, determined on pendulum (*4*).

[b] Treatment consisted in heating with free access to air for 30 minutes at temperature indicated.

Discussion

It must be admitted that the 0° set test will not cover the almost unlimited range of cure that the T-50 test will. However, it is applicable over a good part of the curing range of most present-day tire compounds and for that reason it is not at a practical disadvantage. It has the definite advantage of simplicity in equipment, cooling medium, and manipulation, and as a control test could be operated by a person unaccustomed to chemical laboratory equipment. In gaining this simplicity no precision has been lost.

Literature Cited

(1) Carrington, *Proc. Rubber Technology Conference*, Paper 92, p. 787; *Rubber Chem. Tech.*, 12, 365 (1939).
(2) Duden, unpublished data, Goodyear Tire & Rubber Co.
(3) Dugan, *Ibid.*
(4) Fielding, Ind. Eng. Chem., 29, 880 (1937); *Rubber Chem. Tech.*, 10, 807 (1937).
(5) Garvey and White, Ind. Eng. Chem., 25, 1042 (1933); *Rubber Chem. Tech.*, 7, 89 (1934).
(6) Gibbons, Gerke, and Tingey, Ind. Eng. Chem., Anal. Ed., 5, 279 (1933); *Rubber Chem. Tech.*, 6, 525 (1933).
(7) Goodyear, Charles, U. S. Patent 3633 (June 15, 1844).
(8) *Ibid.*, Reissue 156 (Dec. 25, 1849).
(9) *Ibid.*, Reissue 1084 (Nov. 20, 1860).
(10) Haslam and Klamon, Ind. Eng. Chem., Anal. Ed., 9, 552 (1937); *Rubber Chem. Tech.*, 11, 234 (1938).
(11) Johnson, Ind. Eng. Chem., 20, 904 (1928); *Rubber Chem. Tech.*, 1, 485 (1928).
(12) Sagajello, Bobinska, and Saganowski, *Proc. Rubber Technology Conference*, Paper 14, p. 749; *Rubber Chem. Tech.*, 12, 344 (1939).
(13) Somerville and Cope, *India Rubber World*, 79, 64 (1928).
(14) Somerville and Russel, Ind. Eng. Chem., 25, 449 (1933); *Rubber Chem. Tech.*, 7, 147 (1934).
(15) *Ibid.*, Ind. Eng. Chem., 25, 1096 (1933); *Rubber Chem. Tech.*, 7, 371 (1934).
(16) Tuley, *India Rubber World*, 97, 39 (1939).
(17) Wiegand, Ind. Eng. Chem., 29, 953 (1937); *Rubber Chem. Tech.*, 11, 187 (1938).

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Identification of Commonly Used Waxes in Admixture

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IN THE analysis of commercial wax-containing products such as cosmetic preparations, polishes, etc., the identification of the wax components has proved decidedly difficult and complex. In recent years, with the growth of the wax polish industry and the increased world consumption of waxes for other uses, there has arisen a need for a definite procedure for the analysis of wax mixtures. In view of the comprehensiveness of such a problem, this research was confined to the identification of the more commonly used waxes such as spermaceti, beeswax, carnauba, candelilla, and montan. Cognizance was taken of certain allied substances such as cetyl alcohol, rosin (colophony), and stearic acid which might interfere in the analysis.

Our knowledge of the composition of the natural waxes has been made available largely through the compilations of Lewkowitsch (*14*), Allen (*1*), Grün and Halden (*11*), Lüdecke (*18*), and Better and Davidsohn (*3*). More recently the experiments of Chibnall *et al.* (*4, 5, 6*), Francis *et al.* (*7, 8*), and Piper *et al.* (*20, 21*) with melting point determinations and x-ray crystal spacing measurements of isolated wax fractions have greatly advanced our knowledge of the true composition of many natural waxes. Their work has been summarized by Gisvold and Rogers (*9*).

A comparison of the chemical compositions of the commonly used natural waxes shows that, in general, they consist of similar components; in fact, beeswax, carnauba, candelilla, and montan contain compounds with identical composition—i. e., acids, alcohols, and hydrocarbons with 24 to 34 carbon atoms. The complexity of the problem is further increased by the similarity in properties and relative inertness of the saturated homologous compounds with high carbon content, such as those found in waxes. Separation of the adjacent homologous compounds in the vicinity of C_{24} to C_{34} has been found (*6, 8, 21*) difficult or often impossible. Therefore, any method based on fractionation of these compounds would be impractical for analytical purposes. There are, however, a number of outstanding differences in the composite nature of these waxes as a whole which may be used as a basis for an analytical procedure. These are: variation in proportion of acids, alcohols, and hydrocarbons; difference in chain length of the two components of the ester; and the presence of additional distinctive components such as resinlike substances and ketones.

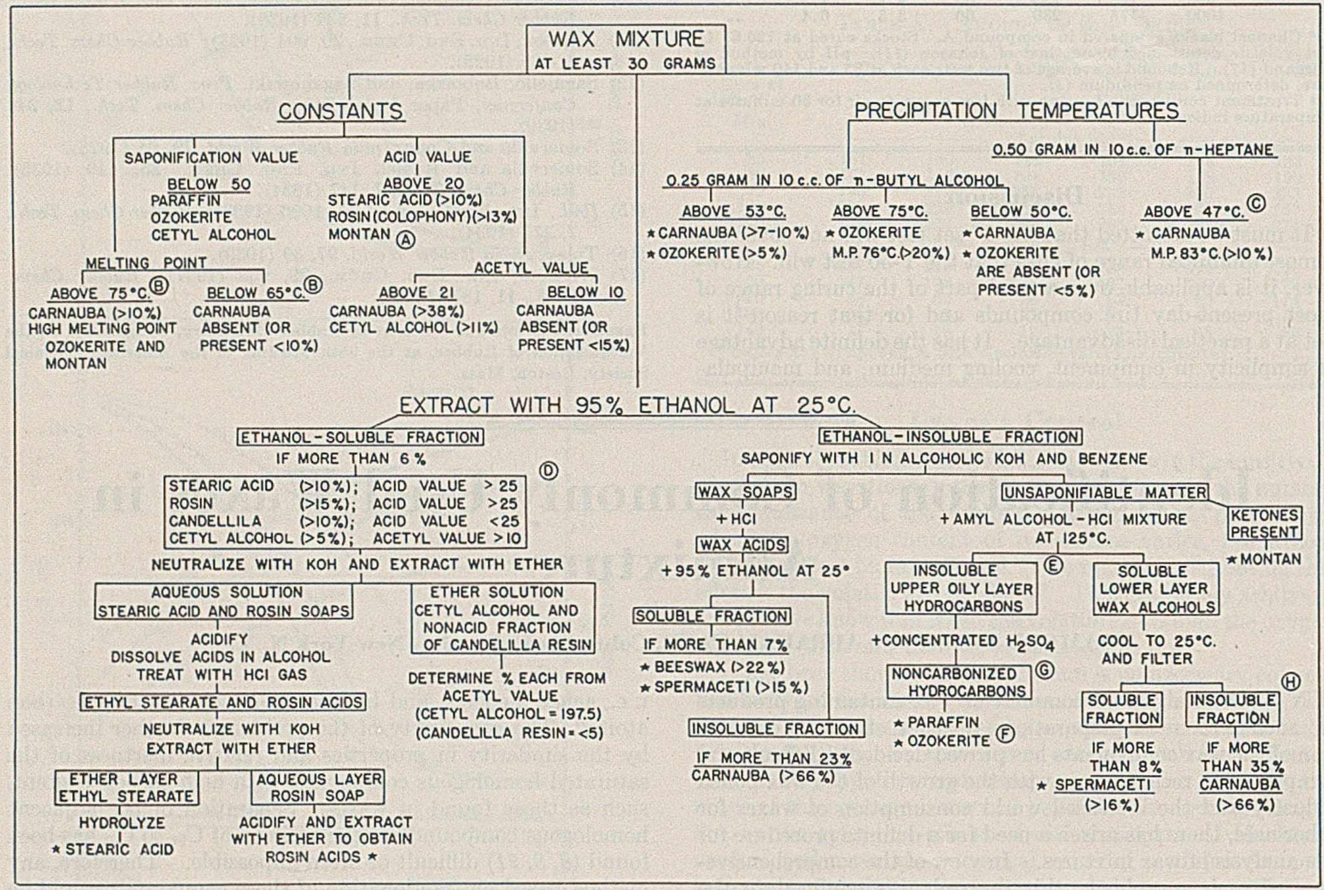
The method outlined here utilizes these differences. Through the following procedures a practical system of identification has been evolved, which is based on (1) the determination of pertinent physical and chemical constants, and (2) the quantitative separation of waxes into groups of homologous compounds and the determination of the properties of the separated fractions.

Physical and Chemical Constants

Of the various constants frequently used for the evaluation of individual waxes, the most indicative for the purpose of analysis of wax mixtures are the melting point, saponification value, acid value, and acetyl value. The information gained as a result of these determinations is described below and summarized in the schematic outline. A physical constant of particular significance, which at present has not been applied to any great extent to waxes, is the dissolution temperature, or more precisely the temperature of precipitation of wax solutions of definite concentration. This constant was found valuable in the detection of carnauba wax and the hydrocarbon wax ozokerite.

PRECIPITATION TEMPERATURES. As used in this paper, this is the temperature at which a wax solution of definite concentration just begins to crystallize as the temperature is gradually decreased. Preliminary experiments with solutions of equal concentrations of various waxes show marked differences in the precipitation temperatures. Solutions of carnauba wax and ozokerite precipitated at much higher temperatures than corresponding solutions of other waxes. Furthermore, it was found that the presence of other waxes admixed with carnauba and ozokerite did not appreciably affect the precipitation temperature. This is in agreement with the results found by Armani and Rodano (*2*) on mixtures of paraffin and ozokerite, and by Waentig and Peschek (*22*) on mixtures of fatty acids in certain solvents.

PROCEDURE. The finely grated wax is weighed and added to 10 cc. of solvent contained in a jacketed test tube (the inner tube



SCHEMATIC OUTLINE FOR IDENTIFICATION. (All per cent figures are based on weight of original sample of wax mixture.)

A. Variations in composition of montan make definite statement concerning quantity impossible.
B. Based on data from Koch *et al.* (*13*) and Lewkowitsch (*16*).
C. Candelilla forms a cloudy solution in *n*-heptane and therefore interferes with determination of precipitation temperatures in this solvent.
D. Rosin and candelilla resin form cloudy solutions in *n*-heptane.
E. Absence of a hydrocarbon fraction (solid at 25° C.) indicates the absence of not only paraffin and ozokerite but also of candelilla (>5 per cent), beeswax (>10 per cent), and montan.
F. 20 to 30 per cent of raw ozokerite is attacked by concentrated sulfuric acid.
G. Hydrocarbons from candelilla, beeswax, and montan are carbonized.
H. Since alcohols of other waxes are also found in this fraction and are closely related to carnauba wax alcohols, this fraction is of value only when a high percentage of carnauba is present (over 60 per cent).

The per cent figure in parentheses indicates the quantity that will always be detected by the determination; when preceded by ">" it indicates that the presence of the quantity stated, or more, will be detected. A smaller quantity may or may not be detected, depending upon a knowledge of the presence or absence of certain other waxes. For example, more than 8 per cent of wax alcohols soluble in amyl alcohol–hydrochloric acid at 25° C. indicates spermaceti (16 per cent). When the spermaceti present in the wax mixture exceeds 16 per cent, the fraction soluble in cold amyl alcohol–hydrochloric acid mixture will always be more than 8 per cent, and spermaceti will always be detected by this determination. However, if the spermaceti in the wax mixture is less than 16 per cent, wax alcohols soluble in amyl alcohol–hydrochloric acid may or may not exceed 8 per cent, depending upon the nature and quantity of other waxes present in the mixture.

Table I indicates that the per cent of the fraction soluble in amyl alcohol–hydrochloric acid for all the waxes determined is: spermaceti, 48 per cent; candelilla, 8 per cent; beeswax, 5 per cent; carnauba, 3 per cent. As candelilla contains as much as 8 per cent of substances soluble in amyl alcohol–hydrochloric acid, spermaceti cannot be determined with certainty unless this fraction is over 8 per cent of the total wax mixture (16 per cent of spermaceti). However, if the approximate quantity of candelilla and/or beeswax is first ascertained, less than 16 per cent of spermaceti can be detected.

Where the name of a substance is starred, that particular determination is of greatest analytical significance for the identification of the substance.

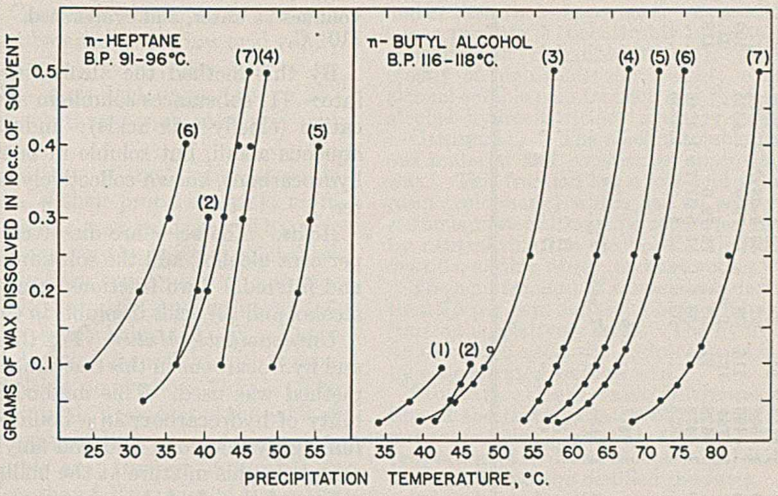


FIGURE 1. PRECIPITATION TEMPERATURES

1 Beeswax, m. p. 60–62° C.
2 Montan, bleached, m. p. 68° C.
3 Candelilla, m. p. 70.5° C.
4 Carnauba refined, m. p. 81.5° C.
5 Carnauba No. 1 yellow, m. p. 83° C.
6 Ozokerite, m. p. 65–67° C.
7 Ozokerite, m. p. 76–78° C.

is 1.5 × 13.75 cm.; the outer, 2.5 × 15 cm.), and then placed in a thermostatically controlled bath which has been previously heated to a temperature at which the wax will dissolve. The temperature of the bath is then allowed to decrease gradually, not more than 1° per minute. The temperature is recorded at the point at which crystals just begin to form. In most instances this point is fairly sharp. In others, however, because of the gradual precipitation the exact temperature is uncertain. The limit of observational error is ±1° C.

RESULTS. The precipitation temperatures in *n*-heptane and *n*-butyl alcohol are plotted in Figure 1. It is evident that the precipitation temperatures of carnauba and ozokerite are much higher than those of other waxes. It may, therefore, be said that if, for example, 0.125 gram of a wax in 10 cc. of *n*-butyl alcohol has a precipitation temperature above 50° C., it probably contains ozokerite or carnauba. When the precipitation temperature of 0.100 gram of wax in 10 cc. of *n*-butyl alcohol is above 64° C., a quantity of high-melting ozokerite is present in the wax mixture. In such a case the presence of carnauba admixed with ozokerite cannot be detected. However, if the wax mixture is then dissolved in *n*-heptane, the order of solubility of the two waxes is reversed and carnauba precipitates at a higher temperature than ozokerite. A determination of the precipitation temperatures of definite concentrations of wax in both *n*-butyl alcohol and *n*-heptane, therefore, will permit the detection of both ozokerite and carnauba. Their presence is further verified by a quantitative separation of the wax components and by the other constants determined.

Beeswax was omitted from the *n*-heptane determinations because it remains dissolved in concentrations specified even at room temperature. Candelilla and rosin (colophony) form cloudy solutions in boiling *n*-heptane; their presence would, therefore, interfere with the determination of the precipitation temperatures in this solvent. However, the precipitation temperatures in *n*-butyl alcohol are not influenced by their presence.

Separation and Comparison of Properties of Wax Components

The methods described below have the advantage of reasonable simplicity and avoid the formation of troublesome emulsions. The properties of the isolated fractions are limited to those of specific value in the identification of the waxes.

ALCOHOL-SOLUBLE FRACTION. Alcohol extraction is an established method for the determination of stearic acid and rosin in beeswax. In order to extend this procedure to the estimation of these substances in other waxes, it is necessary to have a knowledge of the quantity as well as the properties of the alcohol-soluble fractions of all the waxes.

Procedure. Fifty grams of wax are melted in a 400-cc. beaker and extracted by treating with four 150-cc. volumes of boiling 95 per cent alcohol. The alcohol solution is decanted while hot, and allowed to cool to 25° C. The precipitate is then collected on a Büchner funnel, washed twice with 50 cc. of cold alcohol, and combined with the residue that remains from the original hot extraction. The filtrate is evaporated and the residue weighed.

The alcohol-soluble extract of candelilla consists of a clear resinous material with characteristic aromatic odor. It is completely soluble in cold acetone, alcohol, benzene, ether, terpineol, and ethylene chlorohydrin, and partially soluble in hot acetic anhydride and in boiling *n*-heptane and cyclohexane. In 30 parts of *n*-heptane 15 per cent of the resin-like material remains undissolved. A reddish purple color which changes to dark purple on standing is obtained in the Liebermann-Storch test.

The alcohol-soluble material from carnauba consists of a greenish, gummy, and resinlike material with a pungent, aromatic odor. It shows approximately the same solubilities as the candelilla resin, and in 30 parts of cold *n*-heptane 16.5 per cent remains undissolved. The result of the Liebermann-Storch color reaction is similar to that for candelilla resin.

The alcoholic extracts from beeswax, spermaceti, and bleached montan have a soft waxlike consistency, and are completely soluble in *n*-heptane and cyclohexane (the corresponding candelilla and carnauba fractions produce cloudy solutions when dissolved in these solvents).

ALCOHOL-INSOLUBLE FRACTION. Ten grams of the fraction insoluble in 95 per cent alcohol at 25° C. are saponified by boiling for 2 hours with a mixture of 50 cc. of benzene and 25 cc. of alcoholic potassium hydroxide (45 grams of potassium hydroxide in 1000 cc. of absolute alcohol). Fifty cubic centimeters of hot water are added and the aqueous layer is drawn off and washed with three successive volumes of 50, 30, and 30 cc. of benzene. The combined benzene solution is washed with an alkaline aqueous-alcohol mixture (2 to 1). The benzene is evaporated and the unsaponifiable matter dried at 110° C. To the soap solution, 15 cc. of concentrated hydrochloric acid are added and the separated acids are shaken out with hot benzene. The benzene layer, separated from the acid aqueous layer, is washed twice with equal

Table I. Properties of Fractions Separated from Wax

Fraction	Spermaceti				Beeswax				Carnauba				Candelilla				Montan (Bleached)			
	% of entire wax	M. P. ° C.	n_D, 90° C.	Neut. or acid value	% of entire wax	M. P. ° C.	n_D, 90° C.	Neut. or acid value	% of entire wax	M. P. ° C.	n_D, 90° C.	Neut. or acid value	% of entire wax	M. P. ° C.	n_D, 90° C.	Neut. or acid value	% of entire wax	M. P. ° C.	n_D, 90° C.	Neut. or acid value
Entire wax	..	43.5–44.0	1.4252	...	..	60–62.0	1.4327	19	..	83.0	1.4496	7	...	70–70.5	1.4600	22	...	67.5–68.5	1.4270	45
Soluble in cold alcohol	5	32.5–33.0	1.4295	10	5	60.0	1.4391	88.5	3	...	1.4916	19	19	...	1.5115	24	3	52.0	1.4386	29.5
Insoluble in cold alcohol	95	43.5–44.0	1.4252	...	95	62–62.5	1.4326	...	97	83.3	1.4493	...	81	72–73.0	1.4503	...	97	68.5–68.7	1.4270	...
Total acids	45	37.8	1.4199	218	40	56–59.0	1.4308	170	40	78.0	1.4441	...	29–30	80–80.5	1.4496	115	38	77–79.0	1.4325	109
Soluble in cold alcohol	45	37.8	1.4199	218	30	46.6–48.0	....	187	5	73.8	....	193.5	7.5	50–50.3	1.4734	177	2.6	...	....	93.3
Insoluble in cold alcohol	None	...	....	...	9.5	75–78.0	....	105	35	81.6	....	108.5	22.5	82.5	1.4428	91	35.2	78–79.0	....	118
Unsaponifiable matter	48	46–50.0	1.4204	...	55	71–72.0	1.4298	...	55	88.3–89.0	1.4375	...	50	67–68.0	1.4476	...	58.2	51.5–51.7	1.4246	...
Hydrocarbons	None	...	....	...	20	51.7–52.0	1.4264	...	None	...	....	...	30	66.8	1.4325	...	52.6	52.4	1.4236	...
Alcohols (plus other unsaponifiable matter)																				
Insoluble in cold amyl alcohol–HCl	None	...	....	...	30	79–80.0	1.4310	...	52	86–87.0	1.4358	...	11	78.2	1.4417	...	5	...	....	...
Soluble in cold amyl alcohol–HCl	48	44–47.0	1.4200	...	5	...	....	...	3	...	....	...	8	...	1.5136	...	Trace	...	....	...
Acetyl value of entire wax	..	2.6	....	...	..	15	....	...	..	51–60	....	...	...	9–21	....	...	...	11.2	....	...
Saponification value of entire wax	..	128–130	....	...	..	93	....	...	..	79–88	....	...	...	57	....	...	...	77	....	...

volumes of water, and evaporated. The acids are then dried at 110° C.

By this method the alcohol-insoluble fraction is divided into: (1) substances soluble in aqueous alkali after saponification (chiefly wax acids); and (2) substances insoluble in aqueous alkali, but soluble in benzene (chiefly alcohols and hydrocarbons, known collectively as the "unsaponifiable matter").

Acids. The acids are dissolved in twenty parts of hot 95 per cent alcohol, and the solution is allowed to cool to 25° C. and filtered. Two fractions result: (1) acids soluble in cold alcohol and (2) acids insoluble in cold alcohol.

Unsaponifiable Matter. For the separation of the alcohols and hydrocarbons in this fraction, a modification of Leys' (*17*) method was used. This method is based upon the insolubility of hydrocarbons in a boiling mixture of equal parts of fuming hydrochloric acid and amyl alcohol; the alcohols are soluble in this mixture at the boiling point. A further separation of the alcohols is based upon the insolubility in this solvent mixture at room temperature of the alcohols with more than 22 carbon atoms.

The unsaponifiable matter (from 10 grams of wax) is dissolved in 100 cc. of hot amyl alcohol and 100 cc. of concentrated hydrochloric acid (36 per cent) are added. The mixture is stirred and boiled over an asbestos plate for about 5 minutes. The presence of hydrocarbons is evidenced by an oily layer on the surface of the liquid. Upon cooling, a disk of solidified hydrocarbons can be lifted from the lower amyl alcohol–hydrochloric acid layer. The residual liquid is filtered through a Büchner funnel and the precipitate washed twice with 25 cc. of amyl alcohol–hydrochloric acid mixture. The filter paper with the precipitate is placed in a large evaporating dish and boiling water is added. The oily layer of wax alcohols rises to the top and solidifies on cooling. The filtrate containing the soluble alcohols is washed in a separatory funnel with hot water until free from hydrochloric acid. The amyl alcohol is then evaporated or vacuum-distilled, and the alcohols are dried and weighed.

This divides the unsaponifiable matter into three fractions: (1) substances insoluble in hot amyl alcohol–hydrochloric acid mixture (chiefly hydrocarbons); (2) substances soluble in hot amyl alcohol–hydrochloric acid mixture but insoluble in cold amyl alcohol–hydrochloric acid mixture (mainly alcohols of high molecular weight, such as ceryl or myricyl); (3) substances soluble in cold amyl alcohol–hydrochloric acid mixture (mainly wax alcohols of low molecular weight, such as cetyl alcohol).

The properties of the various fractions separated from each wax by the procedure outlined are listed in Table I.

Discussion

The results of the preceding determinations are interpreted below. Allied substances such as stearic acid, cetyl alcohol, and rosin are included, since they are often found admixed with waxes, and their presence may affect the interpretation of the results.

From a knowledge of the constants certain generalities may be inferred—for example, a low saponification value (below 50) indicates the presence of paraffin or ozokerite; a very low acid value (below 3 or 4) excludes the presence of more than 10 per cent of beeswax, montan, or candelilla, and indicates the absence of rosin or stearic acid. Similarly, a low acetyl value (below 10) excludes appreciable quantities of carnauba or free cetyl alcohol; a low melting point (below 65° C.) shows the absence of more than 10 per cent of carnauba (*13*, *16*).

The precipitation temperatures indicate the presence or absence of ozokerite and carnauba.

An examination of the alcohol-soluble fraction yields valuable information concerning a wax mixture—for example, when the quantity of alcohol extract is below 5 per cent, the absence of candelilla, rosin, stearic acid, and cetyl alcohol may be definitely inferred. Candelilla contains 20 per cent of an alcohol-soluble resinous substance with a low acid value. Consequently, the presence of more than 5 per cent of an alcohol-soluble material with a high acid value (above 25) indicates the presence of acid substances such as stearic acid or rosin.

The separation of the constituents of the alcohol-insoluble fraction and the determination of their properties yield more specific information concerning the wax mixture. The wax acids are divisible into two groups on the basis of solubility. The acids soluble in cold alcohol are compounds of low molecular weight, chiefly myristic, palmitic, and adjacent homologous acids, with melting point below 51° C. Those insoluble are compounds of high molecular weight with carbon content from 24 to 34, and melting point above 75° C. The entire acid fraction of spermaceti and 75 per cent of the acids of beeswax are composed of the lower melting point compounds. Therefore, if the alcohol-soluble acid fraction is absent, or present in small quantities (less than 7.5 per cent of the entire wax), spermaceti and beeswax are either absent or present in small quantities. A further verification can be obtained by an examination of the wax alcohols.

The wax alcohols have similarly been divided into a fraction soluble in cold amyl alcohol–hydrochloric acid mixture and a fraction insoluble in this solvent. The entire unsaponifiable fraction from spermaceti is composed of alcohols soluble in cold amyl alcohol–hydrochloric acid, whereas all the other waxes, including beeswax, yield comparatively small percentages of material soluble in this solvent at 25° C. Therefore, the presence or absence of spermaceti would be indicated by the determination of the quantity of material soluble in cold amyl alcohol–hydrochloric acid mixture. Since spermaceti is essentially the cetyl ester of myristic and lauric acids, the ratio of soluble acids to soluble alcohols is approximately 1 to 1. A higher ratio, such as 1.5 or more of soluble acids to one part of soluble alcohols, would therefore indicate the presence of beeswax.

The hydrocarbon fraction offers a means for detecting the presence of ozokerite or paraffin. The wax hydrocarbons are carbonized when heated to 110° C. with concentrated sulfuric acid (*3*, *18*), while the paraffin hydrocarbons are unattacked and can be extracted from the diluted acid mixture with a volatile solvent such as ether or petroleum ether. The quantitative determination of ozokerite and paraffin, when both are present, is difficult. Graefe's method (*10*), often employed for this purpose, is based upon the fact that 50 to 60 per cent of ceresin hydrocarbons are precipitated from their solution in carbon disulfide by the addition of a mixture of ether and alcohol (1 to 1), whereas paraffins remain in solution. Other methods, based on differences in solubility, melting points, and refractive index, are described by Holde (*12*).

The following compilation of the important distinguishing characteristics of each wax is presented as a supplement to this discussion.

SPERMACETI. The unsaponifiable matter, totaling 48 per cent, is found in the fraction soluble in cold amyl alcohol–hydrochloric acid. All the acids are soluble in cold ethyl alcohol. When added to other waxes, spermaceti causes a lowering of the acid value, melting point, and acetyl value. The ethanol-soluble fraction is small, and hydrocarbons are absent.

BEESWAX. Seventy-five per cent of the acids are soluble in cold alcohol. (If spermaceti is present, as indicated by the quantity of cold amyl alcohol–hydrochloric acid fraction, the amount of acids in excess of the combining ratio of alcohols and acids, 1 to 1, which form the ester of spermaceti permits the calculation of the approximate quantity of beeswax.)

CARNAUBA. The precipitation temperatures in *n*-butyl alcohol and in *n*-heptane are much higher than those of other waxes (ozokerite excepted). Hydrocarbons are present in but very small amounts (about 1 per cent). The acetyl value is much higher than that of any other wax studied. The melting point of a wax mixture is considerably increased by the addition of small quantities of carnauba (*13*, *16*). The acids and alcohols are mostly of high molecular weight; consequently, both the cold alcohol-soluble acid fraction and the fraction soluble in cold amyl alcohol–hydrochloric acid are very small.

CANDELILLA. The alcohol-soluble fraction consists of a resinous material and constitutes approximately 20 per cent of the wax. This fraction has a low acid value, in contradistinction to rosin (colophony) which has an acid value of about 160. The resinous material may be separated from rosin and stearic acid by neutralizing the alcohol-soluble fraction with potassium hydroxide, adding water, and extracting with ether or benzene.

The acid fraction of candelilla is dark brown in color and more than 75 per cent is insoluble in cold alcohol. The hydrocarbon fraction is relatively large. The hydrocarbons differ from paraffin or refined ozokerite hydrocarbons in being readily carbonized by concentrated sulfuric acid.

MONTAN. Considerable differences are found in the composition of the three varieties of montan, but all invariably contain montanic acid ($C_{28}H_{56}O_2$), free or combined as an ester. The proportion of hydrocarbons is large, and ketones have been found in the raw and the distilled products. The presence of resinous substances and sulfur-containing compounds differentiates the raw montan from the distilled and bleached products.

Because of the absence of alcohols, the acetyl value of the unsaponifiable matter of distilled wax is for all practical purposes zero, whereas the raw and refined wax contain varying amounts of alcohols of high molecular weight, such as ceryl or myricyl. The presence of ketones in the unsaponifiable matter is an important clue to the identification of montan. Ketones are estimated by reducing with sodium in alcohol to secondary alcohols and determining the difference in hydroxyl value before and after reduction (*3*). They may also be estimated by the method of Mangouri (*19*), which is based on the insolubility in boiling methyl alcohol of the barium salt of a hydrazone formed when the ketones are treated with *p*-hydrazinebenzoic acid.

PARAFFIN. The hydrocarbons are not attacked by concentrated sulfuric acid, whereas wax hydrocarbons are carbonized by this acid. The addition of paraffin to a wax mixture appreciably lowers the saponification value.

OZOKERITE. The precipitation temperatures in *n*-butyl alcohol and *n*-heptane are much higher than those of all the other waxes (carnauba excluded). The hydrocarbons of the refined ozokerite are not attacked by concentrated sulfuric acid.

The precipitation temperatures of the unattacked hydrocarbons can be used to differentiate paraffin qualitatively from ozokerite. Graefe's method (*10*) may be applied to determine whether both are present.

ROSIN (COLOPHONY). Rosin, which is found in the cold alcohol-soluble fraction, has a very high acid value (about 160), and can be differentiated from stearic acid in that rosin acids are not converted into ethyl esters when treated in alcohol solution with hydrogen chloride gas (*15*). Addition of rosin to a wax mixture raises the acid value considerably (10 per cent of rosin increases the acid value by 16). Color reactions for rosin, such as the Liebermann-Storch reaction, are not very reliable since candelilla and montan produce similar colors.

STEARIC ACID. This acid, like rosin, is found in the alcohol-soluble fraction, and is differentiated from rosin as indicated above. The acid value of a wax mixture is increased by 20 when 10 per cent of stearic acid is added.

CETYL ALCOHOL. This alcohol is identified by the high acetyl value of the alcohol-soluble fraction. The acetyl value of the entire wax mixture is increased by 20 for each 10 per cent of added cetyl alcohol.

Summary

The precipitation temperatures of the waxes in *n*-butyl alcohol and *n*-heptane are proposed as criteria for the detection of carnauba and ozokerite in a mixture of waxes.

The quantitative separation involves the isolation of an ethanol-soluble fraction, fatty acids of high and low molecular weight, hydrocarbons, and fatty alcohols of high and low molecular weight.

A schematic outline for the identification of waxes in admixture has been developed on a semiquantitative basis.

Literature Cited

(1) "Allen's Commercial Organic Analysis", Vol. II, 5th ed., Philadelphia, P. Blakiston's Son and Co., 1924.
(2) Armani, G., and Rodano, G. A., *Analyst*, 38, 37 (1913).

(3) Better, E. J., and Davidsohn, J., "Taschenbuch für die Wachs-Industrie", Stuttgart, Wissenschaftliche Verlagsgesellschaft, 1932.
(4) Chibnall, A. C., and Piper, S. H., *Biochem. J.*, 28, 2209 (1934).
(5) Chibnall, A. C., Piper, S. H., Pollard, A., Smith, J. A. B., and Williams, E. F., *Ibid.*, 25, 2095 (1931).
(6) Chibnall, A. C., Piper, S. H., Pollard, A., Williams, E. F., and Sahai, P. N., *Ibid.*, 28, 2189 (1934).
(7) Francis, F., and Piper, S. H., *J. Am. Chem. Soc.*, 61, 577 (1939).
(8) Francis, F., Piper, S. H., and Malkin, T., *Proc. Roy. Soc.* (London), A128, 214 (1930).
(9) Gisvold, O., and Rogers, C. H., "Chemistry of Plant Constituents", Minneapolis, Burgess Publishing Co., 1938.
(10) Graefe, E., *Chem.-Ztg.*, 27, 248 (1903); *Analyst*, 28, 190 (1903).
(11) Grün, A., and Halden, W., "Analyse der Fette und Wachse", Band I (1925), Band II (1929), Berlin, Julius Springer.
(12) Holde, D., "Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes", New York, John Wiley & Sons, 1922.
(13) Koch, J. R., Hable, G. J., and Wrangell, L., Ind. Eng. Chem., Anal. Ed., 10, 166 (1938).
(14) Lewkowitsch, J., "Chemical Technology and Analysis of Oils, Fats, and Waxes", Vol. I (1921), Vol. II (1922), Vol. III (1923), London, Macmillan Co.
(15) *Ibid.*, Vol. I, p. 639.
(16) *Ibid.*, Vol. II, p. 889.
(17) Leys, A., *J. phar. chim.*, 5, 577 (1912).
(18) Lüdecke, K., "Die Wachse und Wachskörper", Stuttgart, Wissenschaftliche Verlagsgesellschaft, 1926.
(19) Mangouri, H. A., *Biochem. J.*, 31, 1978–80 (1937).
(20) Piper, S. H., Chibnall, A. C., Hopkins, S. J., Pollard, A., Smith, J. A. B., and Williams, E. F., *Ibid.*, 25, 2072 (1931).
(21) Piper, S. H., Chibnall, A. C., and Williams, E. F., *Ibid.*, 28, 2175 (1934).
(22) Waentig, P., and Peschek, G., *Z. physik. Chem.*, 93, 529 (1919).

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Computing Titration Blanks

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In 1936 Park (*2*) pointed out that if a series of volumetric determinations is made under exactly the same conditions, except as to the amount of the sample, the value of the blank (at zero sample) may be computed by extrapolation of these data. As an illustration, he cited a series of four titrations of varying amounts of a standardized zinc solution, each in a volume of 200 ml., by means of a potassium ferrocyanide solution.

In order to extrapolate these data analytically, he determined the constants of an equation for a straight line passing through the four points, by solving each of the six pairs of simultaneous equations which could be set up from the four points, and using the averages of the six pairs of constants so computed.

This procedure gives a result which is adequate when the data fall in a straight line and are in such excellent alignment as those used in Park's illustration. In fact, for such data an extrapolation can be made rapidly and easily by graphical means, and the use of a fairly large scale in plotting will ensure the required precision. Park's data, plotted on a condensed scale, are shown in Figure 1 (curve 1), in which the value of the blank (at zero sample) is represented by the intersection of the extrapolated curve on the vertical axis.

As a rule, however, the data do not fall in such good alignment, and may deviate from a straight line nonsystematically. In fitting a straight line to such points by eye, considerable uncertainty may exist as to its exact location, and a significant variation may occur in the apparent value for the blank as determined by graphical extrapolation. In such a case, an appreciable error may also be introduced in computing the value of the blank by the procedure Park used, since constants computed from adjacent data points are given the same weight as those computed from the most widely separated points. Hence, it is preferable to fit the curve to the points by the method of least squares.

Starting with the equation

$$t = as + t_0 \qquad (1)$$

where t is the titration value in milliliters, s the volume or weight of sample taken, a the titration value per unit sample, and t_0 the blank in milliliters, and making n titrations, each on a different sized sample, it can be shown that:

$$t_0 = \frac{\Sigma s^2 \Sigma t - \Sigma s \Sigma st}{n\Sigma s^2 - (\Sigma s)^2} \qquad (2)$$

If it is convenient to weigh out or measure the samples in the ratio 1:2:3, etc., the following simpler equation can be used:

$$t_0 = \frac{2\Sigma^1{}_{n-1}(t)}{n-1} - t_n \qquad (3)$$

This equation can be applied to data of the type reported by Park with considerably less calculation than is required for the method he used, and with greater precision. The data he reported were as follows:

	$K_4Fe(CN)_6$ Solution *Ml.*		Zn Solution *Ml.*
t_1	9.75	s_1	10
t_2	19.13	s_2	20
t_3	28.50	s_3	30
t_4	37.87	s_4	40

Substituting in Equation 3,

$$t_0 = \frac{2(9.75 + 19.13 + 28.50)}{3} - 37.87 = 0.38$$

Since the data in this illustration are in almost perfect alignment, all the above methods (the graphical, Equation 2, or Equation 3) give the same result, and the practical advantage of using Equation 3 lies only in its brevity. However, when there is considerable scatter in the data, the greater precision obtained by using the method of least squares is important.

A close perusal of curve 2, Figure 1, indicates that the points deviate systematically from a straight line. This curve was constructed from the following data (*1*):

	$Ba(OH)_2$ Solution *Ml.*		B_2O_3 Solution *Ml.*
t_1	1.91	s_1	2
t_2	3.47	s_2	4
t_3	5.11	s_3	6
t_4	6.62	s_4	8
t_5	8.14	s_5	10

The blank calculated from these data by means of Equation 3 is 0.415 ml. against a determined blank of 0.27 ml. This is too great a deviation for accurate work and necessitates the introduction of another term in Equation 1, so that

$$t = bs^2 + as + c \qquad (4)$$

where c is used for t_0, inasmuch as it is no longer the blank, but only the intercept of the curve on the t-axis.

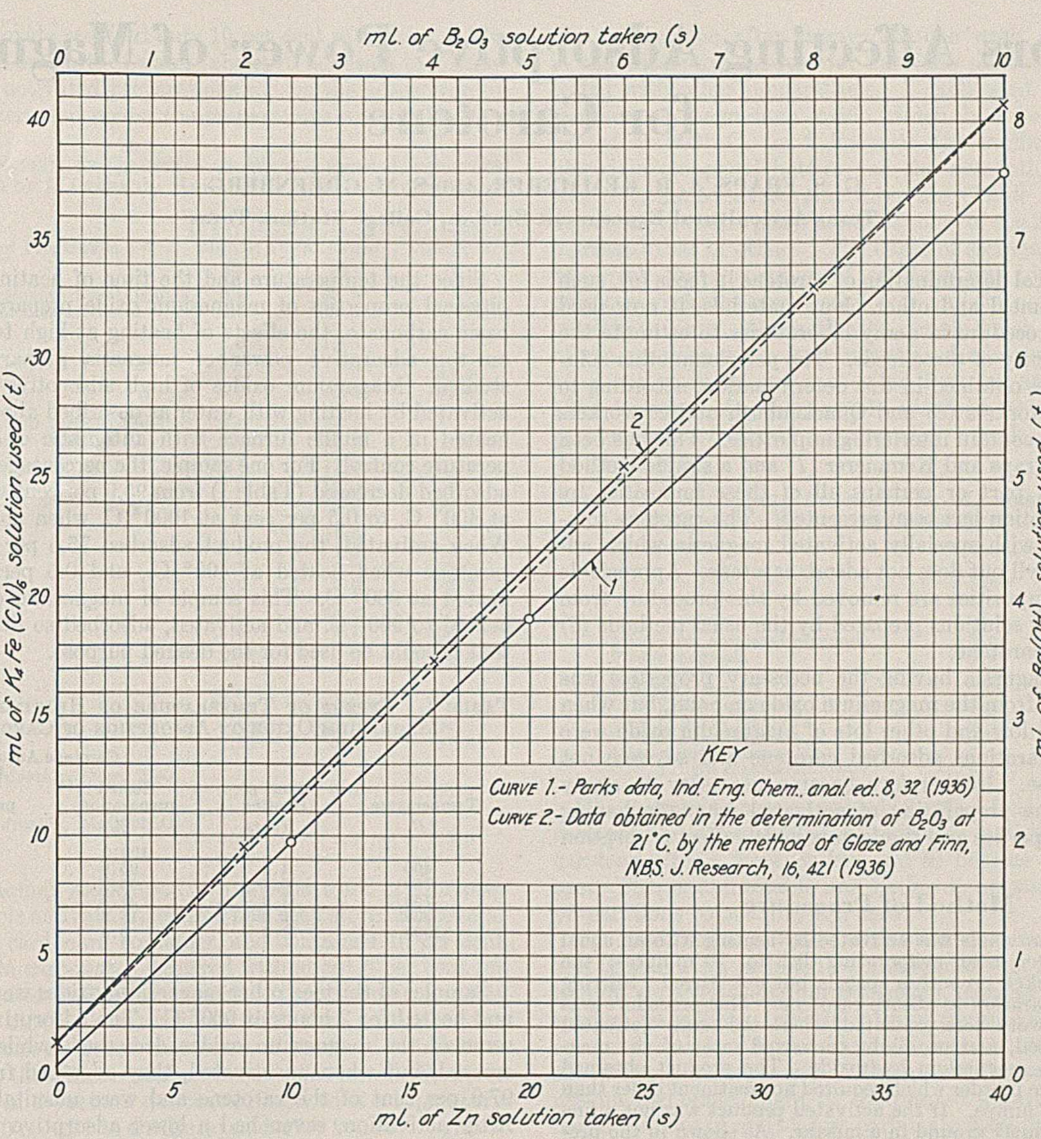

FIGURE 1. TITRATION CURVES OF ZINC BY POTASSIUM FERROCYANIDE AND OF BORON TRIOXIDE BY BARIUM HYDROXIDE

Substituting the above values in Equation 4 and solving for the constants by means of least squares

$$t = -0.00375s^2 + 0.8255s + 0.26$$

It is interesting to note how closely c (0.26) agrees with the determined value (0.27). The curve of this equation can be plotted on a large scale. Then, in making succeeding titrations, the amount of sample, s, can be read off the curve by interpolation for any quantity of the titrating solution, t, provided the conditions under which the titration is made are the same in both cases. If, however, a smooth curve can be accurately fitted to the points by eye, a least squares solution becomes unnecessary. It would seem advisable that any titration data, concerning which there is any question, be graphically analyzed before deciding which of the above methods of correcting for the blank to use or even before applying the blank as ordinarily determined.

For the method of extrapolation to zero sample to be of value, the titrations must be accurately done, or a large number of titrations must be made, so that the variations of the individual titrations will not unduly affect the accuracy of the computed value of the blank. Also, there should be a high ratio (preferably at least 3 to 1) of the spread between the largest and smallest sample to the distance of extrapolation. Where the end point is affected by the volume of solution titrated, the same volume must be used in all cases. Of course, if the end point varies in a nonlinear manner with the size of the sample, linear extrapolation is unsatisfactory, and some method such as that used in connection with curve 2, Figure 1, must be used.

It is felt that blanks evaluated by graphical or "analytical" extrapolation (or indirectly by interpolation when the relation is nonlinear) are in many cases preferable to directly determined blanks, since the former are based on data obtained under the actual conditions of the titration. Also, in the particular case where the relation between the titration value and the size of the sample is not linear, the blank as ordinarily determined is not the true blank, but only the intercept of the curve on the t-axis. In this case it is especially necessary to take precautions to arrive at a correct value for the blank.

Literature Cited

(1) Glaze and Finn, *J. Research Natl. Bur. Standards*, **16**, 421 (1936).
(2) Park, Bartholow, IND. ENG. CHEM., Anal. Ed., **8**, 32 (1936).

Factors Affecting Adsorptive Power of Magnesia for Carotene

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THE chemical determination of carotene in feeds (*6*), such as alfalfa meal and other plant materials, is now used as a regular procedure in many laboratories to estimate the vitamin A potency of these feeds. The petroleum ether solution of carotene obtained in this determination, according to Shinn and co-workers (*8*) and Quackenbush and co-workers (*7*), is likely to contain interfering impurities. This has been confirmed by Fraps and Kemmerer (*1*) and a simple method for eliminating part or perhaps all of these impurities by selective adsorption has been presented. The carotene solution is shaken with specially activated magnesia which adsorbs xanthophyll but does not adsorb carotene. Appreciable quantities of impurities are removed by this procedure from petroleum ether solutions prepared by the usual methods (*6*) for estimating carotene.

Activated magnesia having the necessary properties was easily prepared from the magnesium oxide on hand, but when this supply ran low and other lots of magnesium oxide were tried, the preparations adsorbed carotene and so were not suitable for use. It therefore became necessary to study methods for the preparation of activated magnesia having the desired properties and the factors which affect adsorption of carotene.

Method of Procedure

The magnesium oxide was activated by heating with an equal quantity of water in an evaporating dish for 30 minutes; the mixture was broken up with a spatula but not stirred. Stirring caused the preparation to absorb carotene. This procedure was used in all the work here presented, where the term "activated magnesia" is used, and no doubt converted most of the magnesium oxide to magnesium hydroxide. The product obtained was usually a fine powder which required no treatment other than breaking up the lumps. If the activated product was not a fine powder, it was finely ground in a mortar. As shown in the previous work (*1*), heating longer than 30 minutes, or subjection to a higher temperature such as that of aniline vapor, caused adsorption of carotene.

The determinations of the adsorptive power for carotene were made by shaking 2.5 grams of the powder with 50 cc. of petroleum ether (Skellysolve F, b. p. 30° to 76.7° C., 86° to 170° F.) containing approximately 2 parts per million of purified carotene prepared from S. M. A. crystallized carotene as already described (*1*) and used when fresh, and reading the residual color in a KWSZ photoelectric photometer. A test made by Miller, Zscheile, and Hogness (*4*) showed that S. M. A. carotene did not contain colored impurities, but the authors purified it further by dissolving it in chloroform and precipitating it with methyl alcohol. Adsorption of xanthophyll was determined in a similar way, with use of crude xanthophyll prepared from alfalfa leaf meal as already described (*1*).

Results of Work

Samples of fifteen magnesium oxides and four magnesium hydroxides secured by purchase or by the cooperation of the California Chemical Company and Merck & Company were studied for their adsorptive power as received and after activation, as described above. Although all but one of the oxides adsorbed less carotene after activation than before, all nineteen samples adsorbed carotene and were not suitable for use in the analytical work. The carotene adsorbed ranged from 7.5 to 90 per cent of the quantity used. Preparation of suitable activated magnesia from commercial magnesium oxides or hydroxides by the method described therefore appeared almost impossible.

Since the temperature and the time of heating affect the physical properties of magnesium oxide prepared from the basic carbonate, the effects of heating at high temperatures on the adsorptive power of magnesia preparations were studied. Magnesium oxides of high adsorptive power were activated by heating with water as described above and then heated in a muffle furnace with automatic electrical temperature control. For one sample, the percentage of carotene adsorbed decreased (Table I) from 95.9 per cent when heated at 400° C. to 0.5 per cent at 1000° C. when not activated. When activated, the product adsorbed 75.6 per cent of the carotene when heated at 400° C., and 0.5 per cent when heated at 900° C. This sample of magnesium oxide, when heated to 900° C. and activated, adsorbed so little carotene that it could be used for the desired purpose.

TABLE I. EFFECT OF TEMPERATURE OF HEATING ACTIVATED MAGNESIUM OXIDE ON ADSORPTION OF CAROTENE

Temperature	Time of Heating	Carotene Adsorbed: Heated preparation	Carotene Adsorbed: Activated heated preparation
° *C.*	*Hours*	%	%
..	...	100.0	70.6
400	1.0	95.9	75.6
750	0.5	96.9	25.0
750	1.0	21.3	7.1
900	2.0	18.8	0.5
1000	1.0	0.5	1.2

Samples of thirteen other magnesium oxides were activated and heated for 2 hours at 900° C. The adsorptive power of some of the magnesium oxides decreased, while others increased, but when unactivated, they adsorbed from 18.8 to 97.9 per cent of the carotene and were unsuitable for use. After activation, seven had a lower adsorptive power, two had about the same, and five had a higher adsorptive power than the similar product before heating, but only two did not adsorb carotene and were suitable for use. The other thirteen adsorbed from 1.2 to 99.5 per cent of the carotene. A number of preparations were usually tested at the same time and with the same solution of carotene.

The causes of the differences in the action of supposedly the same kinds of magnesium oxides to the same treatment remain to be discovered. It is claimed (*5*) that at high temperatures (800° C. or above) magnesium oxide tends to change from an amorphous state to a crystalline structure, and that this change is accelerated by such impurities as iron oxide. Presence or absence of iron oxide or other impurities might contribute to differences in action of the various samples.

In preliminary work it was found that additions of water decreased the adsorptive power of activated magnesia for carotene. The effects of different amounts of water on adsorption of carotene by activated magnesia or magnesia hydroxide are given in Table II. Although the proportion of water added to some samples was high, when thoroughly mixed, all the water was adsorbed and a powder resulted. The adsorption of carotene decreased as more water was added until it became zero, but the quantity of water required differed widely with the different samples. The first activated sample required the addition of 90 per cent of water to reduce the adsorption of carotene to zero, the second 40 per cent and the third 54 per cent, while the two samples of magnesium hydroxide required only 10 per cent of water. Additions of small amounts of water (about 10 per cent) to a number of other activated preparations reduce the adsorption of carotene to zero and render the preparations suitable for use.

TABLE II. EFFECT OF QUANTITY OF WATER UPON ADSORPTIVE POWER OF MAGNESIUM HYDROXIDE FOR CAROTENE

Method of Preparation	Water Added to 5 Grams Mg(OH)$_2$	Carotene Adsorbed	Xanthophyll Adsorbed
	Cc.	%	%
C. P. light magnesium carbonate ignited at 400° C. and then activated	0.0	73.9	
	0.3	51.8	
	1.0	29.1	
	2.0	15.6	
	3.0	8.4	
	3.5	1.0	100.0
	4.5	0.0	100.0
C. P. light magnesium carbonate ignited at 900° C. and then activated	0.0	54.5	
	0.3	31.7	
	0.5	19.5	
	0.7	14.1	
	1.0	10.9	
	2.0	0.0	100.0
Activated	2.0	11.5	
	2.5	4.0	
	2.7	0.0	99.0
	3.0	0.0	95.2
Activated	0.0	87.2	
	2.0	7.7	100.0
	2.25	0.0	90.2
	2.50	0.0	73.9
Activated	0.0	94.8	
	1.0	25.8	
	1.25	11.0	99.5
	1.50	0.0	97.3
Magnesium hydroxide, $MgO.H_2O$, activated	0.50	0.0	100.0
Magnesium hydroxide, $MgO.2H_2O$, activated	0.50	1.0	100.0

The magnesium oxide used in previous work (*1*) for preparing suitable activated magnesia had been stored for several months in a cardboard container, and contained 16 per cent of magnesium carbonate compared with about 5 per cent for newly purchased magnesium oxides. It was thought possible that carbon dioxide had combined with that portion of the magnesia which adsorbed carotene and rendered it inactive. Accordingly, the effect of carbon dioxide was tested. Samples were placed in a vacuum desiccator fitted with a separatory funnel and 10 cc. of 1 to 4 sulfuric acid were run into 2 grams of sodium carbonate contained in a small bottle, after the desiccator had been partly evacuated. When the reaction had gone to completion, the vacuum that remained was broken. After the samples remained in contact with the carbon dioxide for one week, they were activated in the usual way. The treatment with carbon dioxide decreased the quantity of carotene adsorbed, and one sample did not adsorb carotene and was suitable for use. The other two adsorbed 4.1 and 7.7 per cent of the carotene, respectively, and the addition of 10 per cent of water reduced the adsorption of carotene to zero and rendered the samples suitable for use.

Since activated magnesia suitable for selective adsorption could be prepared by treatment with carbon dioxide and water, magnesia was exposed to the air in layers 1.25 to 2.5 cm. (0.5 to 1 inch) thick and activated with the results given in Table III. Six of the nine magnesias, after having been exposed to the air 2 weeks and activated, did not adsorb carotene and were suitable for use. The other three had a low adsorptive power, and could be made suitable for use by mixing 10 per cent of water with them.

It is also shown in Table III, that while the freshly prepared reagents might not adsorb carotene, they adsorbed 2.4 to 38.1 per cent of the carotene after storage for one week. The changes in the adsorptive powers for carotene on storage were also tested with other preparations. Unactivated and activated samples of magnesium oxide which had been previously heated at 900° C. for 2 hours in the muffle furnace were placed in stoppered bottles and the adsorption of carotene was determined at several intervals (Table IV). Storage decreased the adsorptive power of some of the 22 samples and increased that of others. The effect of storage was irregular; one week the adsorption of carotene was higher than the previous week, the next week lower, and the next week higher or perhaps lower. One activated sample which adsorbed none of the carotene when freshly prepared adsorbed 23 per cent after one week, 45 per cent after 2 weeks, and 71 per cent after 4 weeks. Another sample adsorbed 13 per cent of the carotene when fresh, 45 per cent after 1 week, and none after 2 and 4 weeks.

TABLE III. CAROTENE ADSORBED BY MAGNESIA EXPOSED TO AIR TWO WEEKS AND THEN ACTIVATED

	Carotene Adsorbed	
	Freshly prepared	After storage 1 week
	%	%
Adsorptive powdered magnesia	0.0	10.7
Plastic magnesia	0.0	22.9
Quick magnesia	0.5	3.4
Reagent magnesia	0.0	10.7
U. S. P. light magnesia	0.0	38.1
U. S. P. heavy magnesia	0.0	2.4
U. S. P. light magnesia	0.0	..
Micron magnesium oxide	2.4	..
U. S. P. light magnesium oxide	5.4	..

The magnesia preparations which when fresh do not adsorb carotene and are suitable for use in this method, may adsorb carotene after a week or less and so become unsuitable for use. This is undesirable and makes it necessary to test all preparations before they are used.

Some preliminary studies with other adsorbents, activated and unactivated, included calcium carbonate, hydrated lime, barium carbonate, barium hydroxide, calcium oxide, dibasic calcium phosphate, tribasic calcium phosphate, calcium sulfate, charcoal, iron hydroxide, fuller's earth, aluminum oxide, and magnesium carbonate. These tests indicated that magnesium carbonate might be the desired adsorbent. A number of samples of magnesium carbonate were therefore tested, with the results given in Table V. Three of the seven samples as received did not adsorb carotene but adsorbed xanthophyll and therefore were suitable for use without treatment. The

TABLE IV. EFFECT OF TIME OF STORAGE UPON MAGNESIUM OXIDES HEATED AT 900° C.

Kind of Magnesia	Carotene Adsorbed					
	Before storage	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks
	%	%	%	%	%	%
U. S. P. special light powder magnesium oxide	95.8	80.5	64.0	..	70.5	77.8
After activation	71.7	82.6	67.5	..	89.3	59.5
U. S. P. light magnesium oxide	97.9	66.7	51.5	..	58.3	75.2
After activation	93.8	89.7	68.0	..	74.8	65.4
U. S. P. light powder magnesium oxide	93.4	50.0	..	78.6	57.0	..
After activation	99.5	67.5	..	70.1	66.0	..
Adsorptive powdered magnesia	34.8	50.8	21.5	..	71.2	19.2
After activation	0.0	22.5	45.0	..	70.5	19.2
Adsorptive powdered magnesium oxide	12.8	44.8	0.0	..	0.0	..
After activation	1.2	33.2	38.5	..	46.5	42.9
Plastic magnesia	41.0	68.4	49.0	..	70.6	46.4
After activation	10.3	68.4	44.1	..	56.2	60.6
Plastic magnesia	29.2	28.9	19.8	..	19.8	..
After activation	11.8	70.2	45.5	..	40.1	62.2
U. S. P. heavy magnesium oxide	43.5	48.7	32.0	..	57.2	32.6
After activation	41.0	71.9	25.0	..	43.9	53.4
Granular magnesium hydroxide	66.2	22.5	..	60.0	22.5	..
After activation	74.9	34.0	..	62.6	25.0	..
Reagent magnesium oxide 90% pure	55.4	..	..	34.3	..	..
After activation	14.4	..	..	68.2	..	..
Reagent magnesium oxide 99% pure	40.6	..	..	53.5	..	..
After activation	12.4	..	..	56.0	..	..

other four samples adsorbed small amounts of carotene as received, did not adsorb carotene after activating or after 10 per cent of water was mixed in, and adsorbed xanthophyll, and so were suitable for use. Two of the samples which did not adsorb carotene had their adsorptive powers so lowered by activation that they did not adsorb all the xanthophyll, so the activated preparations were unsuitable for use.

TABLE V. EFFECT OF TIME OF STORAGE UPON ADSORPTION POWER OF MAGNESIUM CARBONATE

Method of Preparation	Carotene Adsorbed: Original analysis	Carotene Adsorbed: Stored 1 week	Carotene Adsorbed: Stored 2 weeks	Xanthophyll Adsorbed
	%	%	%	%
U. S. P. heavy powder	2.4	...	...	...
0.5 cc. H_2O added to 5 grams	0.0	0.0	0.0	100.0
Activated	0.0	0.0	0.0	100.0
C. P. powder	3.4	...	...	...
0.5 cc. H_2O added to 5 grams	0.0	0.0	0.0	100.0
Activated	0.0	0.0	0.0	100.0
Reagent, low in sulfate	0.0	0.5	0.5	99.5
Activated	0.0	...	...	94.5
Reagent	0.0	0.0	0.0	100.0
Activated	0.0	...	...	94.2
U. S. P. heavy powder	0.0	0.5	0.0	100.0
U. S. P. light powder	1.9	...	...	...
0.5 cc. H_2O added to 5 grams	0.0	0.0	0.0	99.5
Activated	0.0	0.0	0.0	99.5
U. S. P. powder	7.2	...	...	...
0.5 cc. H_2O added to 5 grams	0.0	0.0	0.0	100.0
Activated	0.0	0.0	0.0	99.5

Further experiments with magnesium carbonates indicate that they are more stable than preparations from magnesium oxide, and do not acquire the power of adsorbing carotene so quickly. One sample did not adsorb any carotene after 5 weeks of storage after activation, and, as shown in Table V, other samples are likewise stable. Magnesium carbonate at present seems to be the best reagent for purifying carotene solutions.

In any of the methods outlined above for preparing suitably selective magnesia, the magnesia obtained must be able to adsorb large amounts of the xanthophyll and no carotene. The question then arises as to whether or not such preparations will adsorb other carotinoids which are not so readily adsorbed as xanthophyll but which may still contaminate carotene solutions. The activated magnesia which was found to be suitable in previous work (*1*) and one of the samples heated at 900° C. for 2 hours were shaken with a petroleum ether extract of red tomatoes. Both samples adsorbed 86 per cent of the pigment present. Tomatoes are high in lycopene and since lycopene has only a slightly higher adsorbability than carotene, these two samples of activated magnesia proved to be highly selective.

Discussion

Many samples of activated magnesia adsorb carotene. There is a possibility that the portion of the magnesia which adsorbs carotene may be only a small part of the whole. Adsorption of gases by magnesia (*5*) is known to take place, and it is possible that the adsorption of carotene is partly due to the presence of adsorbed oxygen. The carotene may be partly oxidized by the adsorbed oxygen and changed to such a form that it can be adsorbed. This theory is supported by the work of Gillam *et al.* (*2*) who claim that changes take place in the chemical structure of carotene when solutions of carotene are run through columns of aluminum oxide. Holmes *et al.* (*3*) have shown also that various materials which absorb vitamin A may change its chemical composition.

The action of carbon dioxide and water in reducing the adsorption of carotene may be due to displacement of oxygen or to inactivation of that portion of the magnesia which adsorbs carotene. Treatment with carbon dioxide is more successful when magnesium oxide is used than when magnesium hydroxide is used. This may be explained by the theory that the particles of active magnesium oxide which adsorb carotene combine with carbon dioxide more readily than the remaining magnesium oxide and so are inactivated, but when the oxide has been converted to the hydroxide, the difference in power of the active particles and the other particles to adsorb carbon dioxide is not sufficient to neutralize the adsorptive power for carotene. Why different samples of magnesium oxide should behave differently in the adsorption of carotene is a subject which offers opportunity for further study, and indicates a need for investigation of the adsorptive power of other materials used in chromatographic adsorption work.

Summary

The adsorptive powers of magnesium preparations were studied in order to secure preparations which adsorb xanthophyll and do not adsorb carotene and could be used in the purification of solutions of carotene in petroleum ether. Nineteen samples of magnesia from various sources were tested as received and after activation by heating with an equal volume of water for 30 minutes on a steam bath. All adsorbed carotene and therefore could not be used for purifying carotene solutions. Activated magnesia heated in a muffle furnace at 400° C. and activated adsorbed 76 per cent of the carotene, 25 per cent when the temperature was 750°, and 0.5 when the temperature was 900°. When fourteen other samples were heated to 900° C. and activated, seven had adsorptive powers for carotene lower than before heating, two had about the same, and five had higher adsorptive powers. The adsorptive powers of the magnesias for carotene were lowered as they were mixed with increasing amounts of water, until they became zero for the samples tested. Exposing magnesia to carbon dioxide, or to the air, lowered the adsorptive power of the activated magnesia for carotene. All samples of activated magnesia which did not adsorb carotene when freshly prepared, adsorbed some carotene after a week or less and thus became unsuitable for use in the purification of carotene. Some samples of magnesium carbonate did not absorb carotene when purchased, while others required activation or additions of water. Activated magnesium carbonate appears to be more stable than the preparations from magnesium oxide.

Reagents suitable for the purification of carotene in the method of selective adsorption can be prepared as follows: (1) with a few samples of magnesium oxide or hydroxide by mixing in suitable amounts of water; (2) activating and mixing in suitable amounts of water; (3) exposure of magnesium oxide to the air, activating and mixing water in, if necessary; (4) magnesium carbonate either as received or after activation, or with addition of a small amount of water. The adsorptive power of the reagent for carotene and for xanthophyll should be measured before it is used.

Literature Cited

(1) Fraps, G. S., and Kemmerer, A. R., *J. Assoc. Official Agr. Chem.*, 22, 190 (1939).
(2) Gillam, A. E., Ridi, M. S. E., and Kon, S. K., *Biochem. J.*, 31, 1605 (1937).
(3) Holmes, H. N., and Corbet, R. E., *J. Biol. Chem.*, 127, 449 (1938).
(4) Kraybill, H. R., and Shrewsbury, C. L., *J. Nutrition* (footnotes), 11, 104 (1936).
(5) Mellor, J. W., "Comprehensive Treatise on Inorganic Chemistry", Vol. IV, New York, Longmans, Green & Co., 1923.
(6) Munsey, V. E., *J. Assoc. Official Agr. Chem.*, 20, 459 (1937).
(7) Quackenbush, F. W., Steenbock, H., and Peterson, W. H., *J. Am. Chem. Soc.*, 60, 2937 (1938).
(8) Shinn, L. A., Kane, E. A., Wiseman, H. G., and Cary, C. A., *J. Biol. Chem. Proc.*, 119, LXXXIX (1937).

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Dynamic Fatigue Life of Rubber

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Dynamic fatigue is the gradual deterioration and rupture of a rubber member due to mechanical vibrations imposed on it. The number of repeated mechanical vibrations required to rupture the rubber member is referred to here as the dynamic fatigue life of the member for that particular condition of vibration. Mention has been made in the literature (*1–5*) that the dynamic fatigue life of rubber in extension is less when the minimum of the oscillation cycle falls near zero strain; but heretofore no complete study has been published. The fatigue lives of rubber as a function of the oscillation stroke are examined for minimum distortions varying from high compressions through all possible elongations.

The general dynamic fatigue characteristics of rubber in linear vibration in a dark, dry enclosure are ($L_{\text{min.}}$ = minimum length during the vibration; L_0 = free unstrained length): (1) For a given oscillation stroke the dynamic fatigue life is a minimum when $L_{\text{min.}} = L_0$; (2) for a constant value of $L_{\text{min.}}$ the dynamic fatigue life decreases as the oscillation stroke increases; (3) for given strain limits of oscillation the dynamic fatigue life is usually lower the harder the stock; (4) the dynamic fatigue life depends to a large degree on the rubber temperature.

The dynamic fatigue life of rubber worked in shear can be related to the dynamic fatigue life of rubber vibrated through linear strains.

If a rubber member is continuously vibrated it will sooner or later crack and ultimately rupture, owing to the repeated oscillations to which it has been subjected. The gradual deterioration of physical and chemical properties which accompanies such vibration is called dynamic fatigue. The number of such repeated vibrations required to rupture the rubber member is here defined as the dynamic fatigue life of the member for the particular condition of vibration imposed. The authors wish to outline briefly the general nature of the results they have obtained in their studies on the dynamic fatigue life of rubber and, in particular, to show the critical dependence of the life on the imposed oscillation conditions.

The dynamic fatigue life of rubber which is being vibrated linearly—that is, back and forth along its own length—between constant strain limits will be discussed first. Figures 1 to 3 facilitate a general statement of the problem and also serve to define certain oscillation limits which are of fundamental importance with reference to the dynamic fatigue life. The sketches are conventionalized for the sake of simplicity.

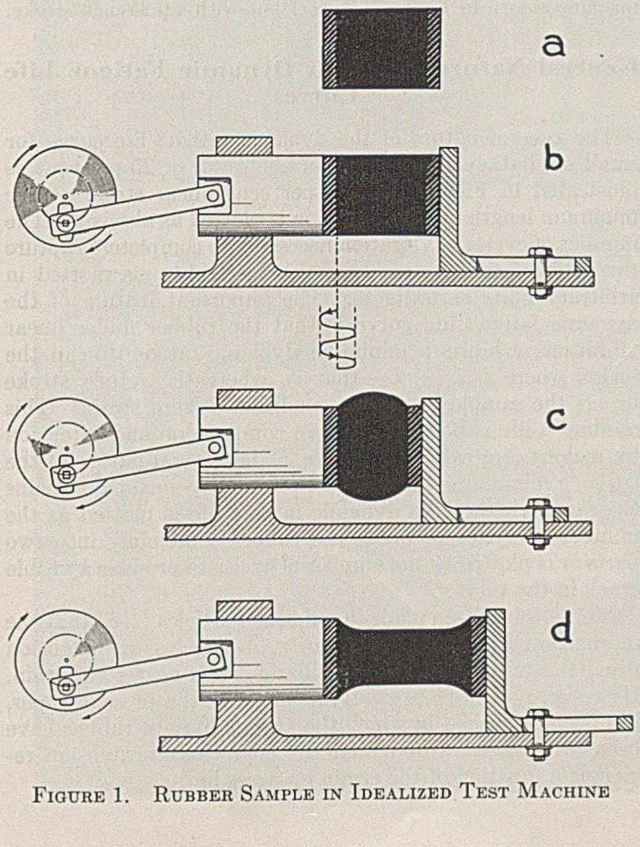

Figure 1. Rubber Sample in Idealized Test Machine

In Figure 1, *a* is a side view of a cylindrical body of rubber bonded between two circular metal end plates. In *b* this rubber member has been placed between two heads of a test machine; the position of the stationary head is adjustable; the other head oscillates back and forth in a direction parallel to the axis of the rubber sample. *b*, *c*, and *d* show various possible test conditions resulting from variation of the position of the adjustable head. Besides the alteration of the adjustable head (which does not change the oscillation stroke) the stroke itself can be changed by varying the position of the eccentric connection on the rotating wheel.

In Figure 2, *a* again represents the rubber sample. Its free unstrained length is referred to as L_0. *b* and *c* show the two extremes in length assumed by the rubber member for a particular oscillation condition. The minimum length, which is the condition in *b*, is referred to as $L_{\text{min.}}$. The maximum length of the sample in the oscillation, as illustrated in *c*, is referred to as $L_{\text{max.}}$. The difference between $L_{\text{max.}}$ and $L_{\text{min.}}$ is the oscillation stroke,

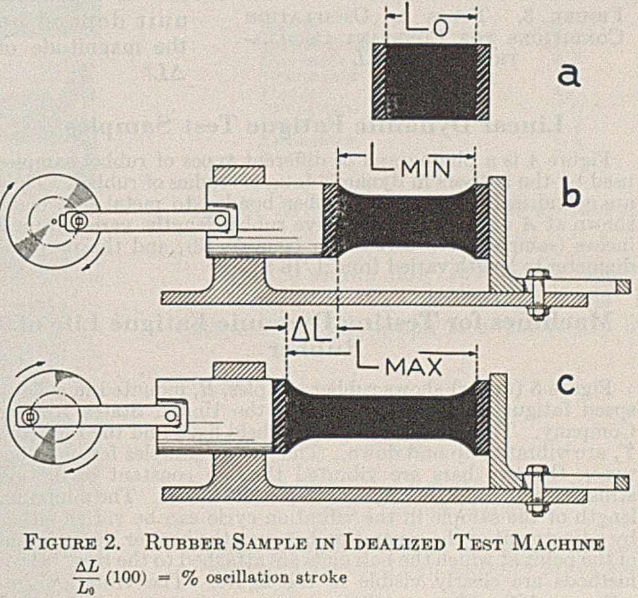

Figure 2. Rubber Sample in Idealized Test Machine

$$\frac{\Delta L}{L_0}(100) = \%\ \text{oscillation stroke}$$

$$\frac{L_{\text{min.}} - L_0}{L_0}(100) = \%\ \text{minimum strain} \begin{cases} + \text{ extension} \\ - \text{ compression} \end{cases}$$

ΔL. The actual fatigue machines used in the authors' experimental testing are designed so that ΔL and $L_{\text{min.}}$ can be varied independently.

In the following discussion "per cent oscillation stroke" and "per cent minimum strain" are mentioned. In order to comprehend the significance of the fatigue data it is necessary that these variables be clearly understood, for in the final analysis they do determine the fatigue life of a sample.

$$\%\ \text{minimum strain} = \frac{L_{\text{min.}} - L_0}{L_0} \times 100$$

$$\%\ \text{oscillation stroke} = \frac{L_{\text{max.}} - L_{\text{min.}}}{L_0} \times 100 = \frac{\Delta L}{L_0} \times 100$$

These definitions involve three specific lengths of the sample (L_0, $L_{\text{max.}}$, and $L_{\text{min.}}$) and are merely certain deformations expressed as percentages of the free unstrained length of the rubber.

Four different types of oscillation conditions for a constant oscillation stroke, ΔL, are illustrated in Figure 3. (*a* shows a compression vibration cycle in which the maximum length in the imposed vibration is less than the free unstrained length of the sample. *b* shows a compression-extension vibration cycle in which $L_{\text{min.}}$ is less than L_0 and $L_{\text{max.}}$ is greater than L_0. *c* shows an oscillation condition in which $L_{\text{min.}}$ is equal to L_0 and $L_{\text{max.}}$ is greater than L_0. *d* shows an extension oscillation cycle in which both $L_{\text{min.}}$ and $L_{\text{max.}}$ are greater than L_0.

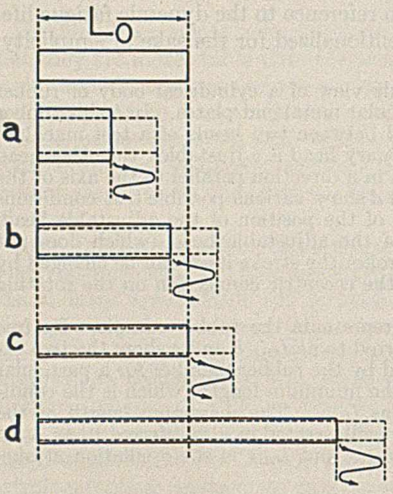

FIGURE 3. TYPES OF OSCILLATION CONDITIONS FOR CONSTANT OSCILLATION STROKE ΔL

The two fundamental problems that have been investigated quantitatively are: (1) If ΔL is kept constant, how does the fatigue life of a rubber unit depend on $L_{\text{min.}}$, for any value of $L_{\text{min.}}$ ranging from high compression to any possible extension? (2) If $L_{\text{min.}}$ is kept constant, how does the dynamic fatigue life of a rubber unit depend on the magnitude of ΔL?

Linear Dynamic Fatigue Test Samples

Figure 4 is a photograph of different types of rubber samples used by the authors in dynamic fatigue studies of rubber. They are cylindrical dumbbells of rubber bonded to metal bolt ends, shown at *A* and *B*. The effective rubber lengths varied from 2 inches (sample 1) to 0.125 inch (sample 13), and the ratios of diameter to length varied from 1/16 to 8.

Machines for Testing Dynamic Fatigue Life of Rubber

Figure 5 (upper) shows rubber samples, *R*, mounted in a slow-speed fatigue machine designed by the United States Rubber Company. The bottom bars, *B*, are held fixed and the top bars, *T*, are vibrated up and down. The rubber samples fastened between the two bars are vibrated through constant oscillation strokes which can have any value up to 3.5 inches. The minimum length of the sample in the vibration cycle can be varied either by adjustment of the separation between the bars or by variation of the point at which the bolt ends are attached to the bars. Both methods are clearly visible in the figure. The vibration frequency is 180 cycles per minute.

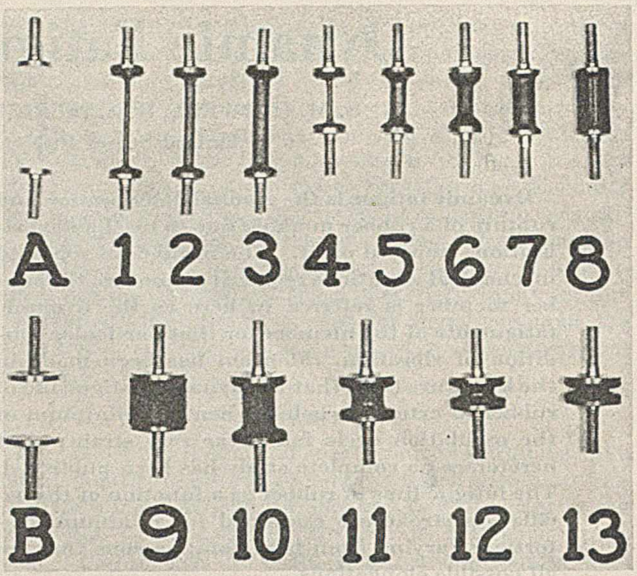

FIGURE 4. TYPES OF RUBBER SAMPLES USED IN LINEAR DYNAMIC FATIGUE TESTS

Figure 5 (lower) shows rubber samples, *R*, mounted in a high-speed dynamic fatigue machine also designed by the United States Rubber Company. The two outer circular heads, *O*, are held fixed and the two inner circular heads, *I*, so-called "wobble plates", are mounted on a shaft arranged to give a nutational motion to the heads, which in turn vibrate all the rubber samples back and forth along their own lengths. The minimum length of the sample in its vibration cycle can be varied by alteration of the separation of the plates, by the screw adjustment shown, or by variation of the point at which the bolt ends are attached to the plates. The machine is adjusted for a 0.5-inch stroke and vibrates at 3600 cycles per minute.

Figure 6 shows a DeMattia fatigue machine with rubber samples, *R*, being vibrated between a stationary head, *S*, and an eccentric driven head, *C;* this fatigue machine has a frequency of vibration of 660 cycles per minute; its stroke can have any value up to 2 inches. The fatigue machine on the right is another high-speed dynamic fatigue machine similar to the high-speed machine shown in Figure 5 (lower) but with a 0.25-inch stroke.

General Nature of Linear Dynamic Fatigue Life Curve

The general nature of the dynamic fatigue life curve for small oscillation strokes, say of the order of 25 per cent, is illustrated in Figure 7. The per cent linear strain at the minimum length in the oscillation is plotted as abscissa. The number of cycles of vibration necessary to completely rupture the rubber—that is, its dynamic fatigue life—is plotted in arbitrary units as ordinate. The important feature of the dynamic fatigue life curve is that the rubber under linear vibrations exhibits a minimum dynamic fatigue life in the region where $L_{\text{min.}} = L_0$—that is, where the return stroke brings the sample back to a condition of zero strain. This minimum life is bounded both in compression and extension by regions of greater fatigue life. The general nature of the curve, a minimum bounded on two sides by maxima, remains the same whether the dynamic fatigue life is plotted as the number of cycles to break the rubber completely into two parts or is plotted as the number of cycles to produce a visible crack in the rubber.

Mention has been made in published articles (*1–5*) that the mechanical fatigue resistance of rubber is less in extension when the minimum of the oscillation falls near zero strain. However, no complete study, as given in the present paper, has been published in which the fatigue lives of rubber have been investigated throughout the compression-extension region as a function of the strain or stress limits.

Linear Dynamic Fatigue Life Curves for a 50 Durometer Stock

Figure 8 is a plot of experimental results obtained on a rubber stock which has a reading of 50 on a type A Shore durometer. The data are for rubber worked indoors in artificial lighting and in the absence of oil, grease, or other deteriorating chemical agents. The per cent linear strain at minimum length in the oscillation is plotted as abscissa. The dynamic fatigue life in terms of the number of cycles for complete rupture is plotted as ordinate on a logarithmic scale. On a linear scale the difference in height between each maximum and its corresponding minimum would be greatly enhanced. For the 25 per cent oscillation, for example, the fatigue life at the minimum is about 6,000,000 cycles, while at the maximum in the extension region it is over 600,000,000 cycles or more than 100 times as great. The graph shows results for a series of different constant oscillation strokes varying from 25 to 350 per cent. Each experimental point represents numerical averages of from 1 to 20 sample breaks. The graph itself contains results on 450 samples of the 50 Shore durometer stock.

For small oscillation strokes, such as 25 or 50 per cent, there are two maximum fatigue regions, one in extension and the other in compression.

For large oscillations—for example, 300 per cent—there is no definite compression maximum.

For a given minimum strain length, the larger the oscillation stroke, ΔL, the lower the dynamic fatigue life of the rubber.

The fatigue life hump in the extension region shifts towards the origin as the oscillation stroke is increased.

This last point is partly due to choice of variables, since for a given stock the per cent elongation at break is a fairly definite quantity and as the oscillation stroke increases the $L_{\text{min.}}$ for which there will be a break in the first cycle decreases. No corrections have been made in this graph for rubber temperature variations resulting from fatiguing at different frequencies or from fatiguing samples of different sizes or shapes. However, when such corrections are made to, say, a rubber temperature of 100° F., the general nature of the curves remains the same.

All rubber stocks considered (which include stocks of hardnesses varying from 30 to 80 Shore durometer, type A) have similar fatigue life curves for constant strain conditions of oscillation. In general, for the same strain conditions of oscillation a harder rubber stock will have a lower fatigue life than a softer stock.

The compound formula for the 50 durometer stock whose experimental dynamic fatigue life curves are given in Figure 8 is the following:

Rubber	100
Carbon black	39
Zinc oxide	5.5
Stearic acid	1.5
Pine tar	4
Antioxidant	0.6
Retarder	0.2
Accelerator	0.8
Sulfur	2.9

Effect of Temperature on Dynamic Fatigue Life

Figure 9 shows how the temperature of the rubber during oscillation affects its fatigue life. The graph is a composite one

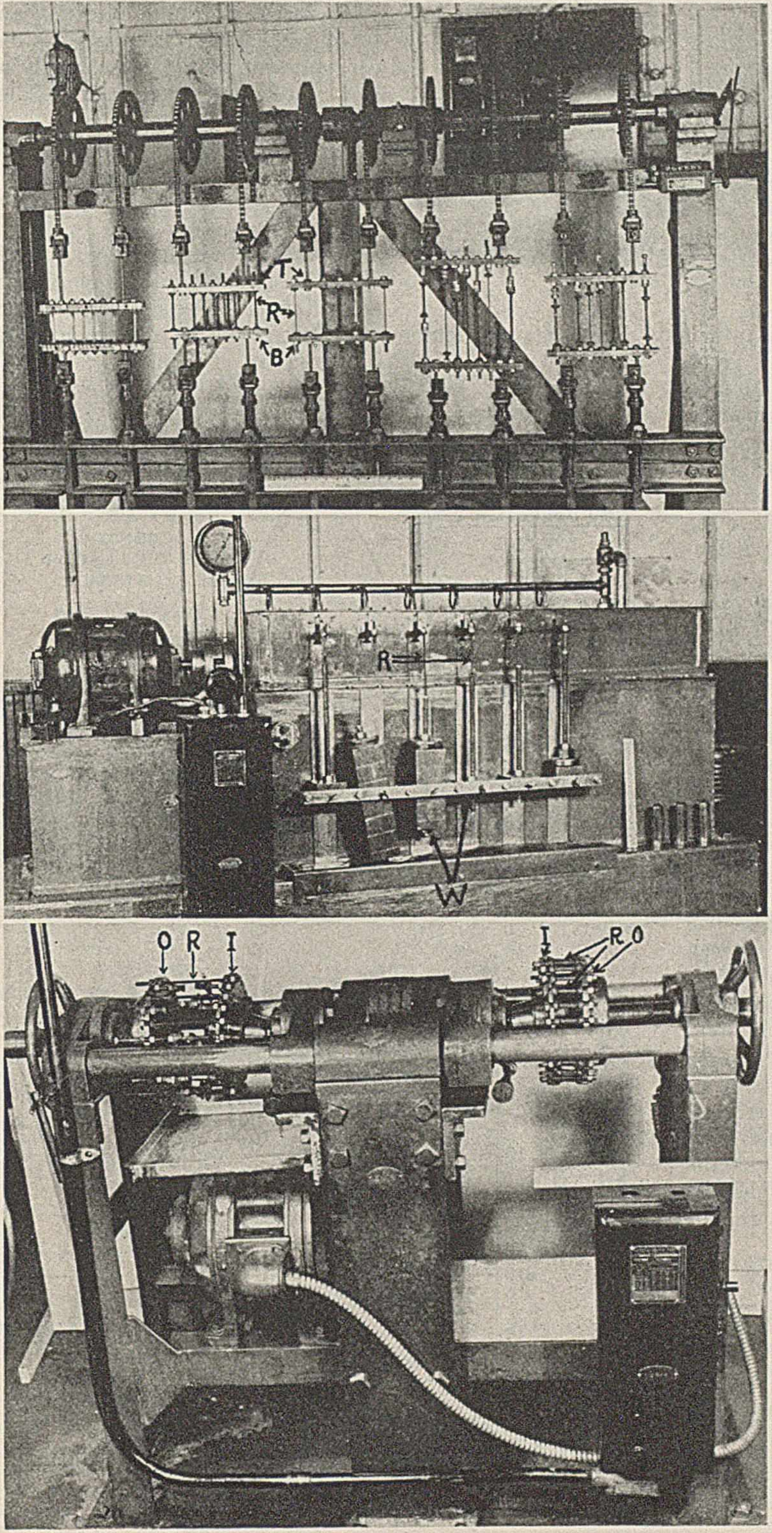

FIGURE 5

(*Upper*) RUBBER SAMPLES MOUNTED IN SLOW-SPEED FATIGUE MACHINE

(*Center*) RUBBER SAMPLES MOUNTED IN HIGH-SPEED CONSTANT-LOAD FATIGUE MACHINE

(*Lower*) RUBBER SAMPLES MOUNTED IN HIGH-SPEED DYNAMIC FATIGUE MACHINE

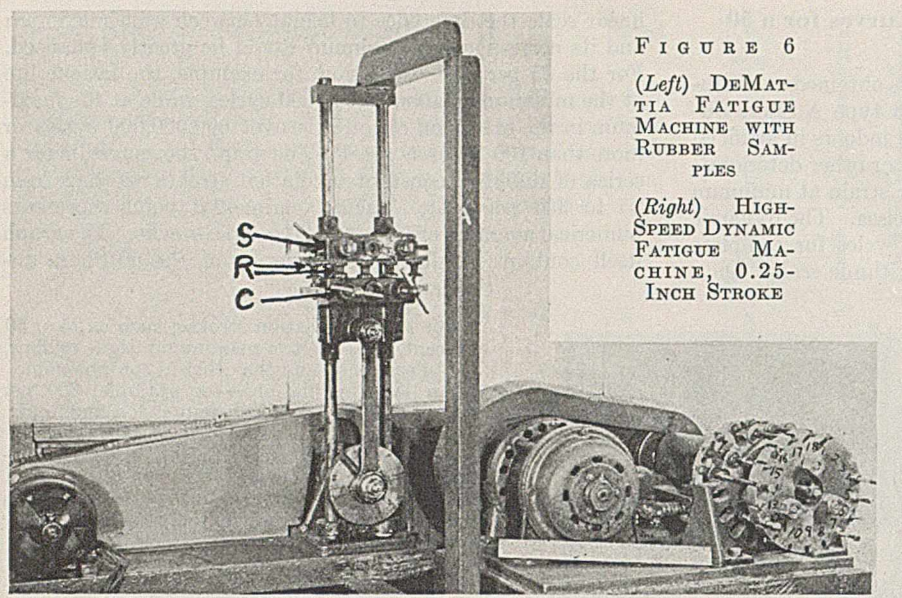

FIGURE 6

(*Left*) DEMATTIA FATIGUE MACHINE WITH RUBBER SAMPLES

(*Right*) HIGH-SPEED DYNAMIC FATIGUE MACHINE, 0.25-INCH STROKE

plotted to cover most of the rubber stocks with which the authors worked. The ratio of fatigue life at a given temperature to that at 100° F. is plotted as ordinate along a logarithmic scale. The temperature of the rubber is plotted as abscissa. The ordinate of the graph, in other words, gives the factor by which the fatigue life of rubber vibrating at a rubber temperature of 100° F. must be multiplied in order to give the fatigue life which would result for rubber vibrating under the same oscillation conditions but at the rubber temperatures given along the abscissa.

The temperature of the rubber under the imposed vibration has a pronounced effect on its fatigue life. Consider a sample vibrating under certain oscillation conditions and at a rubber temperature of 100° F. It will have a given fatigue life corresponding to the ratio =1. If an identical sample is vibrating under the same oscillation conditions but at a much higher rubber temperature, its fatigue life will be less because its deterioration results from several causes. There is first the effect which would result from merely the vibration at 100° F. Then there is the deterioration due to heat aging which would result from keeping the sample at this high temperature without vibration. The total deterioration in all probability is not the sum of these two parts. For example, there may be an interaction between temperature and oscillation which alters the amount of deterioration. Since the relative importance of these variables as well as their interaction cannot be given an evaluation applicable to all cases of rubber testing and compounding, the ratio for high temperatures is indicated as a broad band in Figure 9. Likewise, in the low-temperature region a broad band is also plotted. At the low temperatures the fatigue life depends, among other things, upon the chill characteristics of the rubber stock and the total time during which the rubber member is being fatigued at the low temperature.

Linear Dynamic Fatigue Life under Constant Load Conditions

Figure 5 (center) shows a high-speed constant-load fatigue machine which vibrates the rubber samples at 1800 cycles per minute. The oscillation stroke on this machine can be varied from 0.125 to 0.75 inch. In this type of testing the rubber samples, *R*, are loaded with dead weights, *W*. The top of the rubber sample is vibrated up and down, the weights remaining stationary, owing to the mismatching of frequencies—that is, the frequency of the imposed vibration is very much greater than the natural mechanical frequencies of the weights sprung on the rubber samples.

The distinction between this type of fatigue testing and the constant-strain fatigue testing is that in this case the rubber samples are allowed to drift, or extend in length with time, as they are being dynamically fatigued. However, the general nature of the fatigue life curves obtained under dead loading is similar to the fatigue life curves for constant strain oscillation; and the dynamic fatigue life under "constant load" fatigue conditions can be calculated from data obtained on constant-strain fatigue if changes in length accompanying dynamic drift are taken into account.

Dynamic Fatigue Life of Rubber Vibrated in Shear

Until now we have considered only the dynamic fatigue of rubber worked under linear strains. Similar dynamic fatigue relations have been found for rubber vibrated in shear.

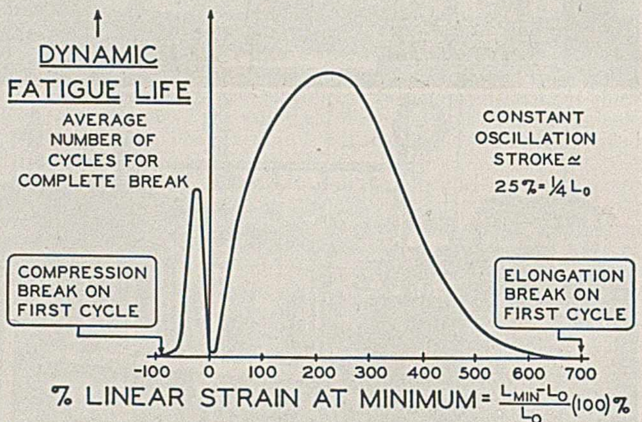

FIGURE 7. DYNAMIC FATIGUE LIFE CURVE FOR SMALL OSCILLATION STROKES

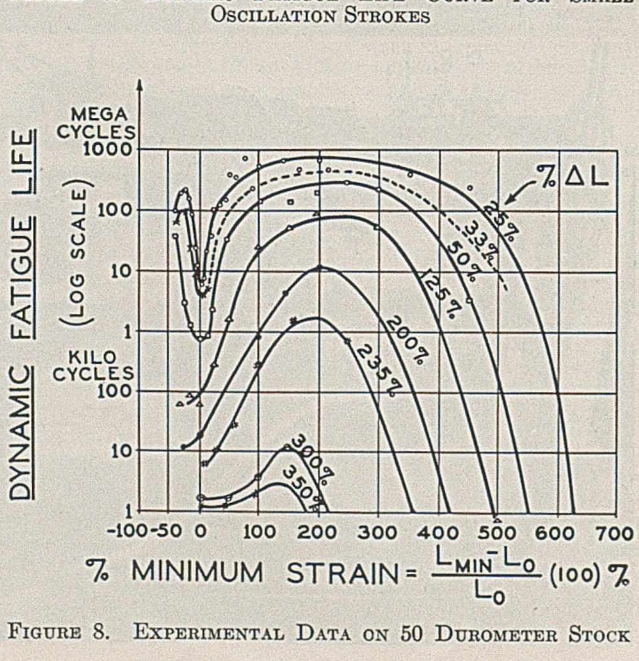

FIGURE 8. EXPERIMENTAL DATA ON 50 DUROMETER STOCK

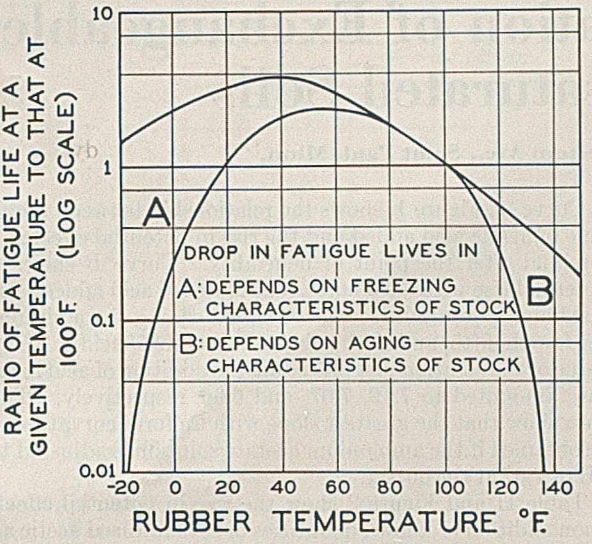

FIGURE 9. EFFECT OF TEMPERATURE ON DYNAMIC FATIGUE LIFE

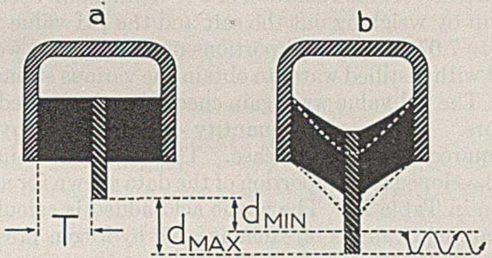

FIGURE 10. RUBBER VIBRATED IN SHEAR

$$\% \text{ minimum shear} = \frac{d_{\text{min.}}}{T}\ (100)$$

$$\% \text{ maximum shear} = \frac{d_{\text{max.}}}{T}\ (100)$$

a in Figure 10 is a sketch of a double shear unit which consists of two identical rectangular bodies of rubber of thickness *T* bonded between two outer metal plates and a central metal plate. If the central plate is displaced a distance *d* relative to the two outer plates the rubber is put in shear; and we express the magnitude of the shear deflection either as the shear ratio d/T or as the shear percentage (d/T) 100. *b* represents the two oscillation extremes of such a unit vibrated in shear. The minimum deflection in the shear cycle is $d_{\text{min.}}$; the maximum, $d_{\text{max.}}$. The shear cycle is then specified as one of vibration between the shear percentages $(d_{\text{min.}}/T)$ 100 and $(d_{\text{max.}}/T)$ 100.

Figure 11 illustrates results obtained on shear samples of the 50 durometer stock discussed above. The two outer metal plates were held fixed, and the central plate was vibrated back and forth along its length between two extremes as shown by the dotted contours. The oscillation length was a 50 per cent shear oscillation. In shear mountings the rubber may be placed in lateral strains which are normal to the center plate. Three conditions of lateral strain are shown in the figure: 0 per cent, 12.5 per cent compression, and 25 per cent extension. The first row corresponds to a −25 to +25 per cent shear cycle; the second row, to a 0 to 50 per cent shear cycle; and the third row, to a 75 to 125 per cent shear cycle.

The striking observation about these test data is that the results in shear fatigue are entirely in accord with what would have been predicted from the linear fatigue data.

Consider samples *B* and *C*. *B*, vibrated between 0 and 50 per cent shear, had a fatigue life of 1,000,000 cycles. *C*, vibrated between 75 and 125 per cent shear, had a fatigue life of 15,000,000 cycles. The shear oscillation cycle for both samples was one of 50 per cent. *C* had a much greater fatigue life than did *B*. This is due to the fact that the rubber elements in *C* were in strain at all times during the shear cycle, whereas those in *B* went back to a condition of zero strain once each cycle. Essentially the elements in *C* were working up on the linear extension fatigue hump, whereas those in *B* were being vibrated at the linear fatigue minimum.

In sample *A* the shear cycle was one from −25 to +25 per cent, a total shear cycle of 50 per cent. The fatigue life of *A* was seven times that of *B*. Actually *A* was subjected to an alternating 25 per cent shear cycle; once from 0 per cent shear to −25 per cent shear, then once from 0 per cent shear to +25 per cent shear. The double 25 per cent shear cycles are essentially two repeated 25 per cent shear cycles. A shear unit of this same 50 durometer stock vibrating through a single shear cycle of 0 to 25 per cent shear has a fatigue life of about 14,000,000 cycles. It is therefore consistent that *A*—each of whose cycles represents two vibrations from 0 to 25 per cent—should last only 7,000,000 cycles.

Sample *D* had a greater life than *A*; *E* had a greater life than *B*. The reason is that the rubber elements were being vibrated essentially with a minimum strain which falls in the compression region, and on the basis of linear fatigue data *D* and *E* should have the higher fatigue lives. In *F*, however, the dynamic fatigue life was considerably less than in *C*. In *F* the rubber elements which under no shear were under lateral compression were essentially relieved from the compression by the extension resulting from the higher shear; and the rubber elements were being worked in a low dynamic fatigue region near the zero of strain.

Sample *G* had a higher fatigue life than *A*; *G* should have a higher life because the rubber elements were always under extension strain during the vibration. Finally, *I* had a higher dynamic fatigue life than did *C*. The rubber elements in *I* were in higher extension than in case *C*; in other words, the shear strain and the lateral extension strain essentially added to place the rubber unit in a more favorable fatigue region.

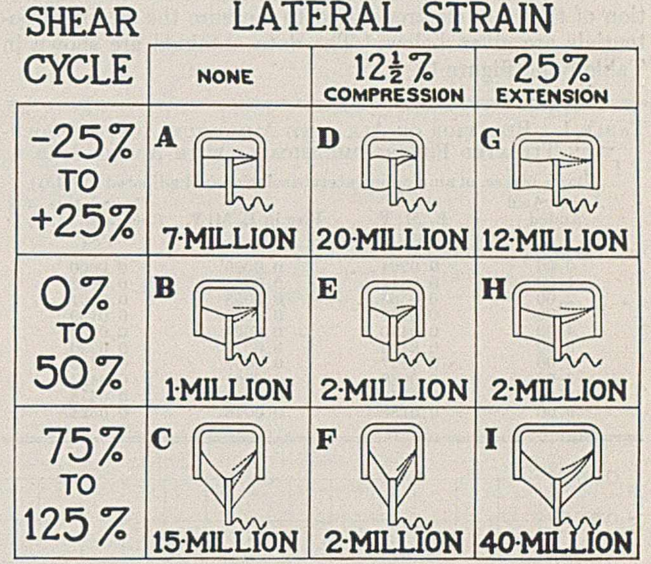

FIGURE 11. DYNAMIC FATIGUE RESULTS ON SHEAR SAMPLES OF 50 DUROMETER STOCK

Many theories can be devised to explain the way the dynamic fatigue properties of rubber vary with the strain and the strain oscillation conditions, but such theories are still conjectures.

Literature Cited

(1) Busse, W. F., IND. ENG. CHEM., 26, 1194 (1934).
(2) Cassie, Jones, and Naunton, *Trans. Inst. Rubber Ind.*, 12, 49 (1936).
(3) Cooper, L. V., IND. ENG. CHEM., Anal. Ed., 2, 392 (1930).
(4) Jenkin, C. F., "Report on Materials of Construction Used in Aircraft and Aircraft Engines", London, H. M. Stationery Office, 1920.
(5) Rainier, E. T., and Gerke, R. H., IND. ENG. CHEM., Anal. Ed., 7, 368 (1935).

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

Potentiometric Determination of Exchangeable Hydrogen in Unsaturated Soils

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A SOIL is considered as being in a state of base unsaturation when its colloidal complex contains hydrogen which can be replaced by other base metals. Base unsaturation has long been acknowledged by soil scientists. Robinson (*4*) states that, under field conditions, unless a soil is in equilibrium with an excess of calcium carbonate, the content of exchangeable bases may fall below that representing saturation. The total exchange capacity of an unsaturated soil, to be correct, must necessarily include the exchangeable hydrogen expressed as milligram equivalents in the same manner as the other exchangeable base metals.

Development of the Method

In this method, the soil is treated with a solution of ammonium acetate which liberates the exchangeable hydrogen as acetic acid. Advantage is taken of the behavior that a neutral ammonium acetate solution exhibits as acetic acid is added to it. Data were first obtained to enable the author to observe the difference in potential effected by adding acetic acid to a solution of ammonium acetate made alkaline with ammonium hydroxide at the outset. The details and operation of the glass electrode used to measure the electrical potentials are given below. The data obtained are shown in Table I and Figure 1.

TABLE I. BEHAVIOR OF ALKALINE AMMONIUM ACETATE SOLUTION TITRATED POTENTIOMETRICALLY WITH ACETIC ACID

[Basis, 500 cc. of ammonium acetate solution (pH adjusted to 7.45)]

Acetic Acid Added *Cc.*	E. M. F. *Volt*	Rise in E. M. F. *Volt*	Cumulative Rise in E. M. F. *Volt*
0.00	0.0264	0.0000	0.0000
1.00	0.0312	0.0048	0.0048
2.00	0.0365	0.0053	0.0101
3.00	0.0423	0.0058	0.0159
4.00	0.0490	0.0067	0.0226
5.00	0.0560	0.0070	0.0296
6.00	0.0627	0.0067	0.0363
7.00	0.0688	0.0061	0.0424
8.00	0.0740	0.0052	0.0476
9.00	0.0788	0.0048	0.0524

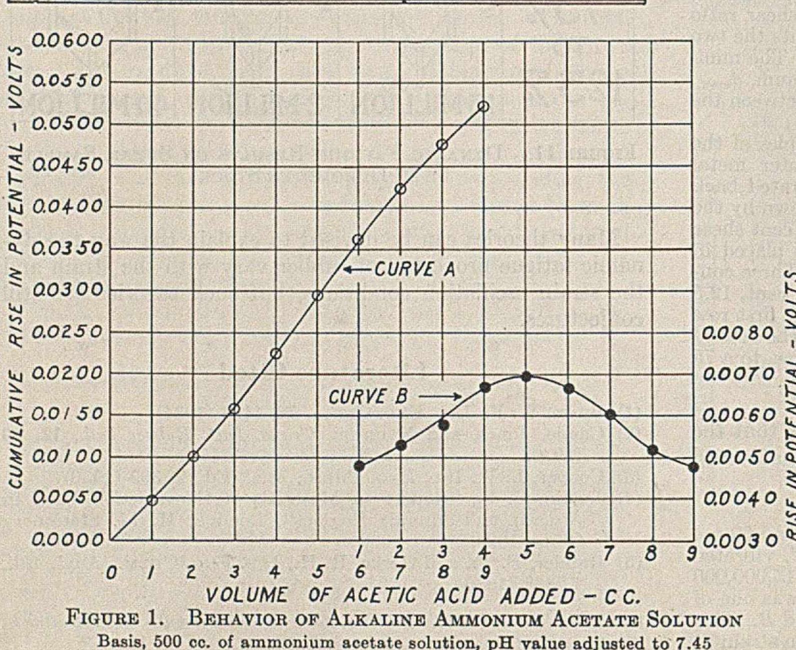

FIGURE 1. BEHAVIOR OF ALKALINE AMMONIUM ACETATE SOLUTION
Basis, 500 cc. of ammonium acetate solution, pH value adjusted to 7.45

Curve *A*, Figure 1, shows the relationship between the volume of acetic acid added and the rise in potential effected before and after the point of neutrality. Curve *B* shows the potential rise with each cubic centimeter of acid added. The maximum potential rise was obtained during the addition of the fourth, fifth, and sixth cubic centimeters of acid. The pH value of the solution just preceding the addition of acid in each case amounted to 7.19, 7.07, and 6.96, respectively. These data show that the greatest slope with uniform curvature will be obtained if the ammonium acetate solution is adjusted to a pH of 7.07 at the outset.

Table II and Figure 2 show the rise in potential effected upon addition of known quantities of standardized acetic acid to ammonium acetate solutions of various strengths. In each case the pH value of the ammonium acetate solution was adjusted to 7.07 with ammonium hydroxide before the titration was started. A stock solution of 2 *N* ammonium acetate was made up by weighing out the salt and the pH value was adjusted to 7.07. Measured portions of this solution were then diluted with distilled water to obtain the various strengths desired. The pH value was again checked and adjusted to 7.07 as before. A very small quantity of ammonium hydroxide was required in the second case. The curve shown in Figure 3 was developed from a portion of the data shown for a normal solution in Table II. The acetic acid added is calculated to milligram equivalents of exchangeable hydrogen present per 100 grams of soil when leaching a 25- and 50-gram sample.

The data shown in Table II and Figure 2 present a very interesting study. At the outset, the rise in potential obtained per cubic centimeter of acid added varied in an inverse manner; however, as the titration was continued the rise in potential reached the same value in all cases. It is evident that solutions weaker than 1 *N* will give a larger potential rise per milligram equivalent of hydrogen exchanged. Although a 1 *N* solution was used by the author for all determinations made thus far, a solution weaker than 1 *N* can, no doubt, be employed to advantage on sandy soils having a low total exchange capacity. If a group of soils containing a large amount of exchangeable hydrogen are to be examined, only the upper portion of the curve will be used. In this case an advantage would be gained by adjusting the initial pH value of the ammonium acetate leaching solution to a point higher than 7.07 (Table I and Figure 1).

The procedure adopted by the author was to digest a 25- or 50-gram sample of air-dried soil with 300 cc. of 1 *N* ammonium acetate solution having a pH of 7.07 for a period of at least 24 hours. The solution was then filtered from the soil by means of a Büchner funnel and transferred to a 500-cc. volumetric flask. During the filtering operation the Büchner funnel was covered with a watch glass to protect the ammonium acetate solution from the atmosphere of the laboratory. The soil on the filter was then washed with 50-cc. portions of the same ammonium acetate solution until a volume of 500 cc. was reached, care being taken not to allow the washing operation to proceed too rapidly. The solution in the volumetric flask was mixed well by shaking and a small portion used to obtain a voltage reading on the glass electrode. The milligram equivalents of exchangeable hydrogen present in the

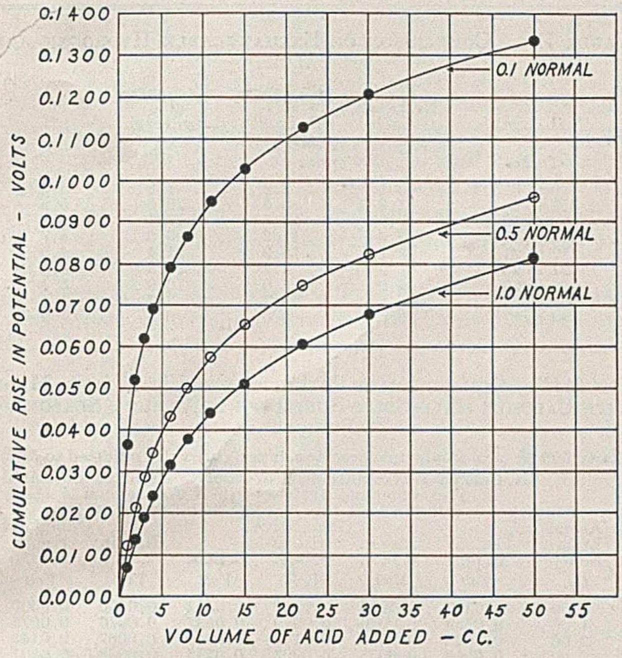

FIGURE 2. RISE IN POTENTIAL ON ADDITION OF ACETIC ACID

Titrations made with N acetic acid on 500-cc. volume of ammonium acetate solution, pH value adjusted to 7.07

TABLE II. BEHAVIOR OF NEUTRAL SOLUTIONS OF AMMONIUM ACETATE TITRATED POTENTIOMETRICALLY WITH ACETIC ACID

[Basis, 500 cc. of ammonium acetate solution (pH adjusted to 7.07)]

N Acetic Acid Added	*N* Solution		0.5 *N* Solution		0.1 *N* Solution	
	Rise in e. m. f.	Cumulative rise in e. m. f.	Rise in e. m. f.	Cumulative rise in e. m. f.	Rise in e. m. f.	Cumulative rise in e. m. f.
Cc.	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1.00	0.0073	0.0073	0.0125	0.0125	0.0370	0.0370
2.00	0.0067	0.0140	0.0093	0.0218	0.0153	0.0523
3.00	0.0058	0.0198	0.0073	0.0291	0.0097	0.0620
4.00	0.0046	0.0244	0.0057	0.0348	0.0070	0.0690
6.00	0.0076	0.0320	0.0089	0.0437	0.0103	0.0793
8.00	0.0060	0.0380	0.0067	0.0504	0.0072	0.0865
11.00	0.0065	0.0445	0.0078	0.0582	0.0082	0.0947
15.00	0.0072	0.0517	0.0073	0.0655	0.0080	0.1027
22.00	0.0091	0.0608	0.0095	0.0750	0.0098	0.1125
30.00	0.0075	0.0683	0.0075	0.0825	0.0082	0.1207
50.00	0.0130	0.0813	0.0133	0.0958	0.0130	0.1337

soil were then obtained from a curve similar to that shown in Figure 3. Since nothing was added or taken away from the solution being examined, it could be returned to the volumetric flask for use in the determination of the other exchangeable bases.

If a 25-gram sample of soil were treated as described above with 500 cc. of the 1 N ammonium acetate solution used in obtaining the data for the curves shown in Figure 3, and the potential rise obtained amounted to 0.0140 volt, the milligram equivalents of hydrogen exchanged per 100 grams of soil would be 8.0. A new curve should be made for each batch of ammonium acetate solution that is made up, as a slight difference in the inital pH value affects the slope of the curve obtained. This fact is clearly brought out by Table I and Figure 1. A variation in the strength of the solution also has an effect on the slope of the curve, as is shown by Table II and Figure 2.

Discussion

Numerous methods for this determination have been suggested and published in recent soil literature. These methods can be placed in two general classes.

1. The exchangeable hydrogen is determined by difference. The exchangeable bases and hydrogen existing on the colloidal complex are removed by treatment of the soil with a solution containing a cation capable of entering the complex other than any present in an exchangeable state originally. The amounts of exchangeable base metals thus removed are then determined quantitatively and expressed as milligram equivalents per 100 grams of soil. The total exchange capacity is determined by analyzing the soil quantitatively for the amount of cation placed on the complex and this is also expressed as milligram equivalents per 100 grams of soil. The amount of exchangeable hydrogen is then obtained by subtracting the former from the latter.

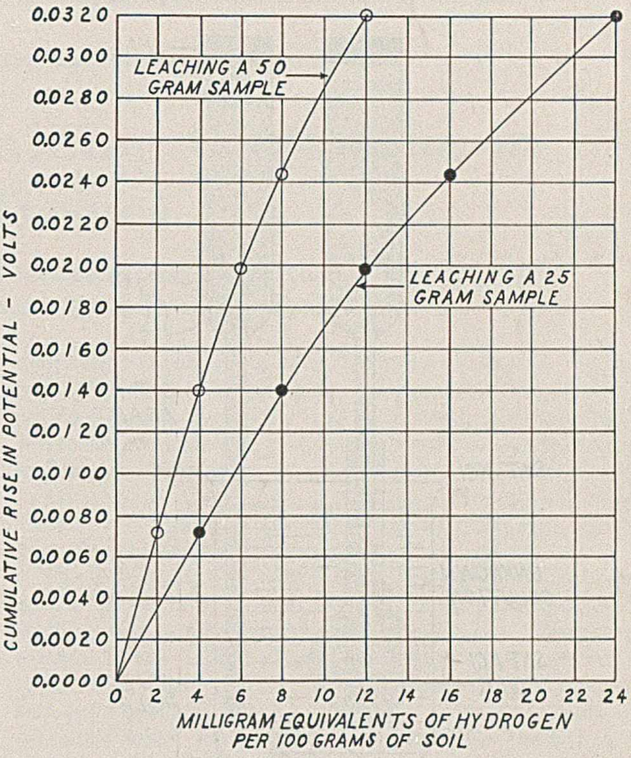

FIGURE 3

While methods of this type are conducive to good results when followed by a competent analyst, they embody some difficulties and undesirable features. All the exchangeable bases must be quantitatively determined before the determination of hydrogen can be attempted. The excess exchange reagent must be completely removed from the soil without removing any of the ions on the exchange complex before the total exchange capacity can be determined. Any errors incurred in the analytical work are also reflected on the exchangeable hydrogen. Included in the methods of this type are those of Kelley and Brown (*2*) and some of those reviewed by Parker (*3*).

2. The exchangeable hydrogen is determined directly. The exchangeable hydrogen together with the other exchangeable cations is brought into solution as before by treatment of the soil with a solution containing a suitable cation followed by a titration. In a method of this type, the solution containing the exchange reagent must exhibit some buffering properties and hence the titration be carried out by means of a potentiometer and suitable electrodes. If this solution undergoes a marked change in pH through the liberation of hydrogen ions, some of the sesquioxides present may be attacked and the determination will run correspondingly low. If the leaching solution contains a measured amount of free base, the excess of which is to be determined after neutralization of the liberated hydrogen ions, some of the secondary

silica present will be attacked and the results obtained will be correspondingly high.

Included in the methods of this type are those of Hissink (*1*) and Schollenberger (*5*), and some of the methods reviewed by Parker (*3*). Schollenberger (*5*) advocates treatment of the soil with a neutral 1 *N* solution of ammonium acetate and titration of the acetic acid formed with standardized ammonium hydroxide using a potentiometer and quinhydrone electrodes.

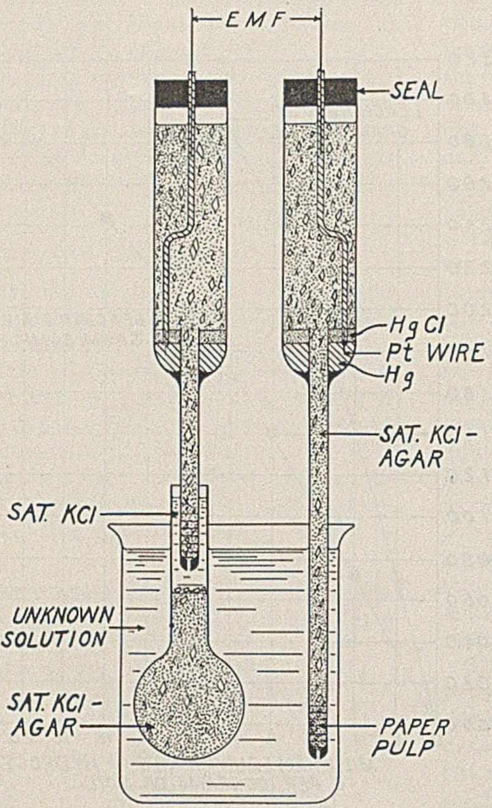

FIGURE 4. GLASS ELECTRODE ASSEMBLY

The method described herein is similar to the latter mentioned in that the same exchange reagent is employed; however, the potentiometric titrations are carried out using a glass electrode and only one potentiometric titration is required for a large number of samples.

In Table III are shown the results obtained on the soils of a profile from the Red River Valley region in Minnesota. Note the agreement between the pH values and the per cent of the total exchangeable material which was found to be hydrogen. A 25-gram sample of soil was treated with a total of 500 cc. of 1 *N* ammonium acetate solution in each case.

Description and Operation of Equipment

This discussion is limited to the glass electrode and potentiometric equipment used. All other equipment required can be found in an ordinary chemical laboratory.

Figure 4 shows the glass electrode circuit used to produce the electrical potentials in the various solutions tested. The potentials were measured on a Leeds & Northrup type K potentiometer which was brought into balance with the aid of a Leeds & Northrup type R suspension galvanometer and light scale.

TABLE III. COMPARISON OF EXCHANGEABLE HYDROGEN AND pH VALUES

Soil Depth	Total Exchange Capacity	Exchangeable Hydrogen	Exchangeable Hydrogen	pH
Inches	*Milligram equivalents per 100 grams*		%	
0 to 3.5	60.1	2.9	4.8	6.9
3.5 to 9	41.3	8.5	20.6	5.5
9 to 13	47.0	12.7	27.1	4.7
13 to 17	47.5	11.2	23.6	4.7
17 to 21	47.7	10.2	21.4	4.8
21 to 25	47.3	8.2	17.3	4.9
25 to 29	46.0	5.0	10.9	5.7
29 to 33	45.8	1.7	3.7	7.1
33 to 37	39.0	0.0	0.0	7.9

TABLE IV. COMPARISON OF POTENTIOMETRIC TITRATIONS MADE WITH CALOMEL HALF-CELLS SUBJECTED TO VARIOUS SEASONING PERIODS

[Basis, 500 cc. of *N* ammonium acetate solution (pH value adjusted to 7.07)]

	Calomel Half-Cell Immersed in *N* Ammonium Acetate Solution for 1 Day			Calomel Half-Cell Immersed in *N* Ammonium Acetate Solution for 12 Days		
N Acetic Acid Added	E. m. f.	Rise in e. m. f.	Cumulative rise in e. m. f.	E. m. f.	Rise in e. m. f.	Cumulative rise in e. m. f.
Cc.	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*
0.00	0.0390	0.0000	0.0000	0.0511	0.0000	0.0000
1.00	0.0469	0.0079	0.0079	0.0587	0.0076	0.0076
2.00	0.0538	0.0069	0.0148	0.0654	0.0067	0.0143
3.00	0.0593	0.0055	0.0203	0.0712	0.0058	0.0201
4.00	0.0638	0.0045	0.0248	0.0757	0.0045	0.0246
6.00	0.0716	0.0078	0.0326	0.0834	0.0077	0.0323
8.00	0.0776	0.0060	0.0386	0.0897	0.0063	0.0386
11.00	0.0849	0.0073	0.0459	0.0966	0.0069	0.0455
15.00	0.0922	0.0073	0.0532	0.1039	0.0073	0.0528

The glass electrode was blown very thin and was of such sensitivity that a deflection of five spaces was obtained on the light scale (stationed at a distance of 120 cm., 4 feet, from the galvanometer) when the potentiometer was thrown out of balance 0.0010 volt. The glass electrode and two calomel half-cells were mounted on a stand which was so constructed that the danger of breaking the electrode was eliminated. At first the glass electrode was filled with a saturated solution of potassium chloride. As evaporation took place, crystals of potassium chloride dropped to the bottom. Further evaporation caused a growth of these crystals until eventually they punctured the side of the electrode. A period of about 18 months was the average life of an electrode of this type. The use of agar solution prevents the formation of crystals on the bottom of the electrode and seems to reinforce the thin glass membrane. No polarization difficulties were experienced.

The calomel half-cell forming the liquid junction was made up using a saturated solution of potassium chloride and agar, as is shown in Figure 3, but was immersed in a solution of 1 *N* ammonium acetate for some time before being put into service. In this way equilibrium conditions were established at the liquid junction, and the potentials were constant with no drifting. When not in use, this half-cell was kept immersed in a 1 *N* ammonium acetate solution.

Until this procedure was adopted considerable difficulty was experienced. Table IV shows the potentiometric titration of an ammonium acetate solution when using a calomel half-cell which was immersed in 1 *N* ammonium acetate solution for 24 hours and the same titration carried out on an equal volume of the same solution after the calomel half-cell had been immersed in 1 *N* ammonium acetate solution for 12 days. The temperature of the solution was the same for both titrations.

When the calomel half-cell was first immersed in the ammonium acetate solution, the potential of the system changed 0.0025 volt on standing for a period of 20 minutes. This change in potential was undoubtedly due to the diffusion of ions across the liquid junction. If any current was drawn from the cell a further change was produced. After the calomel half-cell was immersed for 24 hours the potential change on standing for 1 hour was very small and when small amounts of current were drawn from the system there was no apparent change. After the 12-day period the potentiometer could be thrown out of balance as much as 0.5 volt without changing the potential of the system. During the 11-day period between titrations, the initial potential of the system changed 0.0121 volt. The ammonium acetate solution was stored in a well-stoppered bottle and did not change appreciably, its pH value being checked before each titration was started.

When taking readings, the potentiometer was brought into balance in the regular way; however, the zero point was always confirmed by throwing the potentiometer out of balance equal amounts on each side (usually 0.0010 volt) to note if equal deflections on the light scale were obtained. When once the system was set up, readings were obtained with no more effort than is required to weigh a sample of material on a Chain-omatic balance.

Acknowledgment is given to F. J. Alway and C. O. Rost of the Division of Soils, University Farm, Saint Paul, Minn., for permission to use the division's potentiometric equipment and also to show a portion of the data on a soil profile prior to publication.

Literature Cited

(1) Hissink, D. G., *Trans. Faraday Soc.*, 20, 551 (1924).
(2) Kelley, W. P., and Brown, S. M., "Proceedings and Papers of First International Congress of Soil Science", p. 491, 1928.
(3) Parker, F. W., *Ibid.*, p. 164.
(4) Robinson, G. W., "Soils, Their Origin, Constitution and Classification", 2nd ed., p. 111, New York, D. Van Nostrand Co., 1936.
(5) Schollenberger, C. J., *Soil Sci.*, 30, 161–73 (1930).

A Method for Determining Glutamine in Plant Tissues

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Glutamine is converted to ammonia and pyrrolidone carboxylic acid by hydrolysis in neutral solution. Conditions have been ascertained under which this acid can be quantitatively extracted from the mixture of plant tissue components. On being hydrolyzed, pyrrolidone carboxylic acid is converted into glutamic acid; accordingly the increase in amino nitrogen during this operation furnishes a measure of the glutamine amide nitrogen originally present in the tissue. The details of a method to determine glutamine, founded on these reactions, have been developed and it is shown that satisfactory results are secured. The new procedure is not proposed as a substitute for the convenient and accurate amide hydrolysis method, but as a more specific means of estimating glutamine when present in small amounts or in especially unfavorable conditions, such as in the presence of a large excess of asparagine or other substances that might interfere with the simpler hydrolytic method.

THE method of determining glutamine, originally proposed by Chibnall and Westall (*1*) and subsequently modified in certain details (*3*), depends upon the complete hydrolysis of this somewhat unstable amide when it is heated to 100° C. for 2 hours at a reaction in the range pH 6 to 7. The ammonia liberated under these conditions has been shown to be a reasonably trustworthy measure of the glutamine amide nitrogen present, and the method leaves little to be desired in most practical cases on the scores of convenience or precision. Nevertheless there are other plant components that liberate ammonia, though usually in small amounts, under the same conditions. Urea and allantoin are two that are found in certain plant species, and asparagine, the other widely distributed plant amide, is not entirely unaffected. Accordingly, if reliance is placed on the determination of the unstable amide nitrogen, the results may be misleadingly high in cases where the proportion of glutamine present is unusually small,[1] and especially in cases where the tissues are unusually rich in asparagine. Furthermore, no account is taken of the possibility that unknown plant components that also interfere with the method may be occasionally encountered.

The development of a procedure which depends on a more specific property of glutamine than the hydrolysis of the unstable amide group therefore seemed desirable. The present method is not suggested as a substitute for the convenient amide hydrolysis method, but to be applied as a confirmation both qualitative and quantitative in cases of doubt, and especially when the proportion of glutamine present is unusually small. It is necessary to emphasize that no method of plant analysis short of the isolation of a characteristic crystalline derivative is thoroughly trustworthy in the present inadequate state of our knowledge of plant tissue composition.

When glutamine is heated with water at pH 6 to 7, hydrolysis of the amide group and ring closure to pyrrolidone carboxylic acid take place. The liberation of ammonia is, so far as is known, precisely quantitative, but the ring closure may not be strictly so. The loss of amino nitrogen has been shown, however, to be at least 98 per cent, and the silver salt of pyrrolidone carboxylic acid has been isolated in an amount equivalent to nearly 90 per cent of that calculated from the amount of amide hydrolysis. The hydrolysate obtained was slightly colored, however, and a trace of brown flocculent precipitate separated on the addition of the first drop of silver nitrate. This suggests the presence of a small amount of some by-product of the reaction (*3*). Consideration of the solubility of the silver salt and the conditions under which it was isolated indicates, however, that the amount of glutamine destroyed by side reactions is, for most purposes, negligible.

Pyrrolidone carboxylic acid is a relatively strong imino acid (pK = 3.32, *5*) that can be quantitatively extracted with ethyl acetate from aqueous solution buffered in the range pH 2 to 3. Furthermore it is easily hydrolyzed, when heated for a

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[1] The petioles of rhubarb leaves furnish a case in point. It is shown in another communication (*4*) that the small amount of glutamine present was overestimated by the hydrolytic method since negative values for the calculated asparagine amide nitrogen were obtained. With the present method, the calculated asparagine amide nitrogen values were very small but positive and there is reason to suppose that they were in fact zero.

Test for Magnesium with *p*-Nitrobenzeneazoresorcinol

The Effect of Diverse Ions

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THE qualitative test for magnesium employing the reagent *p*-nitrobenzeneazoresorcinol, commonly called S. and O. reagent, which produces a sky-blue lake in a magnesium solution made alkaline with sodium hydroxide, was first proposed by Suitsu and Okuma (*6*) who claimed that 0.002 mg. of magnesium can be thereby detected.

Ruigh (*4*) found that excess of ammonium salts destroys the sensitivity of the reagent and that nickel and cobalt interfere by giving somewhat similar blue lakes, and stated that after the removal of the heavy metals by precipitation as sulfides the test is absolutely characteristic. Eegriwe (*1*) corroborated the interference of nickel and cobalt and added chromic ion to the list. Stone (*5*) stated that ammonium salts and organic matter decrease the sensitivity. Newell, Pike, and Ficklen (*3*) claimed that the test is not so specific as might be desired and that the sensitivity is only 2 parts per million. They stated that most of the cations of group II and all those of group III interfere, but that only a few of the anions cause trouble.

Engel (*2*) modified the test by causing a blue stain to be formed on the surface of a casserole upon evaporation of the solution and detected 3×10^{-6} gram of magnesium. His test is valid in the presence of any one or all the common ions met in qualitative analysis. Acetates, tartrates, and ammonium salts do not interfere, but do decrease the sensitivity.

TABLE I. EFFECT OF DIVERSE IONS ON MAGNESIUM TEST
(10 mg. of magnesium present)

Ion	Weight *Mg.*	Result
Aluminum	1000	No interference
Ammonium	100	No interference
	500	No interference
	600	No interference
	650	Slight fading
	700	Slight fading
	750	Interference
Antimonous	1000	No interference
Barium	1000	No interference
Bismuth	1000	No interference
Cadmium	1000	No interference
Calcium	1000	No interference
Chromic	10	Green ppt. interferes
Cobaltous	10	Rose-gray ppt. interferes
Cupric	10	Blue ppt. interferes
Ferric	10	Brown ppt. interferes
Ferrous	10	Green ppt. interferes
Lead	1000	No interference
Manganous	10	Brown ppt. interferes
Mercuric	10	Black ppt. interferes
Mercurous	10	Black ppt. interferes
Nickelous	10	Green ppt. interferes
Potassium	1000	No interference
Silver	10	Brown ppt. interferes
Sodium	1000	No interference
Stannic	1000	No interference
Stannous	1000	No interference
Strontium	1000	No interference
Zinc	1000	No interference
Acetate	1000	No interference
Arsenate	10	Brown ppt. interferes
Arsenite	1000	No interference
Borate	1000	No interference
Bromide	1000	No interference
Carbonate	1000	No interference
Chloride	1000	No interference
Chromate	10	Yellow ppt. interferes
Cyanide	1000	No interference
Fluoride	1000	No interference
Iodide	1000	No interference
Nitrate	1000	No interference
Nitrite	1000	No interference
Orthophosphate	1000	No interference
Oxalate	1000	No interference
Permanganate	10	Purple interferes
Sulfate	1000	No interference
Sulfide	1000	No interference
Sulfite	1000	No interference
Thiocyanate	1000	No interference

The purpose of the present work was to make a further study of ion interference with the test when carried out according to Ruigh's directions (*4*).

Preparation of Solutions

p-Nitrobenzeneazoresorcinol solution was made by dissolving 0.5 gram of the solid reagent in a 1 per cent solution of sodium hydroxide and diluting with the solvent to 100 ml.

Test solutions of the cations were prepared from the chloride, nitrate, or sulfate salts, while the sodium or potassium salts were used for the preparation of the anion solutions. Each milliliter contained 10 mg. of the ion in question.

Procedure

The interference studies were made by mixing a given volume of the diverse ion solution with 1 ml. of a magnesium solution containing 10 mg. of magnesium, adding 1 drop of the *p*-nitrobenzeneazoresorcinol solution, and making the solution alkaline with dilute sodium hydroxide solution. If there was no interference a sky-blue precipitate could be seen. As little as 0.002 mg. of magnesium was easily detected in the absence of interference.

The effects on the test of most of the common ions are shown in Table I.

Discussion

Interference is usually due to the formation by the diverse ion of a colored precipitate which masks the blue produced by the magnesium. Black precipitates are given by mercurous and mercuric ions; brown by silver, manganous, ferric, and arsenate ions; green by chromic, nickelous, and ferrous ions; rose-gray by cobaltous ions; yellow by chromate ions; and deep blue by cupric ions. Only arsenate, chromate, and permanganate of the twenty anions tested interfere. The white precipitates formed by aluminum, antimonous, bismuth, cadmium, stannic, stannous, and zinc ions do not interfere because the blue magnesium lake is not masked by white. Ammonium ion does not cause trouble unless present in considerable excess. Sixty times as much ammonium as magnesium by weight may be present without causing fading.

No claim has ever been made by any investigator that the S. and O. reagent is a specific test for magnesium. However, since the interfering ions are easily removed in the usual scheme of qualitative analysis before the test is applied, the test is most satisfactory and useful. Aluminum, barium, calcium, and strontium, traces of which often are present through faulty separations, give a white phosphate precipitate which may easily be mistaken for magnesium ammonium phosphate in the old classical test for magnesium, but in the absence of magnesium they give no blue color whatever when the S. and O. test is applied, nor do they interfere with the test when magnesium is present. Students in the writers' classes get exceptionally good results with the test.

Summary

The effect of forty-four of the common ions upon the *p*-nitrobenzeneazoresorcinol test for magnesium has been studied. Although many of the metals of the first three groups interfere, they will have been removed, in the usual qualitative procedure, before the test for magnesium is made.

Aluminum, barium, calcium, and strontium ions, which give so much trouble in the phosphate test for magnesium through the formation of similar white precipitates, do not interfere at all with the S. and O. test.

Very few anions interfere.

The test, although not specific for magnesium in the strictest sense, is very satisfactory, useful, and efficient when properly applied.

Literature Cited

(1) Eegriwe, E., *Z. anal. Chem.*, 76, 354 (1929).
(2) Engel, E. W., *J. Am. Chem. Soc.*, 52, 1812 (1930).
(3) Newell, L., Pike, N. R., and Ficklen, J. B., *Z. anorg. allgem. Chem.*, 225, 281 (1935).
(4) Ruigh, W. L., *J. Am. Chem. Soc.*, 51, 1456 (1929).
(5) Stone, I., *Science*, 72, 322 (1930).
(6) Suitsu, K., and Okuma, K., *J. Soc. Chem. Ind., Japan*, 29, 132 (1926).

Direct Estimation of Biological Nitrogen Fixation

A Gasometric Method

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DEMONSTRATION of biological nitrogen fixation is usually accomplished by estimating the total nitrogen (before and after incubation) through use of some modification of the Kjeldahl procedure. Although this technique is accurate and reliable whenever a medium initially low in nitrogen is employed, the Kjeldahl method is subject to certain inaccuracies when used with substrates high in organic nitrogen. During the period of incubation, changes in the form of nitrogen occur which may give rise to errors in the determination and thus invalidate the apparent gains in nitrogen observed (*9*). Such errors have caused much confusion and disagreement among workers in the field of biological nitrogen fixation. It has been proposed, therefore, that a direct measure of free nitrogen uptake be a necessary condition for acceptance of claims of nitrogen fixation on substrates initially high in total nitrogen, such as plant extracts, germinating seeds, and nodules from leguminous plants (*8*, *9*).

The chief difficulty in following this suggestion has been the lack of a suitable gasometric method. Although gasometric procedures have been used previously for this and similar problems in biological nitrogen fixation studies (*1*, *2*, *4*, *7*), the majority possess certain disadvantages which have prevented their widespread adoption. Aside from the frequent use of complicated and expensive apparatus, they usually employ rather large culture flasks in order to provide sufficient oxygen for respiration of the biological agent under investigation. Under such conditions, the quantity of nitrogen fixed is ordinarily too small to detect accurately through gas analysis. A second source of error has been the relatively large corrections which must be made in order to allow for changes in the composition and partial pressures of the various gases in the closed system. These objections have been removed through development of a technique based on the principle of constantly renewing the oxygen as it is consumed in respiration.

Method

The apparatus employed is shown in Figure 1; details of the method are best supplied by actual illustration of its use in a test with *Azotobacter*.

To a sterile calibrated Erlenmeyer flask a known volume of sterile nitrogen-free medium is added aseptically and 20 ml. of 40 per cent potassium hydroxide are placed in the inner tube. The connecting glass tube which leads into the potassium hydroxide container holds it upright and reduces danger of contamination from added oxygen. After the flask is inoculated with 1 ml. of a 24-hour-old *Azotobacter vinelandii* culture, it is attached to the Novy-Soule respirometer (*5*) by means of the rubber stopper and glass tube. Heavy-walled rubber tubing and a high-grade rubber stopper impregnated with vaseline are used for connections. The rubber stopper is inserted to a calibration mark on the neck of the flask. These connections are securely wired, glycerol being used to facilitate fitting. Glass stopcocks are carefully greased with Lubriseal, checked for leaks under pressure, and secured in place with stout rubber bands.

When connected, the system is placed in a constant-temperature room at the desired temperature for 4 hours. Stopcocks 1 and 3 are then opened momentarily in order to equilibrate the system; the stopcocks are closed and the test begins. As oxygen is respired, the carbon dioxide evolved is absorbed in the potassium hydroxide; hence the rate and quantity of oxygen consumption can be followed by the changes in the mercury manometer. When the pO_2 inside the apparatus reaches approximately 0.15 atmosphere, as indicated by the reading on the manometer, the flask is shaken for several minutes to absorb the carbon dioxide completely. The Hg level coming to equilibrium, the final reading is taken, and oxygen is added from reservoir *B*. By means of the water system, *A*, the air in the capillary tube, *C*, and the three-way tailcock 3 on the respirometer is displaced with water which in turn is swept out with pure oxygen kept under a slight head of mercury in *B*. When this is accomplished, the tailcock is turned to communicate with the closed system, and oxygen is added to a pressure of zero. This procedure is carried out as often as is required during the period of incubation. In adding oxygen to the system and in filling the oxygen reservoir from the cylinder, great care must be exercised to exclude air completely.

At the end of the incubation period, oxygen is added to zero pressure in the manner just described, stopcock 2 is closed, and samples of gas are removed via stopcock 3 for analysis. In the authors' work these are carried out in a special gas apparatus which requires 15 to 25 ml. (*3*), but any standard gas-analysis apparatus should be satisfactory. A Kjeldahl analysis is then made on the entire contents of the flask.

The gas analysis includes tests for oxygen, carbon dioxide, carbon monoxide, and combustible gases, but in actual practice oxygen and a small quantity of carbon dioxide (about 1 per cent) are the only gases which have been found. It is evident that through use of the technique described not only is the oxygen respired completely replaced, but any free nitrogen fixed will show up in the gas analysis as an increase in the oxygen content. For this reason, the nitrogen fixed can be calculated from the formula:

$$\text{Mg. of N fixed} = \frac{28 \times (G_1 - G_2) \times V \times 273\,(P - vp)}{22.4 \times (t + 273) \times 760}$$

in which G_1 is per cent of total absorbable gases in the experimental flask; G_2 is per cent of total absorbable gases in a suitable

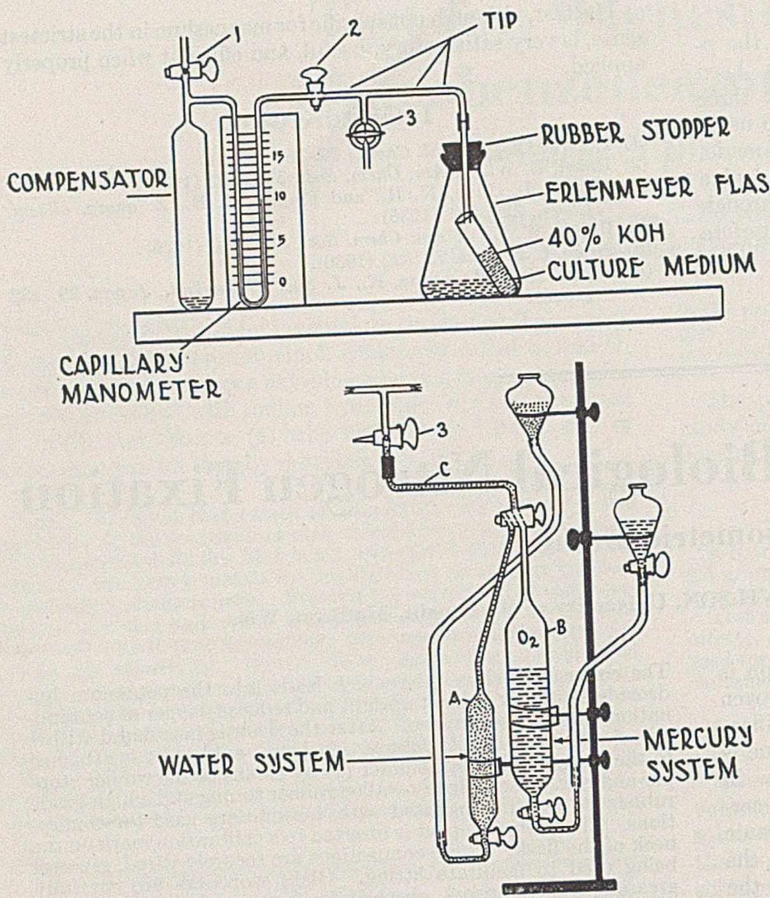

FIGURE 1. GASOMETRIC APPARATUS FOR DIRECT ESTIMATION OF NITROGEN FIXED

control; V is the gas volume (in ml.) of the flask plus "tip" to level of mercury; P is atmospheric pressure at equilibration in millimeters; and vp is vapor pressure at t° C. V is determined by marking the neck of the flask at a point where the lower end of the rubber stopper can be conveniently inserted and calibrating to this mark with water. The volume of the tip is estimated separately. After the apparatus is completely assembled, a check on the calibration can be made by withdrawing a measured volume of air and noting the rise in the mercury level of the manometer. (The use of all-glass connection is suggested, but this refinement would increase the cost of the apparatus. Estimation of V by the two methods agreed within 0.5 per cent, an error much smaller than others in the method.)

In many cases, there is an obvious control—e. g., with *Azotobacter* a culture of the same organism growing on sufficient combined nitrogen to prevent fixation. If no suitable control is available, G_2 becomes the per cent of absorbable gases in an uninoculated control, and correction in the test culture must be made for the small quantity of nonabsorbable gases added with the oxygen.

Test of the Method

Estimation of the quantity of nitrogen fixed by *Azotobacter* in a nitrogen-free medium through use of the gasometric and the Kjeldahl methods gave comparable results. Typical data supplied in Table I illustrate the order of agreement between duplicate gas analyses and between the values obtained for nitrogen fixed by the two methods. In these experiments, *Azotobacter* cultures sup-

TABLE I. TEST OF GASOMETRIC METHOD IN NITROGEN FIXATION EXPERIMENTS BY *Azotobacter vinelandii*

(Final growth experiments in 500-ml. flasks)

Treatment	Age	Oxygen Uptake	Gasometric Analysis Oxygen	Gasometric Analysis Nitrogen fixed	Nitrogen Fixed by Kjeldahl Analysis
	Hours	*Ml.*	*Per cent*	*Mg.*	*Mg.*
Experiment 1					
Control plus NH_4Cl	210	200	20.14 20.10	..	...
N-free	162	472	24.1 24.1	17.0	14.68
N-free	232	590	24.15 24.24	18.0	15.84
N-free	234	754	24.88 24.86	20.9	22.64
N-free	235	790	24.34 24.45	18.9	21.0
Experiment 2					
Control plus NH_4Cl	82	178	20.94 20.94	..	...
N-free	83	338	23.12 23.21	9.80	10.13
N-free	84	319	23.09 22.88	8.99	7.32

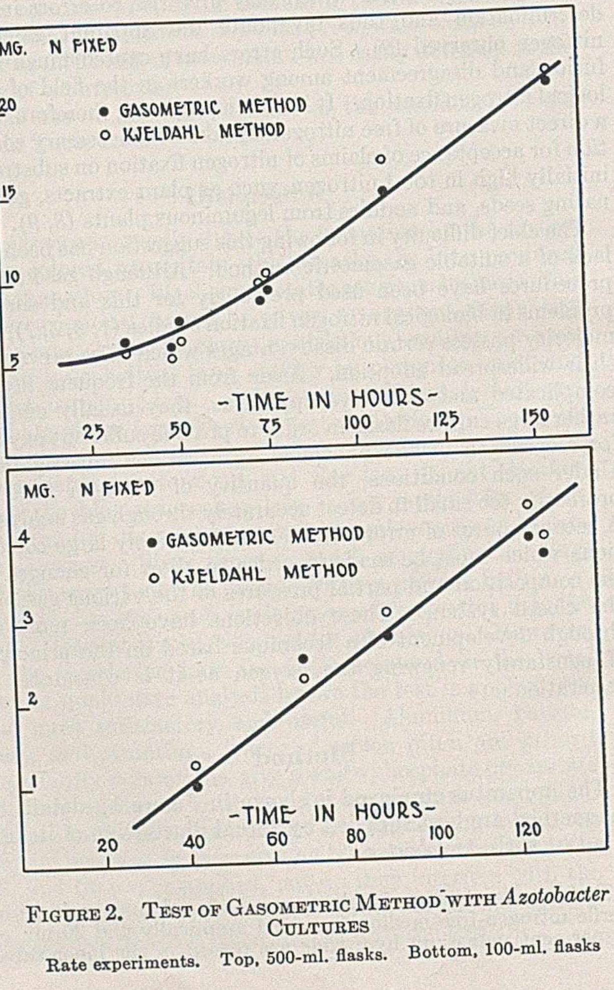

FIGURE 2. TEST OF GASOMETRIC METHOD WITH *Azotobacter* CULTURES

Rate experiments. Top, 500-ml. flasks. Bottom, 100-ml. flasks plied with an excess of ammonium chloride served as a natural control. Similar data are shown in Figure 2 for rate experiments. In the rate experiments a series of cultures was set up, and periodically, one flask (in some cases, duplicates) was removed and analyzed for nitrogen fixed by both the Kjeldahl and gasometric methods—i. e., a Kjeldahl analysis was made on the entire contents of the flask after taking the gas samples.

Accuracy and Sensitivity of Method

Experience with the method using *Azotobacter* cultures, germinating seeds, and root nodules from leguminous plants (*9*) indicates that when 500-ml. flasks are used, the total errors, including those associated with the gas analyses and all necessary manipulation, reach a maximum of about 2.5 mg. of nitrogen. The method has been designed primarily to investigate nitrogen fixation in substrates initially high in organic nitrogen. Since on such substrates it is usually claimed that 10 to 25 mg. of nitrogen are fixed, it is evident that the method is adequate for detection of such quantities. Although the Kjeldahl method may be more accurate for substrates low in organic nitrogen than is the gasometric procedure, the situation is reversed with many substrates high in nitrogen, especially heterogeneous material such as seeds and root nodules. For example, statistical treatment of several hundred analyses of pea seed by various Kjeldahl methods indicated that in a 5-gram sample the estimate of nitrogen has a standard deviation of about 5 mg. (*8*). Therefore, even if quadruplicate samples are taken, the standard deviation of the difference between the means of the controls and treated samples would be 4.1 mg. Since t for 6 degrees of freedom equals 2.45 (95 per cent confidence limit), a difference of 9.9 mg. would be necessary for significance (*6*) if a Kjeldahl method of analysis is used. In contrast, the gasometric method is independent of sampling errors in the initial nitrogen content of seeds since it measures directly the quantity of free nitrogen which disappears from the atmosphere; ordinarily, a loss of 2.5 mg. of nitrogen should be readily detected. For less heterogeneous materials, as nodules, the variance in the samples is less, but the sensitivity of the gasometric method can be increased through use of smaller flasks, so that the latter method still retains its advantage.

Summary

A gasometric method is described for detection of uptake of free nitrogen by biological agents which is based on the principle of quantitatively replacing nitrogen fixed, as well as oxygen respired, with oxygen of known purity. Tests with *Azotobacter* cultures indicate that it is reliable and possesses reasonable accuracy. Its advantages over Kjeldahl methods for use with heterogeneous substrates, as seeds and plant tissues, which are initially high in organic nitrogen are discussed.

Literature Cited

(1) Beijerinck, M. W., *Verzamelde Geschriften*, 5, 264–71 (1922).
(2) Galestin, C. J. A., *Chem. Weekblad*, 30, 207–9 (1933).
(3) Georgi, C. E., and Wilson, P. W., *Arch. Mikrobiol.*, 4, 543–64 (1933).
(4) Krasheninnikov, Th., *Rec. articles sci. dedié au C. Timiriazeff*, 1916, 307–24.
(5) Novy, F. G., Roehm, H. R., and Soule, M. H., *J. Infectious Diseases*, 36, 109–67 (1925).
(6) Rider, P. R., "Introduction to Modern Statistical Methods", New York, John Wiley & Sons, 1939.
(7) Sadasivan, V., and Sreenivasan, A., *Current Sci.*, 6 (5), 216–17 (1937).
(8) Smyth, E. M., and Wilson, P. W., *Biochem. Z.*, 282, 1–25 (1935).
(9) Wilson, P. W., *Ergeb. Enzymforsch.*, 8, 13–54 (1939).

Herman Frasch Foundation in Agricultural Chemistry, Paper No. 200. Contribution from the Departments of Agricultural Bacteriology and Biochemistry, University of Wisconsin.

Determination of Molybdenum in Cast Iron and Steel

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A combination of the alpha-benzoinoxime and lead molybdate methods for the determination of molybdenum in ferrous materials is described. The critical ignition of the alpha-benzoinoxime precipitate is avoided by dissolving it in ammonium hydroxide and precipitating and weighing the molydenum as lead molybdate without further purification.

A MODIFICATION of Knowles' (*2*) alpha-benzoinoxime method for the determination of molybdenum was adopted as a standard procedure in this laboratory during 1935. The method was accurate and more rapid than the former practice, which involved separation by hydrogen sulfide and weighing as lead molybdate. However, the ignition of the molybdenum compound of alpha-benzoinoxime to molybdic oxide at temperatures below 550° C. was troublesome. The operation required at least an hour, and demanded accurate control of the temperature in order to avoid losses of molybdenum. In addition, it was necessary to correct the weight of the oxide for small amounts of impurities.

The authors have succeeded in overcoming these annoyances by dissolving the alpha-benzoinoxime precipitate in ammonia, filtering off the insoluble impurities, and precipitating the molybdenum as lead molybdate. This procedure yields a pure precipitate containing a favorably low percentage of molybdenum, and which may be ignited quickly under easily obtained conditions.

Analytical Procedure

Reagents. The following reagents were prepared, using reagent grade chemicals with the exception of perchloric acid. As a matter of economy the technical grade acid is used in all routine work.

Nitric-Perchloric Acid Mixture. Mix 3 volumes of 68 to 70 per cent technical grade perchloric acid with 1 volume of nitric acid (sp. gr. 1.42) and 1 volume of water.

Potassium Dichromate Solution. Dissolve 1.41 grams of potassium dichromate in water and dilute to 100 ml. Each milliliter contains 5 mg. of chromium.

Ferrous Sulfate, 5 Per Cent Solution. Dissolve 50 grams of ferrous ammonium sulfate hexahydrate in water, add 50 ml. of 1 to 1 sulfuric acid, and dilute to 1 liter.

Alpha-Benzoinoxime, 2 Per Cent Solution. Dissolve 2 grams of alpha-benzoinoxime in 100 ml. of ethyl alcohol.

Lead Acetate Buffer Mixture. Dissolve 4 grams of lead acetate trihydrate in a solution containing 275 ml. of water, 550 ml. of ammonium hydroxide (sp. gr. 0.90), 900 ml. of 50 per cent acetic acid, and 275 ml. of hydrochloric acid (sp. gr. 1.19). Let stand overnight and filter.

Preparation of the Solution. Transfer 3 to 5 grams of steel or cast iron to a 600-ml. beaker and add 50 to 70 ml. of nitric-perchloric acid mixture. Cover the beaker and heat gently until action ceases. Remove the watch glass, and add 1 to 3 ml. of hydrofluoric acid.

Add sufficient potassium chromate solution to cast-iron samples to make the total chromium content of the solution at least 25 mg. The chromium catalyzes the destruction of graphite and carbides by boiling perchloric acid.

Evaporate the solution from the open beaker until heavy white fumes appear. Continue heating until volatile acids are driven from the beaker and the perchloric acid comes to a boil. Cover the beaker with a watch glass and boil gently until carbides and graphite are decomposed. The rate of boiling should not be high enough to cause excessive losses of perchloric acid.

Remove the beaker from the hot plate and allow to cool until the perchlorates crystallize. Dilute the solution to 100 ml. and stir, heating if necessary, until the salts have dissolved. Filter off any insoluble residue.

Precipitation by Alpha-Benzoinoxime. Cool the prepared solution below 20° C. and add ferrous sulfate until the solution has clear blue-green color that is not changed by adding a slight excess. Dilute to 400 ml. and cool to 5° to 10° C. in an ice bath. Pieces of clean ice may be added to the solution itself.

Add 10 ml. of alpha-benzoinoxime solution slowly while stirring. Add an additional 0.5 ml. for each milligram of molybdenum present. Add bromine water while stirring until the solution is tinted a pale yellow, and then add 3 to 4 ml. more of reagent. Let stand 5 to 10 minutes in the ice bath with occasional stirring.

Filter the precipitate on a 15-cm. rapid paper and wash with cold 2 to 98 sulfuric acid containing a few milliliters of reagent. Fill the paper with washing solution and allow it to drain completely before breaking up the cake with the stream from the wash bottle.

Treat the filtrate with more reagent as a check on the complete separation of molybdenum. Needlelike crystals will deposit on standing if sufficient excess reagent has been added.

Reprecipitation of Molybdenum as Lead Molybdate. Transfer the precipitate back to the original beaker by means of a jet of water. Add 10 ml. of ammonia and 10 ml. of 30 per cent hydrogen peroxide, dilute to 75 ml., and boil until the evolution of oxygen ceases. Filter through the original paper and wash the paper and small residue with hot ammonia (2 to 98).

Pour the hot ammoniacal molybdenum solution into 100 ml. of boiling lead acetate buffer mixture slowly while stirring, boil gently until the precipitate coagulates, and allow to settle for 30 minutes. If the precipitate is small, the settling period should be extended to several hours or overnight.

Filter the precipitation on a close-texture paper containing a little paper pulp, wash thoroughly with hot 2 per cent ammonium acetate solution containing a few milliliters of acetic acid, and ignite the paper and residue in a porcelain crucible placed just inside a muffle furnace operating at a dull red heat. Weigh as lead molybdate containing 26.14 per cent of molybdenum.

Analytical Data

The method was established by more than 50 experimental runs on National Bureau of Standards No. 107 Ni-Cr-Mo cast iron and No. 111 Ni-Mo steel. The recommended analyses for these materials are:

Sample	TC[a]	GC[b]	Mn	P	S	Si
107	2.57	1.86	0.706	0.197	0.090	2.34
111	0.202	...	0.662	0.023	0.020	0.292
	Cu	Ni	Cr	V	Mo	W
107	0.074	0.807	0.455	0.015	0.687	0.002
111	0.122	1.75	0.272	0.003	0.215	...

[a] Total carbon.
[b] Graphitic carbon.

Twelve cooperating analysts reported values for molybdenum in the following ranges:

No. 107, 0.676 to 0.70 % Mo
No. 111, 0.20 to 0.223 % Mo

The recommended procedure gave the following results on these samples:

No. 107: 0.687, 0.697, 0.700, 0.687, 0.698, 0.685, 0.689. Av., 0.692% Mo
No. 111: 0.201, 0.208, 0.221, 0.217, 0.214, 0.216, 0.217. Av., 0.213% Mo

Discussion

The authors' work on this method was initiated by the observation that the alpha-benzoinoxime precipitate is freely soluble in fixed alkali. A long series of experiments on essentially the method recommended, but using sodium hydroxide as a solvent, gave results that were consistently high by 0.01 to 0.05 per cent of molybdenum. The error was found to be caused by silica introduced by corrosion of the glassware by the small amount of caustic used. When nickel beakers were substituted for Pyrex the results were normal. By substituting ammonium hydroxide for sodium hydroxide the corrosion of glass was reduced to the point where it could be neglected. However, the precipitate dissolves more slowly in ammonia than in sodium hydroxide, making it essential to remove it completely from the paper for the treatment with ammonia.

The small amount of iron carried down by the alpha-benzoinoxime precipitate is partially precipitated by the alkaline solvent. When hydrogen peroxide is added the precipitation is complete, allowing the impurities to be removed by the subsequent filtration.

Application of the Method

Alpha-benzoinoxime is nearly specific for molybdenum under the prescribed conditions. Tungsten, tantalum, and columbium are the only interfering elements that might be found in ferrous materials. The authors have not tested the method on any of the comparatively rare cases in which one or more of these elements is associated with molybdenum, but the following notes should serve as a guide when such complex alloys are encountered.

An insoluble residue in the normally clear perchloric acid solution of the sample is an indication of the presence of interfering elements. Tantalum or columbium alone would be precipitated and filtered off. The determination would then follow its usual course. If appreciable amounts of titanium were also present, the precipitation of the earth acids would be incomplete. The soluble fraction would be carried down in the first molybdenum precipitation. An abnormally large ammonia-insoluble would be found, and probably recovery of occluded molybdenum would be in order.

The chief offender is tungsten. In some cases it will be completely precipitated by the perchloric acid treatment, but it is never safe to assume this. Any tungsten remaining as a soluble complex with phosphorus or molybdenum itself will be weighed with the lead molybdate. Probably the best line of attack on tungsten steels will include a preliminary separation of molybdenum from tungsten by hydrogen sulfide. Arrington and Rice (*1*) have thoroughly covered this problem.

Occasionally, when the percentage of molybdenum is very high, as in corrosion-resistant nickel-chromium steels, some of the molybdenum is precipitated as the oxide in the prepared solution. The difficulty in such cases is overcome by repeating the determination on a smaller weight of sample.

The useful field of application of the recommended procedure includes practically all of the tungsten-free molybdenum-bearing irons and steels.

Literature Cited

(1) Arrington and Rice, *Bur. Mines Rept. Investigations* 3441, 39-59 (1939).
(2) Knowles *Bur. Standards J. Research*, 9, 1 (1932).

Tie Lines in Two-Liquid-Phase Systems

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THE literature gives many ternary systems, containing one pair of nonconsolute liquids and forming two liquid phases, with limited tie-line data; in order to obtain further data without recourse to experiment, interpolation is necessary.

Direct interpolation on a triangular graph is unsatisfactory, but it may be effected accurately by several indirect methods.

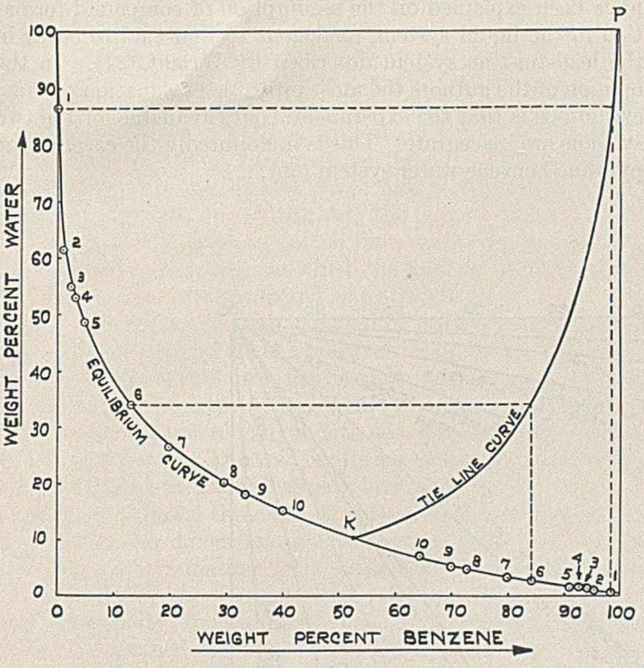

FIGURE 1

A study of ternary equilibrium curves for two-liquid phase systems containing one pair of nonconsolute liquids makes it clear that the critical point is not necessarily at the maximum of the isotherm, and hence the tie lines are not parallel to the base of the triangle. The critical point may, however, be brought to the maximum of the isotherm by altering the units of plotting on the triangular graph. Hand (*3*) gives an interesting account of such a method, whereby tie lines may be obtained parallel to the triangle base and interpolation is simplified.

In the second method described in the International Critical Tables (*4*), lines are drawn from conjugate points of a tie line parallel, respectively, to the two sides of the triangle and intersecting at a point. By repeating for other tie lines, a series of points is obtained forming a conjugate curve from which tie lines may be interpolated.

A similar method has been described by Sherwood (*11*), in which a line is drawn from one conjugate point parallel to the base, to intersect a second line from the other conjugate point parallel to the side of the triangle. A series of points of intersection for several tie lines may be joined to form a conjugate curve from which other tie lines may be interpolated.

In what appear to be the most accurately determined systems (*3*, *6*, *14*, *15*, *19*), the tie lines may be produced to a point focus on the extended base line of the triangle. In many systems, however, the tie lines when produced do not exhibit such a point focus, while in other systems the ex-

TABLE I. TERNARY SYSTEMS

System No.	Temperature, ° C.	System	Reference No.
1	25	Benzene–acetic acid–water	(*3*, *5*, *16*)
2	25	Acetone-chloroform-water	(*3*)
3	25	Toluene–acetic acid–water	(*19*)
4	25	Toluene–methyl alcohol–water	(*6*)
5	25	Acetic acid–chloroform-water	(*21*)
6	0	*n*-Butyl alcohol–water–methyl alcohol	(*9*)
7	15		
8	30		
9	30	Triethylamine-water–ethyl alcohol	(*7*)
10	30	Triethylamine-water–diethyl ether	(*7*)
11	30	Triethylamine-water-phenol	(*7*)
12	25	Pyridine-benzene-water	(*20*)
13	0 and 20	Water–ethyl acetate–methyl alcohol	(*2*)
14		Water–ethyl acetate–ethyl alcohol	(*2*)
15		Water–ethyl acetate–isopropyl alcohol	(*2*)
16		Water–ethyl acetate–*n*-propyl alcohol	(*2*)
17		Water–ethyl acetate–*tert*-butyl alcohol	(*2*)
18	25	Ethyl alcohol–cyclohexane-water	(*15*)
19	25	Methyl alcohol–cyclohexane-water	(*18*)
20	25	Benzene–ethyl alcohol–water	(*1*, *14*, *17*)
21	40 to 60	Water–ethyl alcohol–isoamyl alcohol, etc.	(*4*)
22	25	Glycol-xylene-acetone	(*12*)
23	27	Glycol-toluene-acetone	(*12*)
24	23	Glycol-chlorobenzene-acetone	(*12*)
25	25	Glycol-bromobenzene-acetone	(*12*)
26	27	Glycol-benzene-acetone	(*12*)
27	22	Glycol-nitrobenzene-acetone	(*12*)
28	0 and 25	Ethyl alcohol–ethyl ether–water	(*8*)
29	25	Water–hydrogen bromide–isoamyl alcohol	(*10*)
30	25	Water–hydrogen bromide–isobutyl alcohol	(*10*)
31	25	Water–hydrogen chloride–isobutyl alcohol	(*10*)
32	25	Water–hydrogen chloride–cyclohexanone	(*10*)
33	25	Water–hydrogen iodide–isobutyl alcohol	(*10*)

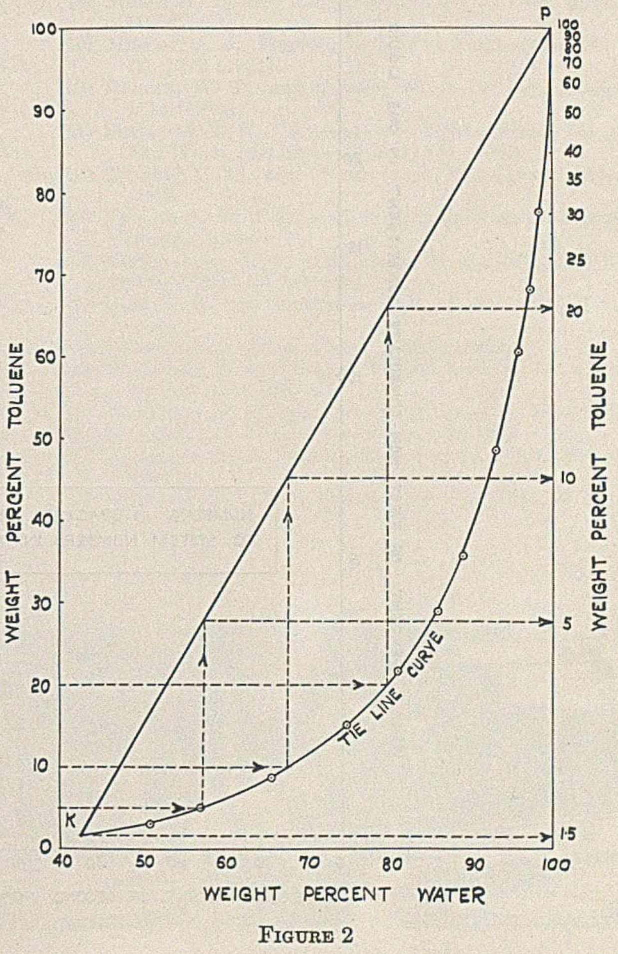

FIGURE 2

tended tie lines appear to be tangential to a curve, as shown by Van Dyck and Saal (*13*).

Insufficient information is available at the moment to determine whether the point focus is a general case and whether any deviations therefrom in a particular system may be due, as is not completely improbable, to inaccurate tie-line data, to the presence of an unsuspected fourth component as an impurity, or to compound formation.

Of these methods, the first three necessitate a knowledge of a considerable amount of tie-line data. The fourth method, where applicable, requires only a knowledge of one accurately determined tie line. The method described in the present paper requires only a knowledge of two accurately determined tie lines.

If the weight percentages of the two nonconsolute liquids are plotted on rectangular coordinates the binodal curve approximates a rectangular hyperbola. This is shown in Figure 1, for the system benzene–ethyl alcohol–water due to Varteressian and Fenske (*14*), where benzene and water are the two nonconsolutes. Points representing tie-line data are located on the curve and numbered. Corresponding numbers are on opposite branches of the hyperbola. These correspondingly numbered points can be joined to form tie lines.

A plot of weight percentage of the first nonconsolute constituent in one liquid phase against the weight percentage of the second nonconsolute constituent in the other liquid phase in equilibrium with the first gives a smooth tie-line curve. This tie-line curve, *KP* in Figure 1, intersects the isotherm at the critical point, *K*, and from its form would appear to have exponential characteristics.

With two exceptions, the thirty-three ternary systems given in Table I gave tie-line curves of similar form. The two exceptions are pyridine-benzene-water (*20*) and ethyl ether–ethyl alcohol–water (*8*), in both of which a change in the slope or direction of the tie lines occurs. Anomalies of this nature have been explained on the assumption of compound formation in the liquid system, analogous to that said to occur in the lead-tin-zinc system described by Wright (*21*). In the opinion of the authors the most probable explanation of these exceptions is that the experimental data available for the two systems are inaccurate. This is undoubtedly the case for the pyridine-benzene-water system (*20*).

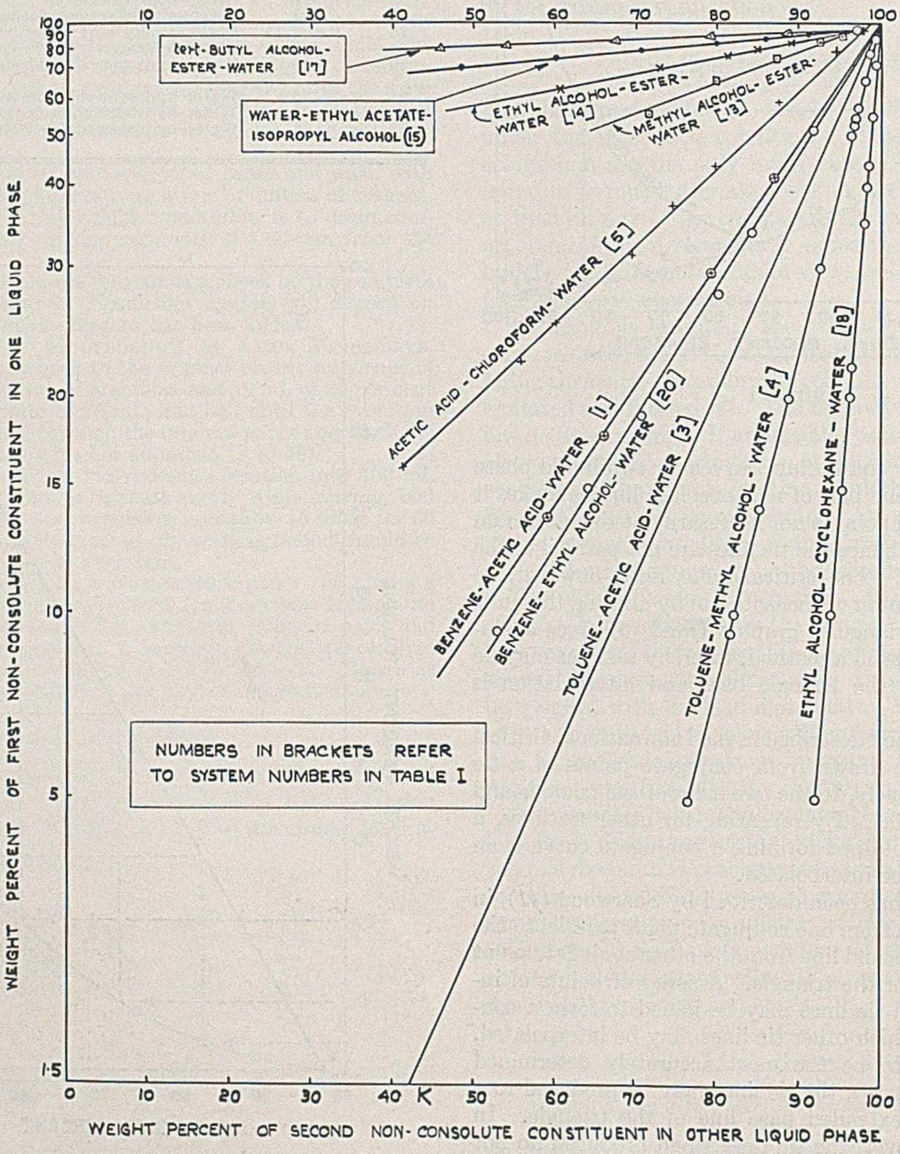

Figure 3

Instead of deriving a general expression which would apply to such tie-line curves in normal ternary systems, a selected system was employed as a standard, and a chart was constructed which would reduce all tie-line curves to straight lines. As a standard it was necessary to employ an accurately determined system from a reliable source. Several such systems are given in the more recent literature (*9, 14, 19*).

The system finally selected was toluene–acetic acid–water, due to Woodman (*19*). In this system, water and toluene are the two nonconsolute liquids and a plot of weight per cent of the first nonconsolute constituent, in this case toluene, as ordinate against weight per cent of second nonconsolute constituent, water, as abscissa gives the usual tie-line curve shown in Figure 2. This curve terminates in the critical point, *K*, and the point, *P*, which represents the mutual solubility of toluene and water.

The tie-line curve reduced to a straight line must contain both *K* and *P*. Therefore *K* and *P* may be joined by a straight line and a special weight percentage vertical scale constructed to replace the original ordinate as shown in Figure 2. Using the original vertical scale on the left of Figure 2 in conjunction with the tie-line curve and straight line *KP*, the new vertical scale on the right of the figure is obtained by the construction shown as dotted lines on the figure. In this way a chart is obtained on which the toluene-acetic acid–water tie-line data can be plotted as a straight line.

It was found that the tie-line data of other systems, when plotted on this chart, also gave straight lines. Examples based on data in the literature for the ternary systems detailed in Table I were tested and, with the exception of the two anomalous systems already mentioned, gave straight lines as shown in Figure 3. To avoid confusion, only a portion of the systems detailed in Table I appear in Figure 3.

It follows, therefore, that by employing a chart of this nature the determination of tie-line data resolves itself into the determination of the critical point and of the mutual solubility of the two nonconsolute constituents. The mutual solubility, together with one, or better two, experimentally determined tie lines would be equally suitable and might often be preferred, owing to the difficulty in determining the critical point.

Although the proposed method appears to be applicable to the systems cited, twenty-six of these thirty-three systems contain water as one of the three components and, until data for more nonaqueous systems are available to test the proposed method more completely, general applicability cannot be claimed. The proposed method has been applied only to ternary systems of two liquid phases containing a closed binodal curve and having a single pair of nonconsolute constituents. There would, however, appear to be no reason why the method should not be applied to ternary systems of two liquid phases containing two or three binodal curves and having two or three pairs of nonconsolute constituents, always providing the closed binodal curves defining the areas of heterogeneity do not overlap.

An interesting case is that of a two-liquid-phase ternary system having two pairs of nonconsolute constituents, where the area of heterogeneity is defined by a band. An example of this is the system aniline-heptane–methyl cyclohexane at 25° C., studied by Varteressian and Fenske (*14*). The treatment of systems of this type in a manner similar to that described above for systems having a closed binodal curve could not be tried, owing to lack of data in the literature. The use of a chart constructed from a system where the area of heterogeneity is defined by a band would be necessary to try out the proposed method for such cases.

A chart constructed from a system where the area of heterogeneity is defined by a closed curve could hardly be applied to the band-type system, and the plotting of Varteressian and Fenske's data for aniline-heptane-cyclohexane on the chart, constructed as described above, does not yield a straight line. The conjugate curves obtained for the aniline-heptane-cyclohexane system by the method of Sherwood (*11*) and by that described in the International Critical Tables (*4*) are both straight lines. If this were general for band-type systems it would afford a simple method of obtaining tie lines from a knowledge of the mutual solubilities of the two pairs of nonconsolute constituents.

Literature Cited

(1) Barbaudy, J., *Rec. trav. chim.*, 45, 207 (1926).
(2) Beech, D. G., and Glasstone, S., *J. Chem. Soc.*, **1938**, 67.
(3) Hand, D. B., *J. Phys. Chem.*, 34, 1961 (1930).
(4) International Critical Tables, Vol. III, 1st ed., p. 398, New York, McGraw-Hill Book Co.
(5) Lincoln, A. T., *J. Phys. Chem.*, 8, 248 (1904).
(6) Mason, L. S., and Washburn, E. R., *J. Am. Chem. Soc.*, **59**, 2076 (1937).
(7) Meerburg, P. A., *Z. phys. Chem.*, 40, 642 (1902).
(8) Miller, W. L., and McPherson, R. H., *J. Phys. Chem.*, **12**, 706 (1908).
(9) Mueller, A. J., Pugsley, L. I., and Ferguson, J. B., *Ibid.*, **35**, (I), 1313 (1931).
(10) Reburn, W. T., and Shearer, W. N., *J. Am. Chem. Soc.*, **55**, 1774 (1933).
(11) Sherwood, T. K., "Absorption and Extraction", 1st ed., p. 242, New York, McGraw-Hill Book Co., 1937.
(12) Trimble, H. M., and Frazer, G. E., IND. ENG. CHEM., **21**, 1063 (1929).
(13) Van Dyck, W. J. D., and Saal, N. J., *World Petroleum Congr.*, **2**, 352 (1933).
(14) Varteressian, K. A., and Fenske, M. R., IND. ENG. CHEM., **28**, 928 (1936); **29**, 270 (1937).
(15) Vold, R. D., and Washburn, E. R., *J. Am. Chem. Soc.*, **54**, 4217 (1932).
(16) Waddell, J., *J. Phys. Chem.*, 2, 233 (1898).
(17) Washburn, E. R., Hnizda, V., and Vold, R. D., *J. Am. Chem. Soc.*, **53**, 3237 (1931).
(18) Washburn, E. R., and Spencer, H. C., *Ibid.*, **56**, 361 (1934).
(19) Woodman, R. M., *J. Phys. Chem.*, 30, 1283 (1926).
(20) Woodman, R. M., and Corbet, A. S., *J. Chem. Soc.*, **1925**, 127, 2461.
(21) Wright, C. R. A., *Proc. Roy. Soc.*, 49, 174 (1891); **50**, 375 (1892).

Tie Lines in Ternary Liquid Systems

IRVIN BACHMAN
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THE direct interpolation of tie-line data on ternary system graphs is inaccurate. Most methods of indirect interpolation require considerable experimental data. The method of Brancker, Hunter, and Nash (*1*), which requires only two experimentally determined tie lines, reduces tie-line curves to straight lines by adopting a variably dimensioned ordinate axis based arbitrarily on Woodman's (*5*) data for the toluene–acetic acid–water system. This method requires considerable plotting to obtain the dimensions of the ordinate axis.

The method described in the present paper requires only two experimentally determined points and reduces tie-line curves to straight lines on rectangular coordinates.

If *A* and *B* are the nonconsolute components of a ternary liquid system, then a plot of weight per cent *A* in the *A*-rich layer against weight per cent *B* in the *B*-rich layer will produce, as Brancker, Hunter, and Nash pointed out, a typical tie-line curve. The equation of these curves, we find, is

$$xy = ax + by \qquad (1)$$

where x = weight per cent A
y = weight per cent B
a and b = constants

This equation, when written in the form

$$x = ax/y + b \qquad (2)$$

shows that a plot of x against the ratio of x to y will produce a straight line. Consequently, if weight per cent A of the A-rich layer is plotted against the ratio of weight per cent A of the A-rich layer to weight per cent B of the B-rich layer, a straight line should result.

Figures 1 and 2 show such plots for a number of ternary systems. For convenience, the lines are plotted to different ordinate scales on the same diagram, and their positions, therefore, bear no relation to each other. A few points which fail to fall in line are near the critical point or near the maximum of the equilibrium curve. The accurate determination of tie lines in these regions is difficult and the experimental data are probably in error.

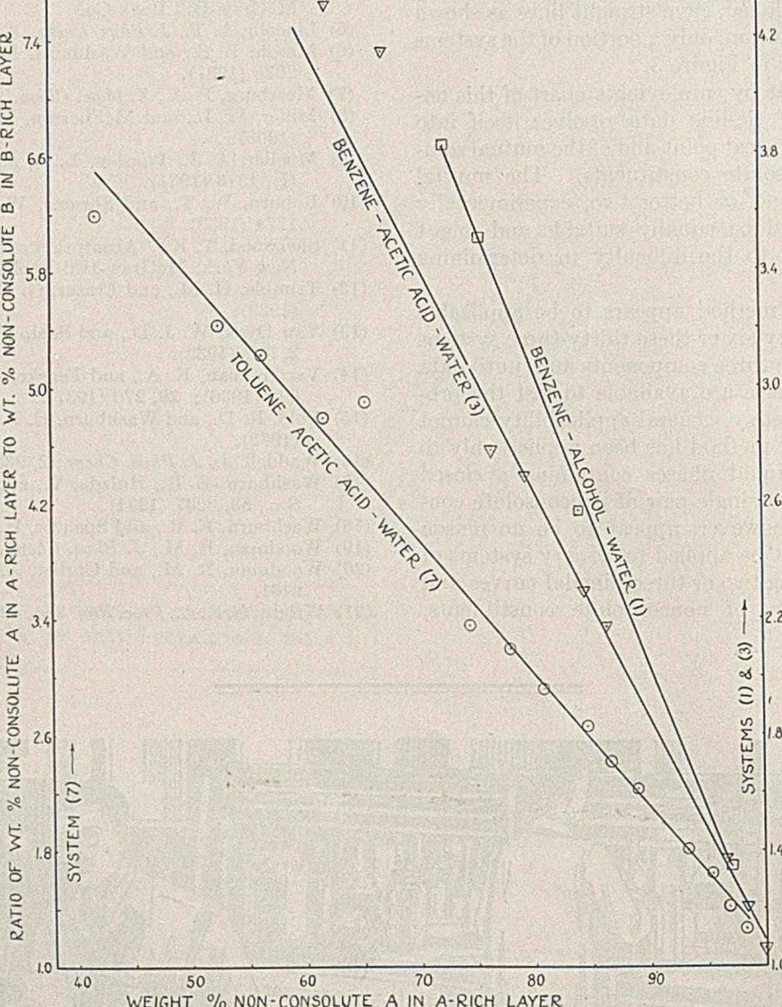

FIGURE 1

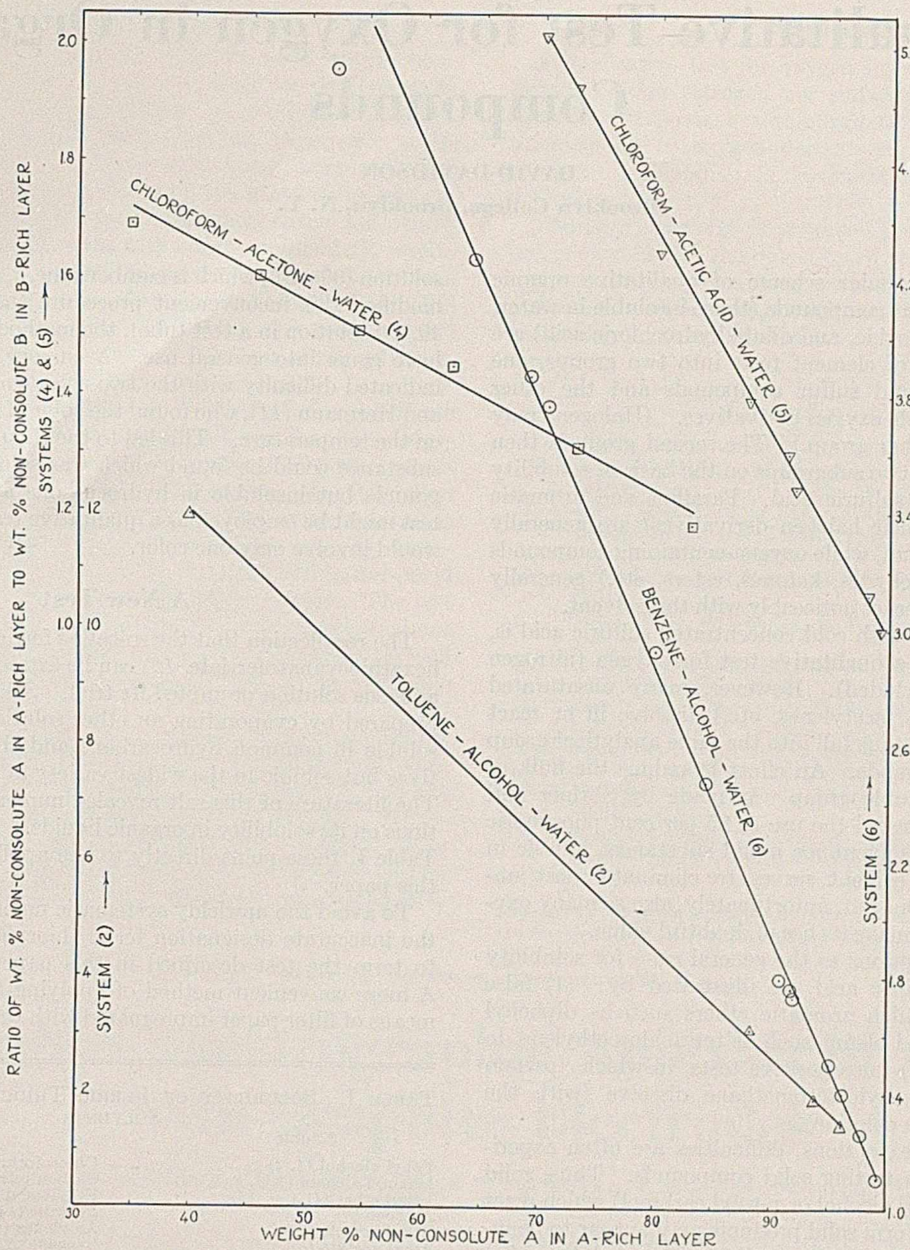

FIGURE 2

The use of the above method in conjunction with the previously determined equilibrium curve to interpolate tie-line data is simple and rapid. From the two experimentally determined tie lines the straight line plot is drawn as shown in the diagrams. The ratio of *A* to *B* may be read from the graphs for any given value of *A*. The value of *B* is then readily calculated. The values of *A* and *B* are sufficient to locate the compositions of the conjugate solutions on the ternary equilibrium curve.

As an alternative method, Equation 2 may be solved for the values of the constants *a* and *b* from the known values for *x* and *y*. The relationship between the nonconsolute compositions shown by Equation 2 may yield a valuable clue as to the nature of equilibrium laws governing ternary systems.

TABLE I. TERNARY SYSTEMS SHOWN IN FIGURES 1 AND 2

System No.	System	Reference No.
1	Benzene-alcohol-water at 20° C.	(3)
2	Toluene-alcohol-water at 20° C.	(3)
3	Benzene-acetic acid-water at 25° C.	(2)
4	Chloroform-acetone-water at 25° C.	(2)
5	Chloroform-acetic acid-water at 25° C.	(6)
6	Benzene-alcohol-water at 25° C.	(4)
7	Toluene-acetic acid-water at 25° C.	(5)

Literature Cited

(1) Brancker, A. V., Hunter, T. G., and Nash, A. W., IND. ENG. CHEM., Anal Ed., 12, 35 (1940).

(2) Hand, D. B., *J. Phys. Chem.*, 34, 1961 (1930).

(3) Tarasenkov, D. N., and Polozenzeva, I. A., *J. Gen. Chem. (U. S. S. R.)*, 8, 76–82 (1938).

(4) Varteressian, K. A., and Fenske, M. R., IND. ENG. CHEM., 28, 928 (1936).

(5) Woodman, R. M., *J. Phys. Chem.*, 30, 1283 (1926).

(6) Wright, Thompson, and Leon, *Proc. Roy. Soc.*, 49, 174 (1891).

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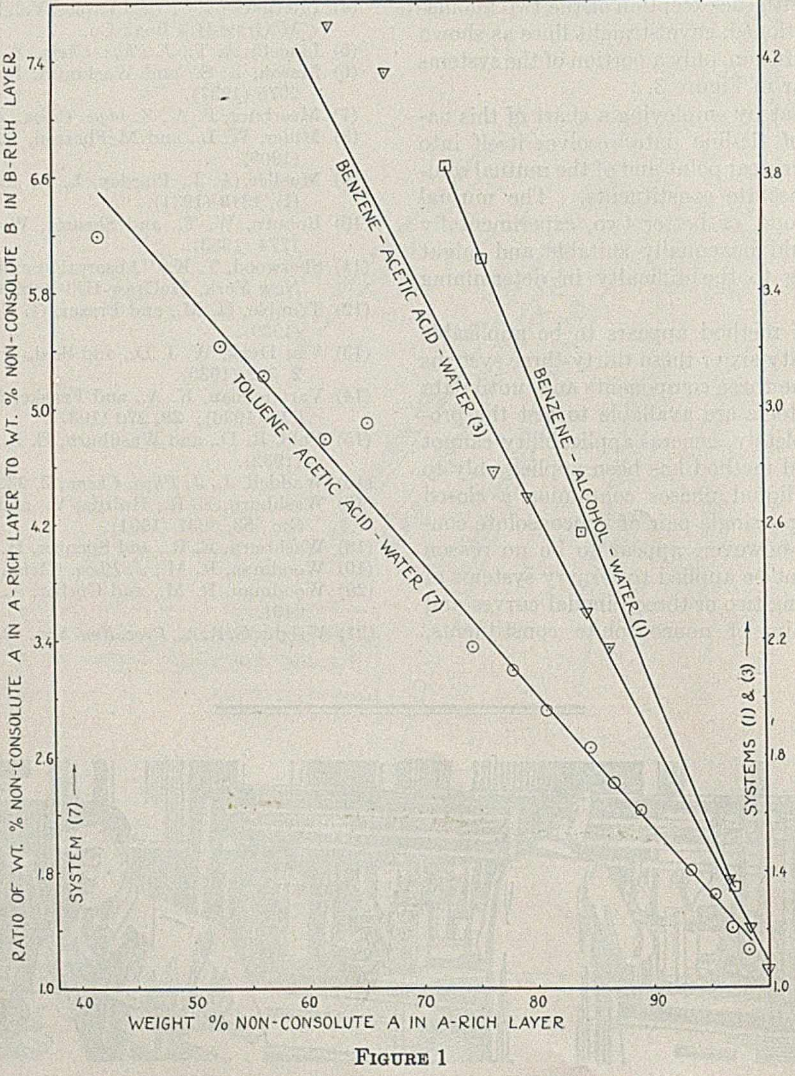

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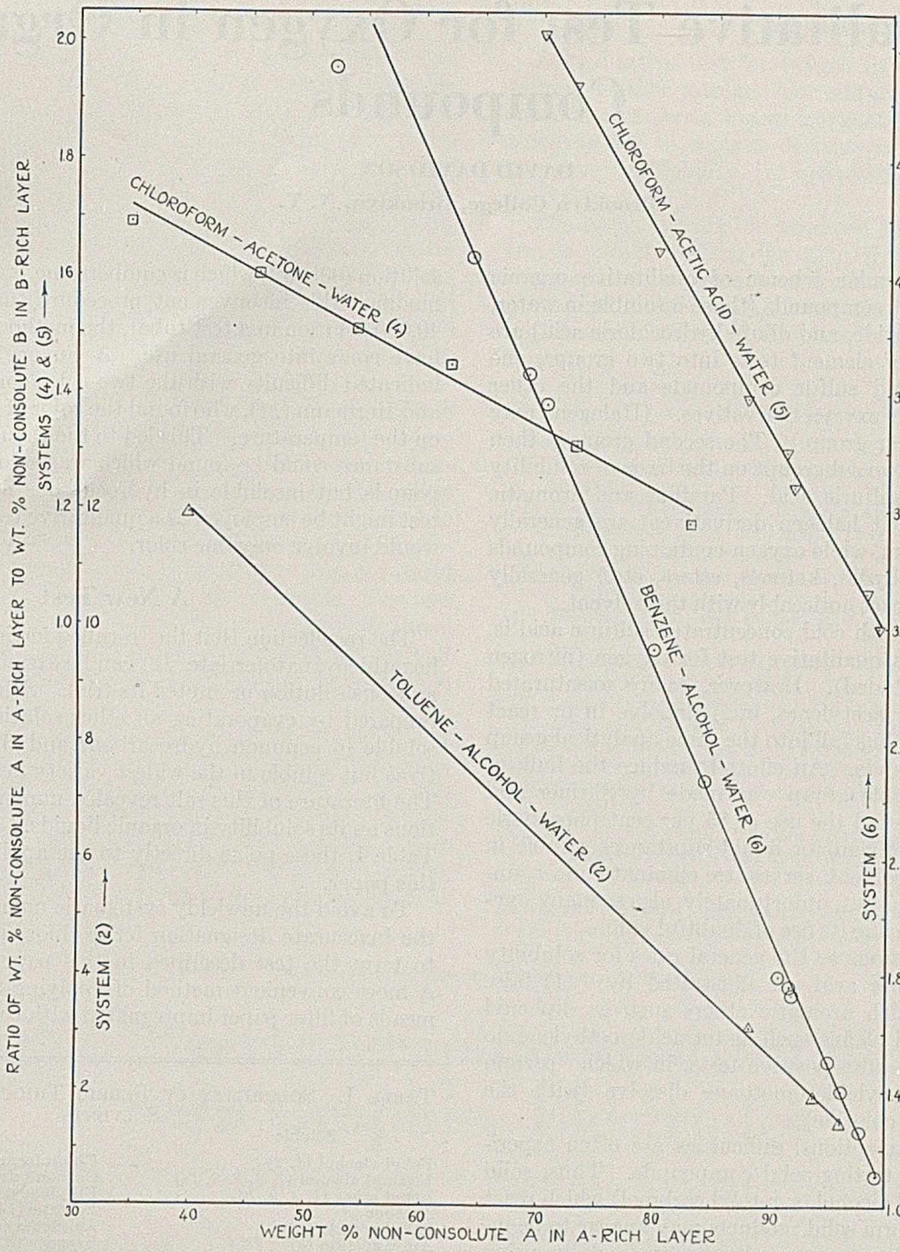

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5	Chloroform-acetic acid-water at 25° C.	*(6)*
6	Benzene-alcohol-water at 25° C.	*(4)*
7	Toluene-acetic acid-water at 25° C.	*(5)*

Literature Cited

(1) Brancker, A. V., Hunter, T. G., and Nash, A. W., Ind. Eng. Chem., Anal Ed., 12, 35 (1940).
(2) Hand, D. B., *J. Phys. Chem.*, 34, 1961 (1930).
(3) Tarasenkov, D. N., and Polozenzeva, I. A., *J. Gen. Chem. (U. S. S. R.)*, 8, 76–82 (1938).
(4) Varteressian, K. A., and Fenske, M. R., Ind. Eng. Chem., 28, 928 (1936).
(5) Woodman, R. M., *J. Phys. Chem.*, 30, 1283 (1926).
(6) Wright, Thompson, and Leon, *Proc. Roy. Soc.*, 49, 174 (1891).

A Qualitative Test for Oxygen in Organic Compounds

DAVID DAVIDSON
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IN KAMM's (*7*) popular scheme of qualitative organic analysis, indifferent compounds (those insoluble in water, dilute potassium hydroxide, and dilute hydrochloric acid) are divided on the basis of element tests into two groups, one containing nitrogen and sulfur compounds and the other hydrocarbons and their oxygen derivatives. (Halogens may also be present in either group.) The second group is then further classified into two subgroups on the basis of solubility in cold concentrated sulfuric acid. Paraffins and aromatic hydrocarbons (and their halogen derivatives) are generally insoluble in this medium, while oxygen-containing compounds (alcohols, ethers, aldehydes, ketones, esters, etc.) generally dissolve in or at least react noticeably with this solvent.

This solubility test with cold concentrated sulfuric acid is, therefore, essentially a qualitative test for oxygen (nitrogen and sulfur being excluded). However, many unsaturated hydrocarbons (olefins, acetylenes, etc.) dissolve in or react with this reagent and thus fall into the same analytical group as the oxygen compounds. An effort to reduce the bulk of this sulfuric acid–soluble group was made by Shriner and Fuson (*13*) who suggested the use of 85 per cent phosphoric acid as an auxiliary solvent for liquid substances soluble in sulfuric acid. This solvent serves to eliminate most unsaturated hydrocarbons but, unfortunately, also so many oxygen compounds as to make its use of doubtful value.

Two types of exceptions to the general rules for solubility in concentrated sulfuric acid are illustrated by: (1) false negative tests, in which aromatic ethers such as diphenyl ether and halogenated olefins such as tetrachloroethylene do not dissolve; and (2) false positive tests, in which "pseudo salts" such as triphenylchloromethane dissolve (with the evolution of hydrogen chloride).

Aside from these exceptions, difficulties are often experienced by students in testing solid compounds. Thus, solid alcohols (such as cetyl alcohol or *p*-tolyl carbinol) which react with sulfuric acid to form solid products may appear to be insoluble. This difficulty may usually be avoided by using very finely divided material and rubbing it vigorously against the wall of the test tube during the test. On the other hand, since some time must be allowed under these conditions even for a truly soluble solid, certain aromatic hydrocarbons which sulfonate readily (acenaphthene, anthracene) may appear to be soluble.

All in all, it appears that, in spite of Kamm's view that tests for oxygen are unnecessary (*7*, p. 137), these circumstances warrant a search for a satisfactory qualitative test for this element in organic compounds or, at least, in those containing neither nitrogen nor sulfur. While this paper was in preparation an article by Bowen, Bourland, and Degering (*2*) appeared, describing a qualitative test for oxygen in organic compounds based on the formation of carbon dioxide on heating the compound with carbon. Since the compounds tested are not mentioned, the generality of the test cannot be judged. Both air and water interfere with the test, entailing considerable care in its execution.

Piccard (*10*) suggested taking advantage of the varied color of iodine solutions in hydrocarbons (violet) and in oxygen compounds (brown). The very dilute solutions recommended (1 to 1,000,000) required examining a long length of solution (90 cm.), which is cumbersome. Although Clarke (*3*) modified this inconvenient procedure (using 10 cc. of 1 to 40,000 solution in a test tube), the method does not appear to have come into general use. A cursory trial by the writer indicated difficulty with the two-color comparison of Piccard and Hermann (*11*), who found the color of solutions dependent on the temperature. This led to the thought that if a colored substance could be found which was soluble in oxygen compounds but insoluble in hydrocarbons an inverse solubility test might be employed as a qualitative test for oxygen, which would involve only one color.

A New Test

The recollection that the so-called ferric thiocyanate (ferric hexathiocyanatoferriate, *12*) can be extracted with ether from aqueous solution prompted its trial. Solid ferric thiocyanate prepared by evaporating an ether solution proved to be insoluble in common hydrocarbons and their halogen derivatives but soluble in the widest variety of oxygen compounds. The literature of this salt revealed numerous earlier observations on its solubility in organic liquids. As will be seen from Table I, these point directly to the application suggested in this paper.

To avoid the unwieldy systematic nomenclature, as well as the inaccurate designation ferric thiocyanate, it is proposed to term the test described in this paper the "ferrox" test. A more convenient method of applying the ferrox test is by means of filter paper impregnated with the complex salt.

TABLE I. SOLUBILITY OF FERRIC THIOCYANATE IN ORGANIC SOLVENTS

Soluble	Insoluble
Ethyl alcohol (*1*, *4*)	Chloroform (*8*, *9*, *14*), bromoform (*8*)
Isoamyl alcohol (*1*, *5*, *8*, *9*, *14*)	Carbon tetrachloride (*14*)
Ethyl ether (*1*, *4*, *9*, *14*)	Ethylene dibromide (*8*)
Acetone (*8*)	Pentane (*14*), petroleum ether (*14*)
Ethyl acetate (*9*)	Amylenes (*6*)
Amyl acetate (*8*)	Benzene (*8*, *9*, *14*)[a]
	Toluene (*8*), xylene (*8*)

[a] Contrary to these reports, Schlesinger and Van Valkenburgh (*12*) claim to have dealt with solutions of ferric thiocyanate in benzene. In the present study benzene remained absolutely colorless in the presence of ferric thiocyanate.

Procedure

One gram of ferric chloride and 1 gram of potassium thiocyanate are dissolved separately in 10 cc. of methanol, and the solutions are mixed and filtered to remove the precipitated potassium chloride. Filter paper is drenched with the resulting solution and air-dried. More than one dipping may be necessary to produce a product having a greenish reflex resembling fuchsine crystals. The paper is then cut into small squares (5 mm.) and preserved in a well-stoppered container protected from sunlight. Under such conditions the test paper may be preserved for months.

In carrying out the test a small square of the ferrox paper is stirred with a few drops of the liquid to be tested. Solids are tested as saturated solutions in hydrocarbons (or halogenated derivatives) in which appreciable solubility is observed. (Caution: Commercial chloroform contains alcohol as a preservative.) A positive test is evidenced by a deep wine-colored solution; hence traces of oxygen compounds in hydrocarbons may be detected. Mineral acids and hydrogen peroxide bleach ferrox paper.

Results

Positive tests were obtained with numerous oxygen compounds, including: benzyl, allyl, cetyl, and *tert*-amyl alcohols, cyclohexanol, glycerol, cholesterol, *n*-amyl ether, methyl-*p*-cresyl ether, phenetole, benzaldehyde, piperonal, acetophenone, benzophenone, 2-acetonaphthone, camphor, ethyl benzoate, butyl phthalate, butyl oleate, ethyl chloroacetate, olive oil, cottonseed oil, stearic acid, and benzoic anhydride. Negative tests were obtained with hexane, mineral oil, terpinene, pinene, benzene, toluene, anthracene, washed chloroform, carbon tetrachloride, bromoform, *s*-dichloroethylene, allyl chloride, propylene chloride, *tert*-amyl chloride, isoamyl iodide, benzyl chloride, 1-bromonaphthalene, diphenyl ether, methyl naphthyl ether, and triphenyl carbinol.

These results confirm those reported in Table I and indicate that positive results are always reliable but that false negatives are obtained with certain aromatic ethers such as diphenyl ether and with triphenyl carbinol. Several alkyl halides supplied by a well-known manufacturer were found to be contaminated with oxygen compounds—namely, cyclohexyl chloride, cyclohexyl bromide, *n*-amyl bromide, *tert*-butyl chloride, isobutyl bromide, and *tert*-butyl bromide. The test has been useful in checking the quality of student preparations of alkyl halides (butyl bromide and *tert*-butyl chloride), as well as to detect the contamination of mineral oil by vegetable oil.

The ferrox test is designed for use with compounds falling into Kamm's analytical group known as "indifferent compounds of C, H, and C, H, O (*7*)". The absence of elements other than these (except halogens) must be assured. Nitrogen compounds such as the amines dissolve the reagent. Few sulfur compounds have been tested, but among these carbon disulfide reacts negatively while benzyl sulfide yields a positive test.

Summary

A qualitative test for oxygen in organic compounds containing neither nitrogen nor sulfur is based on the general solubility of ferric hexathiocyanatoferriate (so-called ferric thiocyanate) in oxygen derivatives as contrasted with its complete insolubility in hydrocarbons and their halogen derivatives.

The name "ferrox" is proposed for this test. The ferrox test is suitable for the detection of small amounts of oxygen compounds in hydrocarbons or their halogen derivatives.

The claim of Schlesinger and Van Valkenburgh that ferric hexathiocyanatoferriate dissolves in benzene could not be confirmed.

Literature Cited

(1) Andrews, *Chem. News*, 70, 165 (1894).
(2) Bowen, Bourland, and Degering, *J. Chem. Education*, 16, 295 (1939).
(3) Clarke, "Handbook of Organic Analysis", 4th ed., pp. 13, 72, London, Edw. Arnold & Co., 1931.
(4) Claus, *Ann.*, 99, 50 (1856).
(5) Curtis, H. A., and Burns, R. M., *J. Am. Chem. Soc.*, 39, 37 (1917).
(6) Durand, J. F., and Bailey, K. C., *Bull. soc. chim.* (4), 33, 654 (1923).
(7) Kamm, "Qualitative Organic Analysis", 2nd ed., New York, John Wiley & Sons, 1932.
(8) Lachs, H., and Friedenthal, H., *Biochem. Z.*, 32, 130 (1911).
(9) Montignie, E., *Bull. soc. chim.* (4), 43, 106 (1928).
(10) Piccard, *Helv. Chim. Acta*, 5, 243 (1922).
(11) Piccard and Hermann, *Ibid.*, 5, 625 (1922).
(12) Schlesinger and Van Valkenburgh, *J. Am. Chem. Soc.*, 53, 1212 (1931).
(13) Shriner and Fuson, "Systematic Identification of Organic Compounds", New York, John Wiley & Sons, 1935.
(14) Urk, A. T. van, *Pharm. Weekblad*, 63, 1104 (1926).

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Qualitative Spectrographic Analysis in the Arc, with Graphite Electrodes

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The methods and apparatus used for qualitative spectrographic analysis with a direct current arc are described. From comparative studies of anode and cathode excitation it is concluded that anode excitation is generally preferable. The factors affecting the sensitivity of detection of an element are discussed, and sensitivity data are given for typical analyses.

THE direct current arc, between graphite electrodes, is the most widely applicable source for qualitative spectrographic analysis. This source may be used equally well for metals and alloys, nonconducting solids, and solutions. Because of the general usefulness of the arc method a study has been made of its applications and limitations.

Equipment

A quartz Littrow spectrograph (Hilger E1) is used for this work, since in many analyses smaller instruments do not possess sufficient dispersion. Accessory equipment includes an optical bench permanently aligned with the slit, a hood to enclose the arc, a lens system for slit illumination, an electrode holder, and a reducing sector. The complete assembly is shown in Figure 1.

The hood is particularly important, for protection of the operator from light and fumes and of the sample from contamination by vaporized metals from previous samples. When an adequate ventilating fan is available, the open-back type, shown in Figure 1, is recommended because it permits ready access to the arc controls at all times. There is a dark-glass window on the side near the operator and a 2-cm. opening on the front.

The source is a 220-volt generator. Experience has shown that steadier arc operation is obtained with 220 volts than with a 110-volt supply, although the arc drop is only 45 volts, at 10 amperes. Two 22-ohm resistors in series with the arc are used for current control. One of the resistors may be shorted, with a snap switch, so that the current can be instantly changed from 5 to 10 amperes after the arc is started.

Various types of slit illumination have been tested; the lens arrangement of Twyman and Simeon (*4*) as shown in Figure 2 has been found very satisfactory, particularly if the same arrangement is to be used for both qualitative and quantitative analyses.

The first lens, L_1, forms a sharp image of the electrodes on a screen which has an opening 3 mm. in height. Only the light passing this opening reaches the slit; the electrode heights are so adjusted that the light from the incandescent carbons is inter-

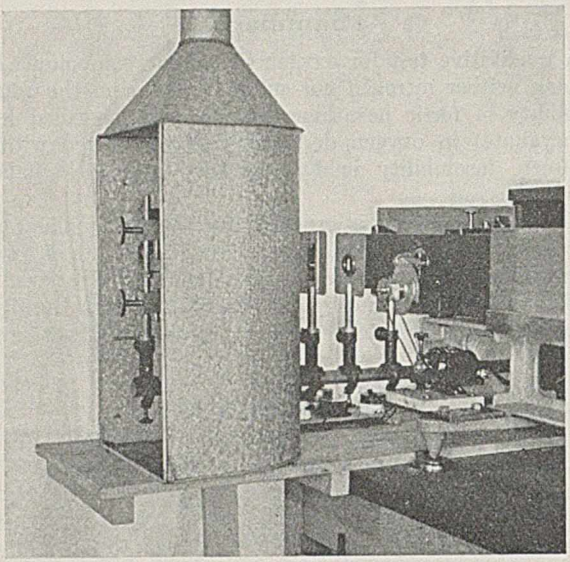

Figure 1. Accessory Equipment

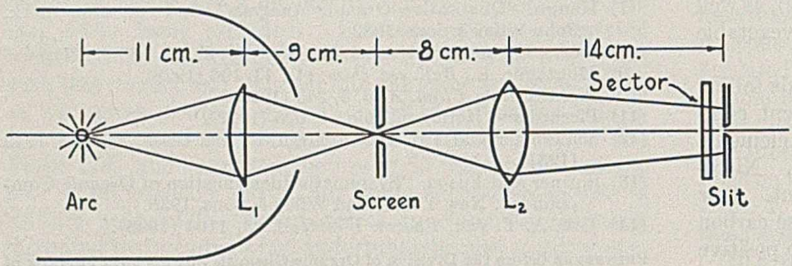

Figure 2. Lens Arrangement

cepted by the screen, and the central portion of the arc column is used for illumination. The second lens, L_2, is arranged to project a slightly convergent beam onto the slit. To adjust the position of this lens the slit is opened wide and the lens so placed that the projection of the screen opening just fills the collimator lens. The advantages of this illumination system are: (1) The intensity is high, (2) the slit is uniformly illuminated from top to bottom, (3) wandering of the arc does not affect spectrum intensity nearly so much as when a single lens is used for slit illumination, and (4) background is reduced by keeping the light of the glowing electrodes from the spectrograph.

The arc stand, Figure 3, was designed to give instantaneous control of the arc position at all times.

Vertical adjustments of the two electrodes are separately made by a rack and pinion movement. Horizontal adjustment of the two electrodes is made simultaneously by turning the stand, which is set in a socket clamp on the optical bench. Details of construction are apparent in the photograph. The side arms are 12.5-mm. brass rods, 15 cm. in length, insulated by mounting on Bakelite blocks. The insulation has been found sufficient for use with an alternating current arc at 2200 volts, and for a moderately high voltage spark. The electrodes are carried by thin-walled stainless-steel adapters, 7 cm. in length, which form spring clamps to grip the tips of the carbon rods. These adapters are advantageous in permitting rapid changing of electrodes, in protecting the insulation from high temperatures, and in economy of electrode material (the projecting portion of the electrode need not exceed 10 mm. in length). An alignment pointer, shown between the two arms, is used for making height adjustments before an exposure. During the exposure the pointer is swung to one side.

Electrodes prepared from commercial Acheson graphite rods are used for most analyses. They are purified by refluxing for two 10-hour periods in equal parts of nitric and hydrochloric acids, then by refluxing in 6 *M* hydrochloric acid, with a change every 10 hours, until a test spectrum shows sufficient purity. Finally the electrodes are rinsed in distilled water and dried on a hot plate in a porcelain evaporating dish. The treated electrodes contain boron and silicon in appreciable amounts, and traces of copper, calcium, magnesium, and sodium. A preliminary 1-minute arcing at 10 amperes will remove nearly all the copper and sodium, greatly reduce the amount of magnesium and calcium, and to some extent reduce the amounts of silicon and boron. This treatment is not advisable when the electrode is to be used for the analysis of solutions, since it leaves the graphite in a very porous condition.

The treated electrodes are, except for boron and silicon, as free of impurities as any of the spectroscopically pure grades which were tested. In fact, use of the treated electrodes is often advantageous because when electrodes are purchased in a purified condition they may become contaminated in the drilling operation. The acid treatment is inexpensive and requires little of the operator's time. For silicon and boron analyses purified graphite electrodes made by high-temperature treatment *in vacuo*, by the Dow Chemical Company, are the best that have been tested. Copper electrodes may also be used for boron analyses.

Two sizes of electrodes are recommended, 6.3 mm. (0.25 inch) for use with solutions, and 4.8 mm. (0.187 inch) for use with solid samples. Before purification craters varying in depth from 5 to 12 mm. are drilled in the lower electrodes. An assortment of depths is prepared with each batch. The crater wall is made as thin as possible in the electrodes for use with solid samples, to reduce the amount of carbon which is vaporized during the arcing of the sample. A wall thickness of about 0.8 mm. is used in the electrodes prepared for the analysis of solutions to prevent leakage of solution through the wall. The drill is set in an end cutting tool, so that the depth of the crater is automatically regulated, and the top edge is made flat in the single operation. Drilling is done in a lathe, with the drill stationary and the electrode rotated at high speed.

Cathode *vs.* Anode Excitation

Comparative studies have been made of anode and cathode excitation for 2-mg. samples of analyzed bronze, silicon, and dolomite, and for electrode blanks. The electrodes were 3 mm. in diameter, since that size is recommended for use with the cathode layer method (*1*). Duplicate spectra were taken by the following arrangements:

1. An enlarged image of the cathode region of the arc was projected onto the slit, by use of a single lens. The lower electrode, containing the sample, was made the cathode.
2. The sample was placed in the anode, and the central portion of the arc column was used as source, employing the same lens arrangement as above.
3. The Twyman-Simeon lens arrangement was used, with sample in cathode. The cathode region of the arc column was permitted to pass the screen.
4. With the lens arrangement as above, the sample was placed in the anode, and the central portion of the arc column used for illumination.

The spectra obtained were inspected for lines showing cathode enhancement, lines appearing only in the cathode region, and relative sensitivity in the various arrangements. The conclusions were:

1. When the amount of sample is very small, as in the electrode blanks, there is a marked gain in sensitivity in the cathode layer method. In the actual analysis of samples all constituents that could be detected by the cathode layer arrangement were also found by anode arcing with the Twyman-Simeon lens arrangement.
2. Arcing conditions are more uniform and reproducible when an anode arc is used. The anode arc burns more steadily than the cathode arc, and strikes directly to the bead of sample when the latter is of conducting material. The cathode arc tends to wander about the rim of the crater and to vaporize more carbon, for a given weight of sample, than the anode arc. In many cases the cathode arc consumed the electrode to such an extent that a portion of the sample rolled from the crater and was lost. Wandering of

the arc is particularly objectionable when the cathode method is used with larger electrodes, such as are required for the analysis of solutions.

3. When the cathode layer method is employed the use of single lens slit illumination is recommended, because the lines obtained are wedge-shaped and can be more readily differentiated from bands than can faint lines of uniform intensity from top to bottom. It is somewhat more difficult to obtain uniform illumination conditions with a single lens than with the Twyman-Simeon arrangement.

4. The cathode layer method is recommended for the detection of impurities in electrodes. For all other types of analysis that have been studied, where the amount of sample is not limited, anode excitation has been found preferable from the viewpoint of convenience and equal to cathode excitation in sensitivity.

Arcing Technique

The most important factor in spectrographic analysis is the technique employed in arcing the sample. In general, conditions are sought that will provide a uniform and continuous vaporization of the sample with a minimum vaporization of carbon from the electrode. The following methods are employed, for the types of sample listed, subject to variations as indicated by experience with particular samples:

Solid Alloys or Metals (oxides or salts that are reduced to metals). The sample of 5 to 20 mg. is placed in the crater of a 4.8-mm. electrode. If volatile constituents, such as mercury or cadmium, are sought the crater is 10 to 12 mm. in depth; otherwise a shallow crater 5 to 8 mm. in depth may be used. An exposure is made with the lower electrode the positive pole, the electrode is removed from the holder, and the crater wall is cut away to expose the bead of sample. The plate is racked down and another exposure is made; this exposure is continued until the sample is completely consumed. With a slit width of 0.01 to 0.02 mm. the exposure time will vary from 60 to 150 seconds in the ultraviolet region, and from 20 to 50 seconds in the visible region, depending upon the speed of the plate employed. When complete vaporization of the sample requires longer time, a reducing sector before the slit is used to make the effective exposure of the correct duration.

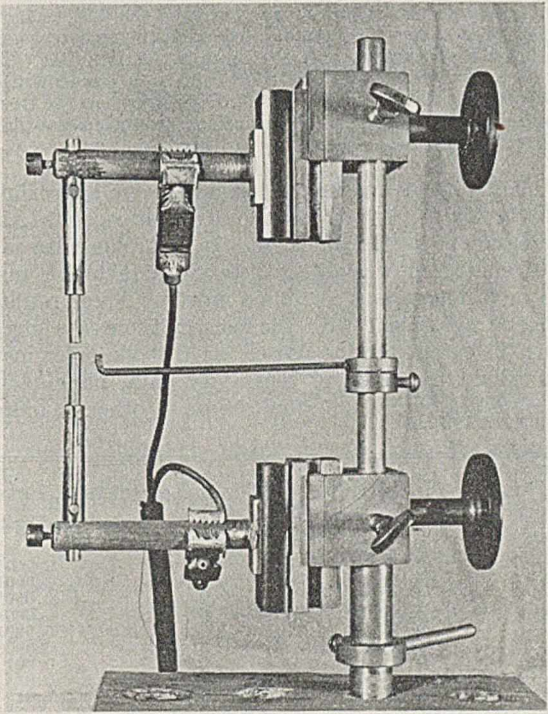

Figure 3. Arc Stand

Nonconducting Solids. The size of sample and electrode and the depth of crater, are the same as specified above. The first exposure is made until the operator can recognize, by the behavior of the arc and the color of the light, that no more sample is being consumed. The electrode is now cut down to expose the lower end of the crater and a second exposure is made until all the sample is consumed. Certain samples are found to sputter from the crater when the arc is first struck; this loss can be minimized by placing 5 to 10 mg. of anhydrous sodium carbonate in the crater, above the sample, to form a flux when the arc is struck.

Solutions. A 6.3-mm. electrode is used, in order that the crater may hold as much as 0.05 to 0.10 ml. of solution. The electrode is treated with a dilute solution of paraffin oil in ligroin or with kerosene, to render the carbon impervious to water solutions. A measured portion of sample is slowly run into the crater from a capillary pipet, with care to prevent entrapping air bubbles, and the solution is evaporated to dryness on a hot plate or in an oven. The dried residue is arced as described above. Steadier arc operation is obtained when the upper electrode contains a crater than when it is pointed.

In the analysis of very viscous solutions flat end electrodes may advantageously be employed. A drop of solution is placed on the end of the electrode and evaporated to dryness. In this case the sample is placed upon both the lower and upper electrodes. If the sample is consumed before a sufficient exposure is obtained, the electrodes are reimpregnated and several exposures made without altering the plate position.

Analysis of Spectra

Every exposure is accompanied by an iron arc reference spectrum, placed directly above the sample spectrum and slightly overlapping it. A Hartman diaphragm is used to impress the two spectra in proper relation without moving the plate holder. The opening for the reference spectrum is 1 mm. in height, and that for the sample spectrum is 1.5 mm.

The method of identification has previously been described *(3)*. The reference and sample spectra are projected, at 10 × magnification, onto charts which contain iron reference lines and analysis lines of the more common elements. When additional elements are sought, such as the rare earths which are not included in the chart, a list of the important analysis lines of these elements is made and the positions of the lines are traced on cardboard strips that can be clipped to the master chart as desired. Reference points on the master charts and the additional cards ensure reproducible placement.

The examination of spectra by projection has been found far more rapid than direct examination of the plate, and can be done without eyestrain. The sensitivity is fully as high as in direct examination of a plate; in general, any line that can be seen by use of a plate lens can be seen in the projected image.

Sensitivity

The sensitivity of spectrographic detection depends upon so many factors that it is impossible to make a general statement regarding the minimum amount of a given element that can be detected. Among the factors which affect the sensitivity the more important are:

Background Intensity. Detection of an element demands that the intensity of its lines be stronger than the background radiation. When graphite electrodes are used there is a background of CN (and other) bands, which is extremely heavy in the region 3400 to 5000 Å. Fortunately the electrode background is much lighter in the region 2500 to 3400 Å., where the best analysis lines for many of the elements occur. Elements whose most sensitive lines occur in the region of heavy background cannot be detected in as low concentration as elements giving lines on the same intensity in a region relatively free of background. Because of this it is sometimes of advantage to employ a metal, rather than a graphite, supporting electrode. The sample can often be obtained in the form of a metal rod, which can be arced or sparked without the use of a supporting electrode; generally such a procedure is desirable when it can be applied. For example, chromium has been detected by sparking the original metal in cases where it could not be identified in arc spectra made with graphite electrodes.

In addition to the background from the electrode there is always some background from the sample, either as bands or as continuous radiation from incandescent particles. The magnitude of this background will vary with the sample. Samples containing a high percentage of silicon are particularly high in background, owing to band spectra.

INTERFERING LINES. Positive identification of an element requires the presence of a sufficient number of lines to minimize the probability of coincidences. When the spectrum of a sample contains few lines identification of an impurity may be made from a single line or characteristic group of lines, but when the sample spectrum is complex a single impurity line does not establish an identification unless it can be shown that this line is not a weak line of some other constituent, and this is often difficult to prove. The sensitivity for a given element depends, therefore, upon the nature of the mixture which is examined. For example, lead can be positively identified in many biological samples by the single strong line at 2833 Å., but the identification of lead in a metal sample containing large amounts of chromium, manganese, etc., may require the presence of a sufficient amount to give several lines.

CONDITIONS OF VAPORIZATION. The conditions under which an element is vaporized may markedly affect the sensitivity of detection. Volatile elements, such as cadmium or mercury, may escape detection if the sample is arced in a shallow crater, whereas high intensity may be obtained if the sample is placed in a deep crater.

At times the sensitivity may be increased by the presence of a foreign element that raises the temperature at which the spectrum is excited. This effect was demonstrated by a series of spectra in which the amounts of trace elements in the arc were kept constant while the amount of a chief constituent was varied. Brass samples having the analysis

Element	Per Cent	Micrograms in Arc	Element	Per Cent	Micrograms in Arc
Cu	88	176	Sb	0.2	0.4
Sn	8	16	Ni	0.1	0.2
Zn	2	4	Fe	0.1	0.2
Pb	1.5	3			

were weighed out in 0.0002-gram portions. Spectra were made of the brass samples alone, and of brass samples with 10 mg. of spectroscopically pure copper added. In the latter case, although the percentages of the trace elements were reduced to one fiftieth the original value, the intensity of lead, tin, zinc, and antimony lines was found to be greatly increased; several weaker lines of these constituents, which were not visible in the spectra of the undiluted sample, appeared in the spectra taken with added copper. The constituents whose intensity is enhanced by dilution are those of greatest volatility, which apparently are lost when the amount of sample is small.

Analysis of Known Samples

Sensitivity tests have been made with various types of samples of known chemical analysis. The results are of interest, not as representing ultimate limits, but as illustrations of the variations in sensitivities that may be encountered.

1. A 25 per cent sodium hydroxide solution (sample and chemical analysis furnished by J. S. Owens) was analyzed according to the method given above for concentrated solutions, with the following results:

Element	Per Cent (Dry Basis)	Found	Element	Per Cent (Dry Basis)	Found
Pb	0.0001	W	Al	0.0007	S
Sr	0.0003	W	Fe	0.00036	S-M
Ca	0.002	S	Si	0.004	S
Ni	0.00013	—	Mg	0.0002	S-M
Cu	0.00014	S	Mn	0.0001	W

S, strong; M, medium; W, weak; —, missing.

The sensitivities are very high because of the simplicity of the sample spectrum and the low background. The dried residue did not penetrate the electrodes deeply, and there was little vaporization of carbon from the electrodes.

2. A dolomite, whose major constituents are calcium and magnesium, was analyzed. The results for the minor constituents are:

Element	Per Cent (as Oxide)	Found	Element	Per Cent (as Oxide)	Found
Fe	0.086	S	Sr	0.01	M
Al	0.069	S	Na	0.08	S
Ti	0.004	—	K	0.03	—
Mn	0.009	S	P	0.002	—

The sensitivities are somewhat less than those found for the sodium hydroxide sample because of greater electrode background; vaporization of the sample from within a crater causes more vaporization of carbon.

3. From a sample of silicon the following results were obtained:

Element	Per Cent (as Element)	Found	Element	Per Cent (as Element)	Found
Si	96.9	S	Ni	0.002	—
Fe	0.65	S	Cr	0.025	W
Mn	0.034	S	Zr	0.025	W
P	0.008	—	Ti	0.10	S
Cu	0.02	S			

The background was very heavy because of bands from silicon compounds. Consequently nickel was not found, although in brass samples it has readily been identified at percentages of 0.001 or lower. Chromium could be identified only by the lines at 4254-75-90 Å.; no other lines could be detected. Only two lines were identified for zirconium. Titanium at 0.10 per cent gave many lines.

4. A pig iron, shown by chemical analysis to contain 0.012 per cent of chromium and 0.08 per cent of phosphorus, was analyzed for these elements. When the powdered sample was arced in the usual manner only two chromium lines could be detected, and these were so faint that identification was doubtful. No lines were found for phosphorus. The greater portion of the iron was removed by dissolving the sample, converting all constituents to chlorides, and extracting ferric chloride with ether. The extracted solution was evaporated to dryness and reanalyzed. The identification of chromium was now positive, but phosphorus was not found. Other elements present, such as manganese and nickel, gave much stronger lines in the concentrated residues.

5. A series of lead samples (provided by J. N. Mrgudich), prepared by adding known amounts of trace elements to a nearly pure lead, was studied. In this series the amounts of the trace elements were halved in each successive dilution, and the sensitivity limits could be accurately determined. The following results were obtained:

Element	Sensitivity Limit, %	Element	Sensitivity Limit, %
Cd	0.003	Bi	<0.0008
Mg	<0.0008	Ag	<0.0008
Sn	0.005	Cu	<0.0001

Practically all the cadmium was found in the first arcing fraction before the crater was cut down. Magnesium was present in the electrode carbon, and the limit is not definite. Copper likewise is present in the electrode, but at a concentration of 0.0001 per cent the sample gives a stronger line than the electrode blank (no electrode absolutely free of copper and magnesium has ever been found in this work).

In all the above analyses the samples were approximately 10 mg. in weight. A percentage of 0.01 corresponds to about 1 microgram of the trace element. In favorable cases as little as 0.01 microgram was detected, but in unfavorable cases as much as 3 micrograms might be missed. These results are in general agreement with the sensitivity results given by Owens (*2*) except for the use of the cathode layer method.

To extend the scope of sensitivity data, permission has been obtained to include some results of other laboratories,

TABLE I. SENSITIVITY FOR TRACE ELEMENTS IN LEAD

Element	Limit, %	Element	Limit, %
Sb	0.001	Ni	0.000X[a]
Cd	0.005	Ag	0.0001
In	0.00X[a]	Sn	0.0005
Hg	0.00X[a]	Bi	0.0003
Pt	0.000X[a]	Cu	0.0001
Tl	0.000X[a]	Mg	0.000005
As	0.01	Pd	0.001
Ca	0.00000X[a]	Te	0.01
Fe	0.001	Zn	0.01

[a] X = > 5

TABLE II. SENSITIVITY FOR TRACE ELEMENTS IN BIOLOGICAL ASH IN SPECTRAL REGION 2500–3400 Å.

Element	Line	Detectable in Arc *Microgram*
Al	3083	0.02
	3093	0.02
Sb	2598	0.40
Bi	3068	0.04
Cd	3261	0.40
Cr	2836	0.50
	2843	0.50
	2986	0.20
Cu	3274	0.02
Fe	3021	0.02
Pb	2833	0.02
Mg	2796 2803 2582	<0.02
Mn	2594 2795 2798 2801	0.02
Hg	2537	0.20
Ni	3051	0.40
Ag	3281	<0.02
Sn	2840	0.02

and these are presented in Tables I and II. The lead analyses were furnished by R. D. McLennan and A. J. Phillips of the American Smelting and Refining Company. Exact experimental details are not available; the sample was arced in a supporting graphite electrode which was made the anode, and in general conditions were about the same as described in this paper. Data for the ash of biological material were furnished by Jacob Cholak, Kettering Laboratory of Applied Physiology, University of Cincinnati, who evaporated a solution of the ash in the crater of a graphite electrode and used an anode arc. The limits given for the biological ash are the lower limits for quantitative analyses and in some cases the lower limit of detectability lies at considerably smaller values. The limits given for the detection of traces in lead samples are not regarded by the authors as ultimate limits, but represent those prevailing under the experimental conditions employed, with samples weighing 25 mg.

Acknowledgments

The writers are glad to acknowledge helpful suggestions from Jacob Cholak, of the University of Cincinnati, J. N. Mrgudich, of the University of Illinois, and J. S. Owens, of Armstrong Cork Company, in addition to the contributors of the sensitivity tables.

Literature Cited

(1) Mannkopff, R. and Peters, C., *Z. Physik*, 70, 444 (1931).

(2) Owens, J. S., IND. ENG. CHEM., Anal. Ed., 11, 59 (1939).

(3) Pierce, W. C., Torres, O. R., and Marshall, W. W., *Ibid.*, 11, 191 (1939).

(4) Twyman, F., and Simeon, F.. *Trans. Optical Soc.* (London), 31, 179 (1929).

Continual Observation of Changes in Weight at Oven Temperatures

An Apparatus for Use in the Study of Drying Rates and in the Oxidation of Oils

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THE apparatus described in this paper was developed for the quantitative study of problems involving a gain or loss in weight. Problems of the first type are chiefly associated with the oil obtained from the soybean because it is used in the drying oil industry where the capacity to absorb oxygen is an index of its usefulness for that purpose, and the decrease of this capacity is an indication of the deterioration of the oil.

Problems of the second type—involving a loss in weight—arise in the study of drying rates. From the curves obtained in such studies, the proper temperature and time for the determination of moisture may be ascertained and the values for the moisture content resulting from the various methods of analysis may be correlated.

It appears probable from preliminary experiments that the sensitivity and versatility of the apparatus should make it useful in many industries where a knowledge of the extent and rate of atmospheric oxidation or dehydration is important. For example, it should aid in the study of the oxidative rancidity in edible fats of both vegetable and animal origin, the aging of rubber, the classification of lubricating oils, the testing of oxidation inhibitors, and the classification of catalysts responsible for the deterioration of lubricating oils and edible oils, or for accelerating the drying of paints.

Description of Apparatus

The apparatus consists essentially of a Jolly spring suspended above an oven and suspending within the oven a suitable container for the sample to be investigated, and a device for accurately observing changes in the elongation of the spring.

The desirability of observing changes in samples exposed to various atmospheres led to enclosing the system, and the sensitivity of the long spring to changes in temperature necessitated a water jacket, *A*, for the circulation of water from a constant-temperature bath. In order to minimize the possibility of convection currents of warm air reaching the spring, *J*, through the tube, *B*, *B* was extended and three baffles, *C*, were introduced just above the oven. The baffles have so efficiently prevented further upward movement of the warm air that practically all the heat is dissipated below the first two. Without water circulating through the jacket, the temperature rise in the spring chamber is less than 2° when the temperature of the oven is raised from room temperature to 105° C. With circulating water, the chamber remains at a constant temperature about 0.2° C. above that of the bath even when the temperature of the bath varies as much as 10° from the room temperature. This close agreement in temperature between the bath and the jacket is made possible by rapid circulation of the bath liquid. The capacity of the jacket is 100 cc. and, since 1 liter of water per minute is circulated through the jacket, a complete change is effected every 6 seconds.

The spring is of the lighter type usually used in the Jolly balance and has a capacity of 9 grams with an elongation of about 5 cm. per gram. This type of spring is designed to give uniform elongation over the entire working range, although in this apparatus the total change in elongation is seldom as much as 1.5 cm. The sensitivity is such that a change of 2 mg. in the suspended weight will produce a change of 0.1 mm. in the elongation. It is advisable to recalibrate the spring at intervals.

Two types of devices for observing the changes in elongation have been used. In the first (Figure 1), a millimeter scale, *D*, is fastened in tube *B*, very near to its center, and a long pointer, *H*, is attached at right angles to the suspension extending from the spring to the sample container. It is necessary to have the pointer rest lightly on the scale in order to avoid parallax, and to tap the tube before taking a reading in order to make sure that the pointer is free. A hand lens is used in making the reading.

The second device (Figure 2) has a scale, *E*, attached to the suspension and, by means of a short-focus lens, an image of the scale is projected onto a small ground-glass screen carrying a fine cross hair. As the scale moves with the change in weight of the sample, its image moves past the stationary cross hair, permitting an accurate determination of the movement. By the proper choice of lens and its position relative to that of the scale, a considerable magnification can be attained, permitting a direct reading without the use of a hand lens.

Two methods of enclosing the sample have been developed. In one type (Figure 1), a desiccator is placed inside the oven, attached by a ground-glass connection to tube *B* extending through the top of the oven. A leveling plate, *G*, must be used beneath the desiccator, since, each time a sample is introduced and the connection is made with the upper portion of the apparatus, it is necessary to realign the entire apparatus to make sure that the spring and suspension are hanging free of the walls of the enclosing tube. The other or vacuum oven type (Figure 2) has the spring enclosure permanently aligned and is attached to the vacuum chamber itself, which eliminates all operations except that of attaching the sample container to the suspension.

Drying Rate Studies

Drying rate curves may be obtained rapidly and with accuracy by the use of this apparatus. The curves shown in Figure 3 represent the drying rate of ground soybeans in an air oven at 105° C. Both curves were obtained on the same afternoon from two 3-gram samples of a single batch of beans. The maximum difference between the two curves is 0.07 per cent of moisture.

Another method of obtaining such curves involves placing a number of weighed samples in an oven, removing specimens at intervals, cooling them in a desiccator, and finally weighing. Besides involving considerable time, the method is subject to several errors, at least one of which is indeterminable. This error is due to the period of cooling in the desiccator, during which time the sample may lose more moisture, or, when dry, actually compete with the desiccant for any available moisture.

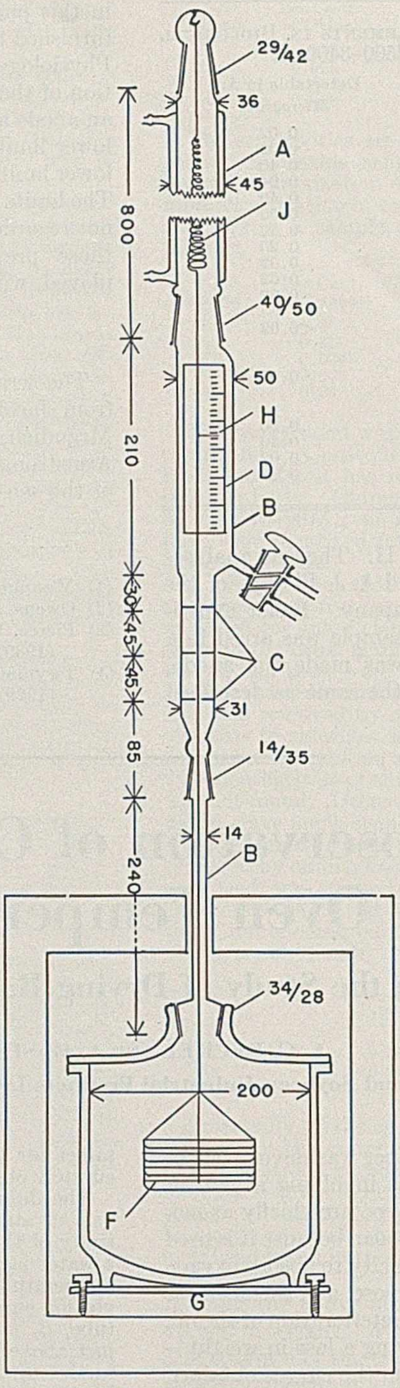

Figure 1

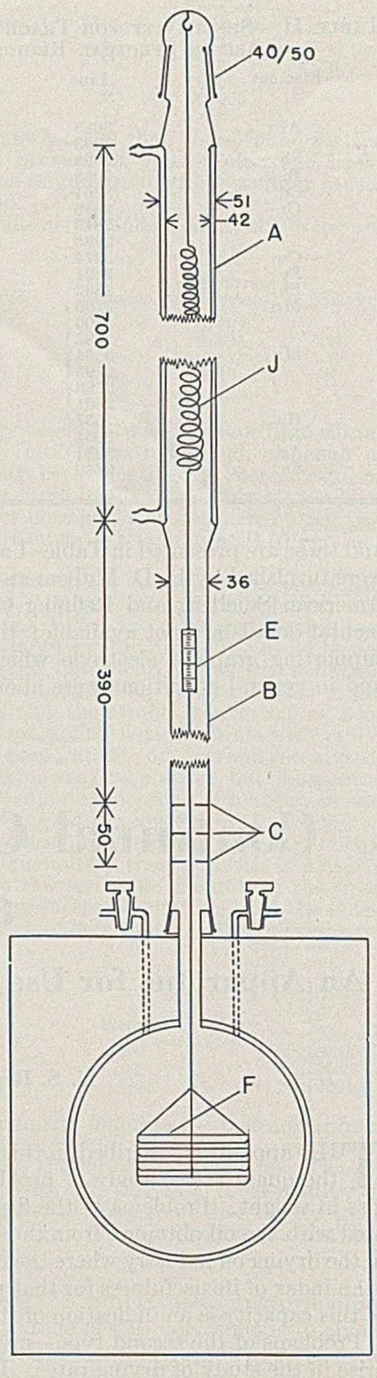

Figure 2

Oxidation of Oils

Semidrying and Drying Oils. Typical of the results obtained by the use of this apparatus are the oxygen absorption curves shown in Figure 4, which were obtained with soybean oil dispersed on filter paper, *F*. The oxidations were carried on in an atmosphere of dry oxygen at a temperature of 80° C. up to the points on the curve marked *A*, at which the temperature of the oven was raised to 105° C.

These curves are presented merely as examples of the usefulness of the apparatus in such investigations and to delineate the approach to the problems involved. From this point of view the curves may be discussed.

The first point to be studied will be the extreme left or "loss in weight" portion of the curve. A preliminary experiment performed in an atmosphere of nitrogen indicated that a loss in weight due to volatile matter and a gain in weight due to oxidation are concurrent. In curve 2 a loss in weight is observed, which is 1.5 per cent greater than is apparent in curve 1, although the observations were made on samples from a single batch of oil which was stored in a glass-stoppered bottle. Curve 2 was obtained from measurements made on a sample withdrawn after the bottle containing the oil had been exposed to the light for a number of weeks.

Following the "loss in weight" portion of the curve there is evident in the case of curve 1 a short "induction" period amounting to 1.5 hours which is followed by oxygen absorption. The period of rapid oxidation seems to proceed at approximately the same rate, but it must be noted that the oil which had been exposed to light, and which suffered the greater initial loss in weight, absorbed 1.76 per cent less oxygen, calculated on the basis of the low point in the curve (volatile matter-free basis), than did the fresh oil. The original oil (curve 1) was stable for the entire period of observation, 13 hours, following the maximum absorption of oxygen, whereas the deteriorated oil reached a maximum and then immediately started to lose some volatile material.

The temperature of 80° C. at which the oxygen absorption was carried out was chosen on the basis of reported evidence (*1*) that the peroxides of soybean oil decompose at 110° C. The very rapid loss in weight, following the rise in temperature of the oven to 105° C., seems especially indicative of abrupt peroxide decomposition in the fresh oil (curve 1) since there was no previous evidence of a loss of volatile matter over a long period of time (13 hours) at 80° C.

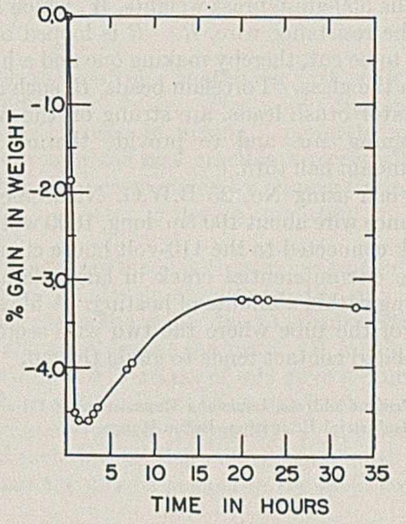

Figure 5. Oxidation of Lubricating Oil

Lubricating Oils. As an example of the application of this apparatus to the investigation of problems other than those that are being conducted in this laboratory, a sample of lubricating oil dispersed on filter paper was oxidized in an atmosphere of dry oxygen at a temperature of 130° C., with the results that have been plotted in the curve shown in Figure 5. After an initial rapid loss in weight due to volatile matter, the sample absorbed 1.44 per cent of oxygen (calculated on the volatile matter-free basis). Because of the importance of oxidation in the "gumming" of lubricants and because of the empirical nature of existing tests, it seems that this apparatus should offer a more rigorous method for comparing the oxidizability of lubricants, as well as providing a method for studying the effect of oxidation inhibitors and various metallic catalysts of these reactions.

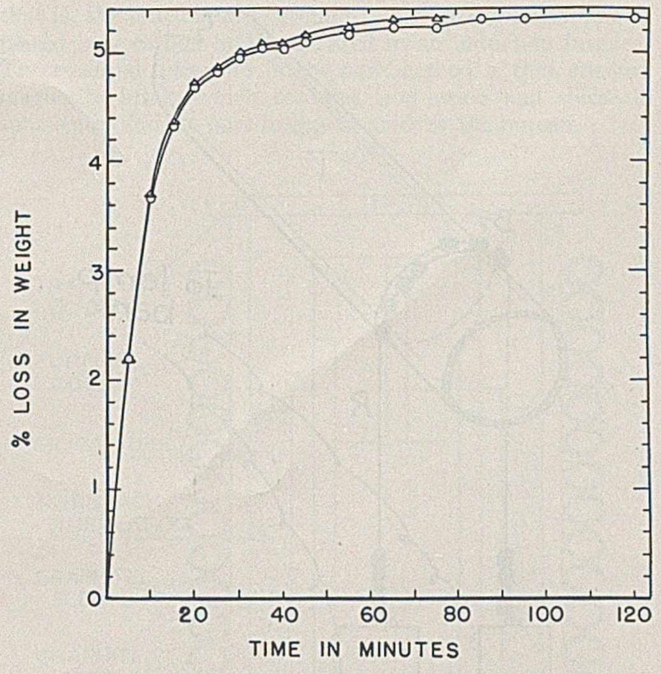

Figure 3. Drying Rate Curves

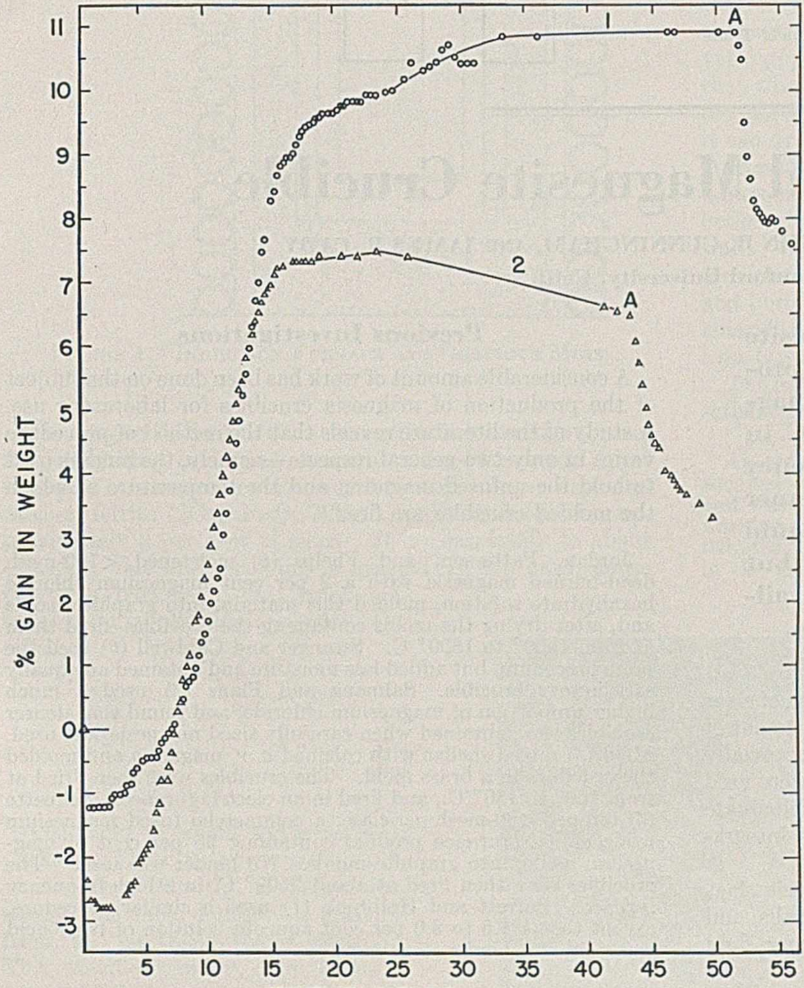

Figure 4. Oxidation of Soybean Oil

Curve 1, ○
Curve 2, △

Literature Cited

(1) Nakamura, Mitsuo, *J. Soc. Chem. Ind., Japan*, 40, Suppl. Bind., 225–9 (1937).

A Hot Wire Cutter for Glass Tubing

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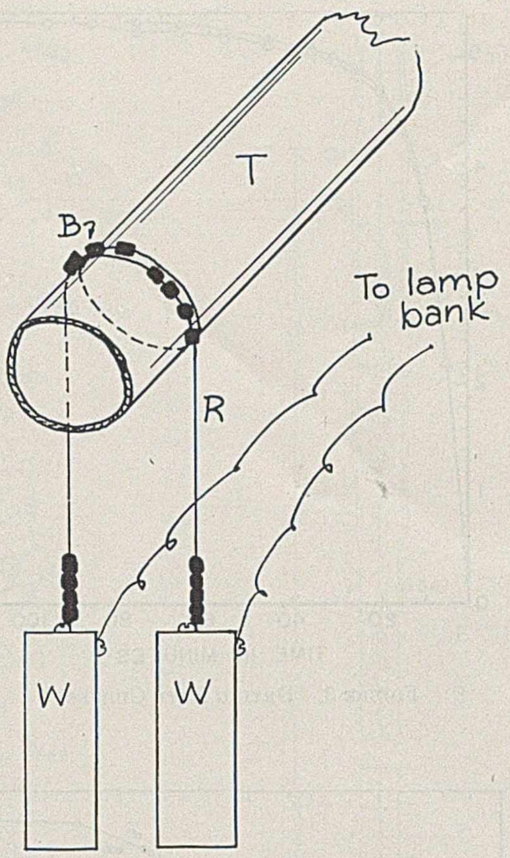
AN EXTREMELY simple glass cutter, by which pressure of a glowing wire looped around the glass shape is secured by means of suspended weights, is shown in the figure. This device produces clean breaks and is instantly adjustable to any size of glass tubing or bottles.

Current is supplied through a lamp bank to binding posts on the 350-gram brass weights, *W*, which hang from the ends of the resistance wire, *R*. *R* is looped once around the object to be cut, thereby making one and a half turns in contact with the glass. Porcelain beads, *B*, such as are used on commutator brush leads, are strung on the wire to separate the adjoining arcs and to provide thermal insulation on the redundant half turn.

When using No. 25 B.W.G. Nichrome or Chromel A resistance wire about 100 cm. long, 1000 watts' load in the lamp bank connected to the 110-volt house circuit produces a complete circumferential crack in large-diameter ordinary glass tubing within a minute of heating. A file scratch made at the top of the tube where the two wire segments approach uninsulated contact tends to guide the cut.



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An Improved Magnesite Crucible

WELTON J. CROOK, JOHN R. CUNNINGHAM, AND JAMES R. CADY
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A new method of producing magnesite crucibles for laboratory purposes is proposed. The base material is crushed magnesite brick which is sintered at 2000° C. in a graphite mold placed in a high-frequency furnace. Crucibles made in this manner have been found to be impervious to liquid basic slags which not only permeate but actually disintegrate commercially available magnesia and magnesite crucibles.

IN CONNECTION with a laboratory investigation of slags which is being conducted in the Mining Department of Stanford University, it was found that the commercially available magnesia and magnesite crucibles, which were used in the production of high-lime slags, were entirely inadequate because of excessive porosity and a tendency to disintegration at working temperatures.

It was desired to produce a crucible in which basic slags could be melted without prohibitive attack on the walls, and which would be sufficiently impervious to hold very fluid slags.

The type of crucible finally produced withstood successfully the conditions of freedom from excessive chemical attack, porosity, and disintegration due to expansion, at a working temperature of 1600° C.

Previous Investigations

A considerable amount of work has been done on the subject of the production of magnesia crucibles for laboratory use. A study of the literature reveals that the method of procedure varies in only two general respects—namely, the binders used to hold the unfused magnesia and the temperature at which the molded crucibles are fired.

Jordan, Patterson, and Phelps (*2*) moistened <100-mesh dead-burned magnesia with a 2 per cent magnesium chloride hexahydrate solution, molded this material into graphite molds and, after drying the molds containing the crucibles, fired them at from 1600° to 1800° C. Swanger and Caldwell (*6*) used the same procedure, but added less moisture and obtained an equally satisfactory crucible. Salmang and Planz (*4*) used a much higher proportion of magnesium chloride, and found that denser crucibles were obtained when carefully sized magnesia was used. Mehl (*3*) mixed shellac with calcined C. P. magnesia and molded the crucibles in a brass mold. The crucibles were then dried at from 100° to 130° C., and fired in an electric furnace. Schuette (*5*) tamped <60-mesh periclase, a commercial fused magnesium oxide electric furnace product containing 95 per cent of magnesium oxide, into graphite molds. No binder was used. The crucibles were then fired at about 2500° C. in a high-frequency furnace. Barrett and Holbrook (*1*) used a similar procedure, except that a 1.5 to 3.0 per cent aqueous solution of boric acid was used as a binder.

Method of Manufacture

The method of manufacture is similar to that used by the U. S. Bureau of Mines in making pure magnesia crucibles—

that is, the crucible mix, ground to the proper grain size, is placed in a carbon mold and fired in an induction furnace. The essential difference in the new method is that crushed magnesite brick, which contains iron oxide and silica, is substituted for the pure magnesia used by the bureau.

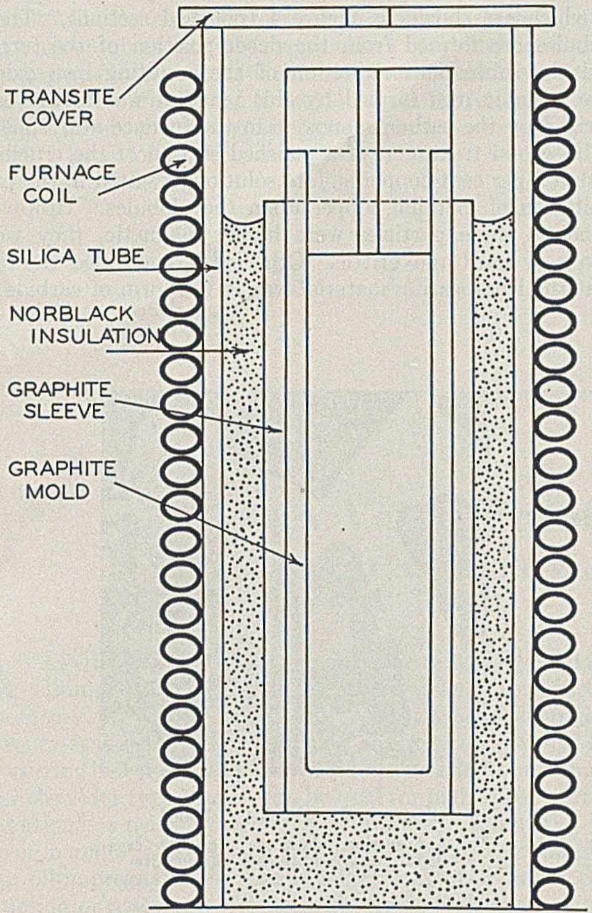

Figure 1. Induction Furnace and Graphite Mold

The magnesite used in the new crucible is a common type of refractory used in furnace construction. It is made up of magnesia grains cemented together with magnesium and calcium ferrite ($2CaO.Fe_2O_3$, $2MgO.Fe_2O_3$), and contains approximately 8 per cent of silica. It crushes easily to about 38 mesh; but finer grinding is resisted by the hard, dense magnesia particles. This brick material has the following analysis:

	%
SiO_2	8.68
FeO	1.78
Fe_2O_3	4.68
CaO	5.99
MgO	78.00
(Total Fe	4.66)

The mold in which the crucible is packed and fired is shown in Figure 1, as it rests within the induction furnace. The mold material is graphite from an electric furnace electrode. This machines easily, and forms a smooth surface.

The first crucibles fired were made with the brick mixture crushed to pass a 38-mesh screen but, as these crucibles were porous, the material was reground to pass a 48-mesh screen. A screen analysis of the reground material gave the following result:

Mesh	Weight *Grams*	%
<48, > 65	306.0	24.6
>100	274.5	22.0
>200	324.5	26.0
<200	343.0	27.3

The various screen sizes were remixed, in the proportions given below, to give grain size proportions that agreed with a mixture found satisfactory by the Bureau of Mines (*1*).

Mesh	%
<65, >100	31.4
>200	30.8
<200	37.8

There is probably an ideal mix containing just sufficient particles of each size to fill all voids. This would correspond with the aggregate sizing used in mixing a perfectly made concrete. Since there is in the new crucible a recrystallization of the magnesia grains accompanied by a precipitation of cementing material, this factor is not so important in this case.

A number of crucibles were made with varying amounts of moisture in the mix; in almost every case the crucibles failed by inward collapse of the walls, due to steam pressure developed between the crucible and the mold. It was found that only 1 ml. of water in 175 grams of mix gave a crucible that was dry enough to resist collapse by steam pressure, and yet damp enough to stand well in the mold. It is essential that this amount of moisture be thoroughly mixed with the dry material, and that the mix be packed in the mold before it can dry out.

In some cases a saturated solution of boric acid was used for dampening the mix, in the expectation that the binding action of the boric acid would prevent collapse of the crucible wall. When the correct amount of moisture was established, no difference could be detected between the use of tap water and boric acid solution. A saturated solution of magnesium chloride was also tried as a binder but, again, no improvement over tap water was observed.

The following method of filling the mold was found the most satisfactory:

An amount of crucible mix between 150 and 175 grams was weighed out, depending upon the height of side walls desired, and was dampened with 1 ml. of tap water by spreading and working with a spatula until the moisture was uniformly distributed. Between 30 and 40 grams of this mix were placed in the mold to form the crucible bottom. A tapered wooden

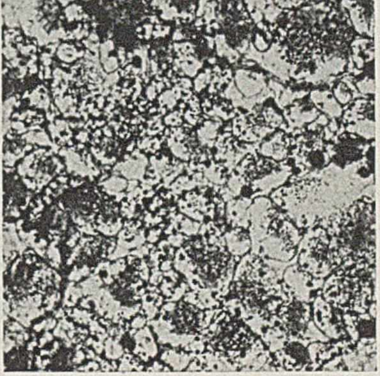

Figure 2. Crucible Wall (× 100), Thin Section

Figure 3. Crucible Wall (× 400), Thin Section

plug was placed in the mold and centered with a spirit level. The remainder of the mix was packed around the plug by lightly tapping the mold on a solid support. The mold, plug, and mix were then vibrated on a "Hum-mer" shaking screen until the plug could be turned with difficulty by the fingers. The mold was placed in its graphite sleeve, in the furnace, before the wooden plug was removed.

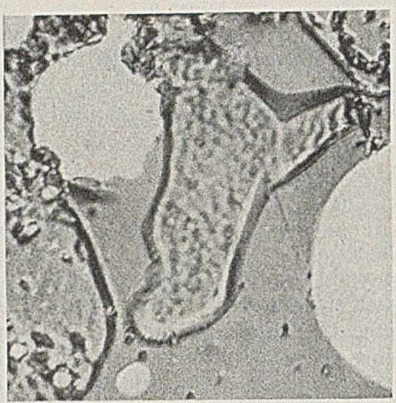

FIGURE 4. CRUCIBLE WALL (× 1000)
Polished section, showing metallic iron, magnesia, and binding material

No difficulty was encountered in heating the crucible to the effective burning temperature of 2000° C. In fact, so great was the rate of heating when the current was full on, that the crucibles were generally cracked about half-way up the side wall. This cracking was caused by a large differential in heating the top and bottom of the mold, which was overcome by slower and more uniform heating. A burning temperature of 2000° C. was selected after some experimentation. Crucibles burned at lower temperatures were found to be porous, and the contained iron readily oxidized when subsequently heated at 1500° C. in the oxidizing atmosphere of a gas-fired melting furnace. Evidently the ferrites in the original mix are not decomposed much below 2000° C. Temperatures higher than 2000° C. were not used for fear of slumping the walls of the crucible. After firing at the proper temperature for approximately 0.5 hour, the current was shut off and the crucibles were allowed to cool undisturbed in the high-frequency furnace.

Character of the Product

The novel properties of the magnesite crucibles produced by this method are due to a complete change in the nature of the original ferrite binding material, accompanied by a recrystallization of the magnesia grains. Ferrites forming the binding material of the original brick are completely decomposed at 2000° C. in the reducing atmosphere of the carbon mold. The calcium and magnesium oxides are set free, and combine with the silica to form dicalcium and dimagnesium silicate. A study of a thin section of the finished crucible revealed this silicate mixture as having parallel extinction and lathe-shaped crystals. This cementing material surrounded the isotropic magnesia particles. It was evident that the magnesia recrystallized and formed grains considerably larger than the original particles in the brick. Surrounding these grains and making a perfect bond with them is the cementing material described above (Figures 2 and 3, thin sections).

Scattered through the cementing material are globules of iron or, more exactly, iron carbide, the shape and character of which are shown in Figure 4 (polished section). These globules are formed from the decomposition of the ferrite and the subsequent reduction of the resulting iron oxide. The metallic iron formed by this reaction was finally carburized by the carbon monoxide in the furnace atmosphere. A 10-second treatment of a polished section of the crucible, with a 5 per cent copper sulfate solution, resulted in the precipitation of metallic copper upon the globules. However, although these particles were highly magnetic, they were also very hard and brittle. Other tests confirmed the fact that the iron-bearing material was in the form of carbide.

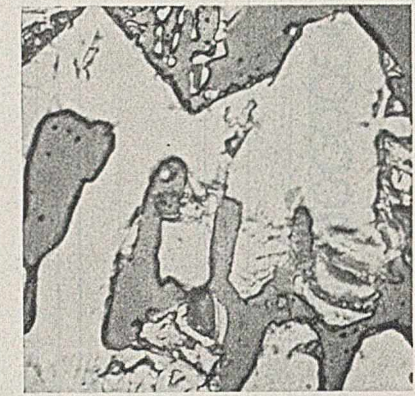

FIGURE 5. SLAG (× 1000)
Polished section, showing magnetite crystals in a matrix of ferrous akermanite

When one of the finished crucibles was heated in an oxidizing atmosphere at 1500° C. for 20 minutes, the zone of oxidation was found to be not over 0.08 cm. (0.03 inch) in depth. The iron particles in this zone were oxidized to ferric oxide and combined with the periclase to form ferrite. Further oxidation seemed to be prevented by the density of the crucible.

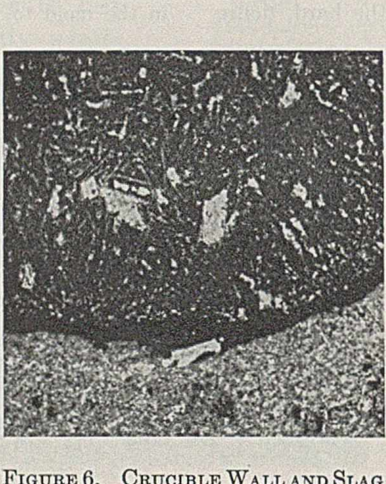

FIGURE 6. CRUCIBLE WALL AND SLAG (× 7)
Thin section. Upper (dark) area is slag.

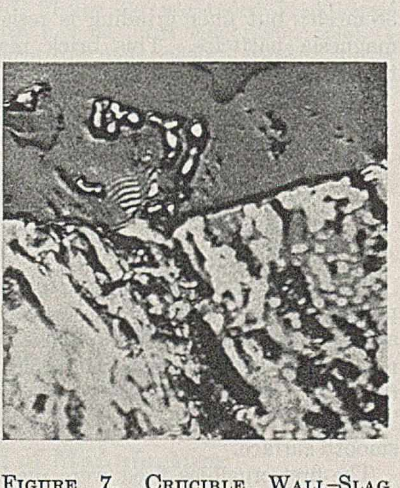

FIGURE 7. CRUCIBLE WALL–SLAG INTERFACE (× 1000)
Polished section. Dark area is slag.

Practical Test of Crucible

To determine the suitability of these crucibles as containers for molten slags, a charge consisting of approximately equal parts of lime, silica, and ferric oxide, which had been found to corrode and permeate commercial magnesia and magnesite crucibles, was melted in one of the new crucibles. The melting time was about one-half hour. A final temperature of 1500° C. was reached. At this temperature a quiet melt had been obtained, and the slag was in a very fluid condition. The gas was then shut off from the furnace, and the crucible and contents were allowed to cool slowly in the furnace.

The analysis of this slag, after melting and slow cooling, was found to be as follows:

	%
SiO_2	26.24
FeO	14.03
Fe_2O_3	21.27
CaO	30.66
MgO	8.53

A polished section showed that this slag contained dendrites of magnetite embedded in a background of ferrous akermanite ($2\,CaO.FeO.2SiO_2$), as shown in Figure 5.

Figures 6 and 7 are micrographs showing the boundary between the slag and the crucible. This boundary is relatively sharp, and the crucible wall was practically impervious to the slag.

Literature Cited

(1) Barrett, E. P., and Holbrook, W. F., Ind. Eng. Chem., Anal. Ed., 10, 91–3 (1938).

(2) Jordan, L., Patterson, A. A., and Phelps, L. H., *Trans. Am. Electrochem. Soc.*, 50, 115–24 (1926).

(3) Mehl, R. F., *Ibid.*, 46, 149 (1924).

(4) Salmang, H., and Planz, N., *Arch. Eisenhüttenw.*, 6, 341–5 (1932–33).

(5) Schuette, G. N., *Bur. Mines Rept. Investigations* 2896 (Oct., 1928).

(6) Swanger, N. H., and Caldwell, F. R., *Bur. Standards J. Research*, 6, 1131–43 (1931).

A Vapor-Proof Laboratory Stirrer

GEORGE CALINGAERT, Ethyl Gasoline Corporation, Detroit, Mich.

A VAPOR-PROOF laboratory stirrer with readily available oil-impregnated bronze bearings has been used in this laboratory, in preference to the conventional glass-in-glass mercury-seal bearing, for carrying out reactions which call for stirring in a closed system. This stirrer is an improvement over the older type since it can be used for high-speed stirring operations, is neither fragile nor cumbersome, eliminates the use of mercury, and does not trap liquid during the operation. The oil-impregnated bronze bearings employed in its construction offer enough resistance to the flow of vapor to prevent leakage, even when the apparatus is operated under slight pressure or vacuum, and it operates much more smoothly than the conventional mercury-seal stirrer.

The latest and best design, illustrated in Figure 1 (left), comprises a 1.59-cm. (0.31-inch) steel drill rod, *A*, fitted at one end with a mixing device such as a small bronze propeller from 2.2 to 7.5 cm. in diameter, depending on the size of the reaction vessel opening. Such a propeller is obtainable in a variety of sizes from shops supplying parts for toy motor boats.

An equally satisfactory type of mixing device is the centrifugal pump illustrated in Figure 1 (center). The combination holder, bearing, and seal is a 25-cm. length of 0.95-cm. (0.375-inch) brass pipe, *C*, equipped at both ends with a pressed-in oilless bearing, *B*, about 1.92 cm. (0.75 inch) long and 1.59 cm. (0.31 inch) in inside diameter. These bearings are available on the market in numerous sizes and from various manufacturers (for example, Bound Brook Oilless Bearing Company, Bunting Brass & Bronze Company, Amplex Division of the Chrysler Corp., Johnson Bronze Company, Nolu Oilless Bearing Company, and Paramount Oilless Bearing Company).

A typical setup using this type of stirrer is illustrated in Figure 1 (right). The brass pipe is fitted into the stopper of the flask, and after this has been lined up and clamped, the upper end of the stirrer shaft is connected to the motor shaft by means of a short piece of heavy-walled rubber tubing.

Stirrers of this type have been used repeatedly in flasks containing boiling organic solvents without any leakage or deterioration of the bearings. When corrosive liquids are used, the stirrer may be constructed of stainless steel or some other suitable corrosion-resistant alloy.

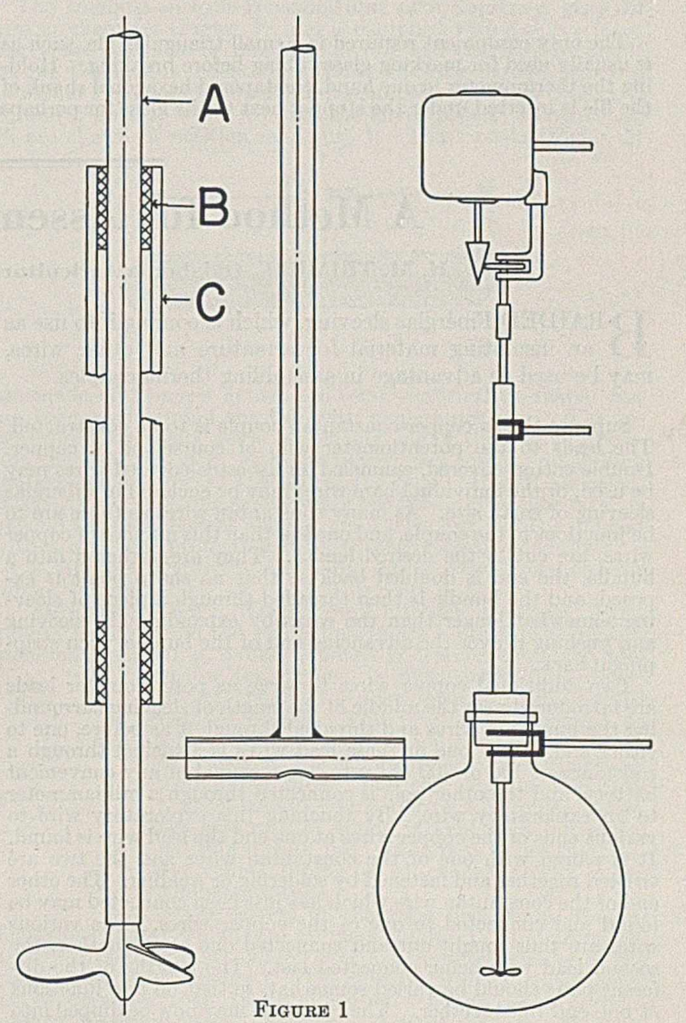

Figure 1

Removal of Adhered Rubber Stoppers

A. J. BAILEY, University of Minnesota, Minneapolis, Minn.

ONE method of removing adhered rubber stoppers from thermometers, Büchner funnels, tubing, etc., is so simple that it appears inevitable that it has been known and used. A search of the literature and a canvass of fellow research men, however, have failed to bring to light any knowledge of existence, and it would appear desirable to emphasize its unusual effectiveness.

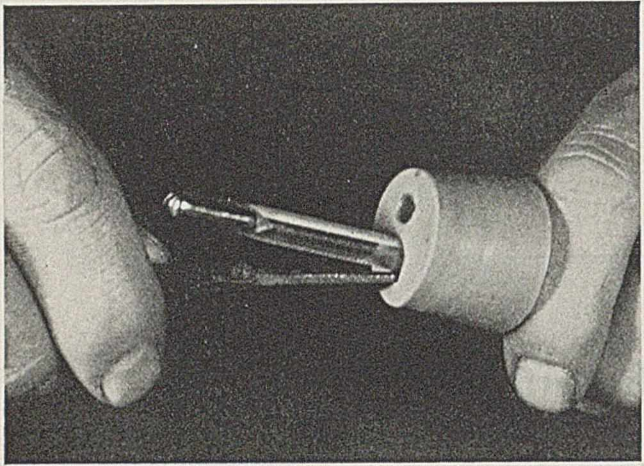

FIGURE 1

The only equipment required is a small triangular file, such as is usually used for marking glass tubing before breaking. Holding the thermometer in one hand, the tapered hexagonal shank of the file is inserted under the stopper next to the glass for perhaps an eighth of an inch. As shown in Figure 1, the top of the technician's right hand is rotated toward his body. Since the shank of the file is pinched between the rubber and the glass, which have widely different coefficients of friction, rotation causes the side next the glass to slide, while that next the rubber merely grips the rubber and sinks in. Continued rotation tears the rubber from the glass by lifting the rubber vertically away from the glass surface. After a portion of the thermometer periphery has loosened, the axis of the file (as shown in Figure 1) is shifted by movement of the technician's hand toward his body, so that as the file shank moves around the thermometer, it becomes inserted more and more under the stopper until finally the tip appears at the opposite end.

In this laboratory, no stopper has failed to yield to this treatment. Stoppers which other workers had been unable to remove (without cutting) were submitted as a test of the method and were removed by a file shank quickly and effortlessly. It has operated on hard stoppers as well as gum stoppers, while size has little or no effect. It is equally effective in removing tubing stuck to high-vacuum apparatus, and not only has greater ease and speed but is much less likely to break complex glass tubing systems than cutting off the rubber tubing with a knife.

Rubber tubing or stoppers close to a neck or side tube may be removed almost as easily, the only modification necessary being that of working almost one revolution in one direction and then reversing until the side tube blocks the way again, with a little manipulation at an angle to loosen the rubber immediately behind the side tube. Partial loosening obtained by some methods necessitates jerking or pulling to remove the rubber, with some probability of breaking. Since the rubber can be completely loosened with a file shank, this danger is eliminated.

A Method for Assembling Thermocouples

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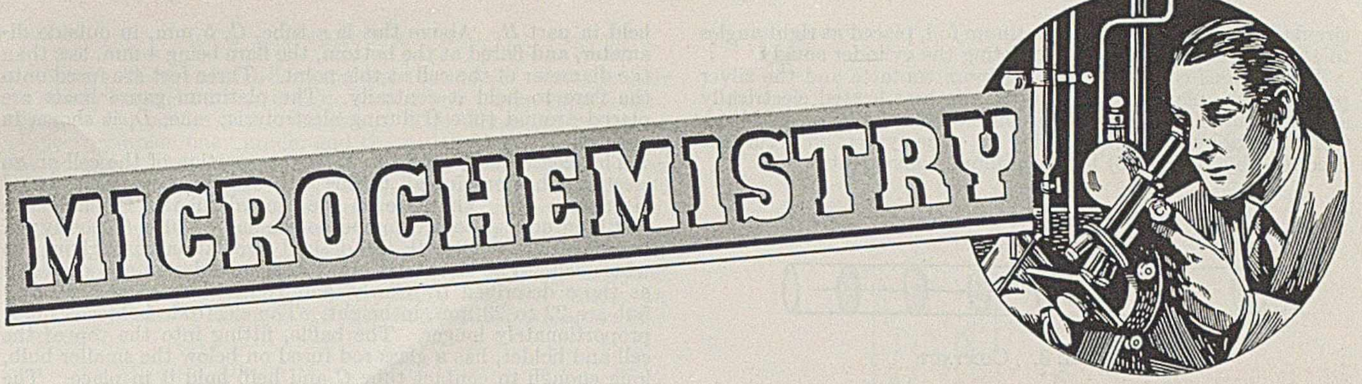
BRAIDED Fiberglas sleeving, which is coming into use as an insulating material for armature and other wires, may be used to advantage in assembling thermocouples.

Suppose that a copper-constantan couple is to be constructed. The leads to the potentiometer will, of course, be of copper. Double cotton-covered, enameled, or asbestos-covered wires may be used, or the individual bare wires may be enclosed in Fiberglas sleeving of small size. As many constantan wires as there are to be junctions in the couple, and one less than this number of copper wires, are cut to the desired length. They are gathered into a bundle, the end is doubled back so that no sharp point is exposed, and the bundle is then threaded through a piece of sleeving somewhat longer than the wires by expanding the sleeving and pushing it over the advancing end of the bundle, then stripping it back.

Two additional copper wires to serve as potentiometer leads are introduced near the middle of the length of sleeving surrounding the bundle of wires and threaded through it as before, one to either end. Now one of these lead wires is attached through a resistance of 100 or 200 ohms to one terminal of any convenient battery, and the other pole is connected through a milliammeter to an exploratory wire. By touching this exploratory wire to various ends of the copper wires at one end the lead wire is found. It is paired with one of the constantan wires and the two are twisted together and fastened by soldering or welding. The other end of the constantan wire which has just been connected may be found and connected to one of the copper wires. The various wires are thus sought out and connected one after another, the second lead wire being connected last. The lengths of the different pairs should be varied somewhat, so that no two junctions at one end fall together. The junctions may now be dipped into insulating varnish which is baked on. The sleeving is drawn snugly over the bundle of wires, and its end is cut off beyond the junctions and closed by binding it with fine wires or with insulating varnish, which is baked on. The lead wires are also threaded through a piece of the sleeving, leaving short projecting ends for attachment to the potentiometer. It is then bound to that containing the bundle of wires with fine wire to complete the couple.

Thermocouples assembled in this way are flexible and readily adapted to various assemblies without the necessity of handling a tangle of loose wires, they occupy less space than those assembled in glass, porcelain, or metal tubes, and they are not readily broken. Their insulation permits their ends to be slipped into wells or metal protecting tubes, with or without paraffin to aid in conducting heat. They have long lives, give relatively low rates of heat leak from apparatus, and are at least as constant in calibration as couples assembled in other ways. Couples with as many as five junctions have been assembled in this manner and used, but still more complex ones offer no difficulties.

Fiberglas sleeving may be had with internal diameters of 0.067 to 0.5 inch. The 0.125-inch size has been found best for the couples which the author has made. When braided with a small percentage of cotton to give it strength it provides satisfactory insulation somewhat above 100° C. When the cotton is burned out it tends to become brittle and to break when flexed, but its intrinsic insulating properties are not impaired.



Determination of Sulfur in Organic Compounds

A New Microchemical Method

E. W. D. HUFFMAN,[1] University of Colorado, Boulder, Colo.

A new method for the determination of sulfur in organic compounds is described and the inherent errors are discussed. The method applies to compounds containing no other elements than carbon, hydrogen, nitrogen, sulfur, and oxygen. The method consists of two parts (1) a reaction between the oxides of sulfur, formed during a catalytic combustion, and metallic silver with the quantitative formation of silver sulfate; (2) the electrodeposition of the silver from the silver sulfate. The plating is carried out in dilute isopropyl alcohol solution. Carbon-hydrogen values may be obtained simultaneously.

IT IS well known that the silver filling in the carbon-hydrogen combustion tube is vigorously attacked when compounds containing sulfur are burned and that silver sulfate is formed. It was found that with compounds containing no elements other than carbon, hydrogen, oxygen, and sulfur good results could be obtained for carbon and hydrogen when only silver was present in the tube filling; evidently all the sulfur was retained. This has recently been confirmed (*8*).

Reactions between the oxides of sulfur and elemental silver in an atmosphere of oxygen have been reported (*2*, *9*). That the reaction with sulfur trioxide is quantitative was pointed out by Dennstedt (*2*), and by Kirner (*4*), who suggested the possibility of using this reaction as a basis for a sulfur determination.

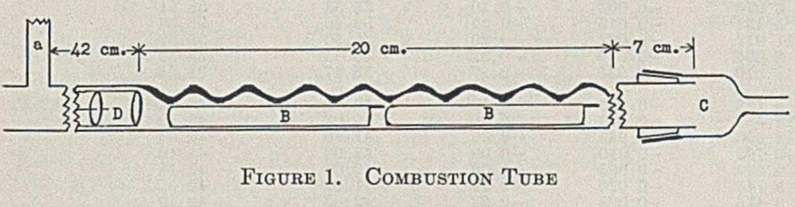


Figure 1. Combustion Tube

The formation of silver sulfate plus a subsequent electrodeposition of the silver from the silver sulfate has been made the basis of a new method for determining sulfur in organic compounds which may contain carbon, hydrogen, nitrogen, and oxygen. The factor, S:2 Ag, is very favorable, 1 mg. of sulfur being equivalent to 6.73 mg. of silver. The method has been in use for about 3 years, during which time many modifications have been studied. The apparatus and procedure described below were found to be the best.

Apparatus

The combustion tube is made from Jena Supremax glass 10 mm. in diameter (Figure 1), and is equipped with a side arm, *a*. Forty-two centimeters from the side arm and extending for about 20 cm. the tube is indented on top so that the indentations dip to within 1 mm. of the top of the platinum-gauze boats (Figure 1, *B*, and Figure 2) which contain the silver pellets. Two boats, *B*, are shown in position in Figure 1. These boats (Figure 2) are made of 52-mesh gauze, are semicylindrical in shape, and are reinforced around the top with a platinum wire. The indentations are easily made by placing one of the boats in position, heating the glass with the oxygen-gas torch, and pulling the glass down toward the top of the boat. If well annealed, this portion is as strong as the rest of the tube. The tube extends beyond the indentations about 7 cm. This exit end is equipped with a cork and protecting tube, *C*, conveniently made from a 13 × 100 mm. Pyrex test tube, and has a drawn-down end for rubber tubing.

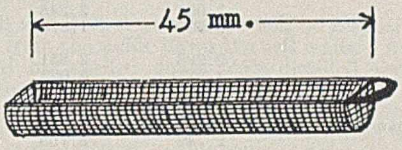


Figure 2. Boat

Combustion Train. Oxygen and nitrogen are used. Running in parallel from the two cylinders are a pressure regulator, precision pinchclamp, bubble counter, and preheater. The preheater for oxygen is filled with "molecular" silver; the one for nitrogen with finely divided reduced copper. The preheaters converge to a three-way stopcock which is connected to the side arm of the combustion tube through an Anhydrone tube. The exit end of the combustion tube is connected to a Mariotte bottle, the side arm of which is kept in a horizontal position during use. It is best to use steamed-out rubber tubing for all connections up to the combustion tube.

The section of the tube just before the indentations contains platinum contacts (Figure 1, *D*) of any type. A very efficient contact, which effects a thorough mixing of the gases, is pictured in Figure 3. The cylinder, which is only slightly less in diameter than the combustion tube, is made of fine-meshed platinum gauze. Strung on a light platinum wire are

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circular baffles made of thin platinum foil, placed at right angles to the axis of the cylinder and fitting the cylinder snugly.

The sections containing the platinum contacts and the silver pellets in the platinum gauze boats are best heated electrically and with furnaces about 20 cm. long which may be pushed back from the tube without disturbing it. The type of long furnace described by Hallett (*3*) has been found convenient.

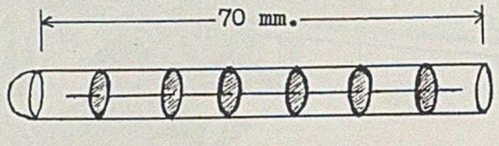

Figure 3. Contact

The contacts are maintained at about 600° C., and the silver at about 450° C. Both furnaces should be equipped with thermocouples, particularly the one for the silver. The section containing the silver may be heated with gas, this part being held in a centrally bored aluminum bar 5 cm. in diameter and the apparatus arranged so that the tube may be pushed forward for cooling.

Electrolytic Apparatus. The assembled cell is shown in Figure 4, *A*. The upper part is made of 28-mm. and the lower of 19-mm. (outside diameter) Pyrex glass tubing. A small amount of ground glass (ca. 40-mesh) is sintered to the bottom, *E*, to aid even boiling. During electrolysis the silver pellets are held in part *B*. Above this is a tube, *C*, 5 mm. in outside diameter, and flared at the bottom, the flare being 4 mm. less than the diameter of the cell at this point. Three feet are fused onto the flare to hold it centrally. The platinum gauze boats are placed around tube *C* during electrolysis; one, *D*, is shown in position.

The electrodes are held in the upper portion of the cell on an electrode holder similar to the one described by Clarke and Hermance (*1*). The flare on the central tube of the holder is just large enough to accommodate the end of tube *C* loosely; if larger, it interferes with the desired circulation throughout the whole cell. The electrodes are of the same design and diameter as those described by Clarke and Hermance (18 and 9 mm.) but are 22 to 23 mm. in height. The electrode holder is made proportionately longer. The baffle, fitting into the top of the cell and holder, has a glass rod fused on below the smaller bulb, long enough to contact tube *C* and help hold it in place. The cell is heated from below with a microburner, a current being set up through tube *C* and the central tube of the holder. To remove the solution after electrolysis a siphon tube (Figure 4, *F*), connected to an aspirator through a suction flask, fits into the cell in place of the baffle and extends into the silver.

Small clips, especially for the cathode, are preferable to mercury cups for connecting the leads.

A conventional electrical hookup is used. The current consumption is very low, so that a bank of three dry cells in series is adequate as a source. Radio volume controls may be used as rheostats. A 0- to 50-milliameter and a 0- to 5-voltmeter are employed.

Table I. Determination of Sulfur

Sample	Sample Weight	Ag Found	Ag Theory	Ag, Difference from Theory		S Uncorrected	S Corrected	S Theory
	Mg.	*Mg.*	*Mg.*	*Mg.*	%	%	%	%
Diphenyl sulfone	3.019	2.979	2.984	−0.005	−0.18	14.66	14.69	14.69
	4.101	4.035	4.054	−0.019	−0.47	14.62	14.65	
	3.555	3.511	3.514	−0.003	−0.08	14.68	14.70	
	3.457	3.413	3.417	−0.004	−0.12	14.67	14.70	
	2.386	2.356	2.359	−0.003	−0.11	14.67	14.70	
	2.004	1.980	1.981	−0.001	−0.05	14.68	14.71	
	1.217	1.199	1.203	−0.004	−0.30	14.64	14.67	
Thiodiphenylamine	1.468	1.579	1.590	−0.011	−0.66	15.98	16.02	16.09
	2.987	3.229	3.234	−0.005	−0.16	16.06	16.10	
	5.176	5.592	5.604	−0.012	−0.22	16.05	16.09	
	4.523	4.882	4.897	−0.015	−0.31	16.04	16.07	
	3.002	3.248	3.251	−0.003	−0.08	16.08	16.11	
	0.996	1.075	1.078	−0.003	−0.32	16.04	16.07	
Sulfanilic acid	2.296	2.851	2.860	−0.009	−0.30	18.45	18.49	18.51
	3.237	4.023	4.033	−0.010	−0.24	18.47	18.50	
	5.275	6.560	6.572	−0.012	−0.18	18.48	18.52	
Benzene sulfonamide	2.758	3.765	3.786	−0.021	−0.55	20.28	20.33	20.40
	2.749	3.768	3.773	−0.005	−0.12	20.37	20.41	
	3.984	5.455	5.469	−0.014	−0.25	20.35	20.39	
	4.236	5.803	5.814	−0.011	−0.20	20.36	20.40	
	1.878	2.570	2.578	−0.008	−0.30	20.33	20.38	
	1.011	1.387	1.388	−0.001	−0.08	20.39	20.42	
Sulfonal	3.052	5.752	5.768	−0.016	−0.28	28.00	28.06	28.08
	2.799	5.285	5.290	−0.005	−0.10	28.06	28.11	
	2.135	4.029	4.035	−0.006	−0.15	28.04	28.10	
	3.996	7.534	7.552	−0.018	−0.24	28.02	28.07	
Benzothiazolethiol	4.188	10.776	10.806	−0.030	−0.28	38.23	38.31	38.34
	3.398	8.747	8.767	−0.020	−0.23	38.25	38.33	
	3.403	8.753	8.780	−0.027	−0.31	38.22	38.30	
	2.112	5.435	5.449	−0.014	−0.26	38.24	38.32	
	2.439	6.286	6.293	−0.007	−0.11	38.30	38.37	
	2.265	5.834	5.844	−0.010	−0.17	38.27	38.35	
	3.010	7.758	7.766	−0.008	−0.10	38.30	38.38	
	1.200	3.094	3.096	−0.002	−0.07	38.31	38.39	
2,2′-Dithiobisbenzothiazole	3.412	8.841	8.857	−0.016	−0.18	38.50	38.58	38.57
	3.984	10.311	10.342	−0.031	−0.30	38.46	38.53	
	2.771	7.184	7.193	−0.009	−0.12	38.52	38.60	
	1.548	4.008	4.018	−0.010	−0.26	38.47	38.55	
	1.185	3.073	3.076	−0.003	−0.10	38.53	38.61	
	2.092	5.415	5.431	−0.016	−0.29	38.46	38.54	
	4.244	10.995	11.017	−0.022	−0.20	38.50	38.57	
	3.118	8.069	8.094	−0.025	−0.31	38.45	38.53	
	5.012	12.975	13.010	−0.035	−0.27	38.47	38.55	
Thiourea	2.871	8.122	8.138	−0.016	−0.19	42.04	42.12	42.12
	5.086	14.387	14.416	−0.029	−0.20	42.03	42.12	
	4.477	12.641	12.690	−0.049	−0.39	41.96	42.04	
	3.810	10.789	10.799	−0.010	−0.09	42.08	42.16	
	3.193	9.045	9.050	−0.005	−0.06	42.09	42.18	
	2.027	5.725	5.745	−0.020	−0.34	41.97	42.05	
	1.226	3.467	3.475	−0.008	−0.23	42.02	42.10	
Dithiooxamide	1.994	7.138	7.159	−0.021	−0.29	53.19	53.30	53.35
	2.341	8.373	8.405	−0.032	−0.40	53.15	53.25	
	2.939	10.527	10.552	−0.025	−0.23	53.22	53.33	
	3.172	11.359	11.388	−0.029	−0.26	53.21	53.32	

Reagents

Silver pellets, 1 mm. in diameter and 1 mm. high, are made with a punch 1 mm. in diameter from sheet silver 1 mm. thick, rolled from a bar at least 5 mm. thick. The silver should be of "spectrographic fine" grade, and the pellets should be as dense as possible. One ounce (31 grams) of the sheet makes enough pellets for two fillings. The new pellets are treated with hot 1 to 1 sulfuric acid to remove foreign matter from the punch, etc.

Molecular silver is prepared in the usual way, and used in the oxygen preheater. Copper, 40-mesh, is reduced in hydrogen and used in the nitrogen preheater. Isopropyl alcohol, analyzed grade, magnesium sulfate heptahydrate, analyzed grade, an oxygen cylinder a nitrogen cylinder, and distilled water are also required.

Procedure

The silver pellets, which are kept under a little isopropyl alcohol in a glass-stoppered test tube, are transferred to the platinum gauze boats with the aid of a glass rod flattened at one end. The gauze boats are best held on a small glass stand, similar in design to the stand usually used for carbon and hydrogen absorption tubes, which is kept in a small petri dish. The boats should be filled just level with the top, so that they will pass easily under the depressions in the combustion tube. The filled boats are placed in an oven (110° C.) for 5 minutes to drive off the isopropyl alcohol and are then transferred with platinum-tipped forceps directly from the oven into the exit end of the combustion tube through which a stream of oxygen (4 to 5 cc. per minute) is passing. They are pushed into place with a platinum wire fastened to a thin glass rod. As soon as the boats are in place and connection is made to the Mariotte bottle, the furnaces, already at the proper temperatures, are pulled over the tube.

A maximum of four boats, each containing 2.5 to 3 grams of pellets, are employed. One boat will handle up to about 0.5 mg. of sulfur; two boats, 1.5 mg.; three boats, 2.5 mg; four boats, 4 mg. (Three boats were used for all samples reported in Table I.)

In 2 to 3 minutes after the furnaces are over the tube the sample is introduced in a platinum boat and the combustion carried out with the usual precautions. After the sample has been burned away, the tube is heated through again, starting about 3 cm. in front of the original position of the wire gauze. The tube is heated directly, the flame encircling it. Although no backlash is usually visible, small amounts of material almost invariably pass backward during combustion, and on the second heating a minute drop or thin white fumes may form as the burner approaches the furnace. After the second heating is completed the three-way stopcock is turned and nitrogen passed through the tube at a rate of 10 cc. per minute. After 50 cc. of nitrogen have passed through the tube the furnaces are pushed back and the silver filling is allowed to cool in the nitrogen stream (the silver may be left in this condition under pressure in nitrogen overnight).

The clean, dry cell with tube *C* in place (Figure 4) is kept in the oven during the combustion. When the silver is near room temperature the cell is removed from the oven (a 150-cc. Erlenmeyer flask is a convenient stand for the hot cell) and a few drops of isopropyl alcohol are added. This volatilizes and displaces most of the air. The boats of pellets are immediately withdrawn from the tube and dropped into the cell, so that they fall around tube *C*, and 3 cc. of isopropyl alcohol are added. The cell is tapped so that the pellets fall out of the boats into the bottom of the cell (Figure 4, *B*). The electrodes on the holder are placed in the cell (Figure 4, *A*) and the cell is clamped on a stand over the microburner. (The cathode is cleaned with hot concentrated nitric acid, rinsed with distilled water, dried in an oven at 110° C. for 10 minutes, cooled, and weighed.) The isopropyl alcohol is heated to boiling and 1 cc. of a 3 per cent magnesium sulfate solution is added, followed by hot distilled water up to the bottom of the electrode holder. The solution is allowed to mix for a minute or so. Meanwhile electrical contact is made, excepting for the electrolyte, and the voltage is set near 1.5 volts. The cell is then filled with hot distilled water to 1 to 2 mm. above the central tube of the electrode holder and the baffle is inserted. The flame is so adjusted that the boiling is vigorous and even. Boiling must be continued throughout the deposition.

The voltage is so adjusted that 15 milliamperes flow (1 to 1.5 volts). In a very few minutes, depending upon the quantity of silver ion present, when about 98 per cent has been deposited, there is an abrupt drop in conductance. The voltage is readjusted (2 to 2.5 volts), so that 20 milliamperes flow and this is continued for 30 minutes, during which there will be an abrupt increase in conductance. However, it is not necessary to readjust the current.

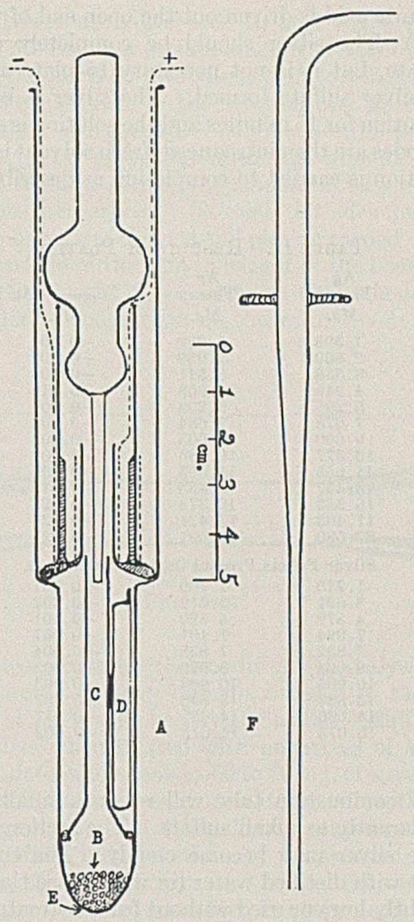

Figure 4

If the cell was well cleaned there will be a continuous flow of condensate from the baffle down the cell walls. Any drops that form should be washed down with distilled water about 15 minutes before the end of the deposition.

At the end of 30 minutes the flame is extinguished, the baffle removed, and the siphon inserted. The solution is siphoned off while cold distilled water is introduced into the cell until the current flow indicates that the electrolyte has been displaced. The cell is then allowed to empty, the electrical contact is broken, and the silver pellets are immediately covered with a little isopropyl alcohol.

The holder with the electrodes is removed to a clean dish, the cathode removed with platinum tipped forceps, and the lead washed with a spray of distilled water. The cathode is hung in the oven for 10 minutes (110° C.), then removed to near the balance, and weighed when cool.

The electrode holder and anode are covered to protect them from dust. It is not necessary to clean the anode between depositions if properly used and protected.

Some of the silver pellets adhere in clusters, which are broken up with a glass rod in either the cell or test tube. These clusters interfere only as they make the filling of the boats more difficult. If another analysis is to follow immediately, the boats are filled directly from the cell; if not, the pellets and isopropyl alcohol are transferred to the stoppered test tube.

Table I presents a recent series of determinations on known compounds, interspersed with determinations on unknown materials. Before calculating the per cent of sulfur an amount equal to 0.2 per cent of the weight of the silver found is added to the weight of the silver.

Setting Up New Apparatus

Before a new setup is used it is necessary to carry out the full procedure, employing a large excess of sulfur and preferably using about 0.05 cc. of concentrated sulfuric acid. (The excess sulfuric acid is driven out the open end of the combustion tube.) The silver should be completely coated with silver sulfate, but it is not necessary to plate all the silver from the silver sulfate formed. The silver is boiled in the plating solution for 15 minutes and the solution is siphoned off. The electrodes are then introduced, fresh solvent is added, and the deposition is carried to completion as described above.

Table II. Results of Plating

Ag_2SO_4 Sample Mg.	Ag Found Mg.	Ag Theory Mg.	Ag Error Mg.	Ag Error %
2.022	1.398	1.399	−0.001	−0.07
4.276	2.960	2.959	+0.001	+0.04
5.117	3.538	3.541	−0.003	−0.09
7.167	4.949	4.959	−0.010	−0.20
8.974	6.205	6.209	−0.004	−0.07
11.106	7.678	7.684	−0.006	−0.08
13.878	9.600	9.603	−0.003	−0.03
15.010	10.377	10.386	−0.009	−0.09
16.854	11.655	11.663	−0.008	−0.07
19.445	13.437	13.455	−0.018	−0.13
23.663	16.352	16.373	−0.021	−0.13
25.182	17.403	17.424	−0.021	−0.12
39.893	27.580	27.601	−0.021	−0.08
Silver Pellets Present during Electrolysis				
2.470	1.710	1.709	+0.001	+0.06
5.231	3.621	3.619	+0.002	+0.06
7.053	4.879	4.880	−0.001	−0.02
10.262	7.094	7.101	−0.007	−0.10
11.314	7.832	7.828	+0.004	+0.05
13.006	8.994	8.999	−0.005	−0.05
15.765	10.905	10.908	−0.003	−0.03
20.006	13.839	13.846	−0.007	−0.05
21.134	14.606	14.623	−0.017	−0.11
23.232	16.073	16.075	−0.002	−0.01

The new combustion tube will retain a small amount of sulfur, apparently as alkali sulfate. The section of the tube around the silver may become cloudy. The tube may be washed out with distilled water (in which case the first result will be slightly low) or used without further treatment.

Treating the pellets with excess sulfur serves to loosen any small adhering fragments and to increase their surface by etching, making a more active filling.

It is essential that the platinum gauze boats be boiled in a solution of silver sulfate.

After the deposition is complete a blank should be run to make sure that the silver is in good condition. The procedure is carried out in full as described, except that no compound is burned (unless it contains no elements other than carbon, hydrogen, oxygen, and nitrogen). A drop of 1 *N* sulfuric acid is added to the plating mixture to simulate the actual conditions of electrolysis. The blank determined in this way should not exceed 0.01 mg. and is usually less than 0.005 mg.

Plating

An anodic deposit of silver peroxide, or peroxysulfate, is formed when silver sulfate is plated from neutral or slightly acid solutions. Reported in the literature are successful analytical methods involving cyanide or ammoniacal solutions. Cyanide dissolves silver readily, and it was found that ammonium hydroxide does to a small extent. A search was made for a solution conducive to good plating which did not attack the elemental silver, so that a separate washing of the pellets would not be necessary.

As the anodic deposit of silver peroxide, formed when only the simple silver ion is present, is a good oxidizing agent, it was proposed to introduce a reducing agent which would set the silver free, so that it would be transferred to the cathode. Ethanol was tried first; no anode deposit was formed but the plate on the cathode was not very adherent, probably because of the formation of acetic acid. Weak acids have a tendency to promote a somewhat inferior plate. A very excellent plate is obtained with a secondary alcohol; isopropyl alcohol has proved the best. An attempt was made to use secondary butyl alcohol, which has a boiling point very near that of the solution, but a number of high results were obtained and it was found that traces of a resinous material, insoluble in water and only difficultly soluble in alcohol and ether, were formed. The reaction is apparently much more complex than was first assumed. If the anode is coated with the peroxide and then an attempt is made to transfer the silver to the cathode using the dilute isopropyl alcohol solution, only small percentages are transferred in long periods of plating. The peroxide is apparently reduced, but the resulting silver is not readily transferred. This may be further illustrated by attempting to transfer elemental silver from the anode to the cathode. No indication of the reduction of the silver sulfate by the boiling isopropyl alcohol has been observed.

It is essential that the solution be at or very near the boiling point throughout the deposition, as the anodic deposit forms at lower temperatures, and that the electrodes complete electrical contact immediately upon immersion. (If the solution cools, the anode must be cleaned before the next deposition.)

It is unnecessary to rinse the cathode with any solvent other than water, but alcohol and ether may be used to speed up the drying if desired.

Results of plating are shown in Table II.

Discussion

The Blank. The nitrogen and the magnesium sulfate are used to control the blank. If the silver is allowed to cool in a stream of oxygen a thin layer of silver oxide is formed, equivalent to about 0.050 mg. of silver for 5 grams of pellets. Silver oxide decomposes with increase in temperature and the decomposition pressure at 450° C. is extremely high (*6*). It reforms upon cooling in the presence of oxygen. If the oxygen is displaced with nitrogen and the silver is allowed to cool in an atmosphere of nitrogen the oxide does not form. The few drops of isopropyl alcohol added to the hot cell serve to displace the air and protect the silver if it has not been allowed to cool completely to room temperature. Even when this factor is controlled there will remain a variable blank amounting to as much as 0.03 mg. for 5 grams of pellets, due to colloidal solution of the silver in the boiling solvent. If an electrolyte is added this effect is minimized and the blank will be about 0.005 mg.

Thirty milligrams of magnesium sulfate heptahydrate, added in solution as a matter of convenience in measuring, have been found sufficient; larger amounts increase the plating time. The magnesium sulfate is not essential to the plating, but is a factor in controlling the blank. The doubly charged magnesium ion is more effective than an ion with single charge.

Because of the tendency of silver to go into colloidal suspension the use of very finely divided silver (molecular silver) is out of the question.

If the pellets are mostly coated with silver sulfate, both factors of the blank are greatly minimized. The coated portion will not be readily attacked by the oxygen, and the silver sulfate is an electrolyte and serves to minimize the formation of colloidal silver. It was found that good results could be obtained in the absence of nitrogen and added electrolyte if the amount of sulfur involved fell within certain limits relative to the amount of silver filling.

The use of preheaters depends on the purity of the oxygen and nitrogen available. There are usually traces of oxygen in the nitrogen. Just what is present in the oxygen that causes the slight increase in blank value has not been determined. In the absence of the preheaters the blank values and analytical results are more variable; the blank value averages slightly higher than 0.01 mg.

A small variable was encountered in connection with the distilled water, which was made in an all-Pyrex glass still having two Kjeldahl traps. Tap water, treated with a little potassium permanganate and distilled once, was satisfactory most of the time, but on two or three occasions increases in blank values were traced to it. If a few pieces of silver foil are placed in the boiling flask the water is consistently good.

The reagents must be free of metals which will be deposited under the same conditions of plating. The only one encountered was iron. One sample of magnesium sulfate was found to contain 0.02 per cent of iron and one sample of silver was contaminated with iron. Both led to high results.

It is best to protect the combustion tube by connecting it to a Mariotte bottle, particularly if gas heating is employed. Apparently sulfurous fumes from the gas diffuse into the open combustion tube, leading to a higher blank value in the silver nearest the exit end.

If the pellets are in daily use the blank value remains low, but if they stand for some time, even in the isopropyl alcohol, a higher result (0.01 to 0.03 mg.) will be obtained on the following determination. Pellets that have stood for some time should be boiled in the plating solution for a few minutes before use.

Combustion. The temperature of the platinum contacts should be maintained at about 600° C. At temperatures exceeding 700° C. low results were obtained and if the platinum contacts were washed the resulting solution gave a test for sulfate—very weak after one combustion, but appreciable after two or three. This phenomenon was not noticed at the lower temperature.

It is recommended that the silver be heated to about 450° C. Quantitative formation of silver sulfate was found to take place at 350° C., but the capacity of the silver filling was very low at this temperature. The silver becomes more and more active as the temperature increases and good results were obtained at 550° C. At temperatures approaching 500° C. and above the silver pellets form clusters that are difficult to remove from the boats. (All temperatures were checked with a high-temperature mercury thermometer.)

Since the temperature necessary for quantitative formation of sulfur trioxide in the system $2SO_2 + O_2 \rightleftarrows 2SO_3$ is 400° C. (*5*), sulfur dioxide may also be quantitatively retained by the silver (*9*).

Correction Factor. As illustrated in Table I, the results are on the average low by an amount very close to 0.2 per cent of the silver theoretically available. (This value was not determined by direct averaging but results were weighted, depending upon the course of the individual determinations.) The error is not so evident where small amounts of sulfur are concerned but is obvious with the larger quantities. This error was made the subject of a rather intensive investigation, but has only been certainly accounted for in part.

One small positive error in the method—the blank—is proportional to the amount of silver surface present but is so small that it can be considered constant. Table II shows that the plating results are all low, as is to be expected. In the absence of the silver pellets this amounts to a little less than 0.1 per cent and in their presence to about 0.05 per cent, about 0.15 per cent of the silver theoretically available remains to be accounted for.

It is essential that the platinum gauze boats be boiled in a silver sulfate solution before being used. Silver is deposited on the platinum during this boiling, primarily in proportion to the amount of platinum surface present. Four gauze boats will increase in weight by about 0.15 mg. If this silver coating is not removed an extremely small amount, if any, is deposited on a second treatment in the boiling solution. If these boats with their silver coating are used to hold the silver pellets during the combustion, a certain amount of this coating will probably be transformed into silver sulfate which would be washed off the platinum in the solution and an equivalent amount of silver redeposited. The fraction of the coating attacked would be proportional to the amount of sulfur involved and consequently to the amount of silver deposited electrically on the cathode. To test this idea part of the surface of the boats was cleaned and plating carried out. The order of magnitude of the gain in weight of the boats and the deficiency in the weight of the silver on the cathode checked with the order of magnitude of the error involved in the method.

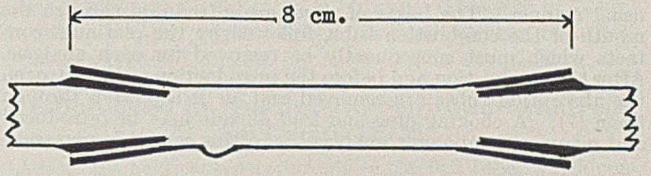

Figure 5

To reproduce accurately the conditions of analysis in these experiments would be very difficult because of the manner in which the silver is attacked by the oxides of sulfur. Five grams of pellets when treated with an excess of sulfur will form silver sulfate equivalent to 60 to 70 mg. of silver. However, a 5-gram filling will retain quantitatively less than 20 per cent of this amount. The silver already coated continues to form silver sulfate, but the efficiency drops more and more as the coating becomes thicker. (It is essential that at least 1 cm. of silver appear free of coating in every analysis.)

Because of this deposition of the silver on the platinum in the boiling solution and the incomplete transfer of silver from the anode to the cathode, the electrodes should complete electrical contact upon being immersed in the solution.

It appeared probable that if porcelain boats were substituted for the platinum ones the difficulty would be surmounted. Through the cooperation of the Coors Porcelain Company and H. W. Ryland of that organization porcelain boats were made, the same size and shape as the platinum boats, and were perforated like the bottom of a Gooch crucible to allow greater access of the silver to the gas stream. The results obtained, however, were low to the same extent as with the platinum. Because of obvious mechanical difficulties these porcelain boats had a much smaller capacity than the platinum ones and a close fit in the combustion tube under the depressions was difficult to obtain. Only small amounts of sulfur could be used. Therefore another scheme was tried.

A combustion tube was constructed with a short removable section in the same position as the indentations in the tube already described (Figure 5). There was no leakage around the ground joints under working conditions. This section of tube containing the silver was removed after the combustion and placed in a cell similar to the one described, except that the lower part was made long enough to accommodate the section. The removable section served to replace tube *C* (Figure 4) after the pellets had fallen to the bottom of the cell. However, the results obtained with this apparatus were still low by a quantity closely equivalent to 0.2 per cent of the theoretically available silver.

Another error may be introduced by the porcelain or glass, but it is curious that the order of magnitude is the same as with the platinum boats.

It is likely that the mechanical difficulties involved with the porcelain boats could be overcome and these used instead of the platinum. The ground-joint apparatus is also usable. The author prefers the platinum boats because of simplicity and ease of handling.

Compounds containing halogen cannot be analyzed for sulfur by this method, because the halogens are also retained by the silver. A somewhat similar method for the determination of halogens is now being studied.

A silver filling worked very well in the carbon-hydrogen combustion tube for substances containing no other elements than carbon, hydrogen, oxygen, and sulfur (*8*). It is obvious that carbon and hydrogen could be determined simultaneously with sulfur on such compounds. Very little modification of the apparatus is required.

The combustion tube is drawn out and a neck sealed on in the usual manner. The boats of silver are introduced through the mouth of the combustion tube, followed by the platinum contacts which must consequently be removed for each analysis. After the combustion and before the introduction of the nitrogen the absorption tubes are removed and air is aspirated through them (*7*). A choking plug and lead dioxide may be introduced and nitrogen compounds analyzed. In this case it is necessary to prepare the usual carbon-hydrogen tube filling, including the silver used for the heat transfer between the furnace and the mortar, cutting this tube about 1 cm. beyond the silver and sealing it onto the combustion tube (Figure 1) just beyond the indentations.

The carbon and hydrogen values obtained are of the usual accuracy.

Literature Cited

(1) Clarke and Hermance, *J. Am. Chem. Soc.*, 54, 877 (1932).
(2) Dennstedt, M., *Ber.*, 30, 1590 (1897).
(3) Hallett, L. T., Ind. Eng. Chem., Anal. Ed., 10, 101 (1938).
(4) Kirner, W. R., *Ibid.*, 7, 363 (1935).
(5) Knietsch, R., *Ber.*, 34, 4069 (1901).
(6) Lewis, G. N., *Z. phys. Chem.*, 52, 310 (1905).
(7) Niederl, J. B., and Niederl, V., "Micromethods of Quantitative Organic Elementary Analysis", New York, John Wiley & Sons, 1938.
(8) Niederl, J. B., and Niederl, V., *Mikrochemie*, 26, 28 (1939).
(9) Uhl, J., *Ber.*, 23, 2151 (1890).

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New Apparatus for Qualitative Semimicroanalysis

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THE steady development and application of semimicromethods to qualitative analysis have demonstrated to both the student and the teacher in analytical courses the possibility of introducing smaller apparatus than is generally used and a change in technique in the filtration, evaporation, and treatment of precipitates with various reagents in ion separations.

The type of equipment required in qualitative semimicroanalysis, which will materially decrease the time of analysis and simplify the procedure, may be easily and inexpensively placed in the hands of each student.

Apparatus

Lipped Test Tube. This tube is a No. 2370 Pyrex test tube which has been lipped to facilitate pouring liquids from it. The test tube fits the cups of the usual semimicrocentrifuges and has been found the most convenient in size for semimicrowork.

Filter Tube. This tube is made from a No. 2370 lipped Pyrex test tube. The side arm is cone-shaped and rimmed to 8 mm. to accommodate the end of a suction bulb.

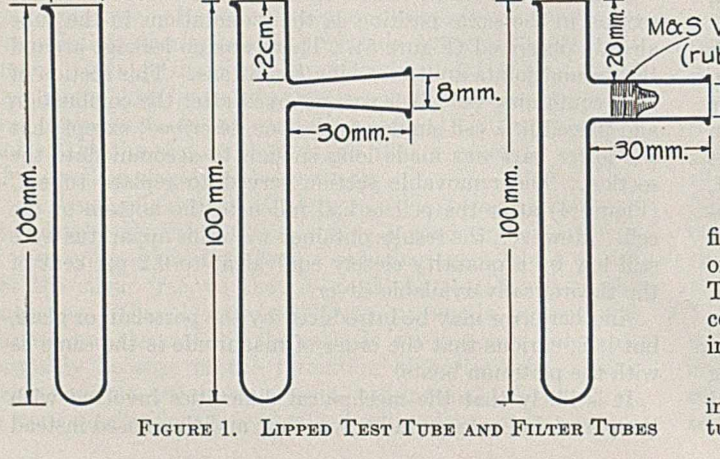


Figure 1. Lipped Test Tube and Filter Tubes

A modified type of this filter tube is also shown. On the inside of the side arm, which has an inside diameter of 8 mm., is placed a small M. & S. valve (rubber) with the point projecting toward the outer end of the arm. This valve limits the flow of air or liquid to one direction: from the tube to the outer end.

Semimicrofunnel. This funnel is of special construction and is designed to be used with the filter tubes. In use the stem above the constricted part is packed with ordinary surgical cotton or Corning Brand fiber glass (No. 008, Catalog No. 9940). The depth and hardness of packing of the filter medium determine the retentiveness of the filter and the rate of filtration. The Monel spatula (No. 7027, of the Wilkens-Anderson Co.) has been found most convenient for packing, as its handle is slightly less than 5 mm. in diameter and may, therefore, be used in pressing down the cotton or glass fiber into the stem of the funnel. When glass fiber is used as a filter medium, it need seldom be changed and is not acted on by chemicals which do not react with glass.

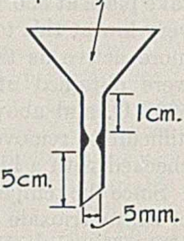


Figure 2. Semimicrofunnel

Pressure Filter Tube. This tube is designed to be used with the lipped test tube and suction bulb. Its outside diameter is slightly less than the inside diameter of the lipped test tube. The volume of liquid held by the pressure filter tube is somewhat less than the volume of the test tube below the constricted end of the filter tube. The top of the tube is flared so that it will rest on the top of test tube No. 2370, when inserted therein. The constricted end of the filter tube is packed with surgical cotton or glass fiber in the same manner as the filter medium in the semimicrofunnel.

In use, the tube is packed with the filter medium and inserted in the tube. The solution to be filtered is poured into the filter tube, and a pressure is applied to the solution by means of the rubber bulb, being easily regulated by the pressure exerted by the hand on the bulb. In case the solution must be hot while filtered, the assembly may be placed in a hot water bath, or a small amount of the filtrate in the test tube may be heated while the solution is filtered. The solution may also be filtered by use of the centrifuge. The need for the centrifuge is eliminated by the use of the pressure bulb in most cases.

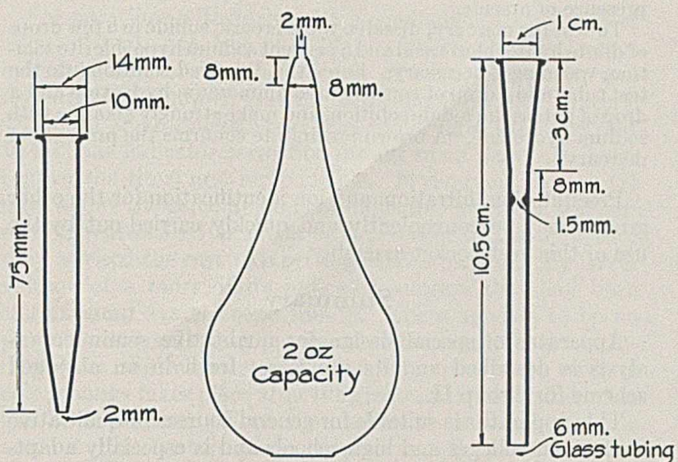


FIGURE 3. PRESSURE FILTER TUBE, VACUUM-PRESSURE BULB, AND FILTER STICK

The experience of the author and students in class work in qualitative semimicroanalysis has proved, to the author's satisfaction, the superiority of the pressure-bulb technique over that of the centrifuge. The advantages are these: (1) Each student may have the 3-piece assembly. (2) The cost of the assembly is about 25 cents. (3) The rate of filtration and clearness of filtrate may be observed and regulated by the pressure applied to the bulb. (4) The solution may be kept hot while filtered. (5) The filtrate is in the lipped test tube and ready for ion testing or treatment. (6) The precipitate is on the filter medium in the tapered tube and is ready for washing and ion testing. (7) Flocculent or light precipitates, which are not thrown out from the filtrate by the centrifuge, may be separated by pressure filtration.

The only disadvantage noted was the possibility of a student's exerting too great a pressure on the bulb during filtration or after the filtrate has passed through the filter. In either case the solution is liable to be blown onto the hands of the operator. Proper precautions must be used here, as in any procedure which involves the use of apparatus and chemicals.

VACUUM-PRESSURE BULB. The vacuum-pressure bulb is a common rubber ear syringe and may be used as a suction pump or as a pressure pump. As a suction pump it is used with the filter tubes. As a pressure pump it is used with the pressure filter tube. The amount of suction this bulb will produce depends on the thickness of the walls of the bulb and the resilience of the rubber used in its construction. The pressure which may be obtained depends on the grip of the analyst, the strength of the bulb, and the strength of the apparatus on which it is used. The ordinary ear syringe has all the strength the average analyst will care to exert when it is used as a pressure pump in semimicroanalysis.

The syringe which best served its purpose is made by the Davol Rubber Company, Providence, R. I., and is the standard ear and ulcer syringe, No. 527, capacity 60 cc. (2 ounces). This bulb, when new, will lift a column of mercury to the height of 8 cm., and a pressure may be easily obtained equal to 30 cm. of mercury. Bulbs that would produce a greater vacuum could be developed.

The taper on these bulbs and the give of the rubber render them particularly suited for semimicrowork. When the bulb is depressed and the end inserted in the side arm of the filter tube, the tube may be set in a rack and filtration allowed to proceed while the analyst turns to other work. When used as a pressure bulb, the filter tube may be lifted out and held in an upright position when the flat end of the bulb is set on the table, thereby eliminating contamination.

FILTER STICK. This type of apparatus finds some use. A plug of cotton or glass fiber is packed into the flared end.

HOT WATER BATH. This apparatus is essentially a holder for test tube No. 2370. The metal part is made from aluminum 1.56-mm. (0.06-inch) sheet. The holes in the upper plate are 14 mm. in diameter, numbered, and spaced 18 mm. from center to center. The holes in the lower-plate are 8 mm. in diameter and set directly opposite the holes in the upper plate. The outside diameter of the plate is 85 mm. This size of holder fits into a 600-ml. Pyrex beaker. A small electric hot plate is most convenient for heating the water in the beaker.

Method Used in Qualitative Semimicroanalysis for Group II (*1*)

Adjust the acid concentration, place the test tube, which contains 1 ml. of filtrate from Group I, in the hot water bath, and precipitate Group II with hydrogen sulfide gas. (The concentration of the unknown solution is 0.01 gram-ion.) Pour the solution and precipitate into the pressure filter tube, which has been placed in a test tube, and filter by the use of the vacuum-pressure bulb. Wash the precipitate in the pressure filter tube with about 1 ml. of acidified hydrochloric acid hydrogen sulfide water, adding a few drops at a time, and set aside filtrate for Group III precipitation.

Place the tube which contains Group II precipitate inside a clean test tube to which has been added 1 ml. of solvent for Division B, Group II, and add 1 ml. of solvent for Division B, Group II. Gently boil the solution in test tube. The solution in the pressure filter tube will be heated and will dissolve Division B, Group II, and run through the filter medium into the test tube. If the precipitate is packed, stir with a rod while heating the test tube. Wash the undissolved portion, Division A, with solvent for Division B. Wash off outside of tube which contains Division A and place it in a clean test tube to which has been added 1 ml. of 1 *N* sulfuric acid. To Division A precipitate add a few drops of concentrated nitric acid. Gently boil the sulfuric acid solution. Division A precipitate will dissolve and the solution is washed through the filter into the test tube which contains the sulfuric acid. Boil off the nitric-sulfuric acid solution and heat to sulfur trioxide fumes.

FIGURE 4. TEST TUBE HOLDER

Cool the tube, add 1 ml. of water, and warm. Filter through cotton filter medium by use of the filter tube–semimicrofunnel assembly, using vacuum-pressure bulb for vacuum. Wash the lead sulfate precipitate, dissolve in ammonium acetate–acetic acid solution, and test the solution for lead by use of potassium chromate.

To the filtrate containing the sulfates of copper, cadmium, and bismuth, add ammonium hydroxide until distinctly alkaline. Filter off the bismuth hydroxide by use of the filter tube–semimicrofunnel assembly. Add a drop of dilute hydrochloric acid to bismuth hydroxide on filter, and then a drop of cinchonine–potassium iodide solution. A yellow-orange precipitate confirms bismuth.

Divide the copper-cadmium solution into two parts. To one add a drop of sodium diethyl dithiocarbamate; brown precipitate confirms copper. To the other tube add potassium cyanide until the blue color of the copper ammonium complex is discharged, and then add 5 drops of sodium diethyl dithiocarbamate; a white precipitate confirms cadmium.

DIVISION B. Reprecipitate the sulfides and filter through pressure filter tube. Treat the sulfides in tube with 6 *N* hydrochloric acid in the same manner as was used for separating Divisions A and B. Antimony and tin chlorides will be in the test tube. The sulfides of mercury and arsenic will remain on the filter medium (glass fiber) in the pressure filter tube.

Divide the antimony and tin solution into two parts. To test for antimony, add 2 drops of saturated solution of potassium nitrite and a drop of rhodamine B solution. A fluorescent reddish violet color shows the presence of antimony. To test for tin, reduce to stannous condition with aluminum and add 2 drops of cacothelein reagent. A reddish violet coloration shows the presence of tin.

Treat the sulfides of mercury (sodium hydroxide–sodium sulfide reagent used for separating Division B from Division A) and arsenic on the filter with 1 ml. of dilute ammonium hydroxide. Use bulb to force the arsenic solution through filter medium into the test tube. The mercuric sulfide remains on the filter.

To test for arsenic, place the test tube in the hot water bath, add 1 ml. of a 3 per cent solution of hydrogen peroxide, and allow to stand for about 1 minute, and add 2 or 3 drops of magnesium nitrate mixture. A white precipitate shows the presence of arsenic. To confirm the presence of arsenic, add to the solution 2 drops of *N* silver nitrate solution, and then add acetic acid drop by drop until the white precipitate just dissolves, and a drop or two in excess. A reddish to deep red precipitate confirms the presence of arsenic.

To test for mercury, dissolve the mercuric sulfide in a few drops of dilute hydrochloric acid and 5 per cent sodium hypochlorite solution, warming if necessary. Force the dissolved solution into the test tube, add a drop of concentrated ammonium hydroxide and a drop of potassium iodide solution, and make strongly alkaline with sodium hydroxide. A brown precipitate confirms the presence of mercury.

Precipitation, filtration, and ion identification for the other groups may be conveniently and quickly carried out by the use of this vest-pocket assembly.

Summary

Apparatus of special design for qualitative semimicroanalysis is described and its use is set forth in an abridged scheme for Group II.

This apparatus is suitable for general courses in qualitative analysis in colleges and high schools and is especially adaptable to field and industrial laboratories and analytical substations.

Literature Cited

(1) Barber, H. H., "Semimicro Qualitative Analysis" (mimeographed), University of Minnesota Press, 1939.

Microdetermination of Iron with the Silver Reductor

SYLVAN M. EDMONDS AND NATHAN BIRNBAUM, College of the City of New York, New York, N. Y.

The hydrogen peroxide interference of iron in the microdetermination of iron with the silver reductor can be avoided by using a considerably smaller reductor column. A simplified procedure is presented for the microdetermination of iron.

THE high precision attainable in the determination of iron using the silver reductor and ceric sulfate was shown (*3*) to extend down to quantities of iron of the order of about 10 mg. Fryling and Tooley (*1*) adapted the reductor to the microdetermination of iron. They found that in determinations involving 1.5 mg. of iron in which the final titer is about 2.5 ml. of 0.01 *M* ceric sulfate the reductor blank was much too large and unreproducible. They demonstrated that this blank was caused by the formation of hydrogen peroxide in the reductor. To overcome this difficulty they designed a reductor in which the operations of reduction and rinsing are carried out under an atmosphere of hydrogen. In this way the hydrogen peroxide blank was reduced considerably although not entirely eliminated. The authors have found that this precaution is unnecessary, provided a small reductor is used. Because of the small size of the column the volume of acid required to wash it free of iron may be reduced considerably and in this way the peroxide blank made negligible.

The micromethod described in this paper is a direct adaptation of the macroprocedure of Walden, Hammett, and Edmonds (*3*), the scale of apparatus having been reduced in proportion to the absolute amount of iron to be determined. The direct application of a well-established macroprocedure to the determination of microquantities of an ion may, as in this case, introduce unexpected errors and difficulties. When, therefore, the absolute quantity of the ion to be determined is lowered, the scale of apparatus should be reduced accordingly.

Materials

Ceric sulfate (0.01 *M*) was prepared by dilution from the 0.1 *M* reagent that had been standardized against Bureau of Standards sodium oxalate by the method of Walden, Hammett, and Chapman (*2*).

A 0.1 *M* ferric alum solution was standardized by reduction in the silver reductor and titration with 0.1 *M* ceric sulfate following the method of Walden, Hammett, and Edmonds (*3*). A 0.002 *M* solution was then prepared by dilution from the 0.1 *M* ferric alum.

Hydrochloric acid (1 *M*) was prepared from the redistilled constant-boiling acid. This precaution was found necessary, since the best grade of acid available contained 0.0001 per cent of iron. Since approximately 3 ml. of this acid would be required in a determination, 0.003 mg. of iron would be introduced, equivalent to 0.006 ml. of 0.01 *M* ceric sulfate.

Silver Reductor

The reductor is of the usual design but approximately 20 cm. in length and 1 cm. in inside diameter. A buret may be adapted for this purpose. About 7 grams of silver are required and are prepared by precipitation with copper (*3*). Experiments showed that with a reductor of this size the wash liquid may be reduced to 20 ml. The hydrochloric acid wash is added in small portions, each being allowed to drain down to the top of the column before the next is added. The first two or three portions are used to rinse the beaker that had contained the iron solution.

Indicator Correction with Phenanthroline-Ferrous Ion

For titrations with ceric sulfate conducted in a volume of about 250 ml., one drop of 0.025 *M* *o*-phenanthroline-ferrous indicator solution is satisfactory. Walden, Hammett, and Edmonds (*3*) showed that for titrations with 0.01 *M* ceric sulfate of small quantities of iron requiring a titer of about 10 ml., the indicator correction is very small (less than 1 per cent of the titer) and reproducible. Fryling and Tooley (*1*) used about the same amount of indicator, but since the correction represented as much as 5 per cent of the final titer they advised the careful pipetting of a correspondingly larger volume of a more dilute indicator solution that had been standardized against ceric sulfate. There appears to be no particular advantage in the use of so large an amount of indicator in the microdetermination, since the most striking color change takes place after the greater part of the indicator has been oxidized. Thus the authors have found that the amount of indicator can be reduced to 2 drops of 0.001 *M* solution. The indicator correction is then only 0.010 ml. of 0.01 *M* ceric sulfate as determined by direct titration in 30 ml. of 1 *M* hydrochloric acid to the disappearance of the indicator color.

Reductor Blank

When 30 ml. of 1 *M* hydrochloric acid are passed through the reductor, the solution is treated with 2 drops of 0.001 *M* *o*-phenanthroline-ferrous indicator, and the mixture is titrated to the disappearance of the indicator color, 0.016 ± 0.001 ml. of 0.01 *M* ceric sulfate is required. Allowing 0.010 ml. as the volume of oxidant required to bleach the indicator, the remaining 0.006 ml. is probably consumed by a trace of peroxide formed in the reductor. The situation is different, however, when the solution passing through the reductor contains iron, for then some iron reoxidized by a trace of peroxide would probably be reduced before it leaves the reductor. Thus the error would certainly be less than that represented by the total reductor blank of 0.006 ml. which would be equivalent to a negative error of 0.003 mg. of iron. Table I shows, moreover, that no correction is needed beyond that for the indicator blank.

Table I. Test Analyses

Fe Taken Mg.	$Ce(SO_4)_2$ Ml.	Fe Found Mg.	Error in Fe Mg.
0.686	1.127	0.687	+0.001
0.686	1.133	0.690	+0.004
0.686	1.122	0.684	−0.002
0.686	1.135	0.692	+0.006
1.372	2.254	1.374	+0.002
1.372	2.253	1.373	+0.001
1.372	2.249	1.371	−0.001
1.372	2.246	1.369	−0.003
1.372	2.249	1.371	−0.001
2.058	3.380	2.060	+0.002
2.058	3.383	2.062	+0.004
2.058	3.381	2.061	+0.003
2.058	3.386	2.064	+0.006
2.744	4.497	2.741	−0.003
2.744	4.505	2.746	+0.002
2.744	4.502	2.744	0.000
2.744	4.505	2.746	+0.002

Method of Analysis

Ten milliliters of 1 *M* hydrochloric acid solution containing the iron as ferric alum were poured through the reductor at a rate of 10 ml. per minute, and the column was rinsed with 20 ml. of 1 *M* hydrochloric acid. Two drops of 0.001 *M* *o*-phenanthroline-ferrous indicator were added and the mixture was titrated with 0.010916 *M* ceric sulfate using a calibrated 5-ml. microburet.

The results of the test analyses are given in Table I. The indicator correction of 0.010 ml. has been subtracted in each case.

Literature Cited

(1) Fryling and Tooley, *J. Am. Chem. Soc.*, 58, 826 (1936).
(2) Walden, Hammett, and Chapman, *Ibid.*, 55, 2649 (1933).
(3) Walden, Hammett, and Edmonds, *Ibid.*, 56, 350 (1934).

Preparation of Microscopic Glass Spheres

C. R. BLOOMQUIST AND A. CLARK, Battelle Memorial Institute, Columbus, Ohio

DURING work on a study of the solid-liquid interface it became desirable to prepare a relatively large quantity of microscopic particles of known surface area. The use of glass spheres was suggested by Bishop (*1*), who mentioned the fact that perfect glass spheres may be prepared by passing powdered glass through the flame of a blast lamp, but did not give details of the process. Recently, Sollner (*3*) described a method of preparing the spheres in a similar manner and collecting them by directing the flame against a water surface so that the fused particles are thrown into the water. He stated that it was impossible to prepare spheres of Pyrex glass in this manner without the use of an oxy-hydrogen flame.

The method used in this work is basically the same as that described by Sollner, but instead of collecting the fused particles in water, the authors have found it more convenient to cool the gases and glass particles from the flame by passing them through a short length of pipe and then drawing them by suction into the bag of an ordinary household vacuum cleaner. In this way it is possible to prepare spheres up to 25 microns in diameter from ordinary Pyrex glass by using a laboratory blast lamp with natural or city gas and compressed air.

The glass powder is prepared by wet-grinding Pyrex tubing in a ball mill with steel balls. After several hours' grinding the suspension is poured into a 2-liter beaker and stirred thoroughly; the particles which have not settled in 5 minutes are decanted and allowed to settle completely. These particles are treated with chromic acid cleaning solution to remove impurities, washed free of sulfate ion, and dried thoroughly.

The apparatus used in preparing the spheres is shown in Figure 1. The glass powder, which has been thoroughly dried at 110° C., is placed in a wide-mouthed bottle of approximately 200-cc. capacity. The gas is ignited and the compressed air turned on gradually until a flame of the proper size is obtained. A large "brush" flame extending about one half the length of the stove pipe works well. The stove pipe is 63.5 cm. (25 inches) long and 12.5 cm. (5 inches) in diameter. As soon as the flame is burning evenly and steadily, the vacuum cleaner motor is turned on and allowed to run until sufficient particles are collected or the vacuum-cleaner bag becomes too hot. A 20-cm. (8-inch) glass funnel attached to the suction end of the vacuum cleaner and closely surrounding the exit end of the stove pipe helps to direct the glass spheres into the collecting bag without any great loss of the particles to the atmosphere.

It is essential that the order of operation be exactly as given above, for if the vacuum cleaner is turned on before a steady flame is obtained the particles collected will generally include some irregularly-shaped powder. The bottle containing the glass powder should be agitated at intervals to ensure a steady stream of the powder through the flame. The spheres removed from the vacuum-cleaner bag are contaminated with lint and dust; this is easily removed by treating with chromic acid cleaning solution and washing until the spheres are free of all soluble material.

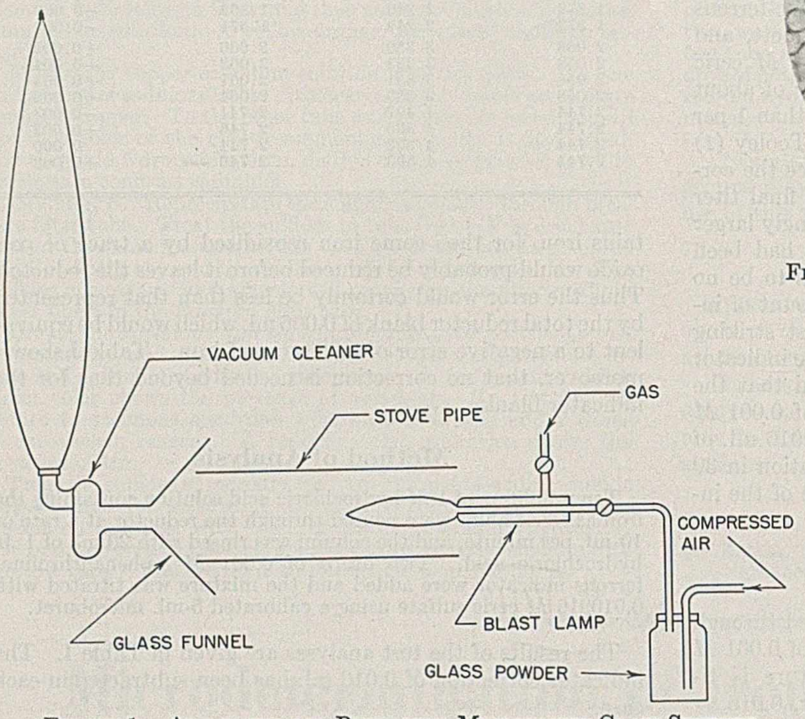


Figure 1. Apparatus for Preparing Microscopic Glass Spheres

The sizes of the spheres prepared in this manner vary from about 25 microns to some so small that they are scarcely visible at a magnification of 1000 diameters. To separate them into fractions of nearly uniform diameter is somewhat tedious but not difficult. The procedure used is an adaptation of that given by Cummings (*2*). All spheres settling in 10 minutes or less are discarded; those settling in the successive 20-, 40-, 80-, and 160-minute intervals are separated and the process of settling and fractionating is repeated on each of these fractions until the supernatant water becomes clear in the settling interval. On the average, it requires 12 to 15 successive decantations to effect complete separation.

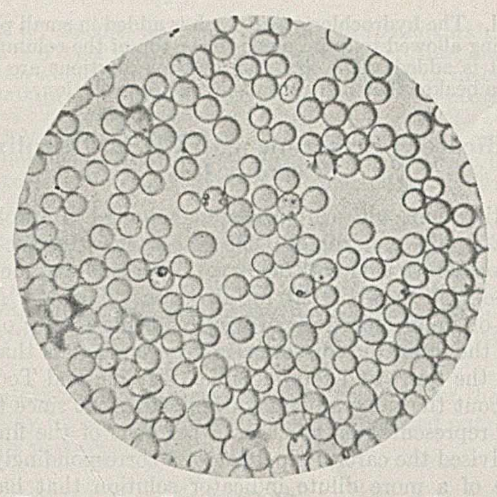


Figure 2. Photomicrograph of Glass Spheres (× 460)

The particles still in suspension after the last interval are allowed to settle overnight and any residue not settling during this time is discarded. About 75 grams of each of the 20-, 40-, 80-, and 160-minute fractions were prepared in 10 days' time.

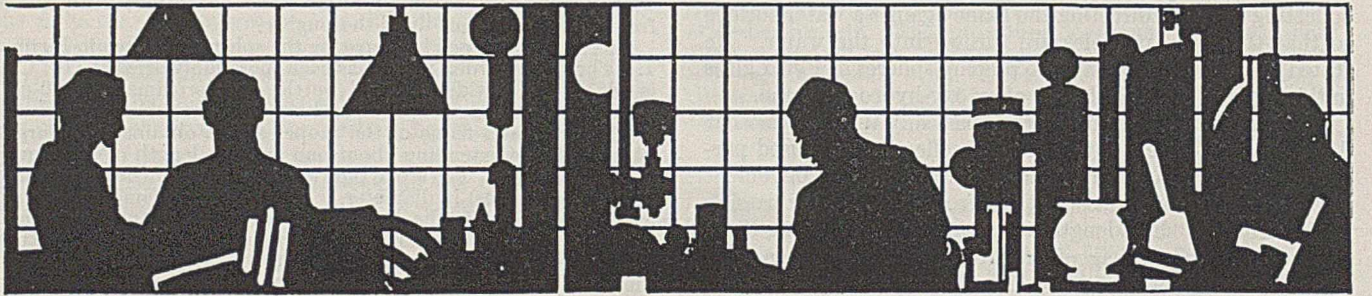
In the final fractions at least 96 per cent of the particles, by actual count, were perfect spheres. A photomicrograph of the particles in the 80-minute fraction is shown in Figure 2. The mean diameters of the particles in each fraction, settled for 20, 40, 80, and 160 minutes, and overnight, respectively, were 15.2, 10.6, 7.2, 5.2, and 3.3 microns. In each fraction at least 90 per cent of the particles were within 2 microns of the average size given. Fractions of more uniform particle size may be obtained by using intermediate settling intervals.

Acknowledgment

Acknowledgment is made to the Battelle Memorial Institute for the support of this work as a part of its program of fundamental research.

Literature Cited

(1) Bishop, D. L., *Bur. Standards J. Research*, 12, 173–83 (1934).
(2) Cummings, D. E., *J. Ind. Hyg.*, 11, 245–56 (1929); quoted by Drinker and Hatch, "Industrial Dust", New York, McGraw-Hill Book Co., 1936.
(3) Sollner, K., Ind. Eng. Chem., Anal. Ed., 11, 48–9 (1939).



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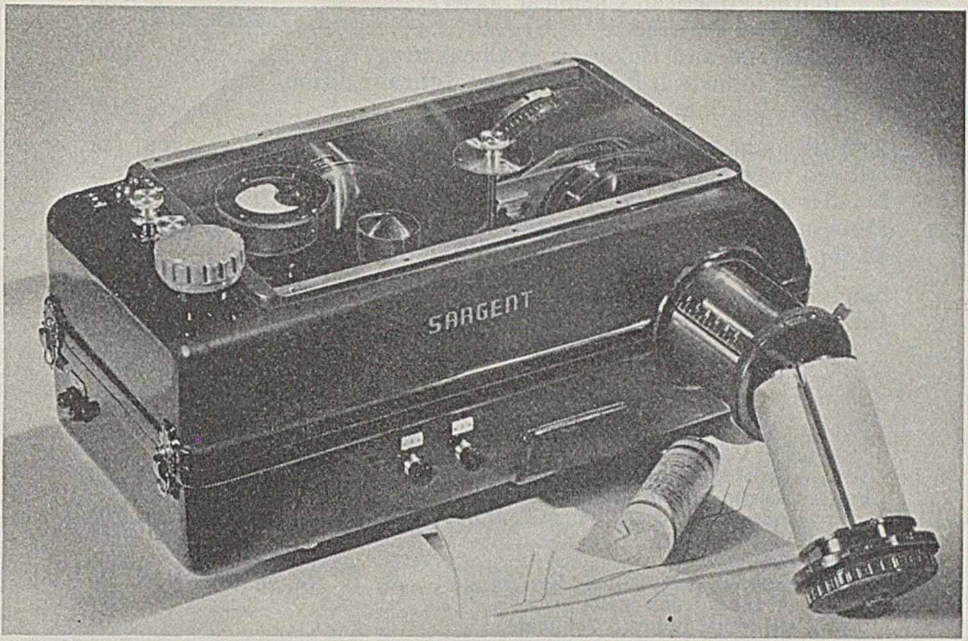

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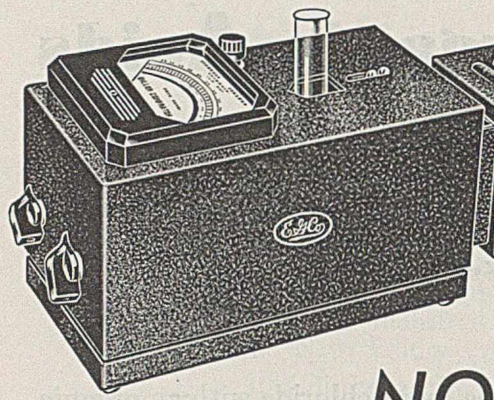

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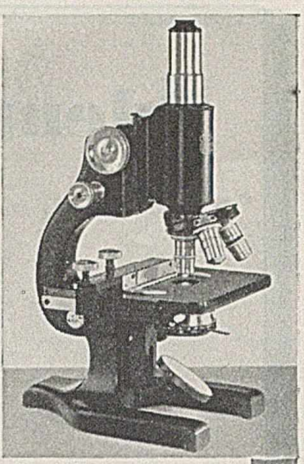

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EDWIN SUTERMEISTER AND FREDERICK L. BROWNE

Second Edition, Completely Rewritten

Technical research on many new casein products has brought about such far-reaching changes in manufacturing processes that a second greatly expanded edition of this Monograph, originally published in 1927, became essential.

In addition to increased use in the paper, leather and glue industries, three spectacular developments have tremendously enlarged the demand for casein, namely, plastics; casein paste paint; and casein fibre, which may soon rival rayon in commercial importance. These recent developments are described in detail and critically evaluated.

On the theoretical side great progress has been made toward a better understanding of this complex protein. The organic and physical chemistry of casein are discussed at length, and avenues for further research are opened up.

Contents—Introduction, Casein in Milk and Its Isolation, The Organic Chemistry of Casein, The Physical Chemistry of Casein, The Manufacture of Casein, Testing and Analysis of Caseins, Storage of Casein, Casein Plastics, Casein Glues, Casein in Paper Making, Casein Paints, Casein in the Leather Industry, Alimentary and Medicinal Uses of Casein, Miscellaneous Uses of Casein and Statistics, Index.

448 Pages A. C. S. Monograph Illustrated $6.50

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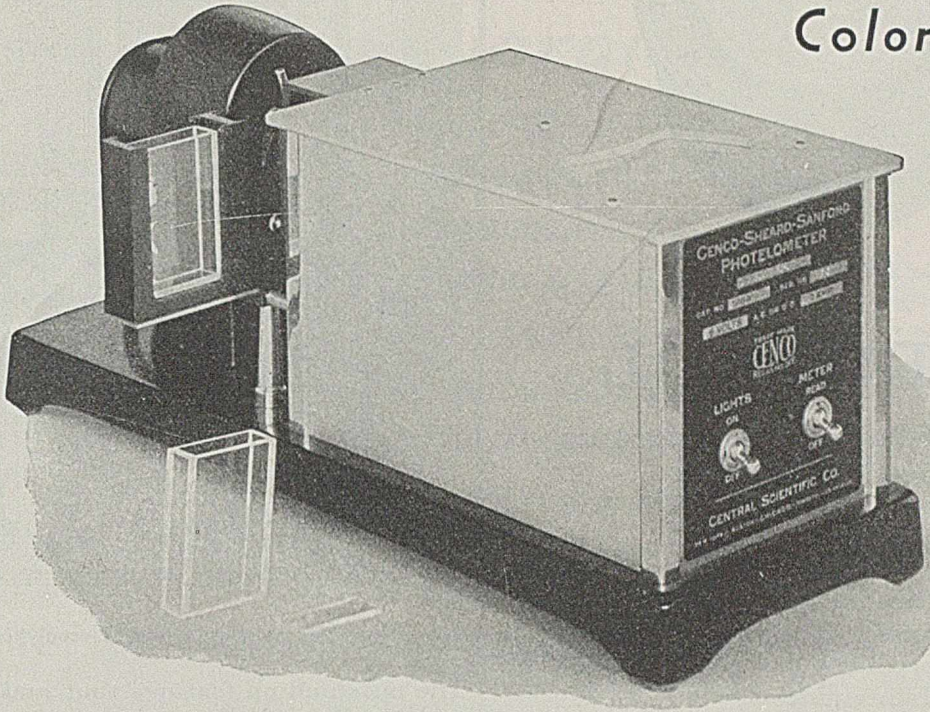

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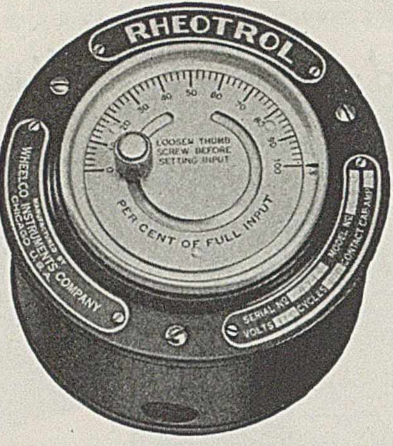

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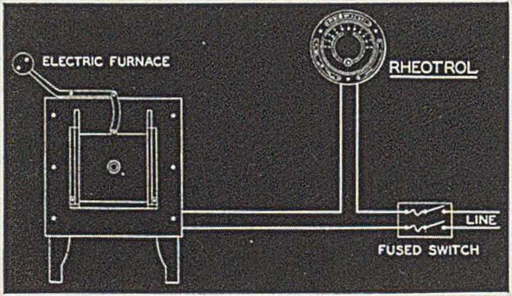

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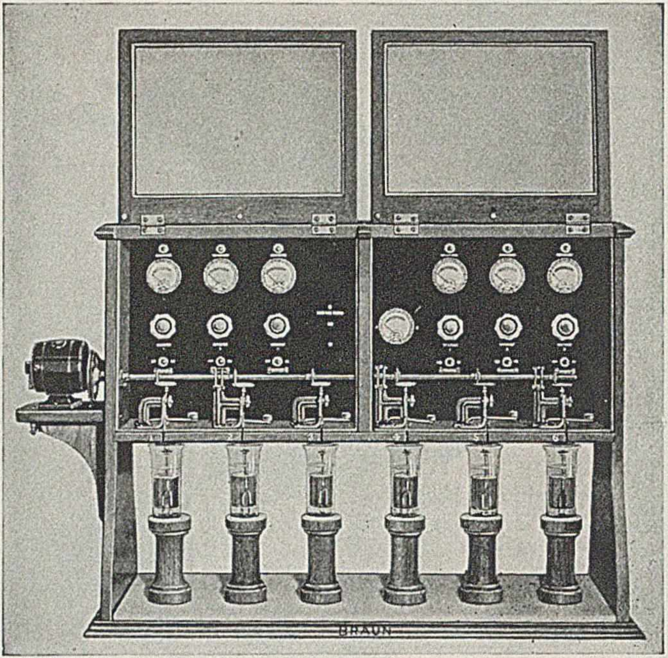

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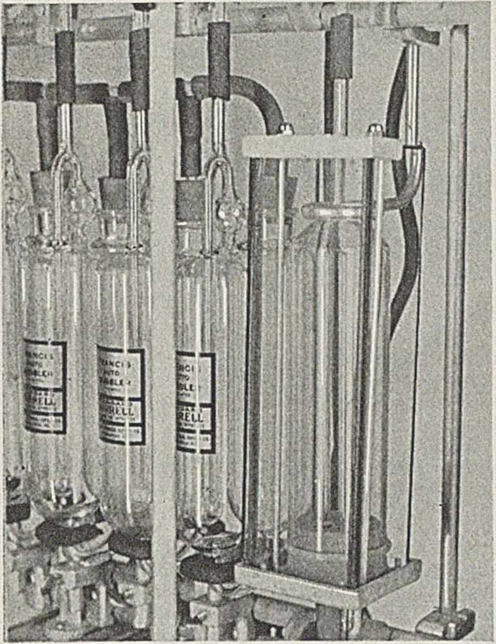

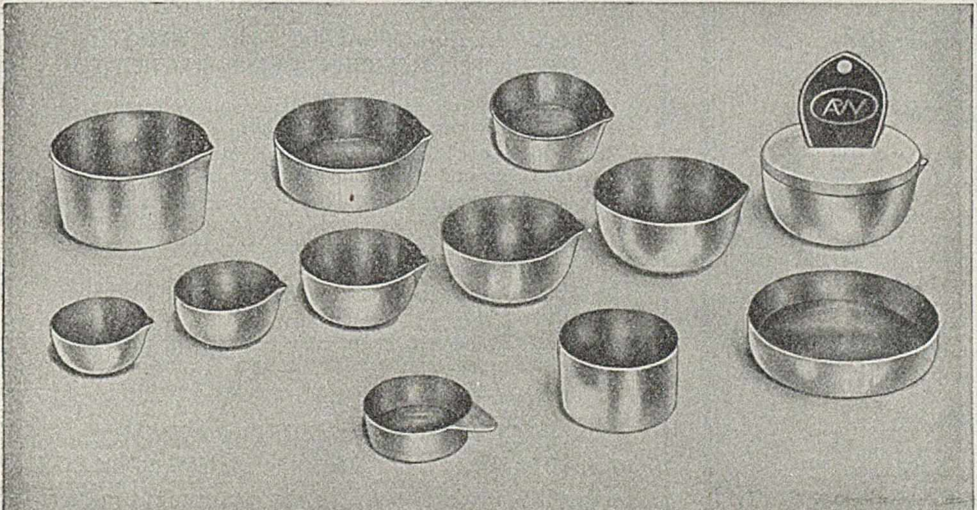

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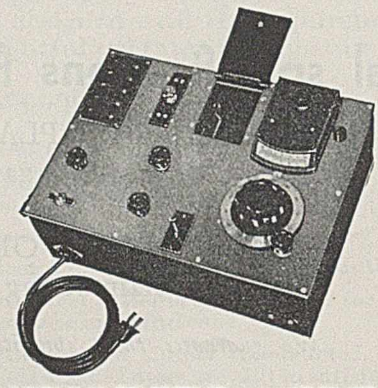

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