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Analytical Edition

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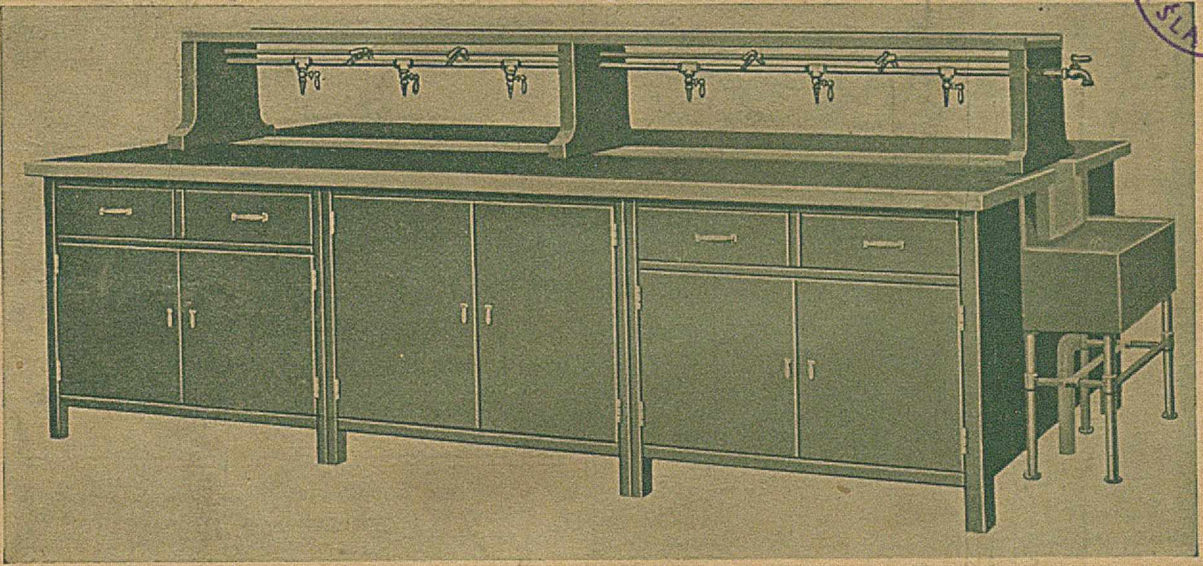

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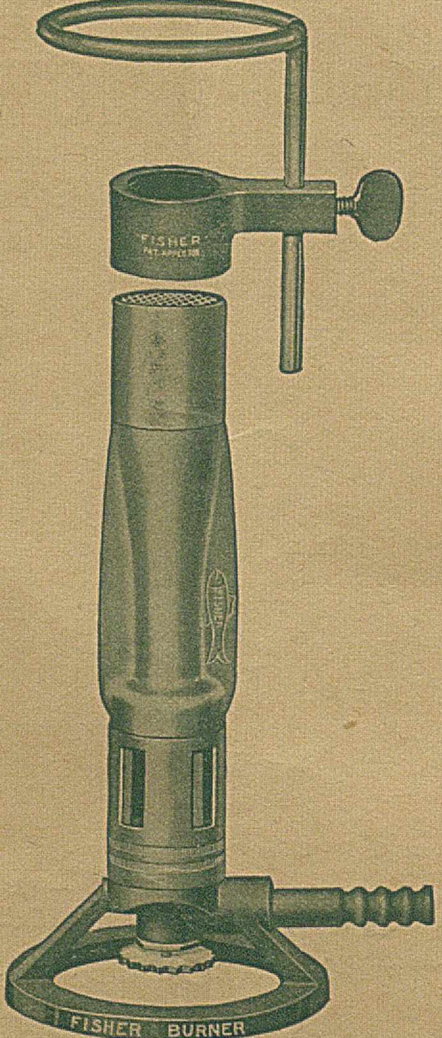

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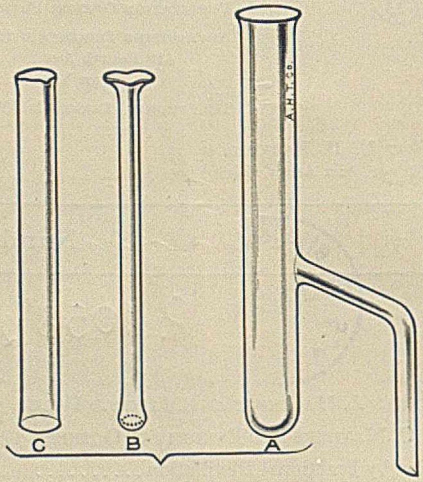

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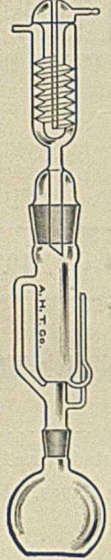

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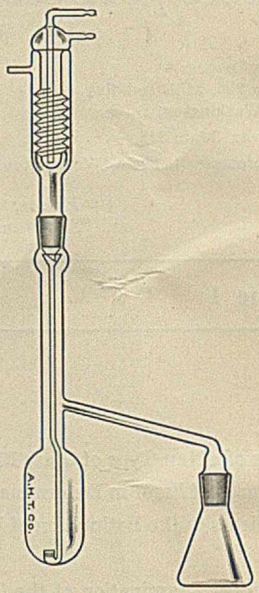

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Tests of a New Type of Glass Electrode

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

Duncan A. MacInnes and Malcolm Dole

The Rockefeller Institute for Medical Research, New York, N. Y.

Glass electrodes have been prepared with active glass surfaces only 0.001 mm. thick. Such electrodes can be made in a very compact and convenient form. Effective electrodes have been made in which the active surface covered the end of glass tubes as small as 0.75 mm. in diameter.

These electrodes were tested by using them in differential electrometric titrations, in which a good order of accuracy was obtained. The electrodes were found to respond only to changes of hydrogen-ion concentrations, being independent of oxidation-reduction potentials existing in the solutions.

GLASS electrodes have been studied by Haber and Klemensiewicz,[2] Hughes,[3] Kerridge,[4] Horovitz,[5] and others.[6] Haber and Klemensiewicz's experimental arrangement is shown in Figure 1. A bulb, *A*, blown on a glass tube, was filled with electrolyte and a platinum wire was inserted as shown. The bulb was then placed in a beaker of solution. The solution also contained a tube leading to a calomel electrode, *B*. Connection was made back to the glass electrode through an electrometer, *E*. It was found that when the hydrogen-ion concentration of the solution was altered the readings of the electrometer changed, roughly at least, in the same way that a hydrogen electrode would change, the characteristic "break" being obtained, for instance, at the end of a titration of an acid with a base.

Hughes has shown that the readings of glass electrodes, made of soft glass, follow changes in the hydrogen-ion concentration quantitatively except in strongly alkaline solutions, the deviations depending on the nature of the positive ions present. Mrs. Kerridge has modified Haber's arrangement by replacing the beaker with a reëntrant, and probably somewhat thinner, bulb blown into the side of the larger bulb. Horovitz and Schiller, however, have shown that with harder, relatively thick glass electrodes the phenomena may become quite complex, particularly in alkaline solutions, the potential observed apparently changing with changes of concentration of sodium or potassium ion rather than hydrogen ions.

Method of Titration

It occurred to the writers that the method of differential electrometric titration,[7] already found useful in other connections because of its advantages in precision and convenience over the direct method of electrometric titration, might be of service in studying the glass electrode. The differential method gives readings which are, very closely, the tangents to the usual titration curves and go through a sharp maximum, instead of a point of inflection, at the end of a titration.

The apparatus used in the differential titrations is shown in Figure 2. It includes two glass electrodes, *E* and *E'*, which are of a novel form to be described below. One of the electrodes is surrounded by a tube, *A*. By means of the simple gas lift pump, *L*, a stream of the liquid from the beaker is kept flowing over electrode *E'* and through the small opening *C*. The gas stream is controlled by means of the special stopcock on the buret, *B*. On partially turning the cock the gas stream is interrupted, thus isolating the solution in the tube *A*. Turning the stopcock still further causes the titrating fluid to flow from the buret. After stopping this flow, but not turning the stopcock back sufficiently to start the stream of gas, the potential beween the electrodes *E* and *E'* can be measured. This potential is that of a simple galvanic cell deriving its energy from the concentration difference between the solution in the beaker and that held back in the tube *A*. If definite increments of solution from the buret are used this potential difference rises as the end point is approached and reaches a maximum at the end of a titration. A typical maximum is shown in Figure 4.

Design of the Glass Electrodes

To adapt the glass electrode to differential titrations, the usual design of that electrode was modified to enable it to be put into the narrow tube *A*. The form of glass electrode thus developed has a number of advantages that would appear to recommend it for general use. An electrode is shown diagrammatically in Figure 3. A thin glass diaphragm, *D*, is fused onto the end of an ordinary glass tube, *B*. This tube is then partly filled with an electrolyte (0.1 *N* hydrochloric acid in the writers' experiments). Into this electrolyte is placed a silver–silver chloride electrode, *C*. This can conveniently be made in the manner described by MacInnes and Beattie.[8] The upper part of the tube is coated inside and

---

[1] Received January 17, 1929.

[2] Haber and Klemensiewicz, *Z. phys. Chem.*, **67**, 385 (1909).

[3] Hughes, *J. Am. Chem. Soc.*, **44**, 2860 (1922); *J. Chem. Soc.*, **1928**, 491.

[4] Kerridge, *Biochem. J.*, **19**, 611 (1925); *J. Sci. Instruments*, **3**, 404 (1926).

[5] Horovitz, *Z. Physik*, **15**, 368 (1923); *Sitz. Akad. Wiss. Wien*, **Abt. IIa, 134**, 335 (1925); Horovitz and Zimmermann, *Ibid.*, **134**, 355 (1925).

[6] Schiller, *Ann. Physik*, **74**, 105 (1924); Elder and Wright, *Proc. Natl. Acad. Sci.*, **14**, 936 (1928). A more complete bibliography is given in Clark's "The Determination of Hydrogen Ions," Williams & Wilkins Co., 1928.

[7] (*a*) MacInnes and Jones, *J. Am. Chem. Soc.*, **48**, 2831 (1926); (*b*) MacInnes, *Z. physik. Chem.* (Cohen Festband), 217 (1927); (*c*) MacInnes and Dole, *J. Am. Chem. Soc.*, **51**, 1119 (1929).

[8] MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

outside with a thin layer of paraffin. The important part of the electrode is, of course, the thin diaphragm *D*. This, in the writers' experiments, is about 0.001 mm. thick, and shows colors due to interference of light waves. The thickness was found by weighing a measured area of the film. The diaphragm can be fused on the end of the glass tube in a simple manner. A bulb is blown on the end of a tube of suitable glass until portions of the resulting film show interference colors. The end of the supporting tube *B* is then heated to a low red heat, the correct temperature being found by experience. The heated tube is then placed against the thin bulb. If the conditions are right, the film of glass will fuse onto the tube. With practice a large proportion of successful electrodes may be made in this manner. Judging from published accounts, these films are fifty to one hundred times thinner than electrodes generally used. The new electrodes are compact and not fragile if care is used in handling them.

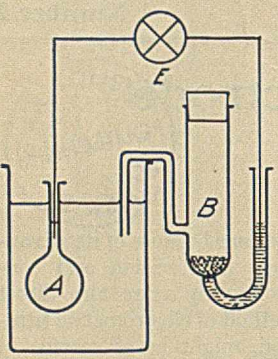

Figure 1—Haber's Electrode Arrangement

Note—Horovitz has made some electrodes that have the same external form as these. However, their mode of manufacture was very different. Relatively thick (0.05 to 0.1 mm.) cover glasses were placed in contact with carefully ground glass tubes and the two fused together in a furnace. This difference of technic may be largely responsible for the difference between his results and those of the writers'.

Results of Titrations

The results of four differential titrations using glass electrodes in the apparatus shown in Figure 2 are plotted on a single curve in Figure 4. These results show the precision already obtained with the glass electrodes and illustrate some of their properties.

(*a*) The change of e. m. f. during the titration of sulfuric acid with sodium hydroxide follows the course that would be obtained with hydrogen or quinhydrone electrodes.

(*b*) The shape of this curve is uninfluenced by the addition of potassium permanganate to the sulfuric acid. This observation shows, in the first place, that the glass electrode responds only to changes in hydrogen-ion concentration and is not influenced by the powerful oxidation potential produced by the presence of the permanganate. The shape of the curve indicates further that permanganic acid is of about the same strength as sulfuric acid, since if the former were a weak acid it alone would be present in solution near the end point and the resulting maximum would be lowered.[9]

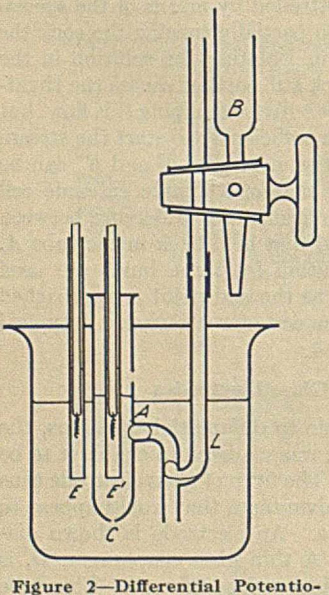

Figure 2—Differential Potentiometric Apparatus

(*c*) On the same curve are shown points obtained in the titration 0.1 *N* nitric acid with sodium hydroxide of the same strength. Here again the glass electrodes give the change in hydrogen ion and are not influenced by the oxidation potential prevailing in the solution.

(*d*) Points are also included for a titration made with some very small electrodes, the active glass surfaces of which were only 0.5 to 0.75 mm. in diameter. As can be seen, these small electrodes can be used for titrations and, of course, equally well for pH measurements. It seems not unlikely that these very small electrodes will further extend the use of the glass electrode to investigations in biology, since in that field it is frequently necessary to work with very small amounts of material or inside small orifices or cavities.

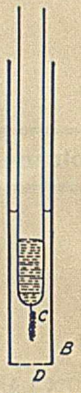

Figure 3—Glass Electrode

Use of Glass Electrodes in Precision Titrations

The method of differential electrometric titration has been shown[7b,7c] to be capable of high accuracy. It seemed worth while to test the method with the new type of glass electrodes to see whether they are capable of yielding results of the same accuracy as has been found possible with the more usual electrodes, particularly as it is frequently desirable to carry out titrations under conditions which make the use of any electrodes other than glass impossible.

To test this matter titrations of 0.1 *N* nitric acid were made with approximately 0.1 *N* sodium hydroxide. Following a procedure described elsewhere,[7c] a weighed amount of the acid, given in column 2 of Table I, was delivered from a weight buret and this was titrated very near to the end point with the sodium hydroxide from another weight buret, the weight taken being given in column 3. The end of the titration was then carried out from a volumetric buret with the hydroxide solution diluted 1 to 20. From this last portion a small correction to the weight of the hydroxide solution was computed (column 4). The ratio of the weight of nitric acid to that of sodium hydroxide is given in the last column of the table. It will be observed that the maximum error of these titrations is 0.03 per cent. Although this is not such high accuracy as the writers have obtained with the differential potentiometric method, it shows that the glass electrodes give surprisingly reproducible results.

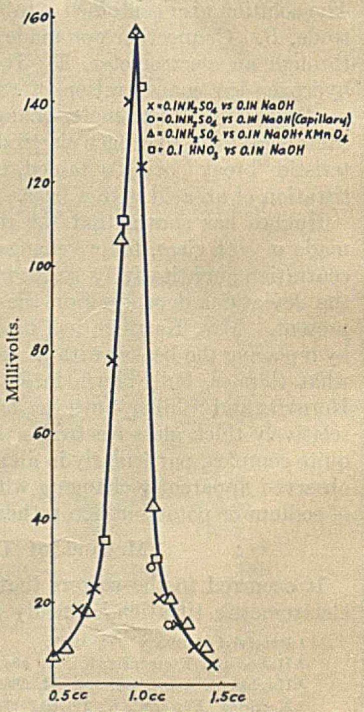

Figure 4—End Point Maxima of Differential Titrations

Method of Measurement of Potentials

The measurements were made with a Compton electrometer. Owing apparently to the relatively low resistances of these electrodes, comparatively little screening from external electrical effects was found necessary. However, the beaker used was surrounded by a grounded wire basket, and the contact key and reversing switch were placed in a grounded tin box, the former being operated from the outside by a glass rod. The leads to the electrometer were insulated wire covered with a grounded lead sheathing. Also, owing to the relatively low resistances, ordinary care in insulation appeared to be ample. However, more careful screening and insulation may occasionally be necessary with the electrodes of capillary size.

---

[9] Hughes, *J. Chem. Soc.*, **1928**, 491, has shown with the glass electrode that permanganic acid and hydrochloric acid have the same strength.

Table I—Titration of 0.1 *N* Nitric Acid with Approximately 0.1 *N* Sodium Hydroxide

EXPT.	WT. HNO_3 SOLN.	WT. NaOH SOLN.	CORRECTION	RATIO $\frac{\text{WT. } HNO_3}{\text{WT. NaOH}}$
	Grams	*Grams*		
1	37.687	37.332	0.071	1.0076
2	33.701	33.426	0.018	1.0077
3	36.448	36.127	0.053	1.0074
4	33.842	33.460	0.124	1.0076

Some preliminary measurements were made with a radio-tube apparatus of the type described by Williams.[10] Though it probably could be used with success for our measurements, it was found to be less convenient than the Compton electrometer.

Resistances of Glass Electrodes

Measurements of the resistances of the electrodes made as described above were carried out by first shunting the electrometer with a 0.5-megohm resistance and connecting it in series with an electrode placed in a beaker containing 0.1 *N* hydrochloric acid and a silver–silver chloride electrode. A known potential (3.7 volts) was then connected to the silver–silver chloride electrode and to one terminal of the electrometer. From the deflections obtained the resistances of the electrodes could be computed. Some results for typical electrodes are given in Table II.

Table II—Resistances of Glass Electrodes

TYPE OF GLASS	DIAMETER OF TUBE	RESISTANCE
	Mm.	*Megohms*
Soft commercial	4	124
Soft commercial	4	103
Soft commercial	4	95
Soft commercial	4	113
Soft commercial	0.75	4000 ±
Pyrex	4	Too high to measure
Special	4	18.7
Special	4	39.7

Certain electrodes which showed very low resistances, possibly owing to cracks or leaks, failed to act as hydrogen electrodes. Other electrodes with very high resistances, including those made of Pyrex, also failed as electrodes. It is of interest to note that the writers' electrodes with about 12 sq. mm. active surface have resistances of about the same order of magnitude as those reported by Elder and Wright[6] for electrodes with approximately one hundred times the area.

Composition of Glass

A few preliminary experiments were also carried out to see whether glasses could not be made that would be better adapted for glass electrode purposes than those at present available. Since low-melting soda glass appears, particularly from the work of Hughes, to be useful for the purpose, a melt was made in an oxygen-gas blast-lamp flame of a mixture producing a glass of the composition SiO_2 72, Na_2O 22, and CaO 6 per cent. This composition is near that given for the lowest equilibrium temperature on the three-component diagram of Morey.[11] Though the temperatures available were probably not sufficient to obtain uniformity in the product, electrodes were prepared which served as hydrogen electrodes and had lower resistances than those made from any samples of glass the writers had been able to find. The data on the resistances of these electrodes are given under "special glass" in Table II.

Future Investigations

It is intended to pursue this investigation, with more adequate equipment and experimental technic, to find the most suitable glass for electrodes. To do this it will be necessary to compare hydrogen electrodes and glass electrodes of varying composition throughout the range of hydrogen-ion concentration from strongly acid solutions to strongly alkaline solutions. It will, further, be necessary and of interest to investigate the various theories that have been proposed to account for the action of these electrodes.

---

[10] Williams, *Proc. Cambridge Phil. Soc.*, **23**, 811 (1927); *Phil. Mag.*, **6**, 325 (1928).

[11] Morey, *J. Soc. Glass Tech.*, **9**, 232 (1925).

A Source of Error in Determination of the Plasticity of Hydrated Lime[1]

Frank C. Mathers and Everett C. Gosnell[2]

INDIANA UNIVERSITY, BLOOMINGTON, IND.

DETERMINATIONS of plasticities of hydrate limes by different experimenters do not check. In general, the same observer can get satisfactory checks on the same batch of lime putty, but very often determinations upon separate batches of putty from the same hydrated lime fail to check. This indicates that there is some variable condition or conditions that should be controlled.

The directions for the preparation of the putty[3] for testing were:

> Soak the dry hydrate for 16 to 24 hours previous to the test with insufficient water for final consistency. At the time of final testing add sufficient water and mix it thoroughly with the putty until the lime putty becomes of standard consistency as determined by a penetration of 20 ± 5 mm. on a Vicat needle.

There is great variation in the amount of stirring of the putty during the addition of these portions of water. If practically the correct amount of water has been used at the beginning of the soaking, almost no stirring may be done at the time of final testing. A very stiff putty may require the addition of several small quantities of water and much stirring may be done after the addition of each portion. The operator may even add too much water to the portion being brought to standard consistency and then be forced to add more of the original thick putty with greatly increased amount of stirring.

The objects of this research were to determine the effects of the following upon the plasticity determinations with the Emley plastometer:

(1) Variations in the amount of stirring of the putty at the time of final test.

(2) Variations in the amount of water used in soaking the hydrate.

(3) The additions of separate small portions of water to the

---

[1] Received May 4, 1928; revised manuscript received January 7, 1929.

[2] Present address, Koppers Company, Jersey City, N. J.

[3] Bur. Standards, *Tech. Paper* **168** (1920); *Circ.* **204** (1925); Briscoe and Mathers, IND. ENG. CHEM., **19**, 88 (1927); Farnsworth, *Ibid.*, **19**, 583 (1927).

thick putty at the time of final test, rather than soaking with the total quantity of water required.

Method and Apparatus

The putty was stirred vigorously by hand with a steel spatula having a 4-inch (10-cm.) blade. The porous plates used on the plastometer had 25 per cent absorption and were bought from the American Instrument Company, Washington. These plates were not standardized; hence the absolute values obtained for plasticity may be in error but the relative values and the conclusions are correct. The end point of each plastometer test was the breaking of the pat, the cracking of the pat and the pointer not advancing for 2 minutes, the scale reading reaching 100, or the pointer dropping back to a previous reading.

Experimental Procedure

The effect of varying the time of stirring is shown in Table I. In each experiment 125-gram portions of the hydrated lime were soaked with 115 cc. of water. As little stirring as possible was done at the time of this mixing. The samples were then allowed to soak quietly for 16 to 24 hours. At the time of final testing each putty was stirred vigorously for the time shown in the table.

Table I—Effect of Varying Time of Stirring

Hydrated Lime	Plasticity Number of Putty after Stirring for:				
	0.5 min.	1 min.	2 min.	3 min.	4 min.
Ohio hydrate No. 1	295	343	357	356	347
Ohio hydrate No. 2	168	243	283	282	262
Pennsylvania mason's	108	124	170	151	158

These results show the marked effect of the stirring upon the plasticity numbers. It was concluded that 2 minutes' stirring was enough for maximum results. The lower values obtained in many cases for the longer periods of stirring were due to the increased fluidity of the putties—a result which was always produced by excessive stirring. This increased fluidity caused slumping, with consequent reduction in the plasticity number, and was especially noticeable with the non-plastic putties. Experiments not given show that the stirring has the same relative effects when the quantities of water are varied from 110 to 125 for each 125 grams of hydrated lime.

Table II gives results when 125-gram portions of Ohio hydrate No. 1 were soaked with varying quantities of water. The stirring was constant at 2 minutes.

Table II—Effect of Varying Quantity of Water

Water	Plasticity No.	Water	Plasticity No.
Cc.		*Cc.*	
100	293	120	323
110	309	125	319
115	335	130	268

This table shows that the actual quantity of water is not important. The water could be varied from 115 to 125 cc. without varying the plasticity number beyond experimental error. With 100 cc. of water the putty was too stiff and with 130 cc. it was too thin; hence the low values in these cases.

Table III shows the effect of adding only part of the water at the beginning and the rest at the time of final test. In each case 125 grams of Ohio hydrate No. 1 and 100 cc. of water were mixed in the beginning, and further quantities of water were added at the time of final testing. The putties were vigorously stirred for 2 minutes at the time of final testing.

This table shows that no apparent variation in the maximum plasticity readings is caused by adding part rather than all of the water at the beginning of the soaking. However, there was less range for variation in the total quantity of water that could be used without lowering the values. Therefore it seems best to add all the water that will be needed at the beginning.

Table III—Effect of Adding Part of Water at Time of Final Test

Water Added at Final Test	Penetration of Vicat Needle in Final Putty	Plasticity No.
Cc.	*Mm.*	
0	0	293
5	3	294
10	10.5	299
15	20.5	334
20	29	325
25	31	303

Table IV shows that the Vicat needle is unreliable as a measure of standard consistency unless previous stirring of the putty for 2 minutes is made a part of the directions. In each experiment 125 grams of Ohio hydrate No. 1 were used.

Table IV—Effect of Stirring upon Vicat Needle and upon Plasticity

Water Used in Soaking	Vicat Needle Penetration	Stirring	Plasticity No.
Cc.	*Mm.*	*Minutes*	
120	20.5	4	308
135	22	0	96
140	27.5	0	111
145	33.5	0	104
150	33.5	0	103
155	33.5	0	96

The Vicat needle readings were made on the soaked putties while still in the vessels in which they were soaked. In the second experiment in this table the Vicat needle reading showed "standard consistency;" yet this unstirred sample of really fine plasticity would have graded as a non-plastic hydrate. Also it should be noted that the first experiment used less water than any of the others, yet it gave the lowest Vicat needle reading and the highest plasticity number. In those experiments where the final putties were not stirred the soaked material was carefully removed from the soaking vessel into the ring on the porous plate at the time of final testing. There was no marked slumping of these test pats. With the large quantities of water used in most of these experiments, very little stirring would have made the putties too thin for testing. This table certainly shows that the stirring, and not the total quantity of water or the consistency as determined by the Vicat needle, is the important factor in making a satisfactory plasticity determination.

Discussion

No doubt most plasticity determinations under the old directions were accurate. It is probable that all experienced operators stirred the putties enough to avoid the very low values that result from a lack of stirring. However, it seems likely that the lack of uniform stirring by different operators on the same lime or by the same operator on the same lime at different times is the cause of distressing variations in the results sometimes obtained. The following changes are therefore recommended in the directions for the Emley plastometer:

Recommendations[4]

The total quantity of water for the test should be added at the start of the soaking. The exact quantity of water required for any hydrate must be determined either by previous test or by the following method: Four separate 125-gram samples of the hydrate should be soaked with 110, 115, 120, and 125 cc. of water, respectively. At the time of final test each of these samples should be stirred vigorously for 2 minutes with a steel spatula.

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[4] This recommendation varies slightly from the Tentative Revisions of the American Society for Testing Materials for 1928, page 853, which say, "It (the putty at the time of final test) shall be vigorously stirred with a trowell or spatula for three minutes; molded, etc." The above tentative changes were adopted after the completion of this paper and after copies of this manuscript had been sent to some of the lime laboratories.

Note—The new tentative directions by the American Society for Testing Materials call for 3 minutes' stirring. No data in this research show that more than 2 minutes' stirring is necessary for maximum value of plastometer reading.

Those samples that are too thin and those that are too thick should be discarded. The plasticity should be determined upon the one or two samples that are free from more than slight slumping and the maximum value should be reported. No hydrate available for these tests required quantities of water outside the range given above. If different quantities of water should be necessary, then the method can be varied accordingly.

The inexperienced operator should finish the tests on all the samples and then report the maximum value. The experienced operator will know the particular sample that should be run. The putty should be stirred vigorously for 2 minutes before using the Vicat needle, if anyone desires to employ that method of determining the right consistency for the determination. If small quantities of water are added to a thick putty to bring it to standard consistency at the time of final test, correct results can be obtained. However, the total quantity of water to be used cannot be varied so widely as when all the water is added at the beginning as recommended above.

Problems in the Estimation of Unsaturated Hydrocarbons in Gases

I—Separation by Fractional Distillation[1]

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Gases rich in unsaturated hydrocarbons are being produced in increasing quantities at petroleum refineries and elsewhere, and their chemical utilization is already the basis for an established industry. Nevertheless, further progress will depend very largely upon the extent to which better methods can be worked out for the accurate estimation and separation of the individual hydrocarbons in the gaseous mixtures.

Fractional distillation of the hydrocarbons into groups containing a few of approximately the same boiling point offers the first approach to the problems. The separation of the individual hydrocarbons in the boiling-point groups necessitates measurements of their relative rates of reaction with various reagents. For these studies the gases must be prepared in a pure state and properly stored.

This paper describes a column composed of a narrow glass spiral surrounded by a silvered vacuum jacket in which liquefied gases can be fractionated almost as easily as ordinary liquids.

Descriptions of the preparation and storage of propene and each of the three butenes are given.

THE present paper deals with fractional distillation through an efficient column at low temperatures, first, as a practical means for the preparation of the gaseous unsaturated hydrocarbons in a pure state, and second, as a method for the separation of mixtures of gaseous hydrocarbons into groups containing only a few species of approximately the same boiling point. Further contributions are planned from research now in progress on this project, which will deal with the utility of various reagents for the separation of the individual hydrocarbons in the boiling-point groups.

The possibilities of fractionation in the analysis of these substances are shown very clearly by the chart, Figure 1, which lists the known gaseous hydrocarbons arranged according to their boiling points on a Centigrade scale. Their number is not great, something over twenty scattered over a temperature range of 170° C. Only a rare mixture, if any, contains them all. In the case of ordinary liquids it would not be difficult to separate by fractionation substances boiling 40° to 60° C. apart, in a comparatively pure state. Note then the positions of methane, ethylene, propene, and the butenes on the chart.

Fractional distillation at low temperatures and mostly at low pressures from one vessel to another without any fractionating column has been used by many investigators for the separation and purification of liquefied gases. It has been applied to the analysis of hydrocarbon gas mixtures.[3] However, it is well known that many distillations in this tedious way are required to obtain results equal to those from one fractionation in a well-designed column. The difficulties which have prevented the general use of fractionating columns for separating low-boiling hydrocarbons lie in their operation below room temperature and in the collection and storage of the products.

Lucas and Dillon[4] fractionated 1-butene to a sharp boiling point −6.7° to −6.5° C. in a glass-packed column kept cool by a surrounding jacket through which chilled brine was circulated.

Frey and Yant[5] fractionated a portion of the 4-carbon-atom fraction of the hydrocarbons in gas from the low-temperature carbonization of coal through a vacuum-jacketed column of glass, filled with 5-mm. brass rings. Controlled reflux was maintained by withdrawing heat from the upper part into liquid air through an annular hydrogen-filled interspace, 1 mm. thick.

Recently Oberfell and Alden[6] have published a valuable

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[1] Presented in part before the Division of Petroleum Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 20, 1928. Received February 1, 1929. Contribution No. 42 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology. This paper contains results obtained in an investigation on "The Relative Rates of Reaction of the Olefins," listed as Project No. 19 of American Petroleum Institute research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

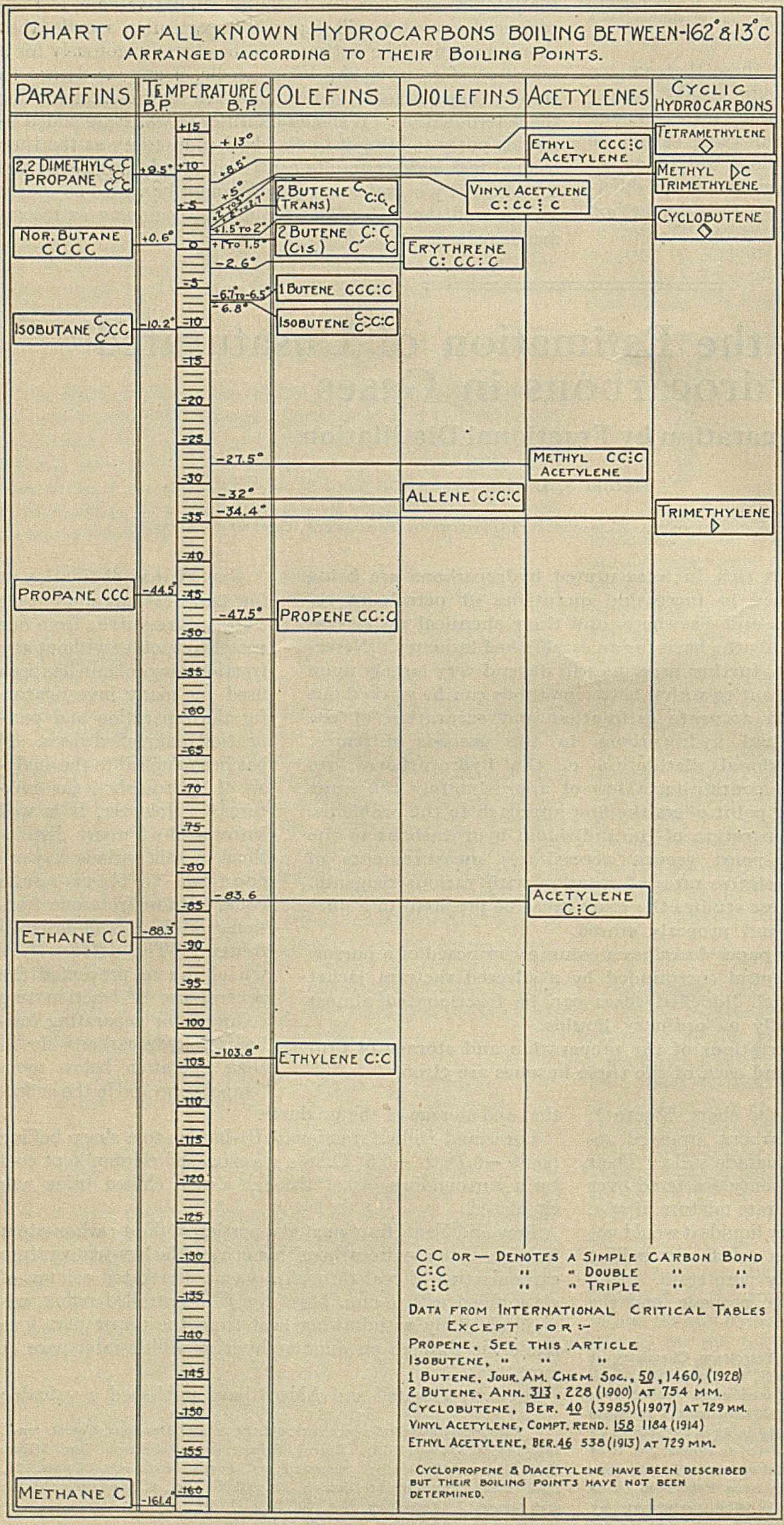
[2] Director and Research Associate, Fellowship No. 19.

[3] Representative references are: Lebeau and Damiens, *Compt. rend.*, **156**, 144, 325, 797 (1913); Burrell, Seibert, and Robertson, Bur. Mines, *Tech. Paper* **142** (1916); Shepherd and Porter, Ind. Eng. Chem., **15**, 1143 (1923); Tropsch and Dittrich, *Brennstoff-Chem.*, **6**, 169 (1925); Coffin and Maass, *J. Am. Chem. Soc.*, **50**, 1427 (1928).

[4] Lucas and Dillon, *Ibid.*, **50**, 1460 (1928).

[5] Frey and Yant, Ind. Eng. Chem., **19**, 489, 493 (1927).

[6] Oberfell and Alden, *Oil Gas J.*, **27**, No. 22, 142 (1928).



CC OR — DENOTES A SIMPLE CARBON BOND
C:C " " DOUBLE " "
C⋮C " " TRIPLE " "

DATA FROM INTERNATIONAL CRITICAL TABLES
EXCEPT FOR:-
PROPENE. SEE THIS ARTICLE
ISOBUTENE, " " "
1 BUTENE, JOUR. AM. CHEM. SOC., 50, 1460, (1928)
2 BUTENE, ANN. 313, 228 (1900) AT 754 MM.
CYCLOBUTENE, BER. 40 (3985) (1907) AT 729 MM.
VINYL ACETYLENE, COMPT. REND. 158 1184 (1914)
ETHYL ACETYLENE, BER. 46 538 (1913) AT 729 MM.

CYCLOPROPENE & DIACETYLENE HAVE BEEN DESCRIBED BUT THEIR BOILING POINTS HAVE NOT BEEN DETERMINED.

Figure 1

description of equipment and procedures for the fractionation of liquefied gases through a vacuum-jacketed column filled with wire packing.

Description of Fractionating Column

A sturdy column[7] in which liquefied gases can be fractionated almost as easily as ordinary liquids is shown in Figure 2. It consists of 3 to 5 meters of 5-mm. glass tubing bent into a spiral of 30 to 40 turns with a low pitch. An upright head at the top is surrounded by a cup in which a cooling mixture is placed. Thermal insulation and mechanical rigidity are secured by a surrounding glass jacket, which is highly evacuated and silvered like a Dewar flask, unsilvered strips being left on opposite sides for observation.

The spiral is not only an effective fractionating means, but it takes up the strains existing in the glass during a distillation.

Note—Spiral tubes have been used for fractionating columns by LaRue,[8] Brown,[9] and Berlemont.[10] Young[11] showed that the effectiveness of a narrow glass tube for fractionating liquids is increased by placing it in a sloping position and is still further increased by bending it into a spiral, and that the spiral, although the most effective for fractionation, actually holds up the smallest quantity of liquid. Previous to the present author's use of spirals, C. R. McCullough had developed at this laboratory a thermally insulated spiral for fractionating liquids.

The silvered vacuum jacket[12] affords a most satisfactory insulation. Even when liquids boiling 100 degrees above or below room temperature are being fractionated, little heat or cold can be felt through the walls.

Note—Dewar[13] found that a good exhaustion reduced the heat influx into double-walled vessels to one-fifth of what is conveyed when the annular space is filled with air and that silvering diminished to one-sixth part the amount entering the exhausted vessel without the metallic coating, the total effect of the high vacuum and silvering being to reduce the ingoing heat to one-thirtieth part.

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[7] Constructed by the Macalaster-Bicknell Co., Cambridge, Mass.

[8] LaRue, *Z. anal. Chem.*, **4**, 243 (1865).

[9] Brown, *J. Chem. Soc.*, **37**, 49 (1880).

[10] Berlemont, *Bull. soc. chim.*, [3] **13**, 674 (1895).

[11] Young, *J. Chem. Soc.*, **75**, 688 (1889).

[12] Silvered vacuum jackets for fractionating columns were first described by the writer, Am. Petroleum Inst., *Bull.* **9**, No. 53, 14 (1928); *J. Am. Chem. Soc.*, **64**, 2779 (1928). Unsilvered vacuum jackets have been used by Marckwald, *Ber.*, **39**, 893 (1906); Robert, *Compt. rend.*, **168**, 998 (1919); Leslie and Geniesse, Leslie's "Motor Fuels," p. 555, Chemical Catalog Co., 1923; Frey and Yant, *loc. cit.*, and Oberfell and Alden, *loc. cit.* The possibilities of all-metal vacuum-jacketed columns should not be overlooked. See Report of the Oxygen Research Committee, *Dept. Sci. Ind. Research* (*Brit.*), *Repts.*, 1923.

[13] Dewar, *Proc. Roy. Inst. Gt. Brit.*, **15**, 341 (1896).

Podbielniak[14] has described vacuum jackets covered with a film of silver thick enough to improve the thermal efficiency about three times but thin enough so that "the packing of the column is distinctly seen by aid of an ordinary flashlight." The writer has used heavy coats with perfectly clear narrow strips on opposite sides for observation. They were left by the well-known method of silvering first one side and then the other leaving unsilvered spaces between.

Operation of Column

The gas was liquefied in the device shown as the condenser III, Figure 2, and forced over by air pressure into a thermos bottle. This was attached to the column by a cork which had been boiled in paraffin under vacuum, the joints being tested against leakage. The heat necessary for distillation was supplied electrically as shown. The rate of distillation could be accurately controlled.

At the start acetone in the Dewar cup *D* at the top of the column was cooled by the addition of solid carbon dioxide.

Note—Oberfell and Alden[6] have also described this cup, which was developed independently by the writer. They used liquid nitrogen dissolved in pentane to cool the head. However, a temperature as low as −70° C. can easily be maintained by a single operator through acetone and lumps of the highly compressed solid carbon dioxide which can now be purchased from most ice-cream companies.

To prevent foaming a small platform of copper gauze was suspended by wires about 0.5 cm. below the surface of the acetone. It was very effective for this purpose; the solid lumps of carbon dioxide dissolved quietly and the thermal currents produced kept the acetone at a moderately uniform temperature throughout.

At first the stillhead *C* was kept so cold that no liquid passed over and after about 30 minutes a steady reflux appeared in the drop indicator at the bottom, showing that the spiral was properly cooled. To obtain the most effective fractionation it was necessary that at all times a reflux showed in the drop indicator; otherwise the lower part of the spiral acted like a flask boiler and the length effective for fractionation was decreased. The temperature of the head was then allowed to rise until distillate appeared and this temperature was maintained until distillation ceased, when it was again permitted to rise, etc.

The distillate was collected in the receiver, *F*, placed in an acetone-carbon dioxide mixture in a Dewar flask silvered except for clear strips. The separate fractions were blown over into suitable vessels, mostly thermos bottles, and finally stored in steel bottles as described below.

Tests on the Effectiveness of the Column

Note—"Effectiveness" refers to the degree of separation of substances accomplished by the fractionation; "efficiency" to the heat required.[15]

BENZENE AND TOLUENE (equal volumes)—Robert[12] has suggested as a measure of the effectiveness of a column for fractionating this solution, the factor $E = \frac{a-b}{v}$, where v is the quantity of benzene in the original mixture and a and b are the quantities of benzene and toluene in the first half of the distillate.

One hundred cubic centimeters of the following solution were fractionated: 50 cc. of benzene (Eastman Kodak Co.) recrystallized once and fractionated from sodium (b. p. 79.7–79.8° C., f. p. 5.5° C.) + 50 cc. of toluene (Eastman Kodak Co.) fractionated from sodium (b. p. 110.5° ± 0.05° C.). The water in the stillhead was kept at 70–74° C. The reflux in the drop indicator remained approximately constant at 175 drops per minute. The distillation rate was about 30 drops per minute for the first 35 cc. and then fell off until at the end it was only 1 drop per minute. The first 50 cc. of distillate boiled at 79.7–81.0° C., and its freezing point was 4.8° C. The toluene content was 0.6 cc.

The following comparison can now be made with the tests of Robert for an over-all distillation rate of 1 drop per second:

	E
Vigreux column with 14 rows of double points	0.73
Robert column, glass-packed and vacuum-jacketed	0.94
Vacuum-jacketed spiral (above test)	0.97

ALCOHOL AND WATER—The first 40 cc. fractionated from a solution of 40 cc. alcohol in 200 cc. of water was 94 per cent alcohol.

PROPENE AND ISOBUTENE—These substances were separated almost quantitatively. See text on the preparation of propene.

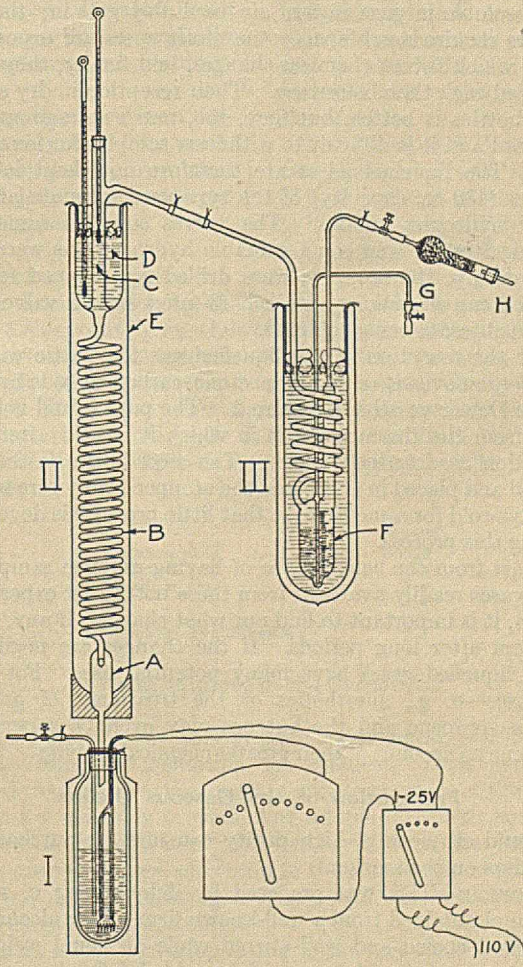

Figure 2—Apparatus for Fractionating Liquefied Gases

I—Thermos bottle from which the liquefied gas is distilled by electric heating.

II—Fractionating column: *A*, drop indicator; *B*, glass spiral; *C*, stillhead with thermometer; *D*, Dewar cup containing acetone cooled by solid carbon dioxide supported on wire platform; *E*, evacuated jacket silvered except for clear strips.

III—Condenser: *F*, graduated receiver; *G*, tube through which distillate can be blown to storage by air pressure at *H*. All immersed in acetone cooled by solid carbon dioxide which is supported on a wire platform in a Dewar vessel with unsilvered strips.

ISOBUTENE AND 2-BUTENE—The following results obtained with a mixture of approximately equal volumes of the pure substances show how effectively these isomers boiling only 8.5° C. apart were separated in a single fractionation. Ninety per cent of the isobutene was recovered in the first half of the distillate.

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[14] Podbielniak, *Oil Gas J.*, **27**, No. 35, 38 (1929).

[15] Leslie, *op. cit.*, p. 121.

ORIGINAL MIXTURE

	Boiling point ° C.	Cc.	Per cent
Isobutene	−6.8	19.7	48.6
2-Butene	+1.5 to 1.7	20.8	51.4

RESULTS FROM ONE FRACTIONATION

	Original mixture	First 9.8 cc.	First 16 cc.	First 20 cc.
Boiling point		−6.8° to −5.8° C.	−6.8° to −5.4° C.	−6.8° to −3.2° C.
	Per cent	*Per cent*	*Per cent*	*Per cent*
Isobutene	48.6	94.6	90.6	89.9
2-Butene	51.4	5.4	9.4	10.1
Per cent of total	100	24	40	50

Time required 1½ hours. Temperature of cooling head, −19° C.

The analyses of the distillates were made on gasified samples by means of 65 per cent sulfuric acid in a Hempel pipet.[16]

Storage of Pure Gaseous Hydrocarbons

It is thoroughly unsatisfactory to hold large quantities of these gases over water or saturated salt solution. Some are quite soluble in pure water; air inevitably gets in; the containers require much space; the moist gases are exposed to light, which favors chemical changes, and finally, they must be dried each time before use. Their reception in dry evacuated bottles is better; but here, too, much storage space is required and it is difficult to withdraw samples for investigation. The liquefied gases are therefore now kept in steel bottles (430 cc. capacity) of the type used commercially for liquid hydrogen sulfide.[17] The valves supplied sometimes leaked after use and some valuable hydrocarbons were lost. Accordingly, the stoppers were drilled and tapped for the attachment of ordinary ⅛-inch (3-mm.) needle valves, the threaded joints being soldered.

For the reception of the liquefied gas the bottle with its stopper removed is cooled by acetone-carbon dioxide mixture in the Dewar vessel III, Figure 2. The pure liquid is blown over from the thermos bottle in which it is held after fractionation as described above. The steel bottle is then removed and placed in a vise and the stopper firmly screwed in. It stays cold for some time, so that little pressure is developed during this process.

Apart from the convenience of having uniform samples of pure gases readily available from these bottles for experimentation, it is important to find out what changes, if any, occur in them after long periods. If the changes are negligible, these liquefied gases have many potential uses. For some purposes—e. g., anesthetics or the treatment of growing plants—propene and the butenes may even be superior to ethylene on account of their greater chemical activity.

Preparation of the Gaseous Olefins

Liquid ethylene of high purity can now be purchased in cylinders on the market.

PROPENE—This was prepared by dehydrating C. P. isopropanol obtained from a well-known firm. The alcohol was kept well cooled and well stirred while an equal weight of phosphorus pentoxide was slowly added. On heating the mixture propene was smoothly evolved.

The gas was collected over water in a 50-gallon (190-liter) drum. It was passed through dilute and concentrated potassium hydroxide solutions, then through calcium chloride, liquefied, and fractionated from sodium. The distillates exclusive of some lower boiling gas were collected as follows:

FRACTION	Cc.	BOILING POINT ° C.
1	440	−47.5 to −47.0
2	3	−47.0 to − 5.8
3	10	− 5.8 to − 3.2
Residue	7	

A part of the third fraction boiling at −5.8° C. was gasified and found to be readily soluble (99 per cent) in 65 per cent sulfuric acid. Evidently it was isobutene, which indicated that the original isopropanol contained 3 per cent or more of tertiary butanol.

Practically all the first fraction on redistillation boiled at −47.3° ± 0.2° C. at 770 mm. The temperatures were taken by an alcohol-filled thermometer, which was compared with a standard pentane thermometer at this point.

Another lot of the isopropanol was dehydrated over active alumina on pumice at 300–325° C. The propene was fractionated in an inefficient vacuum-jacketed spiral of only five turns with a slope too steep. The boiling point after two fractionations was −47.5° ± 0.3° C. at 764 mm.

ISOBUTENE—This was prepared by heating tertiary butanol (f. p. 20° C.)[18] with an equal weight of hydrated oxalic acid. The yield was over 90 per cent of the theoretical. If the alcohol is added in small lots, less oxalic acid is needed.

The gas was washed with water, dried by calcium chloride, and fractionated over sodium. Exclusive of a small residue, the isobutene boiled at −6.8° ± 0.05° C. at 760 mm. (compare −6.6° C., Coffin and Maass[3] and −6.0° C., I. C. T.).

2-BUTENE—2-Butene was prepared from refined 2-butanol made from petroleum gases. This alcohol can be dehydrated by phosphorus pentoxide in the manner described above for isopropanol, giving butene yields over 90 per cent of the theoretical. However, glacial phosphoric acid served very well. The temperature required and the rate of gas evolution depended on the quantity and concentration of the acid used. With 1.5 volumes of 86 per cent phosphoric acid to 1 volume of alcohol a yield of butene over 90 per cent of the theoretical was quickly obtained at about 117° C.

Note—Harries,[19] who found the gas prepared in this way to be pure 2-butene, obtained a yield of only 64 per cent. It is possible that he added the alcohol to the phosphorus pentoxide, a procedure which causes local superheating and polymerization.

The gas was washed with water dried by calcium chloride and fractionated from sodium. Its boiling point was 1.5° to 1.7° C.

1-BUTENE—This butene was made from normal butyl iodide and alcoholic potash, a method which yields a pure product.[20] After washing and drying it was fractionated from sodium through the small vacuum-jacketed spiral described above under propene. The boiling point was −6.9° to −5.5° C. A much closer boiling cut can undoubtedly be obtained in the new column with forty turns in the spiral.

As a preliminary test of the apparatus and methods for the analysis of gas mixtures, a fractionation was made of a sample of light petroleum distillate. It had been recovered at a refinery from a mixture in unknown proportions of field gases and gases from Cross cracking stills. Sharp separations were obtained of the hydrocarbon groups containing 2, 3, 4, and 5 carbon atoms, respectively. Analyses of the constituents in the groups made by methods which will be given later in detail yielded the following results:

	Per cent by weight
Ethylene and ethane	Substantially none
Propane	2.5
Propene	0.4
Trimethylene, allene, allylene	Substantially none
Isobutene	4.5
Normal butenes	8.7
Erythrene	Substantially none

Unfortunately, in an analysis of this kind there is no way to prove the accuracy of the results and further tests will be carried out on synthetic mixtures of pure substances.

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[16] Dobryanskii, *Neftyanoe Khozyaistvo*, **9**, 565 (1925); *C. A.*, **20**, 1576 (1926).

[17] Purchased from The Matheson Co., North Bergen, N. J.

[18] Obtained through the courtesy of Arthur D. Little, Inc.

[19] Harries, *Ann.*, **383**, 181 (1911).

[20] Coffin and Maass, *loc. cit.*

Chemical Examination of the Tissue of the Cornstalk[1]

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An analytical examination of the cornstalk indicates that it consists primarily of lignin (approximately 30 per cent), pentosan (approximately 27 per cent), cellulose (approximately 36 per cent). There is little polyhexose material subject to acid hydrolysis (2 to 6 per cent) and no pectic material could be definitely identified.

Directions are given for the isolation from the cornstalk by alkali extraction of a pentosan fraction (with about 25 per cent impurity as ash and lignin) and of a lignin fraction (apparently containing no carbohydrates).

The shell, pith, and vascular bundles have been dissected from the cornstalk and analyzed. The composition of these tissues does not vary greatly from that of the total stalk. The cellulose pulp prepared from the pith dries to a parchment-like paper.

DURING the last few years there has been a revival in the attempt to utilize the cornstalk commercially as a source of cellulose. Most of the publications regarding this work are of a general descriptive nature,[2] but Jackson[3] gives some analytical data in addition to a general report. Most of the other analytical data available are of an agricultural nature and of little value for commercial purposes.

The following analytical examination of the cornstalk has been made as an orientation for the experimental work in this laboratory. The analytical scheme is fundamentally that recommended by Schwalbe[4] for the examination of plant tissues and the celluloses derived from them. The material used for these experiments consisted of stalks from the baled material selected and cleaned by hand. The selected material was ground to pass a 60-mesh screen unless otherwise indicated. The moisture content of this material was 7.72 per cent on an oven-dry basis of 105° C. The dry tissue ran 3.62 per cent ash and 0.6 per cent ether extractable matter. The data reported below are all calculated on the dry basis.

Lignin Determination

The lignin analyses reported throughout this paper have been obtained by the 72 per cent sulfuric acid method, using the procedure recommended by Schorger.[5] This method gives higher results than does the hydrochloric acid method of Willstätter and Kalb,[6] although it is an easy matter to obtain check results by either procedure. Similar difficulties with flax and hemp were pointed out by Schwalbe and Becker.[7] Determinations of lignin in the cornstalk by these methods gave the following average results:

Method	Per cent
72% sulfuric acid	34.3
Willstätter	26.2

Cellulose in the Cornstalk

The term "cellulose" in carbohydrate chemistry is generally restricted to the inert substance of the same percentage composition as starch $(C_6H_{11}O_5)_x$ but presumedly more highly polymerized. The term is not so restricted in the less technical language, as is indicated by the terms alpha-cellulose, beta-cellulose, and gamma-cellulose used in the analyses of the commercial products. The product obtained by the Cross and Bevan[8] analytical method is reported as cellulose, although it is recognized that this product may contain considerable furfural-yielding material and small quantities of lignin.

The Cross and Bevan determination leaves a residue of 45.5 per cent of the stalk as cellulose pulp. This product contains furfural-yielding material to the equivalent of 17.1 per cent pentosan. The lignin determination by the 72 per cent sulfuric acid method gives 5.8 per cent lignin while the Willstätter method indicates 3.3 per cent. The ash ran 0.6 per cent. Variation in the methods of the treatment will, of course, change these values. If the pentosan, lignin, and ash are calculated to per cent of original stalk and subtracted from the value for Cross and Bevan cellulose, the following results are obtained:

	Per cent
Cellulose pulp	45.5
Pentosan	7.8
Lignin, average	2.0
Ash	0.3
Cellulose, by difference	35.4

Hemicellulose in the Cornstalk

The definition for this group of substances is even less precise than the definition for cellulose. It is generally agreed that they are the group of polysaccharides of the tissue which are insoluble in water but soluble in caustic solution, and are more subject to acid hydrolysis than the cellulose. They are subdivided according to the simple sugars obtained by hydrolysis—xylans, galactans, mannans, and mixtures such as galacto-arabans, etc.

A part of the confusion is due to the fact that alkaline extraction does not give a sharp separation between the cellulose and hemicellulose and also removes a portion of the lignin. As would be expected, the values obtained by alkaline extraction of the tissue do not agree with those obtained by acid hydrolysis of the tissue. These difficulties have led to the postulation of many different kinds of hemicelluloses.

With the cornstalk an approximation has been made by 5 per cent alkaline extraction of the tissue followed by analysis of both the residue and filtrate. The tissue was treated three times for 12, 4, and 4 hours, respectively, with sufficient 5 per cent sodium hydroxide to moisten it at room temperatures. The solutions were pressed off and the residual tissue washed

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[1] Received August 14, 1928.

[2] Rommel, Ind. Eng. Chem., **20**, 716 (1928); *Ibid.*, News Edition, p. 1 (May 20, 1928); p. 7 (July 20, 1928); Kirkpatrick, *Chem. Met. Eng.*, **35**, 401 (1928).

[3] Jackson, *Paper Mill*, **50**, No. 36, 2 (1927).

[4] Schwalbe, *Z. angew. Chem.*, **32**, 125, 229 (1919).

[5] Schorger, "Chemistry of Cellulose and Wood," p. 524, McGraw-Hill Book Co., 1926.

[6] Willstätter and Kalb, *Ber.*, **55**, 2640 (1922).

[7] Schwalbe and Becker, *Z. angew. Chem.*, **32**, 126 (1919).

[8] Cross and Bevan, "Cellulose," p. 94, Longmans, Green and Co., 1916.

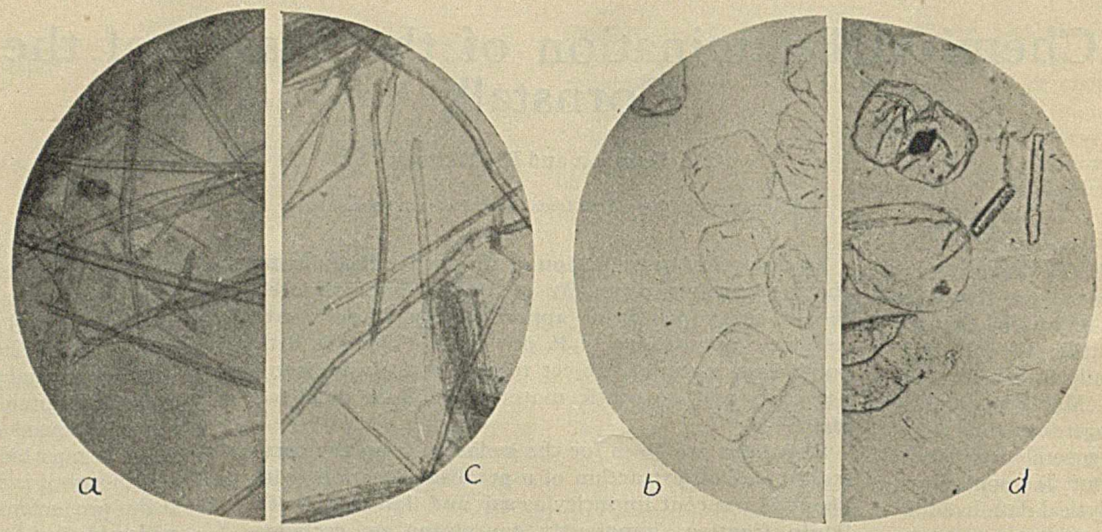

Figure 1—Photomicrographs of Cellulose Pulp from the Cornstalk Prepared by the de Vains Process

a and *b* from vascular bundles and parenchyma carefully dissected out. *c* and *d* from mechanically separated prosenchymatous and parenchymatous tissues.

with warm water after each extraction. This treatment dissolved 46.2 per cent of the stalk, leaving 53.8 per cent as residue. Analyses for pentosans by furfural showed 17.3 per cent of the stalk calculated as pentosans in the extract with 7.1 per cent in the residue. The sum of these results, 24.4 per cent, indicates an unaccountable loss in pentosan equivalent to 3.2 per cent of the stalk, since the original tissue contained 27.6 per cent pentosan. A determination of reducing sugars indicated little, if any, reducing sugars other than those calculated as pentosans.[9]

Table I—Composition of Cornstalk under Various Analytical Treatments

(Results in percentage of original stalk dried at 105° C.)

Designation of Tissue	Original Stalk	5% NaOH Extract of Stalk		Acid Hydrolysis	
		46.2% Fraction (soluble)	53.8% Fraction (not soluble)	40.7% Fraction (soluble)	59.3% Fraction (not soluble)
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Lignins	34.4	26.5 (by diff.)	7.8	14.3 (by diff.)	20.0
Ash	3.6	..	1.6	..	1.4
Hemicellulose:					
Pentosans	27.6	17.3	7.1	20.8	4.1
Hexosans	1.3	None	..	4.9	..
Cellulose, by diff.	33.1		37.3		33.8

An acid hydrolysis of the tissue was run using 2.5 grams of tissue and 20 cc. of 1.125 specific gravity hydrochloric acid in 200 cc. of water at boiling temperatures under reflux for 2$^1/_2$ hours. This treatment dissolved 40.7 per cent of the cornstalk. A gravimetric Fehling's determination gave a copper equivalent of 26.4 per cent glucose in the solution. A furfural determination gave 20.8 per cent pentosan in the solution and 4.1 per cent in the residue. The sum of these values gives 24.9 per cent pentosan, which indicates an unaccountable loss of 2.7 per cent pentosan from that of the original sample. Since the reducing values of glucose and xylose are about the same,[9] a subtraction of the furfural value for xylose of 21.5 per cent from the glucose value would indicate that about 4.9 per cent of the stalk as reducing sugars other than xylose might be present.

The residue from the acid hydrolysis, 59.3 per cent of the original stalk, contained 1.4 per cent ash, 4.1 per cent pentosan, and 20.0 per cent lignin based on the original stalk. This would leave 33.8 per cent cellulose in the stalk by difference.

A summary of the results of the three independent series of analytical procedures is given in Table I. It will be observed that the sums of these various procedures check fairly well for the indicated fractional composition of the cornstalk and that the values for cellulose by difference check roughly with the value 35.4 obtained from the corrected Cross and Bevan value. The analytical procedures upon which these results are based are not considered sufficiently selective to warrant the inclusion of the nitrogenous and ether-soluble fractions, since their magnitudes would be within the experimental error of these values.

Pectin in the Cornstalk

An effort has been made to determine the pectin content of the cornstalk as a means of correlation with retting experiments. A direct isolation failed to give any pectin or pectic acid. An indirect attempt was made by determining galactose on the assumption that all pectins are characterized by yielding mucic acid on oxidation. The quantities of mucic acid obtained were so small that definite identification was doubtful. In this connection attention should be called to the work of Ritter,[10] which shows that the middle lamella of basswood tissue consists of lignin and not pectin or calcium pectate. The question arises as to whether a similar change takes place in the lignification of the cornstalk.

Isolation and Analysis of Pentosans from Cornstalk

In preparing xylan or wood gum it is common practice first to extract the tissue with 1 per cent ammonium hydroxide to remove the water-soluble constituents, coloring matter, etc. Analysis of this extract gave the following results:

	Per cent
Total solids extracted by 1 per cent ammonia	6.00
Total sugars (calculated as glucose)	2.17
Pentosans (by furfural)	0.85
Galactans (by mucic acid)	Indefinite trace

This analysis indicates that the water-soluble hexose carbohydrates, including starch, are not present to more than about 2.0 per cent of the total stalk.

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[9] This statement is based on the equivalent copper value of glucose and xylose as reported by Stone, *Ber.*, **23**, 3796 (1890).

[10] Ritter, Ind. Eng. Chem., **17**, 1195 (1925).

After the preliminary treatment with 1 per cent ammonia, the tissue was extracted with 5 per cent sodium hydroxide as described for the determination of hemicelluloses. Alcohol was added to this extract until precipitation ceased. This usually required a volume-to-volume proportion; in a few cases more alcohol was necessary. The precipitate settled fairly rapidly and was filtered off through paper after about 6 hours' standing. The material was reprecipitated by adding alcohol to a 1 per cent sodium hydroxide solution of the material. The yellow, amorphous powder obtained by drying this residue gave the following analysis:

	Per cent
Moisture (loss at 100° C.)	12.2
Pentosan (furfural distillation)	69.5
Lignin (72 per cent sulfuric acid)	13.1
Ash	8.1
Total	102.9
Reducing sugars as xylan (by Fehling)	69.0

In view of the fact that the reducing sugars and furfural determination check, it seems probable that this material is xylan, with the impurities indicated.

Note—The furfural determinations have been calculated as xylan throughout this paper on this evidence. This fraction is being more closely examined and until that time the furfural values should be interpreted with the usual reservations. Cf. Klingstedt, *Z. anal. Chem.*, **66**, 129 (1925). The work of Brown and Tollens, *Ber.*, **35**, 1457 (1902), indicates that small amounts of arabinose are to be expected.

The same procedure is frequently used and the precipitated fraction designated as "hemicellulose." Varying amounts of lignin can be brought down with this fraction according to the manipulation details.

Isolation and Analysis of Lignin Fraction

The lignins, although insoluble in either water or alcohol, are quite soluble in a mixture of the two solvents. The filtrate from the isolation of the pentosan fraction was fractionally distilled to remove the alcohol, the lignins remaining in solution in the aqueous sodium hydroxide. When the alcohol was removed, the solution was cooled and acidified, the lignins separating at once. They were purified by twice taking up in 1 per cent sodium hydroxide and reprecipitating by acidification.

The lignins (or lignic acids) were obtained as a light brown, amorphous powder. When suspended in water, they softened at 60° C. to a sticky, resinous oil, which immediately solidified upon cooling to a brittle, easily pulverized mass. This characteristic changes with time. The analysis of this fraction was as follows:

	Per cent
Moisture (loss at 100° C.)	22.0.
Pentosans	Indefinite trace
Reducing sugars (hydrolysis)	Indefinite trace
Lignin (by 72 per cent sulfuric acid)	76.1
Ash	1.0
Total	99.1
Methoxy content	14.0

Separation and Analysis of Three Structural Tissues of Cornstalk

The matured cornstalk can be easily separated into three different tissues or combinations of tissues: (*a*) the epidermis and the peripheral vascular bundles or the outer shell of the stalk; (*b*) the pith or fundamental parenchyma of the stalk (the term "pith" as used by Jackson[3] and by Sherwood apparently includes the vascular bundles as well as the parenchymatous tissues); (*c*) the inner vascular bundles interspersed through the pith of the stalk. Of these tissues, the outer shell and the central vascular bundles are predominantly fibrous in structure and of woody appearance. The pith is composed of more or less cubical cells of soft and spongy texture.

It was presumed that most of the lignin content of the cornstalk would be found in the vascular bundles and that the hemicellulose would be largely concentrated in the parenchymatous tissues. The analytical data (Table II) do not support this presumption, the analyses of these different tissues being about the same as that for the total stalk. To obtain these data the outer shell of the stalk was peeled off with a sharp knife, the inner pith cylinder softened in water, and the vascular bundles separated from the pith by carefully pulling out each fiber and scraping away the softer parenchymatous tissue. The separated tissues were then analyzed as previously described for the total stalk except that the cellulose pulp was obtained by a modification of the de Vains process instead of by the Cross and Bevan analytical method. It will be observed that the values for cellulose by difference check roughly with the value reported for the total stalk. (Table I)

Table II—Comparison of Compositions of the Cortex, Vascular Bundles, and Pith of the Cornstalk

	OUTER SHELL	VASCULAR BUNDLES	PITH	TOTAL CORNSTALK
	Per cent	*Per cent*	*Per cent*	*Per cent*
Pentosan	25.9	26.4	27.7	27.6
Lignin	33.5	35.2	32.0	34.3
Cellulose pulp	55.9	50.2	50.1	52.6
Pentosans in pulp	16.6	13.1	12.2	14.2
Cellulose (by difference)	39.3	37.1	37.9	38.4

Although these tissues had approximately the same chemical composition, the physical nature of the cellulose pulp prepared from the pith was very different from that prepared from the other tissues. The pulp prepared from the vascular bundles and outer shell was distinctly fibrous in texture and formed a good mat in filtering. The pulp prepared from the pith had no visible fiber and in appearance resembled the gelatinized celluloses. Photomicrographs of these pulps are shown in Figure 1*a* and *b*. These tissues had no mechanical treatment and it is difficult to believe that treatment with 1 per cent caustic as used in the preparation of the material would cause such a degree of gelatinization. It seems more probable that this property is due to the original subdivision of the tissue into thin-walled, isodiametric cells rather than to the chemical nature of the cellulose.

The tedious task of dissecting these tissues would handicap any great extension of the above studies. Since these results indicated such a decided difference in the physical nature of these tissues, a mechanical device for separating the parenchymatous tissues from the shell and vascular bundles has been developed.[11] The success of the separation can be judged by comparing the photomicrographs *c* and *d* in Figure 1 with those of the corresponding hand-separated tissues.

It should be emphasized that these statements are not to be interpreted to mean that paper cannot be made from the pith of the cornstalk. Sheets prepared from the mechanically separated pith resemble the rice papers of the Chinese. The facts that the pith is very bulky, that it will yield to milder chemical treatment than the rest of the stalk, and that it is almost impossible to bleach it to a white pulp indicate that it would be more economical to separate it from the more fibrous tissues which constitute about 80 per cent of the stalk.

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[11] The machine patented by Sherwood, U. S. Patent 627,882 (1899), apparently separated the shell from the central portion of the stalk, the term "pith" being used to designate the central parenchyma and vascular bundles as well. The same applies to U. S. Patents 720,850 and 720,851 (1903).

Germany to Produce Sugar from Wood—Subsequent to the establishment in July, 1928, of Holzhydrolyse A. G., in Heidelberg, for wood saccharification utilizing the Bergius patents, it is now proposed to erect a plant in Stettin with an estimated capacity of 600 to 700 tons daily.

Cupric Oxide as a Standard in Iodimetry[1]

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Metallic copper, which has been in use as an iodimetric standard for many years, has been subjected to a critical investigation and found to be unreliable because of variable composition. Cupric oxide is suggested as a satisfactory standard, as it is stable, readily obtained uniform in composition, and easily soluble in sulfuric acid.

Cupric oxide has been compared with such accepted standards as potassium permanganate, potassium dichromate, potassium iodate, iodine, copper sulfate solution, and metallic copper, and found to compare favorably with the best in point of precision.

The procedure generally employed in iodimetric titrations, which involves neutralization with ammonia followed by acidification with acetic acid, is found to be unnecessary in cases where the sample is freed of nitrates by fuming. Titrations with thiosulfate may be made with accuracy in the acidities resulting from the sulfuric acid remaining after fuming to dryness.

RELIABLE standards for volumetric analysis have engaged the attention of the research and analytical chemist ever since volumetric procedure came to be generally employed. Certain requirements which a satisfactory standard must fulfil have in the course of time been set up, the essential ones being:

(1) It should be 100 per cent pure or of definitely known purity.
(2) It should be uniform in composition.
(3) It should be stable to air, moisture, and light.
(4) It should be readily soluble in water or simple reagents.
(5) It should be colorless or produce no colored compounds.
(6) It should be non-hygroscopic and have no water of crystallization.
(7) It should have a high molecular weight.
(8) It should be a compound rather than an element so that relatively large samples may be taken and weighing errors reduced.
(9) It should be capable of direct titration.

Of the six generally accepted iodimetric standards metallic copper is regarded as reliable and is almost universally used for the standardization of thiosulfate solutions in industrial laboratories. It is perhaps natural that electrolytic copper wire, such as is used for transmission lines and in electrical instruments, should have been assumed to be 100 per cent pure; for it is well known that even small percentages of impurity in copper greatly increase its electrical resistance and may cause considerable power losses. Numerous tests of supposedly pure copper foils and wire have convinced the authors that this assumption is not tenable. Impurities have been found in the very best electrolytic copper as purchased from supply houses, not only in greater or lesser quantity, but also in very non-uniform distribution. If adjacent strips of foil are used in standardizations, errors of considerable magnitude may occur and perhaps be entirely overlooked, because they may afford perfect checks in titrations and yet deviate greatly from 100 per cent purity. In some instances these deviations have been found to be as great as 1 per cent. An average percentage purity factor for a foil or wire can obviously have no meaning. Surface corrosion adds to this inaccuracy, because it cannot always be entirely removed. The same objections apply to metallic iron, which some investigators still continue to employ in standardizing permanganate or dichromate solutions.

The foregoing facts suggested the desirability of investigating metallic copper to determine the extent of its deviation from purity and of developing a new standard which would obviate, if possible, the difficulties which it presents. If the thiosulfate solution is to be used for copper titrations, it is desirable that the same end conditions shall obtain in the final titration as in the standardization. No work having been published on cupric oxide, this compound was studied in detail and a comparison made of it with the other existing iodimetric standards.

Unreliability of Metallic Copper as a Standard

The first determinations were made on copper foil to establish the extreme variations in its copper content and to ascertain what other elements were present as impurities. The foils were obtained from the following sources:

Foil A. From a well-known supply house by the Department of Chemistry, University of Arizona.

Foil B. From a large copper smelter laboratory in Arizona where it is used as a standard.

Foil C. From the Southwest Station of the U. S. Bureau of Mines, Tucson, Ariz.

After being thoroughly cleaned, the strips of foil were preserved against further tarnish in a desiccator over phosphorus pentoxide. Relatively large samples (about 0.4 gram) were taken, so as to reduce errors in weighing. These were dissolved with 3 cc. of 6 *N* nitric acid and 3 cc. 6 *N* sulfuric acid in 150-cc. electrolytic beakers, and as soon as dissolved were electrolyzed at a normal current density of 0.8 ampere. Urea was added near the end of the electrolysis to remove any nitrous acid formed. The deposits were in all cases bright; completeness of deposition was determined on the solutions with hydrogen sulfide water. The results are summarized in Table I.

Table I—Variations in Copper Content of Copper Foils

Foil	No. of Detns.	Copper Content: Min.	Copper Content: Max.	Copper Content: Deviation
		Per cent	*Per cent*	*Per cent*
A	19	99.00	100.08	1.08
B	19	99.43	100.08	0.65
C	17	99.41	100.09	0.68

The electrolytic method by which the above data were obtained affords an accuracy which is well within 0.1 per cent. There was therefore justification in concluding that the extreme variations recorded in Table I are not due to experimental or instrumental errors, but truly indicate a very non-uniform distribution of impurities throughout the foil. An average of these figures to obtain a so-called "purity factor" can be little better than a rough approximation.

In the analysis of the foils the authors avoided the removal of the impurities prior to the electrolysis, for two reasons: (1) They are never so removed in process of standardizing a solution; and (2) successive precipitations and filtrations to remove small amounts of impurity were believed to introduce indeterminate errors into the results. The procedure as used would yield a pure copper deposit in the presence of iron, arsenic, or zinc; if silver or lead were present it would, of

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[1] Presented before the Physical Sciences Section of the Southwestern Division of the American Association for the Advancement of Science, Flagstaff, Ariz., April 13 to 16, 1928. Received August 14, 1928.

course, deposit along with the copper. Qualitative tests were accordingly made on the foils, with results as shown in Table II.

Table II—Impurities Present in Copper Foils

	Foil A	Foil B	Foil C
Iron	Trace	Trace	Trace
Arsenic	None	...	None
Silver	0.5%	None	None
Lead	None	None	None

Experiments with Cupric Oxide

Cupric oxide was found to fulfil most of the conditions for a satisfactory standard, particularly that of uniformity. Uniformity of composition is more important than 100 per cent purity, because a purity factor can be determined which will be constant and definite. Attention was accordingly directed to working out a method of preparation which would prevent, as far as possible, occlusion and adsorption during the precipitation, but would also insure complete dehydration on ignition without reduction to the metallic form.

With the needs of both plant control work and of the most precise analytical work in mind, various samples of oxide were prepared as follows:

(1) Baker's technical oxide was washed, screened in water suspension through a 200-mesh sieve, dried, and subsequently ignited in a current of oxygen at about 400° C. for 4 hours.

(2) Kahlbaum's cupric carbonate was ignited in a current of dry oxygen.

(3) Cupric hydroxide was precipitated from copper sulfate solution with potassium hydroxide, washed, dried, and ignited as in (1).

(4) Cupric hydroxide was precipitated from cupric nitrate solution by fresh ammonia distilled into the solution. Fifty per cent potassium hydroxide solution was added, and the suspension boiled to cause the partially hydrated oxide to settle out. After drying it was ignited as in (1). After the ignition, the products were rolled on cloth or in ball mill to insure complete mixing.

The purity of the oxide was determined electrolytically, and in some instances the deposited copper was titrated with thiosulfate as a check. A weighed sample was simply dissolved in 3 to 5 cc. of 6 *N* sulfuric acid, 3 cc. of 6 *N* nitric acid were added, the sample was diluted to 50 cc. and electrolyzed. No metallic copper particles were observed in any of the oxides. A microscopic examination, made by F. N. Guild, of the University of Arizona, of a polished specimen obtained by embedding some of the oxide in hard wax, also established the absence of copper. Table III summarizes the data so obtained.

Table III—Uniformity of Cupric Oxide for Use as a Standard

Detn.	Sample (1)	Sample (4)	Sample (W)
	Per cent	*Per cent*	*Per cent*
1	79.65	78.77	79.45
2	79.76	78.87	79.30
3	79.68	78.83	79.40
4	79.64	78.87	79.45
5	79.80	78.79	79.30
6	79.65	78.80	
7	79.76	78.83	
8	79.80	78.87	
9	79.80	78.87	
Mean	79.73	78.84	79.38

The theoretical percentage of copper in cupric oxide is 79.89 per cent. The data in Table III indicate that the oxides used in this investigation were not pure, owing perhaps to non-volatile substances present or incomplete removal of water of composition in the ignition. They do, however, indicate satisfactory uniformity of composition. Sample (W) was kindly furnished by F. S. Wartman, assistant metallurgist of the Southwest Station of the U. S. Bureau of Mines, for purposes of comparison. A test of the hygroscopic nature of the oxide was made by placing it over water in a desiccator for several days; under these conditions it adsorbed moisture only to the extent of 0.04 per cent of its weight. The oxides were free from iron and any other impurities which might liberate iodine. On the basis of these findings, the authors now consider the oxide trustworthy as a standard and employ it as such in all thiosulfate standardizations.

Comparison of Cupric Oxide and Copper Foil with Other Iodimetric Standards

Numerous papers have appeared in the literature bearing on these various iodimetric standards by the following authors: Bray,[2] Popoff and Chambers,[3] Popoff and Whitman,[4] Schroeder,[5] all on potassium permanganate and potassium bromate; Bray,[2] and Bruhns,[6] Jander and Beste,[7] and Vosburgh[8] on the use of potassium dichromate; and Parsons and Whitmore[9] on iodine. The suggestions given by these authors have, except for minor modifications, been followed in making this comparison. The potassium dichromate and iodate were recrystallized and dried. The "electrolytic" copper was the copper which had been deposited on a platinum cathode, dissolved off, and titrated. The copper sulfate solution was prepared from the recrystallized salt and was nitrate-free. The normality of the thiosulfate (about 0.2 *N*) was chosen so that large samples could be used and weighing errors reduced. The normality was determined against the oxide by dissolving in dilute sulfuric acid, diluting with water, and completing the titration with thiosulfate in the usual way. Table IV gives the results of this comparison.

Table IV—Comparison of Various Iodimetric Standards

No.	Standard	Amount Taken	Purity or Normality	Volume of Thiosulfate	Normality of Thiosulfate
		Gram	*Per cent*	*Cc.*	
1	Copper foil B	0.2165	100	17.74	0.1921
		0.2273	(assumed)	18.55	0.1930
		0.2400	(assumed)	19.61	0.1925
		0.2039	(assumed)	16.64	0.1935
		0.2504	(assumed)	20.38	0.1935
				Av.	0.1929
2	CuO (1)	0.5000	79.73	32.65	0.1922
		0.5000	79.73	32.66	0.1921
		0.5000	79.73	32.67	0.1921
		0.5000	79.73	32.66	0.1921
				Av.	0.1921
	(W)	0.2000	79.38	13.03	9.1921
		0.2000	79.38	12.99	0.1922
		0.2000	79.38	12.98	0.1923
				Av.	0.1922
		Cc.			
3	$CuSO_4$ soln.	50.04	0.005000 g./cc.	20.49	0.1921
		50.04		20.51	0.1919
		50.04		20.50	0.1920
				Av.	0.1920
		Gram			
4	Electrolytic copper	0.3880	100	31.77	0.1921
		0.4742	100	38.84	0.1920
		0.3522	100	28.86	0.1921
		0.3968	100	32.56	0.1919
				Av.	0.1920
		Cc.			
5	Iodine soln.	49.96	0.10002 *N*	26.04	0.1920
		49.96	0.10002 *N*	26.06	0.1920
		49.96	0.10002 *N*	26.04	0.1920
				Av.	0.1920
6	$KMnO_4$ soln.	50.01	0.1397 *N*	36.45	0.1917
		50.01	0.1397 *N*	36.46	0.1917
		49.94	0.1260 *N*	32.84	0.1917
		49.94	0.1260 *N*	32.85	0.1916
				Av.	0.1917
		Gram			
7	KIO_3	0.3403	100	49.76	0.1919
		0.3652	100	73.37	0.1921
		0.2476	100	36.16	0.1920
				Av.	0.1920
8	$K_2Cr_2O_7$ (solid)	0.1793	100	19.03	0.1921
		0.3133	100	33.30	0.1920
		0.2621	100	27.75	0.1923
				Av.	0.1921
		Average of all determinations			0.1921

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[2] Bray, *J. Am. Chem. Soc.*, **46**, 2206 (1924).

[3] Popoff and Chambers, *Ibid.*, **45**, 1358 (1923).

[4] Popoff and Whitman, *Ibid.*, **47**, 2259 (1925).

[5] Schroeder, *Z. anal. Chem.*, **68**, 233 (1926).

[6] Bruhns, *Ibid.*, **70**, 128 (1927).

[7] Jander and Beste, *Z. anorg. allgem. Chem.*, **133**, 73 (1924).

[8] Vosburgh, *J. Am. Chem. Soc.*, **44**, 2120 (1922).

[9] Parsons and Whitmore, *Ibid.*, **33**, 1933 (1911).

The normalities as determined by means of copper foil not only vary over a wide range, but are in most cases higher than the mean or true normality, which is consistent with the fact that the foil contains less than 100 per cent copper. Calculation of these normalities by the use of a "purity factor" does not render the data perceptibly more concordant with the true value. The oxides yield strikingly concordant values, which, moreover, are in agreement with the mean normality obtained with the other standards. The writers' results for the standardization against permanganate, obtained according to the conditions prescribed by Bray,[2] were uniformly low, yielding an average value of 0.1917 *N*. This cannot be attributed to loss of iodine before or during titration, for it is evident that loss of iodine would occasion a smaller volume of thiosulfate and a consequent high value for the normality. In fact, to prevent any loss of iodine in these determinations, cracked ice was used in the solutions titrated. The titrations with iodine as a standard hold equally well for the solid as for the solution. The authors occasionally prefer to weigh out the iodine in a weighing bottle containing potassium iodide solution, as suggested by Olsen.[10]

Titration of Copper in Presence of and in Absence of Ammonia and Acetic Acid

The question is occasionally raised as to the necessity of neutralizing with ammonia the sulfuric acid remaining after fuming a copper sample to dryness and then adding acetic acid before the potassium iodide is introduced. One answer, of course, is that nitrate ion is more vigorous in its oxidizing action in strong acid solutions, and far less so in acetic acid solution. The action of atmospheric oxygen under these conditions is perceptible but slow. Thiosulfates also decompose into sulfur and sulfurous acid in strong acid solutions. The effect of acidity upon the thiosulfate-iodine titration has been studied by Bray[11] and Schupp.[12] Schupp has shown that iodimetric titrations can be made with accuracy in acidities up to 2 normal, and evidence from Bray's work shows that thiosulfate is oxidized to sulfate in neutral or alkaline acid solution but only to tetrathionate in acid solution. It is thus necessary that titration be made in acid solution. In the absence of nitrates this titration could be made in relatively strong acid solution, and certainly in one which would be obtained on redissolving the copper samples in water after fuming to dryness. To determine the magnitude of such acidity, the actual amount of acid remaining after fuming was determined on several samples to which 3 cc. of 6 *N* sulfuric acid had been added. On diluting the respective residues to 50 cc. (iodimetric titration volume) the acidities were found to be 0.35 *N*, 0.10 *N*, and 0.25 *N*, which are well within the limit of 2 normal. A series of titrations made under the two sets of conditions is given in Table V.

Table V—Titration of Copper with Thiosulfate at Different Acid Concentrations

CuO Taken *Gram*	Acidity	Thiosulfate Required *Cc.*
0.5000	NH_4OH + HAc (excess HAc, 1 *N*)	32.60
		32.61
		32.60
0.5000	H_2SO_4 (0.1 *N*)	32.60
	H_2SO_4 (0.1 *N*)	32.59
	H_2SO_4 (0.2 *N*)	32.62

These data justify the omission of ammonia and acetic acid from the classic copper titration method. The elimination of these two reagents not only obviates the troublesome effect of ammonium acetate upon the iodine-starch end point, but also effects a saving of considerable time, labor, and expense.

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[10] Olsen, "Quantitative Chemical Analysis," p. 325, D. Van Nostrand Co., 1904.

[11] Bray, *Z. physik. Chem.*, **54**, 471 (1906).

[12] Schupp, *Science*, **65**, 284 (1927).

Analysis of Chrome Ores[1]

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Methods for the determination of chromium, iron, silica, alumina, lime, and magnesia are described. Perchloric and sulfuric acids are used to decompose the sample. Alumina is separated from iron by means of cupferron and is determined by precipitation with ammonia after oxidation of chromium to the hexavalent state by potassium chlorate.

THE exact analysis of chrome ore is a matter of some difficulty, involving the separation and determination of large amounts of chromium, iron, aluminum, and magnesium. Although chromite is one of the most stable of the common minerals, complete decomposition may be obtained by heating the ore with perchloric and sulfuric acids or by fusion with sodium peroxide or a mixture of sodium carbonate and borax. The methods here described for the determination of chromium, iron, silica, alumina, lime, and magnesia offer the advantages of exceptional accuracy and simplicity of manipulation.

Determination of Chromium

Chromium can be determined more quickly and more accurately on a separate portion of the sample than on the same portion used for determining the other constituents. One (1.0000) gram of the 100-mesh ore, which has been dried for 2 hours at 105–110° C., is weighed, preferably from a weighing bottle, transferred to a 30-cc. Armco iron crucible, and fused over a gas flame with about 8 grams of dry sodium peroxide. The fusion should be made by revolving the crucible around the outer edge of the flame of a laboratory burner until the contents have melted down quietly; the temperature is then increased to a medium red heat for 3 to 5 minutes and a rotary motion is given to the fused material to prevent spraying. Suitable iron crucibles, containing only a trace of chromium, can be obtained from the Consolidated Manufacturing Company, Dayton, Ohio. Ordinary iron crucibles, which may contain significant amounts of chromium, should be avoided.

When the crucible has partly cooled, and while tightly covered, it is tapped on an iron plate to loosen the fusion in a solid cake. This is transferred to a 600-cc. covered beaker and treated with 200 cc. of warm water. The crucible is also rinsed with water. The solution is treated with 60 cc. of sulfuric acid (1:1) and 5 cc. of nitric acid (sp. gr. 1.42) and is then boiled for several minutes until all iron scale from the crucible has dissolved. From 20 to 25 cc. of a 0.5 per cent solution of silver nitrate, 1 or 2 drops of strong potassium permanganate (25 grams per liter) and 3 to 5 grams of ammonium persulfate (to oxidize the chromium completely) are

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[1] Received September 4, 1928.

added and the liquid is then boiled for 5 minutes. Twenty cubic centimeters of a 10 per cent solution of sodium chloride are introduced and the solution is boiled for 5 to 10 minutes after the permanganate or any manganese dioxide has completely disappeared, to make sure that all chlorine has been expelled. The solution is cooled to room temperature, treated with 3 cc. of phosphoric acid (sirup, sp. gr. 1.725), and an excess of 5 cc. of 0.1 *N* ferrous ammonium sulfate solution is added from a 100-cc. buret. This will cause the reduction of the chromium to the trivalent state, as shown by the following equation:

$$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$$

The buret reading is noted and 0.1 *N* potassium permanganate solution is run in with vigorous stirring to the first faint permanent darkening of the clear green color.

The excess of ferrous ammonium sulfate naturally is oxidized to ferric sulfate; wherefore, subtraction of the volume of 0.1 *N* potassium permanganate used from the volume of 0.1 *N* ferrous ammonium sulfate taken gives the volume of 0.1 *N* ferrous ammonium sulfate required to reduce the chromic acid. The ferrous ammonium sulfate solution is prepared by dissolving 39.2 grams of the salt in 1 liter of water (1 cc. = 0.001733 gram chromium) and it is standardized against 0.1 *N* potassium permanganate; this standardization must be made every day the solution is used, as this gradually grows weaker as a result of oxidation. The 0.1 *N* potassium permanganate is standardized against sodium oxalate obtained from the Bureau of Standards.[2]

Determination of Iron and Alumina

One-half (0.5000) gram of the sample, which has been ground to an impalpable powder in an agate mortar and dried for 2 hours at 105–110° C., is weighed preferably from a weighing bottle, and treated in a 300-cc. covered casserole with 50 cc. of sulfuric acid (1:4) and 5 cc. of perchloric acid (sp. gr. 1.54). The liquid is heated gently until fumes of sulfur trioxide are freely evolved. This treatment should result in a complete decomposition of the ore except some chrome ores which contain quartz.

An alternate method of decomposition is to fuse a 0.5000-gram sample of the dry agate-ground ore with a mixture of 5 grams of sodium carbonate and 2 grams of powdered fused borax ($Na_2B_4O_7$) in a covered 50-cc. platinum crucible. The fusion must be maintained at a temperature of approximately 1100° C. for 20 minutes, while a rotary motion is given to the crucible from time to time to stir up any unattacked particles of ore on the sides or bottom. When cool, the melt is dissolved in 50 cc. of hydrochloric acid (1:4) contained in a 300-cc. covered casserole. Forty cubic centimeters of sulfuric acid (1:1) are added and the solution is concentrated to a volume of 40 to 45 cc.; 25 cc. of methanol and 10 cc. of hydrochloric acid (sp. gr. 1.19) are added, and the evaporation is continued slowly until fumes of sulfur trioxide are given off. The methanol causes the volatilization of boron which, unless removed, might cause erratic results.

After partial cooling, about 150 cc. of water and several cubic centimeters of sulfurous acid are added to reduce chromium to the trivalent state, and the solution is boiled for several minutes until all salts have dissolved. The gelatinous silica is then filtered on a 9-cm. paper and washed thoroughly with hot water. The silica is ignited in platinum, first at a dull red heat until the carbon has burned and finally at 1100° C. for 10 minutes. The crucible and silica are cooled in a desiccator, weighed, and treated with 1 drop of sulfuric acid and 1 to 2 cc. of hydrofluoric acid (48 per cent), and the solution is evaporated to dryness. The crucible is again ignited for a few minutes at 1100° C., cooled, and weighed. The loss in weight multiplied by 200 gives the percentage of SiO_2 in the sample. The small residue which usually remains is fused with about 0.5 gram of potassium pyrosulfate, then dissolved in a few cubic centimeters of dilute hydrochloric acid and added to the filtrate from the silica.

The solution is treated with 1 cc. of nitric acid (sp. gr. 1.42) and boiled several minutes to oxidize the iron to the ferric state. Five grams of ammonium chloride and a considerable quantity of ashless paper pulp are introduced, and the solution is rendered very faintly ammoniacal by the addition of dilute, filtered ammonium hydroxide (1:4). The solution is heated to boiling for 1 or 2 minutes (no longer), the precipitate is allowed to settle, and is then filtered and washed ten or twelve times with a hot 2 per cent solution of ammonium chloride. The precipitate is rinsed from the filter back into the beaker with a jet of warm water, dissolved in 75 cc. of hydrochloric acid (1:4), and the solution diluted to 200 cc. A second ammonia separation is made in a similar manner, the precipitates being filtered on the same paper. The two filtrates are combined and reserved for the determination of lime and magnesia.

The hydroxide precipitate is dissolved in 60 cc. of hot sulfuric acid (1:4) and the solution made up to a volume of 150 cc. Some ashless paper pulp is added, the liquid is cooled to about 20° C., and the iron and titanium are precipitated by the addition (dropwise and with constant stirring) of a freshly prepared, cold, 6 per cent solution of cupferron [ammonium nitrosophenylhydroxylamine, $C_6H_5(NO)ONH_4$] in slight excess. An excess is known to be present when a drop of the precipitant forms a white precipitate which goes quickly into solution.

The precipitate is filtered on an 11-cm. paper with the aid of gentle suction, washed thoroughly with cold 10 per cent sulfuric acid, and ignited at a low temperature in a porcelain or silica crucible. The resulting oxides are treated in a 150-cc. beaker with 10 cc. of hydrochloric acid (sp. gr. 1.19) and heated until the iron oxide has all dissolved. Iron is determined in this solution by the Zimmerman-Reinhardt method. If the determination of titanium is desired, the ignited oxides are fused with potassium pyrosulfate, the melt dissolved in sulfuric acid (1:4), and the titanium determined colorimetrically. The iron is then determined in this solution by one of the approved methods.

The filtrate from the cupferron precipitate, which contains all of the aluminum and chromium, is concentrated to a volume of 40 to 50 cc.; 100 cc. of nitric acid (sp. gr. 1.42) are added, and the evaporation is continued slowly until the volume has again been reduced to 60–75 cc. Potassium chlorate is next added, a few crystals at a time, to the slowly boiling solution until its color changes from green to clear reddish yellow, indicating that the excess cupferron has been completely oxidized and the chromium converted to the hexavalent state. The solution is then diluted with 300 cc. of cold water, approximately 5 grams of ammonium chloride and some ashless paper pulp are introduced, and the aluminum is precipitated by the addition of ammonium hydroxide (1:4) in very faint excess. The liquid is boiled for 1 or 2 minutes (no longer) and the precipitate, after having been allowed to settle, is filtered and washed ten or twelve times with hot 2 per cent ammonium chloride solution. The aluminum hydroxide is dissolved in 50 cc. of hot hydrochloric acid (1:1) and the precipitation with ammonia and filtration repeated as previously described. The precipitate and filter paper are placed in a weighed, covered platinum crucible and ignited first at a low heat and finally to constant weight at 1100° C. The increase in weight represents the amount of Al_2O_3 present in the ore plus a very small amount of Cr_2O_3 and all of the P_2O_5 in the ore.

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[2] McBride, *J. Am. Chem. Soc.*, **34**, 393 (1912).

The phosphorus content of the chrome ores usually encountered is so low that the error introduced by its inclusion with the alumina is negligible, except when the highest accuracy is desired. To make correction for chromium, the oxides are fused with 6 to 8 grams of sodium carbonate, the fusion is dissolved in water and filtered, and chromium is determined colorimetrically by comparison with a standard solution of potassium chromate prepared by dissolving 1.867 grams of anhydrous potassium chromate in 1 liter of water (1 cc. = 0.0005 gram Cr). The chromium found, calculated to Cr_2O_3, is deducted from the weight of the impure alumina, and the remainder is calculated to percentage of Al_2O_3 in the ore. If desired, phosphorus may be determined in the solution after the estimation of chromium, calculated to P_2O_5, and deducted from the alumina.

Determination of Lime and Magnesia

The combined ammoniacal filtrates from the iron and aluminum hydroxide precipitates are made slightly acid with hydrochloric acid, evaporated to a volume of approximately 150 cc., and cooled to 15° C. Twenty cubic centimeters of a 10 per cent solution of diammonium phosphate are added and ammonium hydroxide (sp. gr. 0.90) is then slowly introduced, drop by drop, with vigorous stirring until the solution is ammoniacal and a crystalline precipitate appears. Fifteen cubic centimeters of ammonia (sp. gr. 0.90) are added, the liquid is stirred thoroughly and finally chilled by surrounding the beaker with crushed ice. After standing for several hours with frequent stirring, or preferably overnight if allowed to stand at room temperature, the solution is filtered on a 9-cm. blue ribbon paper, and the precipitate is washed three or four times by decantation with cold 2.5 per cent ammonia water. Twenty-five cubic centimeters of hydrochloric acid (1:1) are poured through the filter, the filtrate being collected in the original beaker containing the bulk of the precipitate, and the filter is washed thoroughly with 5 per cent hydrochloric acid. The solution is diluted with cold water to a volume of 150 cc., 3 cc. of a 10 per cent solution of diammonium phosphate are added, and the precipitation is repeated as previously described. The precipitate is allowed to stand for 2 hours surrounded by crushed ice, filtered, washed ten or twelve times with cold 2.5 per cent ammonia water, and ignited in a weighed platinum crucible, first at a dull red heat until the carbon has been burned, and finally to constant weight at 1000–1050° C.

The pyrophosphate precipitate thus obtained—which will contain all the lime, magnesia, any manganese present, and small amounts of silica—is dissolved in 20 cc. of hot dilute (1:4) hydrochloric acid, the solution is filtered on a 7-cm. paper to remove silica, and the filter is washed well with hot water. The paper and silica are ignited and the silica determination is completed in the usual manner. The weight of silica found is deducted from the weight of the magnesium pyrophosphate obtained as previously described.

Ten cubic centimeters of sulfuric acid (1:1) are added to the filtrate from the silica and the solution is evaporated to fumes of sulfur trioxide. Five cubic centimeters of water and enough absolute alcohol to constitute 90 to 95 per cent of the total volume are added, and the solution is stirred vigorously for several minutes. After the calcium sulfate precipitate has settled for 2 or 3 hours, preferably overnight, it is filtered on a 9-cm. blue ribbon paper and the paper and precipitate are washed free from phosphoric acid with 80 per cent alcohol. The calcium sulfate is dissolved in 25 cc. of hot 10 per cent hydrochloric acid and the solution is heated to boiling. One-tenth gram of oxalic acid is added and the lime is precipitated by the slow addition, with vigorous stirring, of dilute ammonia (1:3) in slight excess, the determination being completed in the usual manner. The weight of calcium oxide found is calculated to tricalcium phosphate ($Ca_3(PO_4)_2$) by multiplication by 1.8447, and this amount is deducted from the weight of the magnesium pyrophosphate obtained as previously described.

The alcoholic filtrate from the calcium sulfate is evaporated until strong fumes of sulfur trioxide are evolved and all organic matter is destroyed. After the solution has cooled, the residue is dissolved in 25 cc. of nitric acid (sp. gr. 1.135) and finished for manganese by the bismuthate method. Any manganese found is calculated to manganese pyrophosphate ($Mn_2P_2O_7$,) (factor, 2.5847), and this is deducted from the weight of magnesium pyrophosphate. The weight of $Mg_2P_2O_7$ is multiplied by 0.3621 and by 200 to obtain the percentage of MgO in the sample.

Rapid Dehydration of Alcohol Using Barium Oxide and Metallic Calcium[1]

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THE many applications of absolute ethyl alcohol in experimental research and in the operations of quantitative analysis, particularly with the alkali and alkaline-earth metals, make a convenient and rapid method for the dehydration of 92 to 93 per cent ethyl alcohol desirable. No claims to originality are made for this paper. Rather the attempt is made to indicate the serviceability of barium oxide as a rapid and practical alcohol drier. This fact has not been indicated in previous investigations as far as could be learned. Metallic calcium is further advocated for the rapid removal of the last half per cent of water.

The bibliography of the literature on alcohol and alcoholometry has been most completely compiled down to a recent date by McKelvy.[2] An extensive investigation by Osborne, McKelvy, and Bearce[3] on the preparation of pure anhydrous ethyl alcohol, the determination of the thermal expansion of mixtures of ethyl alcohol and water, together with density data for the same aqueous alcohols, accompanies McKelvy's bibliography.

General Considerations

The heat of reaction for the hydration of barium oxide is greater than that for calcium oxide. This fact suggests its use in the dehydration of alcohol with resultant increase in the heat and rate of reaction. Formerly the cost of barium oxide as compared with lime in addition to its threefold molecular weight per unit of hydration served as a deterrent to its use.[4] Certain known reactions of barium oxide and alcohol, to be subsequently tabulated, indicate undesirable characteristics.

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[1] Received October 1, 1928.

[2] McKelvy, U. S. Bur. Standards, *Bull.* **9**, 436 (1913).

[3] Osborne, McKelvy, and Bearce, U. S. Bur. Standards, *Bull.* **9**, 327 (1913).

The increasing use of practically dry alcohol in analytical chemistry as well as for a multitude of other purposes makes the improvement of the conditions under which it may be produced attractive. This paper demonstrates that, from the point of view of speed, economy, and simplification of manipulation, barium oxide, which is now obtainable cheaply in any quantity, is attractive. Previous objections to its use for this purpose have been shown to be overemphasized and not practicable deterrents to its use. The chief objection, that of poor yield, has been shown to be invalid. A discussion of the various chemical reactions encountered and a further advocation of metallic calcium as a finishing reagent for complete dehydration has been made and data concerning its rate of reaction with alcohol are given.

Absolute alcohol can be prepared from hydrated alcohol at ordinary temperatures if a sufficiently large excess of lime and extended time intervals are employed. Two such experiments are given by Crismer[5] and the results are presented graphically in Figure 1. Curve I shows the gradual dehydration of aqueous ethyl alcohol using four times the theoretical amount of lime while curve II gives similar data for nine times the theoretical amount. Even in the second case 21 days were required to obtain absolute alcohol starting at 98.75 per cent. Curve III represents experiments using the theoretical amount of barium oxide with other conditions comparable. Starting with 93 per cent ethyl alcohol, 99.61 per cent alcohol was produced in 3 days. The yield of dried alcohol is much greater than for the dehydrations using excess of lime.

The heat of reaction between aqueous alcohol and barium oxide can be demonstrated in the following manner: If 200 to 300 cc. of 92 to 93 per cent ethyl alcohol are poured over twice the theoretical quantity of barium oxide, using as container an unsilvered Dewar flask provided with a reflux condenser, and the contents are thoroughly mixed and allowed to stand, the heat of reaction will cause the alcohol to boil and this boiling will continue for approximately 1 hour.

The dehydration of 92 to 93 per cent alcohol is always carried out in two stages. Lime is generally employed for the first stage and the conditions are adjusted to produce an alcohol of approximately 99.5 per cent strength.[6] The "absolute" alcohol thus obtained is further dehydrated to 100 per cent with a special dehydrating agent,[7] metallic calcium probably being the most convenient and rapid.[8] By the use of barium oxide in the place of lime it has been possible to shorten the time interval from 12 hours to 2 hours.

Experimental

Preliminary Dehydration—One thousand cubic centimeters of 93 per cent (by weight) ethyl alcohol in a 2000-cc. flask were treated with 500 grams (theoretical assuming formation of barium hydroxide) of barium oxide and allowed to react on the steam cone for specified periods using a reflux condenser. The heat of reaction together with a moderate flow of steam quickly brought the reaction mixture to boiling, at which point the steam was regulated to maintain a vigorous refluxing action. After various periods of reaction the reflux condenser was replaced by a 60-cm. condenser and the reaction mixture rapidly distilled using a small Hopkins distilling trap between the flask and the condenser. After 1 to 1$^1/_2$ hours' distillation the density of the distillate was determined.

Density Determination—A 25-cc. Ostwald pycnometer, previously calibrated, and thermostat accurate to 0.01 degree at 25° C. were employed. After temperature equilibrium was reached the pycnometer and contents were withdrawn from the thermostat, chilled momentarily, rapidly dried, and placed in a tared weighing bottle with a thoroughly ground glass stopper and weighed. From the data thus obtained the density of the alcohol corrected to 25°/4° C. was calculated. The percentage of water present was found from the tables given by McKelvy.[2] The apparatus employed, the calibration of weights, pycnometer, and thermometers, vacuum corrections, etc., indicated an accuracy of ± 0.01 per cent in the water content determined.

Treatment with Metallic Calcium—Since the turnings were not sufficiently finely divided to present a large surface compared with the total weight of metal, a proportionally large excess of calcium was suspended in the boiling alcohol using a wire gauze basket. The basket of turnings was suspended by a fine wire through the reflux condenser and when the reaction was thought complete the excess metallic calcium was withdrawn. The metal turnings and basket were then placed in a well-stoppered bottle and used for later reactions. The alcohol thus prepared was distilled and its water content determined in the same way as for the distillate of the preliminary dehydration.

Discussion of Results

The results of several runs which illustrate points in question sufficiently are given in Table I.

Table I—Dehydration of 93 Per Cent Ethyl Alcohol Using Barium Oxide and Metallic Calcium

RUN	ALCOHOL	BaO	TEMP.	TIME	YIELD	ALCOHOL BY WT.
	Cc.	*Grams*	*° C.*	*Hours*	*Cc.*	%
1	1000	500	25	72	750	99.61
2	1000	400	b. p.	2	850	99.40
3	1000	400	b. p.	1$^1/_2$	855	99.04
4	1000	500	b. p.	2	807	99.39
5	1000	500	b. p.	3	760	99.42
6	500 (99.56%)	50 (Ca)	b. p.	15 min.	...	100.00
7	400 (99.34%)	10 (Ca)	b. p.	60 min.	...	99.52
8	500	500	25	9	...	99.21
	1000	500	25	20	...	99.36

The data of Table I may be most profitably discussed in connection with the following reactions:

$$\mathrm{BaO} + \mathrm{H_2O} = \mathrm{Ba(OH)_2} \tag{1a}$$

$$\mathrm{Ba(OH)_2} + 8\mathrm{H_2O} = \mathrm{Ba(OH)_2{\cdot}8H_2O} \tag{1b}$$

$$2\mathrm{C_2H_5OH} + \mathrm{BaO} = \mathrm{(C_2H_5O)_2Ba} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{Ca} + 2\mathrm{H_2O} = \mathrm{Ca(OH)_2} + \mathrm{H_2} \tag{3}$$

$$\mathrm{Ca} + 2\mathrm{C_2H_5OH} = \mathrm{(C_2H_5O)_2Ca} + \mathrm{H_2} \tag{4}$$

$$\mathrm{(C_2H_5O)_2Ca} + \mathrm{H_2O} = \mathrm{C_2H_5OH} + \mathrm{Ca(OH)_2} \tag{5}$$

The theoretical amount of barium oxide required for the amount of alcohol dehydrated in Table I according to reaction 1*a* is 500 grams. Reaction 1*b*, if obtained during the early stages of the dehydration, provides for the use of less barium oxide. The reversal of reaction 1*b* is not appreciable at steam-bath temperatures. Runs 2 and 4 of Table I bring out these points.

Reaction 2 takes place when barium oxide is added to absolute alcohol, resulting in the dilution of the alcohol with water, 0.4 to 0.6 per cent depending on the temperature. The dehydration of alcohol at room temperature (run 1, Table I) shows that barium alcoholate is not formed when alcohol of less than 99.6 per cent strength is treated with barium oxide. At the boiling point reaction 2 proceeds at an alcohol strength of 99.4 per cent. Treatment longer than 2 hours gives no appreciable concentration of the alcohol (runs 2 and 5). One and one-half hours' refluxing with barium oxide is too short a period for maximum dehydration. Three hours' treatment is not better than 2 hours' refluxing (runs 3 and 5).

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[4] Technical grades of lump barium oxide can now be purchased in small or large amounts at 10 cents per pound or less. A sample for this investigation was kindly supplied by the J. H. R. Products Company, of Willoughby, Ohio. Acknowledgment of this courtesy is hereby made.

[5] Crismer, *Bull. soc. chim. Belg.*, **18**, 18 (1904).

[6] Noyes, *J. Am. Chem. Soc.*, **45**, 857 (1923).

[7] See reference 2 for a list of suitable dehydrating agents.

[8] Winkler, *Ber.*, **38**, 3612 (1905).

Reactions 3 and 4 were studied by Winkler.[8] Reaction 3 is very slow with compact metal. If the metal is finely divided and the alcohol heated, a rapid reaction takes place. The reaction is the less rapid the more nearly absolute the alcohol. Reaction 3 is rapid, however, on 93 to 95 per cent alcohol. The calcium hydroxide formed is insoluble, causing alcohol to turn milky, but the calcium hydroxide does not coagulate.

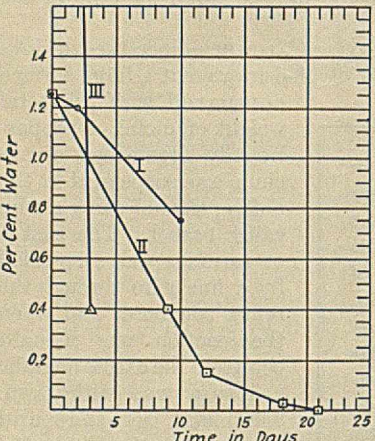

Figure 1—Dehydration of Ethyl Alcohol with Lime at Room Temperature

Reaction 4 attains appreciable proportions only with alcohol above 99.5 per cent.

Reaction 5 follows rapidly after as well as simultaneously with reaction 4. The precipitate in suspension is coagulated, gelatinous, and grayish white. Hydrogen is rapidly evolved and may be tested for at the opening of the reflux condenser in the usual manner. Too great an excess of calcium after reaction 4 has progressed materially should be avoided.

Runs 6 and 7, Table I, show the rates of reactions 4 and 5, starting with 99.56 and 99.34 per cent alcohol, respectively.

The yield of alcohol given in Table I is for 1 to $1^{1}/_{2}$ hours' distillation. More alcohol could be obtained if more time were given. Counting the water absorbed, the yield of pure alcohol for run 2 is 90 per cent. With a few additional hours' heating on the steam cone several per cent additional alcohol could be recovered. The yield of alcohol using barium oxide is as good and generally better than that obtained using lime. The yield of alcohol in run 9 is 92.5 per cent, if a last fraction of slightly less strength after 12 hours on the steam cone is included.

General Directions

Condensed working directions for the preparation of dry alcohol are:

(*a*) Reflux 1000 cc. of 93 per cent alcohol on a steam cone in a 2000-cc. flask together with 400 grams of barium oxide for 2 hours. Replace the reflux condenser by a 30-cm. (12-inch) straight condenser and distil the alcohol $1^{1}/_{2}$ hours. Yield, 855 cc. of 99.40 per cent alcohol. More alcohol of slightly less strength is obtained by distilling for longer periods.

(*b*) Allow 1000 cc. of 93 per cent alcohol and 500 grams of barium oxide to react cold for 72 hours with occasional shaking and distil as in (*a*). Yield, 750 cc. of 99.61 per cent alcohol.

(*c*) The directions in (*b*) may be duplicated with 20 hours reaction. Yield, 800 cc. of 99.36 per cent alcohol.

For absolute alcohol reflux any of the products obtained in (*a*), (*b*), or (*c*) on the steam cone with 50 grams of metallic calcium (turnings or wire) suspended in 1 liter of the alcohol by a wire gauze basket hung through the reflux condenser. When the reaction of dehydration is complete, as indicated by the formation of a gelatinous gray precipitate of calcium ethylate, the rapid evolution of hydrogen, and a noticeably exothermal reaction, remove the excess of metallic calcium and distil the product. One hour is always sufficient for the reaction and much less time is generally sufficient. The product thus obtained will be found to be absolute.

Advantages of Barium Oxide as Dehydrating Agent

1—The preparation of 99.4 per cent alcohol is accomplished with barium oxide using the theoretical quantity of reagent by refluxing less than one-fifth the time required for the preparation of alcohol of approximately the same strength using calcium oxide.

2—Theoretical amounts of barium oxide reacting without addition of heat produce 99.6 per cent alcohol in 72 hours.

3—The yields using barium oxide are in general better than those obtained using lime.

4—The increased cost of barium oxide over lime is slight and the profitable recovery of the resulting barium hydroxide (not discussed) as well as the saving in alcohol yield lessen this apparent disadvantage.

A Self-Regulating Gas Flowmeter[1]

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IN THE course of some work upon the vapor phase oxidation of benzene, it became necessary to have a means for obtaining a constant flow of air. The well-known device of a T-tube with one arm opening under water will give an approximate regulation of air pressure, but it is not very accurate. The apparatus described in this paper, although originally constructed as a makeshift to serve while more elaborate instruments were in preparation, proved so efficient that it was used for over a year and with complete satisfaction. It was designed to deliver air at velocities up to 500 cc. per minute, and proved capable of continuous operation over periods of a week or more.

Description of Apparatus

The essential parts are an electrically operated gas valve, a flowmeter consisting of a capillary tube with a manometer connected across it, and means for operating the valve by the changes in the manometer level.

The valve mechanism is shown in Figure 1. *B* is an electric bell from which the bell proper has been removed. The valve *A* is an ordinary automobile high-pressure tire valve. To one of the flat sides of *A* is soldered a bolt, which serves to fasten the valve to the bell frame. A portion of the end of valve *A* is cut away so that the stem, *C*, projects. The valve is so placed that *C* is hit squarely by the bell clapper, *D*, when this is depressed. It did not prove necessary to have this clapper vibrate and therefore the wires from the bell's magnet coils were connected directly to the binding posts. However, the end of *C* should be a little distance from *D*, so that when the coils are energized the clapper will gather a little momentum before hitting the valve stem. This whole bell-valve combination is suspended in the jar, *J*, by means of the lead-in wires, *H*.

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[1] Received November 20, 1928.

Air entering the apparatus is carried by means of the rubber tube *E* directly to the "tire end" of the valve *A*. When the valve is open, the air passes into the jar, *J*, and out through the exit tube, *F*. The stopcock, *G*, serves as a by-pass valve, and makes it possible to obtain a much larger flow of gas than would normally pass through *A*.

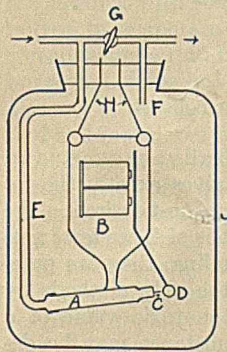

Figure 1

The air from the valve is run through a 20-liter bottle to smooth out the irregularities in flow caused by the intermittent operation of the valve.

From this reservoir the air passes to the flowmeter shown in Figure 2. Here *O* is the capillary. The flask, *K*, contains mercury, below the level of which dips the end of the manometer tube, *L*. In order to increase the sensitiveness of the apparatus, *L* is inclined at a small angle to the horizontal. If the angle whose sine is 1/13—about 4.5 degrees—is chosen, the pressure read along *L* in centimeters of mercury is the same as the pressure that would be indicated by a vertical water manometer. A centimeter scale may be glued to the back of *L*. If the level of mercury in the flask *K* varies fairly uniformly with the change in level of the mercury in the manometer tube, which will usually be the case, the use of a fixed scale will not change the calibration curve (manometer scale readings plotted against rates of flow) from an approximately straight line.

The upper end of the tube *L* is large enough to take a rubber stopper, *M*, through which passes a long glass tube of small diameter, *N*. Through the lower end of *N* there is sealed a tungsten or platinum wire, *P*. (In the drawing no distinction is made between the wire point, *P*, and the tube *N*.) The hole in the stopper *M* is lubricated with glycerol so that the tube *N* will slide readily.

The capillary *O* should be placed above the manometer as indicated, so that if the valve ever sticks open the back pressure of mercury in the vertical tube connecting the upper part of *L* with *O* will counterbalance the air pressure and prevent mercury from being blown entirely out of the manometer.

Electrical connection with the mercury reservoir is made by means of the iron wire, *Q*.

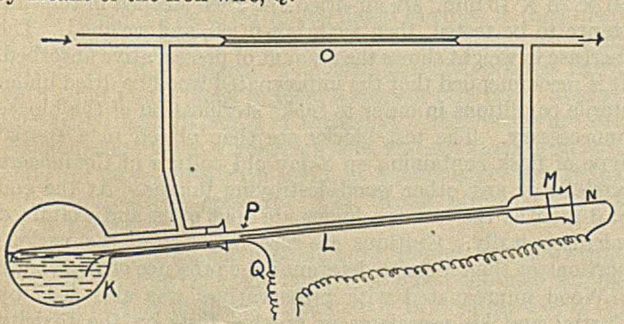

Figure 2

The flowmeter circuit operates a 250-ohm telegraph relay, which in turn operates the air valve. The relay contacts are so arranged that when the flowmeter circuit is open the valve circuit is closed. The relay draws so little current that it is not necessary to connect a condenser across the flowmeter circuit. It may be necessary to clean the point *P* every 6 months or so. On the other hand, the bell coils in the valve mechanism draw a quantity of current, and therefore the batteries in the valve circuit, if batteries are used, must be watched to see that they do not go dead during an experiment. When the apparatus is not in use, the valve circuit must be broken.

Performance

The operation of the apparatus should be clear from this description. If the supply of air or gas available has more than a moderate pressure, the apparatus should be protected by some sort of safety valve, such as a tube opening under a meter or two of water.

The efficiency of this self-regulating flowmeter is indicated by its performance under the conditions in which it was actually used. As employed in the work for which it was designed, the flowmeter was operated to furnish a constant stream of air, which was passed through a constant thickness of liquid benzene heated to a constant temperature in a thermostat. It was especially desired to vaporize under constant conditions a definite weight of benzene in a given time, and to have the results reproducible.

During the course of the work a number of blank runs were made in which the vaporized benzene was condensed under standard conditions, and weighed. This served as a check on the functioning of the whole set-up, of which the flowmeter was only a part. However, the consistency of the experiments indicates the dependability of the flowmeter itself. The accompanying table gives the results of some pairs of these blank runs made over a period of 8 months. In most cases a number of other experiments intervened between the two blank runs of a pair. It will be understood that only the two runs of a pair are to be compared with each other. In going from one pair to another, various changes, such as in the flowmeter setting and temperature of benzene, were made.

Checks on Flowmeter Operation

Duration of Run	Weight of Benzene Recovered	Duration of Run	Weight of Benzene Recovered
Hours	*Grams*	*Hours*	*Grams*
4	(*a*) 270 (*b*) 272	8	(*a*) 365 (*b*) 365
24	(*a*) 165 (*b*) 165	8	(*a*) 393 (*b*) 393
7	(*a*) 415 (*b*) 414	8	(*a*) 378 (*b*) 379
8	(*a*) 340 (*b*) 342		

A Convenient Method for Preparing Na-K Alloy[1]

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When maximum reactivity, at relatively low temperature, is desired of an alkaline metal, the liquid sodium-potassium alloy is very useful. The most common method of preparation is to melt the metals together under kerosene. This method is not satisfactory, for it tends to divide the alloy into small particles coated with dirt.

The alloy is easily prepared by placing freshly cut sodium and potassium in slightly wet ether and slowly agitating. It keeps clean under ether, and may be pipetted from the bottom of the container in substantial purity.

Although the alloy catches fire when exposed to air and must consequently be handled with care in the presence of ether, experience has shown that this association is less dangerous than the association of the alloy with benzene, since the rapid evaporation of the ether has a cooling and a blanketing effect, which reduces the tendency of the alloy to ignite.

[1] Received December 7, 1928.

Laboratory Methods of Testing the Toxicity of Wood Preservatives[1]

With a Suggested Improvement of the Agar Plate Method

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The various methods which have been used to determine the toxicity of wood preservatives are critically reviewed. It is apparent that no single method has yet been devised which is entirely satisfactory. The determination of the toxicity of relatively volatile substances, such as coal-tar creosote, is particularly difficult, owing to the control of the loss of preservative during the sterilization process. In order to prevent this loss, it is proposed to place the preservative in small sealed glass ampuls, which are later broken to liberate the preservative to form preservative-agar mixtures of any desired concentration.

During the past fifteen or twenty years the toxicity to fungi of a large number of substances has been determined. These determinations have been made primarily to ascertain the efficacy of fungicides and wood preservatives. Unfortunately, many different methods and fungi have been used in making these tests, thus making it practically impossible to compare the results. Unfortunately, too, there seems to be no unanimity of opinion regarding the uses, limitations, or value of toxicity studies.[2]

The fact that a wood preservative must be able to kill or inhibit the organism against which protection is desired is almost universally recognized. A wood preservative must also be permanent, it must be easy to inject into the wood, must not injure the wood or attack steel, etc.

Toxicity studies deal only with the poisonous properties of a wood preservative, and therefore they do not give a complete picture of the value of any particular substance as a wood preservative. Furthermore, the results are usually expressed in terms of the relative amount of the material necessary to stop the growth or kill the fungus under certain more or less controlled conditions. These conditions may vary considerably, and each variation to some extent modifies the results. Nevertheless, by the use of standardized methods it is possible to get results that are comparable, thus permitting a comparison of the toxic or poisonous properties of any given number of substances.

For commercial work, however, it is of interest to know the amount of material that must be initially injected into the wood in order to maintain the desired amount of preservative for a definite period of time. Laboratory studies of the toxicity of wood preservatives do not give this information. Attempts to calculate the amount of material which must be injected into the wood from laboratory studies of toxicity are, therefore, based upon an erroneous conception of the value of such studies.

General Methods of Determining Toxicity

Broadly speaking, the toxicity of wood preservatives may be determined by either of two general methods. The first consists of determining the resistance to decay of wood impregnated with the toxic material. The wood may either be *en masse* or in the form of a fine sawdust or wood flour. The second method consists of adding the toxic material to nutrient agar, emulsifying the mixture, when necessary, by shaking, and determining the inhibiting effect of the toxic material. Both of these methods have certain advantages and disadvantages, and neither gives exactly the information most desired. The limitations of these tests notwithstanding, they are practically the only methods by which the toxic value of a given substance may be determined in a short time and, when the same procedure and the same organisms are used, it is possible to get relative values of the toxic properties of a number of substances.

Impregnated Wood Methods

Subjecting injected wood to the action of the wood-destroying fungi is probably the oldest method for determining the toxic properties of wood preservatives. As early as 1848 de Gemini[3] reported the results of a series of experiments in which shavings injected with coal-tar creosote had been placed in a rotting pit, in order to determine the efficacy of coal-tar creosote as a wood preservative. Boulton[3] used a similar method in his work, but kept his cultures under observation for more than four years. This method cannot, therefore, be used when quick results are essential.

Malenkovic[4] and Netzsch[5] also used impregnated wood to determine the toxicity of wood preservatives. The methods followed by these investigators are not greatly different than those proposed by Boulton. Falck,[6] however, has recently proposed a standard method which he uses in all tests of volatile wood preservatives. Small blocks of pine sapwood, 50 × 25 × 15 mm., are air-dried and then steeped in the substance to be tested, then again air-dried, and weighed. The increase in weight shows the amount of preservative absorbed. It is recommended that the impregnated wood be dried under sterile conditions in order to make sterilization of the blocks unnecessary. The test blocks are then placed in a special type of flask containing an 8-day old culture of *Coniophora cerebella* or any other wood-destroying fungus. At the end of 3 months the test specimens are split open and examined microscopically. Cultures are also made from the various portions of the blocks to determine the presence of mycelium.

Wood impregnated with preservatives was also used by Curtin[7] and his associates in making tests on the toxicity and permanence of certain wood preservatives. Long sticks of treated wood were introduced into test tubes containing 5 cc. of nutrient gel in the bottom and inoculated with *Fomes annosus*. These tests were not made to determine the exact toxic value of the preservative in question, but were designed to show its relative permanence. The method does not vary

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[1] Received October 12, 1928. Published with the approval of the director as Paper 804 of the Journal Series of the Minnesota Agricultural Experiment Station.

[2] Bateman, *Proc. Am. Wood-Preservers' Assocn.*, **24**, 35 (1928).

[3] See Boulton, "Preservation of Timber by Use of Antiseptics," New York, 1885.

[4] Malenkovic, *Mitt. Gegenst. Artil. Geniew.*, **35**, 311 (1904).

[5] Netzsch, *Naturw. Z. Forst- Landw.*, **8**, 377 (1910).

[6] Falck, *Hausschwammforschungen*, **8**, 17 (1927).

[7] Curtin, Kline, and Thordarson, Ind. Eng. Chem., **19**, 1340 (1927).

greatly from that proposed by Falck, but the application is different.

The use of impregnated sawdust, in order to insure a more even distribution of the preservative in the wood, has been suggested by Schmitz and Zeller.[8] Coal-tar creosote is dissolved in redistilled 95 per cent ethyl alcohol and added to the sawdust with constant stirring. The alcohol is then permitted to evaporate by exposing the impregnated sawdust, spread out in a thin layer, to the air. The desired amount of impregnated sawdust is then placed in a culture flask, a known amount of distilled water added, the flask and contents sterilized and inoculated with *Lenzites sepiaria*. Since the culture must be kept under observation for from 4 to 8 weeks, the cotton plugs are covered with paraffined paper in order to reduce the rate of water loss. It is important that the inoculum be placed near the inner wall of the flask in order that it may be examined with the aid of a strong hand lens.

The sawdust method has been modified in the toxicity test made recently in this laboratory, eliminating the sterilization of the impregnated sawdust. After the creosote-alcohol solution has been added to the sawdust in the manner described above, the impregnated sawdust is placed in previously sterilized culture flasks. The alcohol is permitted to evaporate through the cotton plug. This usually requires 8 to 10 days, during which time the flasks are frequently shaken to prevent the accumulation of creosote on the upper surface of the sawdust. After the alcohol has evaporated, a known amount of hot, sterile, distilled water is added to each culture flask. The moist impregnated sawdust is then thoroughly mixed with a sterile spatula and the culture flask is ready for inoculation. When due care is used in adding the water to the flasks and when the impregnated sawdust is mixed with the spatula, the number of contaminations is small.

This modification eliminates some, but not all, of the shortcomings of the method. The most obvious weakness of the method is that considerable time is required for the alcohol to evaporate, during which an appreciable loss of creosote, particularly of the lighter fractions, also occurs.

Impregnated sawdust was also used by Reeve[9] to determine the toxicity of a number of wood preservatives. The oil to be tested is first dissolved in c. p. benzene, the solution being prepared in such concentration that from 15 to 30 cc. will introduce the desired percentage of preservative when mixed with 10 grams of sawdust. After impregnation, the sawdust is spread on large watch glasses and allowed to dry at room temperature for 24 hours. The dried impregnated sawdust is then mixed with a predetermined optimum amount of distilled water and spread over the bottom of a Petri dish and pressed lightly with a flat metal block to form a smooth firm layer, approximately $^1/_8$ inch (3 mm.) in thickness. The dishes are then covered, clamped in a wooden frame, and sterilized in an autoclave for 20 minutes with steam at 5 pounds per square inch ($^1/_3$ atmosphere) pressure. The dishes after cooling are ready for inoculation.

The concentrations necessary to inhibit the growth of wood-destroying fungi are quite high when obtained through the use of this method. Bateman,[10] in a discussion of the method, calls attention to the fact that the use of sawdust is quite a different thing than the use of wood, because it is impossible to get fungi to grow on sawdust, if the concentration of water is much below 200 per cent, while wood containing only 50 per cent is very susceptible to decay. Consequently the values obtained from sawdust cannot be expected to check with those obtained from wood *en masse*.

Bateman also suggests that, since the oil is dissolved in benzene when it enters the wood, it is possible that there is not sufficient contact between the oil and the water to permit the oil to exert its full toxic effect.

A modification of the impregnated sawdust method has also been used by Curtin[7] and his associates. A suspension of sawdust prepared from treated wood is made in standard malt agar. Curtin calls attention to the fact that this type of test is of no importance in the case of the less toxic preservatives, since it is possible for the fungus to grow in the gel between particles of wood. In cases where complete inhibition is accomplished, however, the results are considered to be significant.

By the use of impregnated wood in the determination of the toxic properties of a wood preservative, experimental conditions more or less closely resembling, but not identical with, the conditions of treated wood in actual use are obtained. This method also has some very definite limitations, one of the most important of which is the difficulty, if not the impossibility, of obtaining an even distribution of the preservative through the wood. It is, of course, true that the sapwood, and for that matter the heartwood, of certain tree species is quite permeable to coal-tar creosote, and in such cases the entire wood can be injected with the creosote. To inject even such wood with small amounts of creosote, evenly distributed, would necessitate dissolving the creosote in some solvent such as alcohol or benzene and then permitting the solution to evaporate. Getting rid of the solvent would require considerable time, during which a considerable loss of creosote would occur. Although it is possible to determine the amount of creosote in impregnated wood after the solvent has been evaporated, provided the original dry weight of the wood is known, nevertheless the composition of the creosote in the impregnated wood after the solvent has evaporated may be quite different from that of the original sample. More important still, the movement of the solvent in the wood during drying would cause an uneven distribution of the creosote.

With more experimental work, the impregnated wood method of determining the toxicitiy of wood preservatives could undoubtedly be materially improved. This is an important field of investigation and should receive more attention.

Nutrient Agar Methods

During recent years there seems to be a decided trend toward the use of nutrient-agar preservative mixtures, emulsions, and solutions to determine the toxicity to wood preservatives. The technic used in making these tests is being constantly modified and improved.

One of the earliest studies made of the toxicity of wood preservatives in which the method was used was made by Malenkovic.[4] The preservatives are added to a 10 per cent gelatin or a 2 per cent agar culture medium in known amounts. These mixtures are not sterilized, but are inoculated directly with a common mold fungus. That concentration on which no growth of mold developed in 14 days is considered to be the toxic concentration. It is now known, however, that the resistance of molds to toxic agents may be quite different from that of the true wood-destroying fungi. Even strains of the same species of fungus may exhibit considerable variation in their resistance to toxic agents.

Malenkovic's method was slightly modified by Netzsch[5] in so far as a true wood destroying fungus was used in the tests. Netzsch also extended the incubation period from about 10 days to approximately 4 weeks. The results are presented on the basis of the number of liters of culture media which must be added to 1 gram molecule of the preservative to prevent fungous growth. This basis of presenting the results of toxicity studies has many drawbacks from a practical point of view, and it cannot be used when the toxicity of mixtures such as coal-tar creosote is studied; but from a technical point of view it is superior to the percentage basis, since it shows the relative toxicity of different chemical units.

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[8] Schmitz and Zeller, Ind. Eng. Chem., 13, 621 (1921).

[9] Reeve, *Proc. Am. Wood-Preservers' Assocn.*, 24, 42 (1928).

[10] Bateman, *Ibid.*, 24, 50 (1928).

Weiss[11,12] and Rumbold,[13] the latter at least in part, used methods more or less similar to those of Netzsch. The organisms used, however, differed in each case. Weiss used *Bacillus subtillus*, *Saccharomyces glutinis*, and a species of *Pencillium*, while Rumbold used a true wood destroyer, *Fomes annosus*. Rumbold sterilized the agar preservative mixtures, which is now known to modify their toxic properties materially. He also used toasted bread soaked with the antiseptic solution as a culture medium, a procedure not to be recommended in the present state of our knowledge concerning the subject.

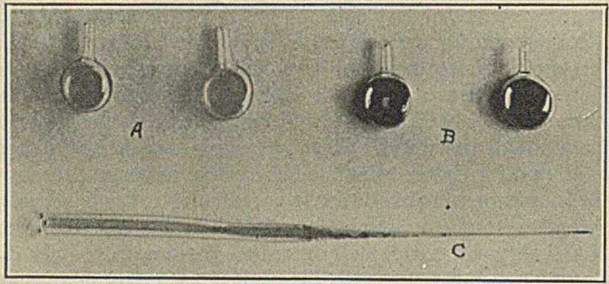

Figure 1—Type of Bulbs Used in Making Toxicity Tests of Volatile Wood Preservatives
A—Unfilled bulbs, half actual size
B—Bulbs containing creosote with necks sealed
C—Capillary tube used in placing creosote in the bulbs

In 1912 Falck[14] reported the results of a rather extensive study in which a large number and variety of substances were tested with reference to their toxic properties, when mixed with a nutrient culture medium.

It is extremely difficult to secure an even mixture of some creosote oils in an agar or gelatin medium. Some creosotes emulsify readily with an agar culture medium when vigorously shaken while hot, while with others, particularly creosote-tar and creosote–crude-oil mixtures, it is practically impossible to secure a uniform distribution of the preservative in the medium. In order to facilitate emulsification, Dean and Downs[15] suggested the use of creosote–gum arabic emulsions. Humphrey and Fleming[16] have shown, however, that the gum arabic materially reduces the toxicity of creosote. There does not seem to be much question that any colloidal gel, such as agar-agar or gelatin, introduces certain errors which may differ in magnitude with each substance used. This fact must always be taken into consideration when the agar plate method of determining toxicity is used to evaluate the merits of any toxic substance as a wood preservative.

It has further been shown by Fitch[17] that the addition of even a relatively inert substance, such as ground glass, modifies the toxicity to *Pencillium glaucum* of copper sulfate. Furthermore, the size of the glass particles influences the magnitude of the modification. The action of solid substances in reducing deleterious effects of poisonous solutions is attributed to the process of "absorption."

The work of Dean and Downs and of Fitch raises some questions of great importance. Does the wood absorb a part of the preservative, whether an inorganic salt or coal-tar creosote, and thus remove it from the sphere of action? Do different woods absorb different amounts of preservative and are different preservatives absorbed to different degrees? Theoretically these are all possibilities, if not probabilities, and they are questions of sufficient importance to warrant careful study.

Weiderpass and Kogerman[18] have also proposed a modification of an agar plate method of determining the toxicity of preservatives to fungi, which overcomes some of the difficulties experienced in emulsifying creosote agar mixtures. A creosote emulsion is first prepared by adding 2.10 grams of oil, 2 grams of fat, 20 grams of sodium hydroxide, and 68.0 grams of water. This stock solution is then added to the culture medium to make any desired concentration of the oil. The addition of fat and sodium hydroxide, however, introduces errors very difficult of evaluation.

The work of Humphrey and Fleming[16] marks the beginning in this country of carefully controlled toxicity tests. In this work a standard malt agar was used as a culture medium. The culture medium and the preservative are sterilized separately under conditions which supposedly prevent the loss of either preservative or culture medium. After sterilization, the preservative and the culture medium are mixed and vigorously shaken until about ready to gel, when they are quickly poured into cold Petri dishes. This procedure hastens gelation and in part prevents the separation of the emulsion. The incubation period is also extended, in some cases running over 10 weeks. The toxicity of these mixtures to *Fomes pinicola* and *Fomes annosus* was tested. The latter fungus is now used in all the toxicity experiments at the Forest Products Laboratory.

When the toxic properties of a volatile substance, such as certain fractions of coal-tar creosote and, as a matter of fact coal-tar creosote itself, pyridine, etc., are tested, the Petri dish is not entirely satisfactory since it permits the loss of considerable of the volatile material. This loss can be reduced somewhat by placing the inoculated dishes under small bell jars set on glass plates. If hard vaseline is applied at the point of contact between the bell jar and the glass plate, volatilization can be limited to the volume of air contained under the bell jar. It is not good practice, however, to place Petri dishes containing different concentrations of the toxic material under the same jar, since a gradual distillation from the higher to the lower concentrations occurs.

The use of glass-stoppered Erlenmeyer flasks in place of Petri dishes in toxicity tests has been recently recommended by Bateman and Henningson.[19] Closed flasks of this type make it possible to calculate, when the vapor tension of the substance is known, the amount of toxic substance which will be lost from the culture medium and taken up by the air in the flask. Enough oxygen is contained in the flask to permit considerable growth of the fungus. The toxic properties of certain volatile and very toxic substances can be accurately studied only when the factors mentioned above are taken into consideration.

Falck[6] has recently proposed another modification of the agar plate method for testing the toxicity of substances which act as "respiration poisons." The fungus is grown on a malt-agar medium in low, wide-mouthed flasks for 8 days. The desired amount of toxic substances is placed in a low dish which is set on a cork, the cotton plug is removed, and the culture flask inverted over the dish containing the substance to be tested. At intervals of 1, 2, 4, and 8 days transfers are made for the fungus culture to determine if it has been killed. Since there is no question that some of the volatile substances will be taken up by the agar culture medium, the results obtained with this method are of extremely doubtful value in so far as they may indicate that a given substance is a "respiration poison." If such a culture flask were maintained under constant conditions for a considerable length of time, an

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[11] Weiss, *J. Soc. Chem. Ind.*, **30**, 190 (1911).

[12] *Ibid.*, **30**, 1348 (1911).

[13] Rumbold, *Naturw. Z. Forst- Landw.*, **10**, 429 (1911).

[14] Falck, *Hausschwammforschungen*, **6**, 338 (1912).

[15] Dean and Downs, *Orig. Com. 8th Intern. Cong. Appl. Chem.*, **13**, 103 (1912).

[16] Humphrey and Fleming, U. S. Dept. Agr., *Bull.* **227** (1915).

[17] Fitch, *Ann. Mycologici*, **4**, 313 (1906).

[18] Weiderpass and Kogermàn, *Naturforsch. Ges. Univ. Tartu*, **33**, 28 (1926).

[19] Bateman and Henningson, *Proc. Am. Wood-Preservers' Assocn.*, **19**, 136 (1923).

equilibrium would be reached between the amount of the volatile substance taken up by the agar medium and the amount of the air above it. The exact ratio would, of course, depend upon the solubility of the particular substance, its vapor pressure, temperature, and other factors. The opening of the flask for the purpose of making transfers also introduces an error which might be eliminated by preparing a number of such flasks from each of which only one transfer is made. On the whole, the method has little to recommend it either from a practical or scientific point of view.

A modification of the Petri dish method to test the toxicity of relatively insoluble substances has been devised by Curtin.[20] In connection with certain tests of the toxicity of barium carbonate, a double-strength nutrient solution was prepared, and to 10 grams of this were added 5 grams of sodium carbonate solution containing the required quantity of carbonate. Then, after shaking, 5 grams of solution containing the proper amount of barium chloride were added, with shaking. The barium was immediately precipitated as carbonate in the hot solution and the cooling of the jelly held it in place with a minimum aggregation and settling out. This method is claimed to be very satisfactory in preparing cultures of certain relatively insoluble substances, but some compounds cannot be handled in this way, because other undesirable chemical reactions take place. Such materials must be treated in the powdered form.

A very important advance in toxicity tests has been made by Bateman[21] which greatly simplifies the determination of the toxic concentrations of any substance by the modified agar plate method. It has been shown that there is a definite relationship between the concentration of a preservative and the percentage retardation of the growth of the fungus. This relationship is such that a straight line is obtained when the logarithm of the concentration is plotted against the logarithm of the percentage retardation. Falck[22] had previously shown that under constant conditions the rate of radial growth of fungi is constant. Hence it is only necessary to prepare two concentrations below the toxic limit of the substance and to plot the logarithm of the concentration used against the logarithm of the percentage retardation. This curve, being a straight line, may be extended to determine the concentration necessary to inhibit entirely the growth of the fungus.

Modification of Agar Plate Method

One of the outstanding difficulties in any of these methods of testing toxicities of wood preservatives is in connection with the sterilization of the preservative itself. This is particularly true when the preservative is volatile, as coal-tar creosote. When the preservative is a liquid, or a solid in a concentrated solution, it is not necessary to sterilize the preservative, because ordinarily these substances are toxic enough to be sterile. It is necessary, however, to sterilize the container in which the preservative is placed before addition of the nutrient agar. The common practice is to place known amounts of the preservative in tightly stoppered bottles or flasks and sterilize them. It is extremely difficult, however, to prevent the loss of more or less of the preservative by volatilization. During heating the air in the flasks expands, causing considerable internal pressure in the flasks. If a cork stopper is used, it softens during steaming, permitting the loss of some preservative. When glass-stoppered bottles are used and the stopper is tight, the internal pressures are often sufficient to burst the flask.

In order to overcome these difficulties and to prevent the loss of any preservative during sterilization, it is proposed that known amounts of preservative be placed in small glass bulbs or ampuls of known weight, which are then sealed and weighed. The sealed bulb is then placed in a glass-stoppered Erlenmeyer flask with a sufficient amount of nutrient culture medium to make the concentration desired. During sterilization the flask is plugged with cotton, the glass stopper being tied to the flask by means of a string. After sterilization, the cotton plug is removed and the bulb containing the preservative is broken by means of a sterile glass rod. The glass stopper is then inserted and, after very gentle shaking to permit some of the expanded air to escape, is tightly inserted and the flask violently shaken to emulsify the mixture. When about ready to gel, the upper portion of the flask is flamed in order to expand the air in it and thus permit the easy removal of the glass stopper, and the emulsion is poured into cold sterile Petri dishes.

This method of testing the toxicity of wood preservative has been tried in this laboratory and found to be very satisfactory. Only one difficulty was experienced, which consists of the preservative getting into the neck of the bulb. It is quite difficult to break the small neck of the bulbs by means of a glass rod, as previously mentioned. It can, however, be easily broken by the use of sterile tongs.

Care must be taken in filling the bulb not to get any preservative on the inner wall of the neck, since a portion of this would volatilize and be lost when the neck is sealed. The preservative can easily be placed in the bulbs by use of an ordinary capillary tube shown in Figure 1, *C*. After a little experience the amount of the preservative added to the bulb can be estimated fairly accurately by counting the number of drops from the capillary tube.

This modification of the regular agar plate method of determining the toxicity of volatile wood preservatives is rapid, simple, and eliminates all possibility of loss of preservative during sterilization.

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[20] Curtin, Ind. Eng. Chem., 19, 1159 (1927).

[21] Bateman, Private communication on data to appear soon.

[22] Falck, *Hausschwammforschungen*, 1, 53 (1907).

Modification of Hempel Gas Pipet[1]

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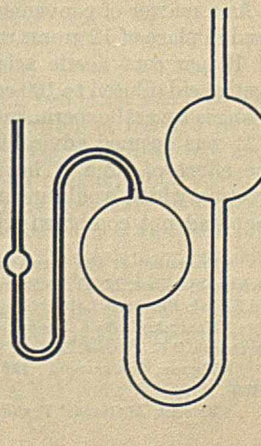
Every analyst who has used a Hempel gas pipet knows how difficult it is when employing mercury in the gas buret to prevent such substances as alkaline pyrogallol, fuming sulfuric acid, etc., from running up the capillary tubing in the pipet and coming into contact with the rubber at the juncture between the pipet and the buret, when the level of the mercury in the buret and the leveling tube is being adjusted. Furthermore, as the gas is run back and forth through the pipet, droplets collect in the capillary tubing and these are frequently sucked back into the buret when the gas is being aspirated into it. The author has found that a small bulb about 0.5 cc. in volume blown in the capillary tubing, as shown in the accompanying sketch, causes these bubbles to be broken, and as it takes a few moments for the bulb to fill one has plenty of time to level the mercury in the buret.



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[1] Received February 11, 1929.

The Reaction of Cellulose with Phenylhydrazine Acetate[1]

C. J. Staud and H. LeB. Gray

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The first observation of a reaction between cellulose and phenylhydrazine appears to have been made in 1892 by Nastjukoff,[2] who found that when cellulose was treated with phenylhydrazine hydrochloride in the presence of sodium acetate, it took up phenylhydrazine and assumed a yellow color which could not be extracted with alcohol or ether. The reaction was subsequently investigated by Vignon.[3] Finally it was the subject of experimentation by Knecht, who attempted to use the reaction in the estimation of the degradation of cellulose by the so-called "osazon method."[4] The procedure employed by Knecht was the treatment of cellulose with an excess of phenylhydrazine solution followed by back titration using titanous chloride.

It was deemed of interest to attempt to correlate the values obtained with the copper numbers of cellulose, and an investigation of the problem of the action of phenylhydrazine acetate on cellulose was first made using as a basis the procedure of Vignon.[3]

Vignon Procedure

In the first experiments the method employed by Vignon was carefully followed. Five grams of sulfite pulp which had been degraded by the action of nitric acid and thoroughly washed and dried were placed in a solution consisting of 7.5 grams of glacial acetic acid and 12 grams of phenylhydrazine diluted to 100 cc. with distilled water. After $^1/_2$ hour on the water bath the cellulose was filtered with suction and washed on the filter by slow addition of 200 cc. of distilled water followed by 200 cc. of 95 per cent ethyl alcohol. It was then subjected to vacuum filtration for several minutes, after which it was dried. The last of the alcohol used for washing was of a definite yellow color. The residue was bright yellow and had a pronounced odor of phenylhydrazine. The nitrogen content, however, was determined by the modified Devarda method, to be described herein, and found to be 1.24 and 1.33 per cent.

Although fair agreement in the nitrogen content with values given by Vignon was obtained, it appeared that the procedure led to erroneous results because of the short time of heating and the rather obviously inadequate extraction employed.

Improvement in Vignon Procedure

As a matter of convenience 15 cc. of phenylhydrazine were used in place of 12 grams recommended by Vignon and 100 cc. of 10 per cent acetic acid in place of 7.5 grams of glacial acetic acid diluted to 100 cc. with distilled water. With these changes several experiments were made.

It was deemed advisable, before attempting to determine the effect of time of heating, to develop a method of extraction which would insure removal of the phenylhydrazine that had not combined with the cellulose. By heating the cellulose for a short period with an excess of phenylhydrazine acetate, removing the major portion of such excess by washing on a filter with 50 to 100 cc. 95 per cent ethyl alcohol, and subjecting to extraction in a Soxhlet extractor, a point was reached where the extract was colorless. The time of extraction differed with various materials as well as with the tightness with which it was packed in the extraction thimble, but the period required was usually between 4 and 8 hours. After the extract had become colorless, the alcohol was changed and the material was extracted for $^1/_2$ to $^3/_4$ hour with fresh alcohol which was examined for color; if colorless, the extraction was discontinued. The efficiency of this procedure may be appreciated by noting two runs in one of which extraction was continued for 4.5 hours and in the other 7.5 hours; the nitrogen values were 0.73 per cent for the former and 0.75 per cent for the latter, which is within the experimental error.

In the matter of heating the materials it was thought preferable to use a ring-necked flask instead of the Erlenmeyer designated by Vignon. The flask was placed in the steam bath in such a position that it was surrounded by steam above the level of the liquid. It is believed that in this way more uniform heating was attained.

Effect of Time of Heating

With the changes described above the effect of time of heating on the amount of phenylhydrazine combining with the cellulose was studied.

Five grams of cellulose, in the form of sulfite pulp which had been degraded by the action of nitric acid, were used. The samples were dried at 105° C. for 16 hours, weighed to the nearest decigram, and placed in a 500-cc. ring-necked flask. A solution consisting of 15 cc. of phenylhydrazine (E. K. White Label) and 100 cc. of 10 per cent acetic acid, prepared by diluting glacial acetic acid 99.7+ per cent with distilled water, was added. The flask was equipped with a reflux condenser and immersed below the level of the liquid in a steam bath. After heating, the contents were filtered by gravity and the excess of phenylhydrazine acetate was removed by washing with 50 to 100 cc. of 95 per cent ethyl alcohol. The cellulose was then transferred to a Soxhlet extractor, where it was extracted until the returning liquid was colorless. The alcohol was then changed and extraction was continued for $^1/_2$ to $^3/_4$ hour longer. The nitrogen content was then determined.

The effect of time of heating on the phenylhydrazine combined, as indicated by the nitrogen content of the products, is given in Table I.

Table I—Nitrogen Content of Treated Sulfite Pulp Heated with Phenylhydrazine Acetate

TIME OF HEATING	NITROGEN CONTENT OF PRODUCT
Hours	*Per cent*
0.5	0.49
3.0	0.61
16.0	0.75
46.0	0.73

From the data it is seen that heating for a period longer than 16 hours apparently does not increase the nitrogen content. This period was accordingly used in later experiments.

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[1] Presented at the Intersectional Meeting of the American Chemical Society, Syracuse, N. Y., October 19, 1928. Communication No. 376 from the Kodak Research Laboratories.

[2] Nastjukoff, *Bull. Mulhouse*, **62**, 493 (1892); and "Lehrbuch der Cellulosechemie," E. Heuser, 3rd ed., p. 124.

[3] Vignon, *Compt. rend.*, **128**, 579 (1899); *Bull. soc. chim.*, [3] **21**, 60 (1899).

[4] Knecht, *Melliands' Textilber.*, **6**, 507 (1925).

Values for Standard Cellulose

By the method described above, two experiments were carried out using standard cellulose prepared according to the method of Corey and Gray.[5] The nitrogen contents were 0.03 and 0.06 per cent, which is considered as satisfactory agreement for values of such low magnitude. This material apparently contains an exceedingly small amount of material which reacts with phenylhydrazine acetate.

Miscellaneous Materials

Various other materials were subjected to the same procedure. The results are given in Table II.

Table II—Nitrogen Content of Various Cellulose Materials after Phenylhydrazine Treatment

NUMBER	MATERIAL	NITROGEN CONTENT OF PRODUCT I	II	AV.
		Per cent	*Per cent*	*Per cent*
1	Sulfite pulp treated with nitric acid	0.74	0.72	0.73
2	Hydrocellulose A	0.08	0.09	0.08
3	Hydrocellulose B	0.22	0.23	0.23
4	Crude linters, 1% NaOH hot, followed by nitric acid	0.39	0.40	0.40
5	Linters, mercerized, treated with nitric acid	0.51	0.52	0.52
6	Hydrocellulose C	0.19	0.19	0.19
7	Hydrocellulose D	0.22	0.24	0.23
8	Crude linters, hot 1% NaOH	0.04	0.02	0.03
9	Standard cellulose	0.03	0.06	0.04

Comparison with Copper Number Values

Since the copper number is also used as a criterion of the degree of degradation, it was thought of interest to draw a comparison between these values and the nitrogen contents of the same materials after treatment with phenylhydrazine.

The copper numbers given in Table III were determined according to the method of Staud and Gray.[6]

Table III—Comparison of Copper Numbers with Nitrogen Content after Treatment with Phenylhydrazine

NUMBER[a]	COPPER NUMBER I	II	AV.	NITROGEN CONTENT
				Per cent
1	9.55	9.30	9.42	0.73
2	2.3	2.0	2.15	0.08
3	2.1	2.2	2.10	0.23
4	6.57	6.10	6.33	0.40
5	14.10	13.59	13.84	0.52
6	4.26	3.97	4.12	0.19
7	3.20	3.14	3.17	0.22
8	0.024	0.018	0.021	0.03
9	0.005	0.006	0.005	0.04

[a] Numbers refer to samples listed in Table II.

There appears to be a general trend of agreement in that high copper numbers are associated with high nitrogen content.

In another paper Gray and Staud[7] have shown that the copper number of cellulose depends to a great extent upon the character of the surface of the material upon which the copper number is being determined. This may account for some of the apparent failure in correspondence between copper number and nitrogen content. In the same paper data are given which indicate that alkali has the property of destroying or converting to an inactive form the reducing substances in cellulose which give rise to the copper number. In this connection attention is drawn to the results of Number 8, in which crude linters were treated with hot 1 per cent sodium hydroxide. The copper number is low, as is also the nitrogen content. Although it is impossible to theorize from one example, the result appears significant.

Altogether the results obtained by the action of phenylhydrazine acetate on cellulose appear more trustworthy than the copper number values. In Numbers 2 and 3 the same linters were treated for equal intervals of time with identical mineral acid solutions. The temperature employed in the former, however, was 50° C., whereas the latter was heated to 70° C. The copper numbers of the two samples are the same, within experimental error. The nitrogen value for the sample heated at the lower temperature was 0.08 per cent, while that heated at the higher temperature had a nitrogen content of 0.23 per cent.

Modified Devarda Method for Determination of Nitrogen in Cellulose and Cellulose Nitrate

Weigh out from 0.5 to 2 grams (depending upon the estimated nitrogen content). Make moisture determinations on separate samples. Place the samples in an Erlenmeyer flask (750 cc.) and heat on the steam bath for about 45 minutes with 2 to 3 cc. ethyl alcohol, 30 cc. of 12 per cent hydrogen peroxide, 50 cc. of sodium hydroxide solution ($d = 1.31$), and about 50 cc. of distilled water. After removal from water bath allow to stand for 1 to 2 hours and then heat with open flame for a few minutes, to break down hydrogen peroxide, and finally cool.

Fit the flasks with a distilling head and condenser leading into a flask containing a measured amount of standard 0.1 *N* hydrochloric acid. Then add quickly 5 cc. of ethyl alcohol and 2.5 grams of Devarda alloy and after the first vigorous reaction has subsided start distilling and distil until most of the liquid has been distilled over into the hydrochloric acid solution. Titrate the excess hydrochloric acid with standard 0.1 *N* sodium hydroxide and calculate the results.

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[5] Corey and Gray, IND. ENG. CHEM., **16**, 1130 (1924).

[6] Staud and Gray, *Ibid.*, **17**, 741 (1925).

[7] Gray and Staud, IND. ENG. CHEM., **19**, 854 (1927).

Laboratory Method for Measuring Relative Adhesive Qualities of Fungicidal Dusts[1]

Robert C. Williams

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IT IS of considerable importance to be able to evaluate relative adhesive qualities of fungicidal dusts. Other things being equal, the dust which adheres best to foliage will function most efficiently over a period of time. Long-drawn-out field tests, which require the greater part of a growing season, are at best scarcely equal as a measure to a simplified laboratory method.

The following method was used to test sulfur dusts, many of which contained small percentages of inert or adhesive ingredients or added toxic substances.

A convenient number, eight or ten, of weighed shellacked microscope slides were placed under a bell jar. The dust was introduced through a glass tube in the top of the bell jar by means of a test-tube atomizer. Various quantities were used and were calculated to give deposits ranging from 0.001 to 0.01 gram per slide. The glass tube in the top of the bell jar had a somewhat upturned tip, so as to cause a more uniform distribution of dust particles and to divert lumpy particles from striking the slides. The tube was held in place by a cork stopper which had an opening to allow the escape of the air blown in. Compressed air forced the contents of the atomizer into the jar.

After the dust had settled, the slides were weighed indi-

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[1] Received December 26, 1928.

vidually to determine the amount of dust on each. They were moistened by holding them in a jet of condensed steam and then dried in the open. Without this treatment all dusts were subsequently washed off almost completely instead of partly as desired. The moistening might be looked upon as comparable to dew under field conditions. Tests without dust upon the slides showed no appreciable effect on the shellac provided they were not held in the hot part of the condensing steam jet.

The slides were next dipped individually ten times, five times from each end using forceps, into a beaker of water which was a little deeper than the full length of the slide. This washing action removed quantities of dust from the slides which varied from 10 to 50 per cent of the dust applied, depending on the kind and amount used. Individual variations for a given grade of sulfur dust were rarely more than 5 per cent. The slides were then dried either in a desiccator or in the open and weighed to determine the loss. Blanks subjected to the same treatment showed no appreciable change in weight. The aggregate washings of ten slides containing the same kind of dust were analyzed by filtering, drying the residue, and isolating the sulfur by dissolving it in carbon tetrachloride. This analysis indicated the part played by added ingredients.

The shellac surface (ordinary commercial white shellac dissolved in methanol) was chosen rather than the plain glass surface itself or a variety of other surfacing substances tried because it emphasized differences in the adhering qualities, is insoluble in water, and quite approximates the character of foliage surfaces in that it acts similarly when wet.

A similar series of experiments was carried out using apple leaves, instead of slides, which were cut to a definite size (2 by 1 inch). They were treated in the same way except that the leaves were not weighed. The aggregate washings from each sample were weighed and analyzed. The amount of dust used in these experiments was approximately the same per unit area as that used previously.

Results

The results are in good agreement with regard to rating dusts in the order of adhering values. The laboratory tests are also in accord with tedious field tests even though conditions of experiment were at variance.

In the following table the ranking of the dusts found by the laboratory tests is compared with the ranking found by the field tests. In each case the sulfur was 300-mesh ground sulfur. For example, 90–10 lead arsenate means 90 parts of 300-mesh ground sulfur and 10 parts of lead arsenate. The dusts are listed according to their adhesion.

TEST	LABORATORY TESTS	TEST	FIELD TESTS
1	98 ± ½–2 ± ½ potassium permanganate	1	98 ± ½–2 ± ½ potassium permanganate
2 or 3	100 sulfur, 300-mesh 75–25 "Kopper's" process sulfur	2	100 sulfur, 300-mesh
4	90–10 "Manganar" (manganese arsenate)	3 or 4	75–25 "Kopper's" sulfur 90–10 "Manganar"
5 or 6	90–10 "Kopper's" process sulfur 90–10 Bentonite	5 6	90–10 dry lime–sulfur 90–10 Bentonite
7	90–10 lead arsenate	7	90–10 "Kopper's" sulfur
8	90–10 dry lime–sulfur	8	90–10 lead arsenate

The ranking of dusts in the field tests was determined by averaging the results of the several separate tests during the course of one growing season under various conditions. The variations in percentages of loss, considering the different dusts, encompassed a range of no more than 15 per cent, so a single set of results was not very significant. Losses were in general 80 to 95 per cent of the dust applied.

The tests with slides, however, emphasized the difference in adhering qualities in that a range of differences of 30 to 40 per cent was encompassed, and the percentages of loss were smaller (10 to 50 per cent).

The method is of greater value where a dust is tested which is made up from the standpoint of obtaining one which adheres well rather than that of obtaining one which is more toxic.

A New Automatic Pipet[1]

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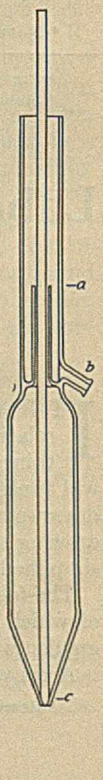
A PIPET to deliver an exact quantity of carbon tetrachloride from a vessel immersed in a constant-temperature bath was vainly sought by the writer. The usual form of pipet is not satisfactory for accurate work on account of the error introduced by the cooling effect while the liquid is being drawn into the bulb and during the time needed for adjustment to the line. Any instrument having a stopcock is also unsuitable on account of contamination from the lubricant. The instrument described here has neither of these disadvantages and was ideally suited to the purpose in hand.

It consists of two parts—(1) the bulb with overflow arrangement, and (2) the valve rod which is ground in at the exit orifice to make a liquid-tight seal. In operation, the bulb is lowered into the liquid, the rod being out, until the level *a* is reached or exceeded, and the rod is dropped in place. As the pipet is raised out of the liquid, the surplus discharges through the overflow tube, *b*. The capacity of the instrument is the volume contained between the points *a* and *c*, minus the volume of the rod between those points. To deliver the contents the rod is simply lifted.

An instrument of this type was tested for constancy of delivery with the following results:



WEIGHT OF LIQUID DELIVERED AT 30° C.

	Carbon tetrachloride *Grams*	Water *Grams*
	76.50	48.49
	76.53	48.46
	76.52	48.49
	76.52	48.47
	76.51	48.46
	76.52	
	76.52	
Average	76.52	48.47
Deviation	± 0.02	± 0.02

These data show that the delivery is quite constant.

The obvious advantage of this instrument is that it automatically takes up and delivers a definite volume of liquid with a high degree of accuracy. The personal factor is entirely eliminated as there is no adjustment to a fixed line, and this fact is especially appreciated in routine work where a given volume is repeatedly required. In addition, the sanitary aspect is important, as it is undesirable to draw up many types of liquids by mouth.

The writer believes this instrument may have application in other fields and welcomes suggestions for its further use. Patent protection has been applied for.

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[1] Received February 8, 1929.

Studies of Destructive Light Sources for Use in Accelerated Weathering Systems[1]

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As part of the general problem of developing a more satisfactory destructive light source for use in accelerated fading and weathering test systems, the relative darkening tendencies of a series of lithopones are shown as obtained under (1) the carbon arc, using impregnated carbons; (2) the mercury arc; and (3) sunlight. A relationship is noted between the spectral characteristics of the light source used and the different degrees of darkening developed. The difficulty of establishing a so-called standard sunlight exposure is quite evident.

A filter of ultra-violet transmitting glass around the mercury burner to eliminate the very short wave lengths gives promising results.

Mercury arc lamps are being built of a less highly fused quartz than is normally used. The running characteristics of these are detailed. Measurements of the changes during service in the spectral distribution of the energy emitted indicate that a wattage control scheme is applicable for maintaining a constant total intensity.

An automatic starting mercury burner of simple design is shown.

As INDICATED by previously published work,[2,3] the application in accelerated weathering systems of moisture (humidity and rain), temperature changes, and treated atmospheres (carbon dioxide, sulfur dioxide, oxygen, and ozone) has advanced further than the perfection of destructive light sources. Improvement in the latter is essential for a satisfactory correlation of results, and would prove valuable also in the allied subject of fading and color testing. The two light sources generally used are the flaming arc, with pure carbon electrodes, and the quartz mercury arc.

With the introduction into therapeutics of the impregnated carbon electrode there has become available a light source whose spectral characteristics can readily be controlled. A correlated study of reactions induced by these impregnated carbons and other light sources, as well as sunlight, would prove worth while.

Carbon Arc Studies and Comparison of Results with Those of Mercury Arc and Sunlight

To obtain a satisfactory means of measuring the various reactions is one of the greatest difficulties encountered in a subject such as weathering. The action of the various light sources was compared by means of a modification of the method generally used for testing the light resistance of pigments.[4] Owing to the sensitivity of nitrocellulose films to the ultra-violet, a clear lacquer was substituted in the test for the usual China wood oil vehicle. It was so formulated that with the addition of a pigment it became a finished lacquer. The pigment-vehicle ratios were varied so that approximately a uniform consistency was obtained for all the tests. The lacquers, spread on white porcelain palettes, were heated for 30 minutes at 50° C. before exposing. To avoid temperature effects, the palettes were mounted 2 feet (61 cm.) from the light source. To insure a definite high humidity the test surfaces during exposure were saturated with cold running water. Four experimental lithopones (*W*, *X*, *Y*, and *Z*) with different degrees of light resistance were prepared for this investigation.

Exposures under Carbon and Mercury Arcs—Six impregnated carbons were selected[5] which were known to have well-distributed spectral sections of maximum intensity, particularly in the violet and ultra-violet. The experimental work included a comparison of these arcs with (1) the regular untreated carbon arc; (2) the 6-inch (15-cm.), clear-quartz, vertical Cooper-Hewitt mercury arc; and (3) the so-called special mercury arc, which will be described later.

Carbon arcs used for weathering and fading test purposes generally are run at 10 to 15 amperes, using 13 mm. diameter electrodes. Since changes occurred too slowly, 30 amperes were used for all the tests. This is the maximum load which 13-mm. carbons will satisfactorily carry. An ordinary automatic feed mounting was used giving an arc approximately 1.5 inches (3.8 cm.). No globe surrounded the arc. From a photographic record of the results the chart as shown in Section I, Figure 1, was assembled.

The color tone of the darkening under any one type of light was approximately the same, but it varied under the different ones and ranged from pure gray to a distinct yellow.

An analysis of the results readily permits three classifications:

(1) Exposures which cause equal darkening on *W* and *X* and considerably more on *Z* (*Y* was not affected in any case).

(2) Those which cause *X* and *Z* to darken equally and *W* less.

(3) Those which cause *W*, *X*, and *Z* to darken different degrees, in the order named, with *Z* in every case most pronounced.

Table I is a grouping of the light sources according to the three classes of results.

Table I—Grouping of Light Sources

Light Source	Sections of Spectrum Intensified	Tone of Darkening
GROUP 1—*w* AND *x* ABOUT EQUAL WITH *z* WORSE		
Carbon *B*	2300 to 3000 Å.	Gray
Carbon *K*	Extreme ultra-violet particularly about 2500 Å. and below	Gray
6-inch vertical Cooper-Hewitt clear quartz arc	Near and far ultra-violet, particularly about the 2536 Å. line	Gray
10-inch vertical special arc	Near and far ultra-violet, but considerably weaker in far section than the previous light	Gray
GROUP 2—*x* AND *z* ABOUT EQUAL AND *w* CONSIDERABLY LESS		
Carbon *D*	Infra-red and near ultra-violet (3500 to 4200 Å.)	Yellow
Carbon *E*	Visible red and to a less extent in the near ultra-violet to 3300 Å.	Yellow
Carbon *H*	Visible red and green and to a less extent in the near ultra-violet to 3200 Å.	Yellow
Untreated carbons	Mainly in the near ultra-violet to 3500 Å. shading off gradually to 3200 Å.	Yellow
GROUP 3—*w*, *x*, AND *z* OF DIFFERENT DEGREES IN ORDER NAMED, *z* WORSE		
Carbon *A*	Infra-red, visible and to a less extent in the ultra-violet to 2900 Å.	Yellowish gray

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[1] Presented before the Division of Paint and Varnish Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Nelson and Schmutz, *Proc. Am. Soc. Testing Materials*, **24**, 920 (1924).

[3] Nelson and Schmutz, Ind. Eng. Chem., **18**, 1222 (1926).

[4] Breyer, Nelson, and Farber in paper by Gardner and Holt, *Paint Mfrs'. Assocn. U. S., Tech. Circ.* **194**.

[5] Obtained from National Carbon Co., Cleveland, Ohio.

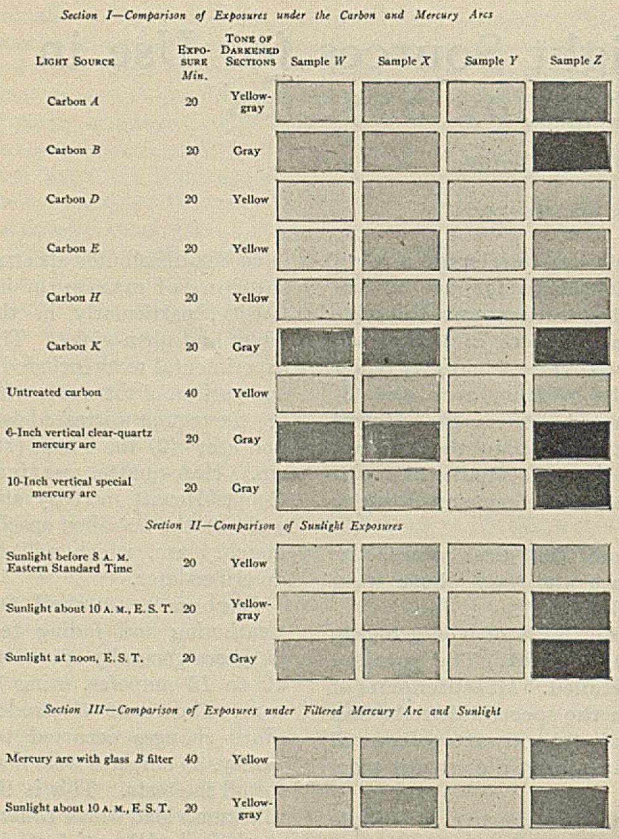

Figure 1

As has been anticipated, because of the predominance of the ultra-violet, Group 1 showed the severest darkening. The difference between W and X (as a group) and Z, with carbon K and the 6-inch, clear-quartz mercury arc was not very marked. This may be due to the strength of the far ultra-violet, particularly about 2500 Å.

The changes in Group 2 were least, especially with the untreated carbons which needed a 40-minute exposure. Carbons D, E, and H, with different distributions of maximum energy in the infra-red and visible, and the untreated carbons, relatively weak in these regions, produced results of the same order. Thus changes as noted must be attributed to whatever violet and ultra-violet is present down to 3200 Å.

Carbon A, Group 3, covers, in addition to the spectral regions emphasized by the light sources of Group 2, the section 2900–3200 Å. A spectroscopic examination of this section showed that most of the intensity was concentrated about 3200 Å. and that the lines and bands faded out as 2900 Å. was approached. The increased darkening under this carbon as compared with Group 2, and particularly the marked increase of sample Z, must be due to the intensification in the vicinity of 3200 Å.

To summarize:

(1) Intensification of the infra-red and visible has but little influence.

(2) Intensification between 3200 and 4200 Å. has an equal effect on both X and Z, weaker at the longer wave lengths but with increasing intensity toward the shorter. W shows practically no response.

(3) Intensification between 3000 and 3200 Å. makes Z more sensitive than X and affects W also to a noticeable extent.

(4) Intensification below 3000 Å. causes W, X, and Z all to show up poorly. The darkening on W and X are equal, and on Z more pronounced. With the far ultra-violet (2500 Å.) also included in the energy increase, the differences in darkening become less marked.

SUNLIGHT EXPOSURES—Sunlight is the ultimate criterion of comparison. Preliminary data obtained during November, 1927, proved rather unreliable because of poor weather conditions. The tests were repeated in August, 1928. Section II of Figure 1 is a comparison of results obtained between sunrise and noon. The results between noon and sunset agreed with these.

The extent of the variation in results for different hours of the day is rather surprising. The early morning results are similar to the darkening obtained in Group 2, Table I; those of the middle of the morning approach Group 3, and those over the noon, Group 1.

According to experiments by Dorno at Davos, Switzerland,[6] the variation in the solar ultra-violet (2900–3100 Å.) for different hours of the day in the summer time is very great. At the particular location of Davos the extremes for July 15 are from 200 arbitrary units before 7 A. M. to 1150 units a little before noon. For January 15 these figures became less than 100 arbitrary units for 10 A. M. and about 200 units for just past noon. At the altitude of Palmerton these summer extremes would not be so great; nevertheless they must be sufficient to account for the variations observed. At no time in November were results obtainable of the type produced at noon in August or as under Group 1, Table I. Of the four light sources in Group 1, carbon B and the 10-inch special mercury arc both have the lesser amounts of energy in the far ultra-violet. Results under these agree well with sunlight at noon. The 10 A. M. results are most closely approximated by carbon A, those of the early morning, by the untreated carbons.

It seems evident that in our continued endeavor to simulate June noon sunlight as the ideal destructive light source we may be attempting to standardize upon a natural condition not sufficiently prevalent over the whole year. Thus deteriorations occurring under the ideal light source are not likely to be in harmony with those occurring under outdoor exposures over the year as a whole.

Modification of Mercury Arc

Because of the excessive heat generated, the carbon arc at 30 amperes has not been successfully operated in a closed exposure system, as used in the writers' laboratory,[2] without elaborate cooling arrangements. Hence, the mercury arc is more conveniently applied, but from a spectral viewpoint a decrease in the far ultra-violet is essential for this light source. Recent developments in ultra-violet transmitting glasses suggest a means of accomplishing this improvement, but such a glass, as a filter, must maintain constant transmission characteristics while in service. To determine this property ultra-violet light exposures both at 60° and 500° C. (approximately the temperature of the mercury arc) were run upon three makes of glass. These had an original transmission limit of about 2600 Å. The results are briefly summarized in Table II.

Table II—Lower Limit of Transmission[a]

Ultra-Violet Light Exposure		Glass A	Glass B	Glass C
Hours	° C.	Å.	Å.	Å.
Unexposed		2580	2600	2690
77	60	2700	2710	2700
149	60	2700		
72	500	2490	2560	2690
149	500	2490		

[a] Measurements by C. C. Nitchie, of this laboratory.

The luminous section of the mercury arc was next enclosed in a tube of glass C.[7] Darkening tests were similar to sunlight results (Section III, Figure 1). The rate of darkening was very slow—about on a par with the untreated carbon arc. Measurements show that a reduction in thickness markedly increases the percentage of energy transmitted by glass *C*, particularly between 2900 and 3200 Å. (Table III). Thus a decrease in the thickness of the tube wall would accelerate the light action. The thickness of the tube used was about 2.0 mm.

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[6] Dorno, "Physik der Sonner und Himmelstrahlung;" also Clark, "Lighting in Relation to Public Health," p. 154, Williams & Wilkins, 1924.

[7] Obtained through the coöperation of Corning Glass Co., Corning, N. Y.

Table III—Transmission of Glass *C* at Different Thicknesses

THICKNESS	2900 Å.	3000 Å.	3100 Å.	3200 Å.
Mm.	*Per cent*	*Per cent*	*Per cent*	*Per cent*
4.95	1	8.5	30	42
2.06	4.5	28.0	59	70

It would be necessary to reënforce the ends of the thinner tubes with metal to guard against breakage.

Accelerated weathering exposures were run upon house paints, using in the one case the unfiltered arc and in the other the glass filter, keeping the other weathering factors the same. After 21 days the test surfaces under the first light showed heavy chalking without pronounced checking, while under the modified light they showed much less chalking with more checking. Since the possibilities of a filtered mercury-arc light source are very promising, it might prove feasible to build the burners of the light-filtering material. Experiments along this line are now under way. Globes of this type of glass should also prove interesting for the carbon arc.

VARIATION IN LIGHT CHARACTERISTICS OF MERCURY ARC WITH CHANGES IN DESIGN—For accelerated weathering work a rugged burner with a long luminous tube length is essential. It also had been thought that the energy distribution, particularly as applied to the far ultra-violet, could be varied by changes in design of the burner. Subsequently there have been gradual developments[8] in the design and construction of the burners used in our accelerated weathering system.[2]

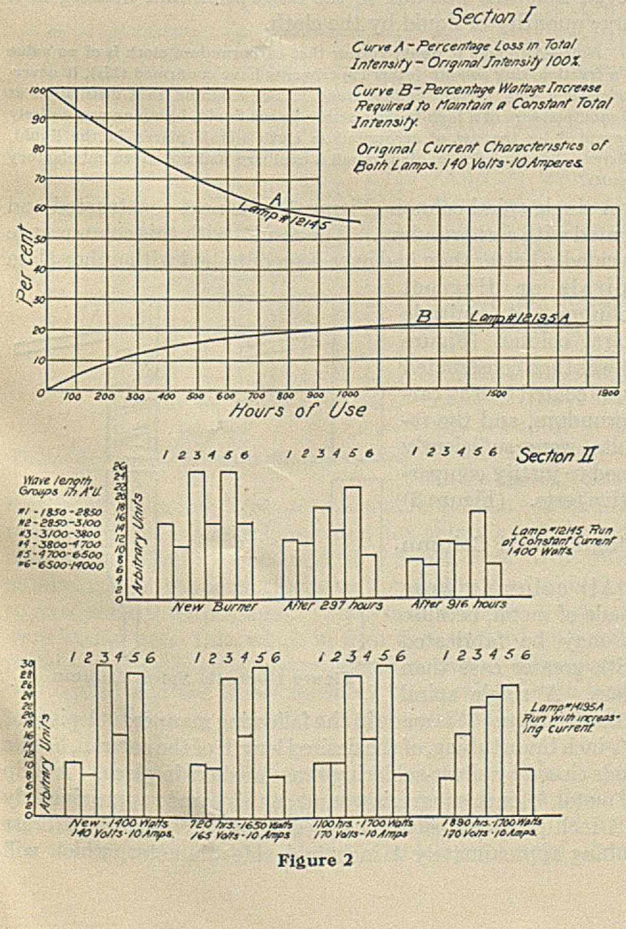

Figure 2

In the place of clear quartz generally used in 6-inch burners, a vitrified, less highly fused, type (known as Thermal Syndicate stock quartz) has been adopted, which is not so clear and does not so completely transmit the far ultra-violet. Being more rugged and thick, longer effective luminous tube lengths can be built (Table IV).

Table IV—Various Sizes of Burners Now in Use

BURNER	LUMINOUS TUBE		MERCURY WELL AT CATHODE	
	Length	Internal Diameter	Length	Internal Diameter
	Inches	*Inches*	*Inches*	*Inches*
Clear quartz	6½	½	1½	1
Special No. 1	10½	¾	2¾	1¾
Special No. 2	19¾	¾	2¾	1¾
Special No. 3	29¾	¾	3½	1¾

According to Stockbarger,[9] "the quartz mercury arc when used primarily as an ultra-violet light source should have as large a tube diameter as possible, the arc voltage and current should be as high as lamp construction will permit and the luminous tube should be maintained at a high temperature." Temperature measurements (Table V) indicate that the longer burners run at lower temperatures.

Table V—Average Running Temperatures of Luminous Tubes (Middle Section)

BURNER		CURRENT CONSUMED	TEMPERATURE
	Inches	*Watts*	*° C.*
Clear quartz	6	608	485
Special	10	890	523
Special	20	1056	429
Special	30	1450	321

This more than counterbalances any ultra-violet efficiency of the lamp induced by the greater tube diameter. The light emitted by these burners shows a reduction in the percentage of far ultra-violet (Table VI).

Note—The results were obtained by the thermopile and filter method as outlined by Stockbarger. (See footnote 9.) The filters used were Uviol, G86B, Uviol O, Uviol C, and Wratten filter No. 70, designating the spectral sections as indicated in Table VI.

Table VI—Comparative Energy Distribution of Light Emitted by Various Burners

BURNER		1850–2850 Å.	2850–3100 Å.	3100–3800 Å.	3800–4700 Å.	4700–6500 Å.	6500–14,000 Å.
	Inches	%	%	%	%	%	%
Clear quartz	6	28.0	9.4	22.0	10.6	20.8	9.2
Special	20	14.8	10.4	25.0	14.8	24.6	10.4
Special	30	12.4	9.2	28.0	15.2	26.1	9.1

The light efficiency of the special burners decreases with tube length (Table VII).

Table VII—Light Efficiency of Various Burners in Terms of Current Consumed

BURNER		CURRENT CHARACTERISTICS			LIGHT ENERGY, IN ARBITRARY UNITS	
					Total	Per watt current consumed
	Inches	*Volts*	*Amperes*	*Watts*		
Clear quartz	6	140	4	560	350.0	0.62
Special	10	140	7.5	1050	307.0	0.29
Special	20	140	8.5	1190	202.0	0.17
Special	30	145	10	1450	148.0	0.11

Stabilization of Light during Continued Service

It is generally agreed that the 6-inch clear-quartz burner after continued use changes in spectral characteristics and shows a loss in total intensity for the same current consumption. A study was made covering the continued running characteristics of the special 30-inch burner. A new burner (No. 12,145) run for 1000 hours at the 140 volts and 10 amperes showed a decrease in total light intensity (Section I, Figure 2, curve *A*). On the basis of 100 as the original total intensity, this decreased to 57.

The rearrangement in the spectral distribution of the energy is indicated in Section II of the same figure. The blocks are graphic comparisons of the total energy between the wave lengths indicated. A marked change has occurred in the shorter wave lengths.

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[8] In coöperation with L. J. Buttolph, of Cooper-Hewitt Electric Co.

[9] Stockbarger, *J. Optical Soc. Am.*, **14**, 356 (1927).

The wattage consumed by the lamp can be increased by decreasing the external control resistances. Experiments were run to determine whether a constant total intensity could be maintained by a wattage increase. Curve *B*, Section I, Figure 2, indicates the per cent increase over the original wattage required. As shown in Section II, the rearrangement in energy distribution is not marked except after long service, when an actual browning of the lamp tube becomes evident. This browning is probably due to a deposition from the tungsten electrodes.

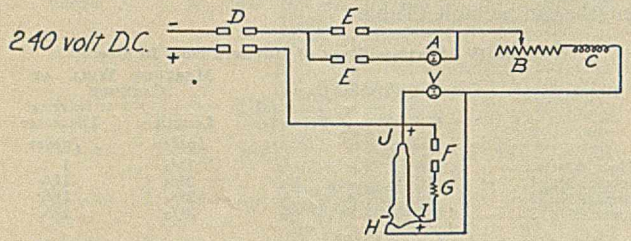

Figure 3—Automatic Lighting Mercury Arc

A—Plug connector for ammeter
B—25-Ohm variable resistance (280 feet No. 12 nichrome wire)
C—High inductance
D—D.P. switch 250 volts, 20 amp.
E—S.P. snap switch 250 volts, 20 amp.
F—S.P. switch 250 volts, 10 amp.
G—155-Ohm resistance, 2 amp.
No. 12 asbestos-insulated copper wire used

Since simplicity is essential in any maintenance scheme, only the required wattage control without the more involved voltage and amperage factors was determined. The lower original fusion and running temperature may account for the more uniform behavior of the quartz in the special burner, as compared with the 6-inch clear-quartz burner.

Automatic Lighting Mercury Arc

To eliminate the necessity for handling the 20- and 30-inch light units and also to facilitate developing semi-automatic weathering apparatus, an automatic lighting mercury arc has been developed[8] (Figure 3). The changes are (1) the addition of a positive electrode, *I*, at the level of the mercury in the well; (2) a high-resistance, *G*, in this electrode circuit; and (3) a high inductance, *C*, in the other positive electrode line. A slight quiver of the mercury establishes an arc between *H* and *I* which jumps to *J*, because of the resistance and the inductance. The circuit through the auxiliary electrode can then be cut.

Coated Spiral Fractionating Columns[1]

Thomas Midgley, Jr.

Thomas & Hochwalt Laboratories, Dayton, Ohio

SOME time ago it was observed that a Hempel column filled with a material which would behave as a "boiling stone" in the liquid being distilled gave better results than did the customary glass beads. At that time, and without further investigation, crushed antimony was selected to serve in this capacity, because of the ease with which it could be prepared. The present development is an outgrowth of this earlier observation.

Comparative Efficiency of Various "Boiling Stones"

It was believed that varying degrees of efficiency might exist among different materials which behave as "boiling stones." To determine this, the following experiment was conducted: A 2-liter round-bottom flask was mounted beneath a reflux condenser and half filled with a mixture of equal parts of benzene and toluene. A thermometer, reading in tenths of a degree, was placed in the liquid and constant heat applied to the flask. After refluxing started, the temperature was observed until it became constant. This procedure was repeated with various materials as "boiling stones," with the following results:

MATERIAL	TEMPERATURE °C.	MATERIAL	TEMPERATURE °C.
No boiling stones	94.0	Glass beads	94.0
Crushed antimony	93.8	Steel strips	94.0
Crushed porcelain	92.6	Etched brass	94.0
Carborundum cloth	88.7	Etched steel	94.0
Brass strips	94.0		

It is evident that many other materials may well be investigated in the preceding manner, and it is quite likely that results superior to those obtained with carborundum cloth will be found.

A Hempel column was then filled with small scrolls of carborundum cloth and the fractionation of benzene and toluene attempted. The results were quite unsatisfactory. It is believed that this was due to the absorption and holding of a large quantity of liquid by the cloth.

Note—Although it would appear that carborundum cloth is of no value in a fractionating column (other experiments have confirmed this), it nevertheless is a very useful "boiling stone." For example, in a distillation at 20 mm. pressure of a high-boiling, semi-viscous liquid, bumping was entirely prevented by the use of carborundum cloth spirals placed in the liquid, whereas the admission of air through a capillary had not given satisfactory results.

A single spiral column (Figure 1) was next constructed and coated with carborundum. The results with this column were decidedly better than had ever been obtained with either plain spirals or Hempel columns. A multiple spiral column (Figure 2) was then constructed and coated with carborundum, and the results were sufficiently good to justify comparative tests. (Figure 3)

Single Spiral Column

All columns were made of metal, because it may be fabricated with greater ease than glass. A single spiral column (Figure 1) is made in the following manner: A piece of $^3/_4$-inch brass tubing, of the desired length of the column, has its ends closed by silver-soldering brass washers in place. A strip of metal, $^1/_8$ inch square, is wound on this core to approximately a 1-inch pitch and silver soldered in place. A piece of brass tubing approximately 1 inch in inside diameter, which will

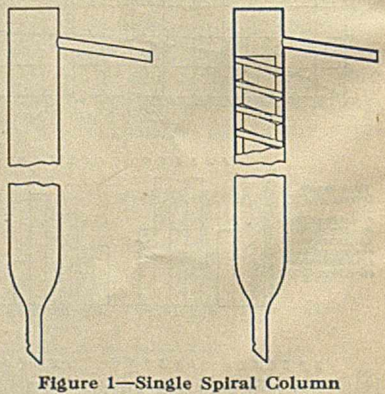

Figure 1—Single Spiral Column

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[1] Presented before the Division of Organic Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

fit snugly, is slipped over the assembly and cut to length. Suitable ends are soldered to the column to fit thermometers, condensers, and distilling flask.

COATING WITH CARBORUNDUM—The column is filled with a dilute solution of shellac in alcohol and drained. It is mounted on a stand and connected to a source of air saturated with alcohol by placing a wash bottle filled with alcohol in the air line. The air is turned on and blows out the excess shellac solution. After the excess shellac solution has drained from the column, a round-bottom flask containing 60-mesh carborundum is placed in the air line and so connected to the air supply that carborundum particles are carried from it by the air stream to the column. After a few minutes carborundum particles come through. The alcohol wash bottle and carborundum flask are removed from the air line and air is blown through the column until the odor of alcohol almost disappears from the air as it leaves the column. The column is next mounted for distillation and benzene distilled through it until all traces of alcohol in the distillate disappear.

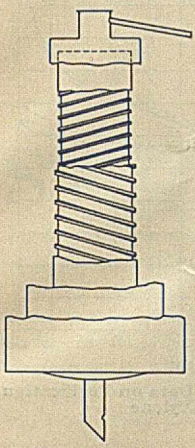

Figure 2—Multiple Spiral Column

VARIATIONS OF CONSTRUCTION AND COATING—It is obvious that a column using shellac for a binder is unsuited to alcohol distillations. In such cases a column using water glass as a binder may be constructed. It is obvious also that for other special purposes better binders may be selected than either shellac or water glass. It likewise is apparent that metal columns cannot be used where corrosive materials, such as strong acids, are to be distilled. However, in the general field of organic research, particularly with hydrocarbons where maximum efficiency in fractionation is essential, metal columns with shellac binders are quite applicable. It is suggested that a column made from Pyrex, coated with carborundum sealed to the glass, would have a very wide application.

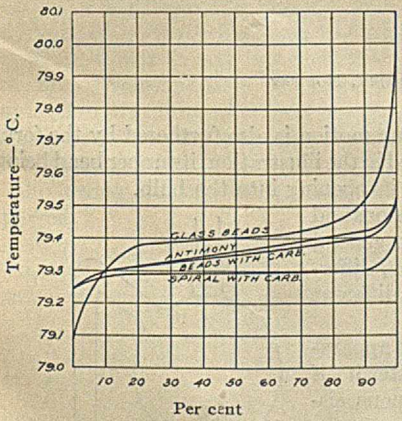

Figure 3—Comparative Distillation Curves

Multiple Spiral Column

Multiple spirals are fabricated in substantially the same manner as single spirals, except that larger diameter cores are used and more than one spiral is wound thereon. The column used for obtaining the results reported in Figure 3 consisted of a 3-inch core with three parallel spirals wound clockwise on it. A thin sheet of copper covered these three passages. Three counter-clockwise spirals were wound upon this, which in turn were covered with sheet metal and suitable ends silver soldered in place. The column was coated and the whole assembly was insulated with magnesia pipe covering and felt, giving an outside diameter of 6 inches (15 cm.).

The passages of multiple spiral columns should be coated separately, since simultaneous coating fails to give uniform results. Separate coating can be done with ease only before the end connections are in place. The temperature of silver-soldering is too high for organic binders to stand. Therefore it is desirable to construct multiple columns with flanged ends, to which the end connections may be bolted after the passages are coated.

Adiabatic Coated Spiral Column

The description so far covers only columns designed to replace elementary Hempels. It becomes apparent that if improvements are made on the elementary Hempel column such improvements can be incorporated with the recognized principles used in adiabatic and partial-condensation columns.

For this purpose a single spiral column, 4 feet (122 cm.) long, was built and coated. An air space was provided around the column as shown in Figure 4. Ample nichrome heating coils were provided around the air space and the assembly was insulated by asbestos and felt. A thermometer was placed in the air space and during operation was held in substantial agreement with the distillation temperature. The superstructure at the top of the column was an adaptation of a principle of partial condensation received in private communication from F. H. Rhodes, of Cornell University.

This column was used for the separation of hydrocarbons produced in the destructive distillation of rubber. Components boiling within 4 degrees of each other were detected on the initial fractionation. Three re-runs were required to purify such components sufficiently so that subsequent identifications were made possible.

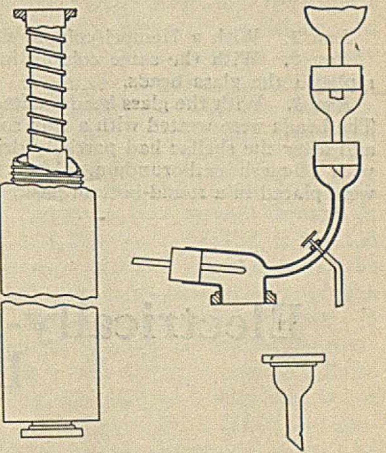

Figure 4—Adiabatic Coated Spiral Column

To measure the efficiency of this column, 150 cc. of pure benzene and 150 cc. of pure toluene were mixed and distilled. The over-all rate of delivery was 1 cc. per minute. The distillation curve is shown in Figure 5. Ninety-four per cent of the benzene and 86 per cent of the toluene were recovered, of practically the same purities as were the original materials. The Engler distillations, specific gravity, and freezing point of the recovered materials are recorded in Figure 6. Figure 7 represents the results of purifying meta-xylene.

Inasmuch as the "residue" from these columns is larger than could be desired, this type of column does not appear to be adaptable for use in separating a component present in small quantities (30 cc.).

Comparative Tests of Fractionating Column

A column 15 inches (38 cm.) high was mounted with the customary condenser and thermometer (reading in tenths of a degree) on top of a 500-cc. round-bottom flask. Two hundred cubic centimeters of a selected commercial benzene (f. p. +2° C.) were placed in the distilling flask. The heating rate was adjusted to deliver 2 drops per second from the condenser. The condensate was collected in 10-cc. cuts and freezing points were determined. At the end of the run the ten cuts of highest freezing points were mixed (in all cases this 100 cc. represented a consecutively delivered cut), and an Engler distillation was made in an A. S. T. M. gasoline distillation apparatus (standard except that a tenth of a degree thermometer was used). Four runs were then made as follows:

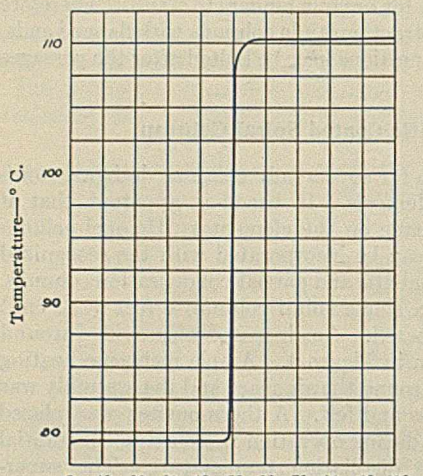

Figure 5—Distillation of Benzene-Toluene Mixture in Coated Spiral Column

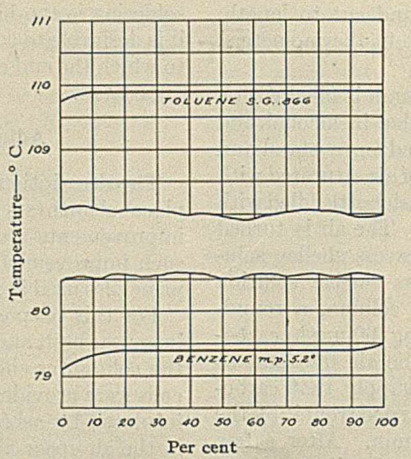

Figure 6—Distillation Data for Materials Recovered from Distillation of Benzene-Toluene Mixture in Coated Spiral Column

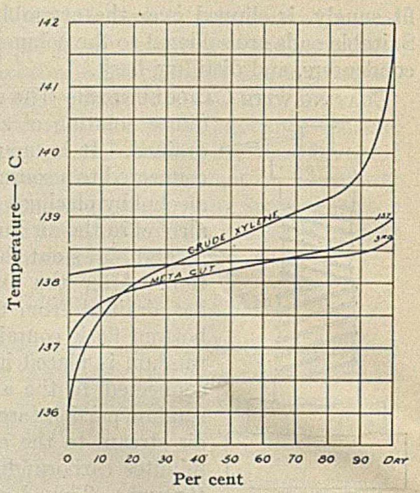

Figure 7—Distillation Data on Purification of Meta-Xylene

Run 1. With a Hempel column filled with glass beads.

Run 2. With the same column in which crushed antimony replaced the glass beads.

Run 3. With the glass beads coated in the following manner: The beads were wetted with a thin solution of shellac in alcohol and after the shellac had partially dried the beads were shaken with 60-mesh carborundum. After further drying the beads were placed in a round-bottom flask, covered with benzene, and the whole distilled until all evidence of alcohol in the distillate had disappeared, after which the beads were removed and dried.

Run 4. In the coated multiple spiral column, which was the same height as the Hempel column previously used.

The resulting curves of the Engler distillation are plotted in Figure 3.

Electrically-Heated Thermocirculator for Hot Leaching and Digesting[1]

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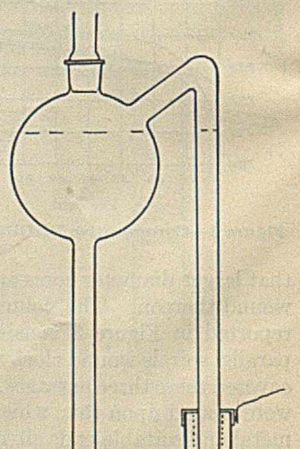
DURING laboratory investigations of methods for leaching certain ores, an apparatus was wanted permitting continuous leaching with exceedingly corrosive, boiling liquids. For this work an all-glass construction as illustrated proved very useful.

The apparatus, which is easily made out of a round flask and some glass tubing, consists of a glass bulb connected with a reflux condenser at the top and a circulation tube between the bottom and the upper part. The lower part of the tube is covered, as the illustration indicates, by a layer of asbestos sheet around which a nichrome wire is coiled. This heating coil is insulated and protected on the outside by mica-mantled asbestos fastened with brass caps carrying contact screws and connected with an adjustable resistance.

For use the apparatus is filled with preferably preheated leaching liquid to a little below the upper opening of the circulation tube and the current is switched on. Soon a local steam generation drives the liquid into the bulb with considerable force and thus starts a circulation. The material to be leached is then charged through the top opening and the condenser replaced. If the apparatus is of correct dimensions, the circulation should not be continuous—as, for instance, in an air lift—but markedly pulsating. In that way not only is the liquid circulated, but—and this is the special feature of the device—the material to be leached is itself brought into vigorous circulation, even when of high specific gravity. The pulsating motion is also furthered by the form of the lift tube indicated in the illustration, its upper bend being somewhat higher than its opening into the bulb.



As to the best dimensions and the current needed no general directions can be given, different liquids demanding different working conditions.

The principle of the apparatus—the leaching matter itself being kept in continuous circulation—should insure the best possible contact between liquid and solid and thus give a maximum of leaching efficiency. The circulation may be carried on for days without loss of liquid and without danger of breakdown, the apparatus being entirely free from moving parts. The apparatus needs no supervision and may be left working during the night without fire hazard.

The apparatus should also be well adapted for carrying out reactions between immiscible reactants at boiling temperature.

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[1] Received September 8, 1928.

Determination of Free Sulfuric Acid in Light-Oil Sludge[1]

F. S. Bacon[2]

Arthur D. Little, Inc., Cambridge, Mass.

SLUDGE obtained from the treatment of light oils contains a large percentage of free sulfuric acid. No satisfactory method was found in the literature for determining the amount of this acid in sludge. Such a method would be of considerable use in refinery operation.

In the course of this work five different methods have been developed, all of which give reasonable check results on the sludges tested. Several of these methods are open to objections when considered in the light of information available in the literature. In the case of one of these—namely, that in which aniline is used—a series of experiments has been carried out which seem to refute these objections and to establish the validity of the method. We appreciate the fact that check results obtained by all five procedures may possibly indicate that some fundamental error exists in all of them, but so far none has been found. Further work is contemplated, but these results are presented at this time in order to obtain helpful criticism.

In any method which might be developed it was considered necessary to avoid the presence of water on account of the ease with which alkyl sulfuric acid esters were said to hydrolyze. Work recently completed at the Massachusetts Institute of Technology, but which has not yet been published, has shown that sulfuric acid esters of high-molecular-weight primary olefins hydrolyze with great difficulty, and even those of secondary olefins but slowly. In the course of this same work some evidence was obtained that sulfuric esters of tertiary bodies of high molecular weight were formed but that they hydrolyzed instantly on contact with water. This hydrolysis is much slower in acid solution than in neutral or alkaline media. Experiments in this laboratory have indicated that at least in the sludge which was being used, tertiary esters were either absent or the amount present was too small to affect the results.

Following are the various methods which have been employed:

A—Gravimetric determination as barium sulfate.

B and C—Titration methods in which the sulfuric acid is titrated with alkali, each under different conditions.

D—A method in which the heat of dilution of the sludge with water is determined and the amount of free sulfuric acid estimated by comparison with data on the heat of dilution of pure sulfuric acid.

E—A method in which the sludge is treated with a boiling solution of aniline in chloroform with the formation of aniline sulfate, which is filtered off and analyzed either for aniline or sulfuric acid by titration or for sulfate by a gravimetric method.

Method A

In Method A, a water extract of a fresh light-oil sludge is treated in the cold with a 10 per cent barium chloride solution strongly acidified with hydrochloric acid in order to precipitate all SO_4 ions as barium sulfate. Just what happens to the alkyl sulfuric esters is problematical. If the acid esters are soluble in water and do not hydrolyze, then the determination of the free sulfuric acid by barium sulfate precipitation is satisfactory. If, however, they hydrolyze whether soluble or not, the results will be high. The fact that the precipitation is made in the cold and with acidified barium chloride, so that the solution is always on the acid side, tends to prevent a rapid hydrolysis at any rate. Also, during the procedure the time for possible hydrolysis is short, and even if acid esters of moderate molecular weight are present the probable hydrolysis is slight. The literature in regard to high-molecular-weight sulfuric acid esters such as might be found in sludge is practically nil.

Methods B and C

Methods B and C are titration methods in which the sulfuric acid is titrated with alkali under different conditions. In Method B the sample to be analyzed is weighed on a very thick mat of asbestos in a Gooch crucible. Chloroform is then poured through this until the washings are colorless, thereby removing the tar and the alkyl sulfuric esters and leaving the sulfuric acid adhering to the asbestos. The excess chloroform in the asbestos is removed by gentle suction. About 200–250 cc. of hot water are then poured through to remove the sulfuric acid, and this water solution is titrated with standard alkali for the acid content. Even by using the utmost care to prevent the acid from passing through the mat with the chloroform, the results are invariably low. If the chloroform solution is then titrated and the results combined, they check reasonably well with the other methods. For convenience this is called the isolation method and is not so accurate as the others. The alkyl sulfuric esters and neutral esters are completely soluble in chloroform, as will be shown later in this paper.

In Method C, which is an outgrowth of Method B, the sludge is thoroughly mixed with chloroform and dumped into ice water. It was observed that, at least in the case of the several light-oil sludges available, when fresh they are easily soluble in chloroform or carbon tetrachloride, but on aging they become less and less soluble in these solvents. This difficulty would probably not be encountered in refinery laboratories.

The ice-cold solution is immediately titrated for total acid with standard alkali, using phenolphthalein as indicator. This step gives the free sulfuric acid present plus one unreplaced hydrogen ion of the alkyl sulfuric acid. The neutralized solution is then boiled for at least 30 minutes and again titrated with standard alkali. This second titration gives the amount of alkyl sulfuric acids alone, since one replaceable hydrogen is freed by the hydrolysis. This is equivalent to the amount originally present and titrated in the cold, so that the free sulfuric acid present can be determined by subtracting the hot titration from the cold. The amount of sulfuric esters can also be determined by this method. Certain difficulties arise with this procedure owing to the unknown solubility and hydrolysis of the alkyl sulfuric acids. If any of the esters are soluble in water and hydrolyze in the cold, or are soluble in the chloroform and do not completely hydrolyze on boiling, or if sulfonic acids are present, the results will probably be high. This method is therefore open to criticism but, as is shown later, it worked very well on the particular sludge under investigation.

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[1] Presented before the Division of Petroleum Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Present address, Monsanto Chemical Works, Monsanto, Ill.

Pilat and Starkel,[3] after treating the sludge with water, titrated the water extract for total acid with 0.1 *N* caustic soda. They also made a gravimetric determination by precipitating the sulfate with barium chloride and assumed that the difference between the two determinations was due to alkyl sulfuric and sulfonic acids. This procedure is open to the same criticism that was discussed for Method A, estimation of the acid as barium sulfate—namely, the possibility of hydrolysis of the alkyl sulfuric esters present under the conditions of the procedure.

Method D

Method D is a quick method, which gives a result accurate probably within 1 per cent for acid concentrations above 60 per cent. Some details will be given in connection with this method, as it is not an ordinary procedure.

When sulfuric acid of various strengths is mixed with equal parts of water, the temperature rise corresponding to any strength of acid is definite. Plotting this temperature rise against the per cent strength (by weight) gives a smooth curve. The results are fairly accurate for acids of more than 50 per cent strength, but below that concentration the nature of the curve is such that a slight error due to radiation or inaccurate reading of the final temperature causes a large error in the acid strength. In the case of light-oil sludges the free acid may be less than 50 per cent, but the strength of the aqueous portion is normally greater than that.

It was found that on dilution the temperature rise from any sludge was definite and probably depended almost entirely on the heat of dilution of the free sulfuric acid present. On account of the large amount of heat produced in the formation of alkyl sulfuric acids, it is reasonable to assume that on hydrolysis they will produce little if any additional heat, and consequently it has been neglected in the calculations.

The heat of dilution of the sulfuric acid portion and water added raises the temperature, not only of the acid-water mixture, but also of the tar present in the sludge. A correction must therefore be applied to the observed temperature rise, which is the amount of heat employed in raising the temperature of the tar. To determine this the following assumptions are made—namely, that the tar has a specific gravity of 0.9 and a specific heat of 0.5, and also that the strength of the sulfuric acid present (neglecting the presence of the tar) is 60 per cent and therefore after dilution 30 per cent. The fact that the strength is usually somewhat greater than this introduces no appreciable error, for the increase in specific gravity is compensated by the decrease in specific heat.

For convenience, the derivation of the formulas for determining the actual temperature rise is given for both Fahrenheit and Centigrade degrees.

To raise the temperature of 100 cc. of 30 per cent acid 1° F., 57.1 calories are required. To raise the temperature of X cc. of tar 1° F. there are required $X \times 0.9 \times 0.5 \times 0.55$ calories, where 0.55 is the ratio of Fahrenheit to Centigrade degrees. Then if ΔT_o is the observed rise in temperature in degrees Fahrenheit, the corrected rise is

$$\Delta T_c = \Delta T_o \left[57.1 + \frac{(X \times 0.9 \times 0.5 \times 0.55)}{57.1} \right]$$

Similarly, to raise the temperature of 100 cc. of 30 per cent acid 1 ° C., 103.8 calories are required. To raise the temperature of X cc. of tar 1° C. there are required $X \times 0.9 \times 0.5$ calories. Then, if ΔT_o is the observed rise in temperature in degrees Centigrade, the corrected rise is

$$\Delta T_c = \Delta T_o \left[\frac{103.8 + (X \times 0.9 \times 0.5)}{103.8} \right]$$

The volume of tar, X, in a given volume of sludge may be estimated in two ways after a preliminary extraction with water:

(1) By dissolving in a known volume of carbon tetrachloride or chloroform and noting the increase in volume.

(2) By dissolving in carbon tetrachloride, transferring to a weighed flask, and distilling off the tetrachloride followed by weighing the sludge directly. From this weight the volume may be estimated by assuming a specific gravity of 0.9. During the distillation the temperature should be raised to 300° F. (149° C.) to avoid occlusion of water in the tar.

Following the estimation of the amount of tar present, a known volume of sludge is taken—conveniently, that containing 50 cc. of aqueous portion—and mixed in a Pyrex vacuum flask with a volume of water equal to that of the aqueous portion of the sludge. ΔT_o is observed and ΔT_c is calculated. The strength of acid in the aqueous portion (by weight) is then determined by comparison with the temperature-rise curve for pure acid, and the strength of acid in the whole sludge is found by multiplying the above figure by the percentage by weight of the aqueous portion in the sludge. One light sludge examined by this method showed 18.1 per cent of tar and 81.9 per cent of aqueous portion by weight and 27.4 per cent of tar and 72.6 per cent of aqueous portion by volume. 68.9 cc. of sludge (94.9 grams) which contained 18.9 cc. of tar and 50.0 cc. of aqueous portion were mixed with 50 cc. of water. The temperature rise observed, ΔT_o, was 51° F. (22.6° C.) and the corrected rise 55° F. (24.5° C.) From the heat of dilution curve for pure acid the percentage of acid in the aqueous portion is found to be 74 per cent. Multiplying this figure by the percentage of aqueous portion in the sludge—81.9 per cent—the percentage of free sulfuric acid in the sludge is calculated to be 60.6 per cent. Analysis of this same sludge by the gravimetric method (A) showed 59.5 per cent free acid.

Method E

In Method E the sludge is treated with 10 per cent aniline in boiling chloroform with the formation of aniline sulfate. This is filtered off and analyzed for aniline or sulfuric acid by titration or for sulfate by a gravimetric method. This method gives results checking within 0.2 or 0.3 per cent.

One to two grams of sludge are weighed into a 100-cc. beaker and to this are added 50 cc. of a 10 per cent solution by volume of freshly distilled or water-white aniline oil in boiling chloroform. A vigorous reaction takes place, forming aniline sulfate, the chloroform dissolving the tar, esters, sulfonic acids, and dialkyl sulfates. The mixture is carefully stirred to insure a complete reaction with the sludge. By treatment at the boiling point of the chloroform the aniline sulfate comes down in a form that filters readily through a Gooch crucible. The asbestos is suspended in chloroform instead of water, for obvious reasons. The beaker is carefully policed and washed with either chloroform or ethyl ether, the washings being run through the same Gooch, which is then washed with chloroform or ether until the washings are colorless. Air is sucked through to evaporate the solvent and then 100 to 200 cc. of boiling water are poured through to dissolve the aniline sulfate completely. Small specks of carbon or insoluble tar are usually left on the asbestos.

The filtrate and washings are then made up to 1 liter and an aliquot is taken and titrated with 0.5 *N* bromide-bromate solution for aniline content, from which the sulfuric acid can be calculated; or the acid may be determined gravimetrically as barium sulfate.

The formula for calculating the sulfuric acid content by titration of the aniline is as follows:

$$\frac{(\text{cc. KBr.KBrO}_3\text{ soln.}) \times F \times 0.0155 \times (\text{cc. aniline sulfate soln.}) \times 0.526 \times 100}{(\text{wt. sludge taken}) \times (\text{cc. sample titrated})}$$

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[3] Pilat and Starkel, *Petroleum Z.*, 6, 2177 (1911).

where F = normality factor of bromide-bromate solution
0.0155 = grams of normal aniline per cubic centimeter bromide-bromate solution
0.526 = gravimetric factor of aniline to sulfuric acid

The bromide-bromate solution is made up with 14 grams potassium bromate and 50 grams potassium bromide per liter and standardized against a known weight of pure aniline. One mol of aniline requires 3 mols or 6 equivalents of bromine.

Following is a typical example of the results obtained by this method:

Sludge (1.83 grams) was treated with 50 cc. of a solution of chloroform containing 5 cc. of aniline. The precipitated sulfate was washed thoroughly with chloroform dissolved in boiling water and made up to 1 liter. The 20-cc. aliquot taken required 5.5 cc. of 0.484 N potassium bromide–bromate solution. Calculating by the formula, we find

$$\frac{5.5 \times 0.484 \times 0.0155 \times 50 \times 0.526 \times 100}{1.83} = 59.2 \text{ per cent } H_2SO_4$$

Three determinations showed these checks: 59.2, 59.3, and 59.2 per cent. Between 30 minutes and an hour is required to make a determination.

Experiments to Check Validity of Method

Objections have been made to this method on the ground that the aniline would react to form a precipitate insoluble in chloroform, not only with the free sulfuric acid, but also with other materials present in the sludge, such as the alkyl sulfuric acids, the sulfonic acids, and neutral sulfates. In order to verify the validity of this method and that aniline gave a precipitate insoluble in chloroform on reacting only with the free sulfuric acid, the following experiments have been carried out:

(1) Taking the possible sulfuric acid derivatives in order, the writer has found that the aniline salts of the alkyl sulfuric esters are soluble in chloroform. This was shown by the following procedure: A sample of sludge was heated under reflux with chloroform for 15 minutes; the suspended matter was allowed to settle for 1 hour and then separated by decantation. The residue was washed with chloroform by decantation until the washings were colorless. The chloroform extract was then filtered through powdered calcium carbonate to remove any free sulfuric acid in suspension. This may have neutralized some of the alkyl esters, but it is hardly probable. On adding to the filtrate a quantity of freshly distilled water-white aniline and refluxing for 5$^3/_4$ hours, no precipitate was formed, indicating that there was no free sulfuric acid in the filtered solution. The solvent was then evaporated, water and hydrochloric acid added, the whole was refluxed 2 hours and then steam-distilled to remove the hydrolysis products of the acid esters. The residue was then make alkaline and the aniline removed by steam. The residual solution was again acidified with hydrochloric acid, filtered, heated to boiling in a moderate volume of water, and hot barium chloride solution added. A heavy cloud of barium sulfate was thrown down. This shows that the aniline salts of the alkyl sulfuric esters are soluble in chloroform.

In another experiment using the same sludge it was found that the hydrolysis of these esters was quite slow, since 15 minutes' refluxing produced only a turbidity with barium chloride solution. This also seems to show that Method A, precipitation with barium chloride, is not very much in error since the time of manipulation is very short.

(2) Another experiment was made to check the above observation, in which the sludge was treated with aniline in boiling chloroform and then filtered. Sulfuric acid was carefully added to the filtrate until no more precipitate was formed. The precipitate was found to be aniline sulfate. The filtrate, then, should contain only the aniline salts of the acid esters and any neutral sulfates that were present in the sludge. An excess of sulfuric acid was added and the mixture refluxed for several hours. No further precipitate formed. The chloroform was evaporated and water added. This was refluxed, filtered, and then steam-distilled. A quantity of oily material distilled over, but no attempt was made to identify it as it was probably alcohol. The residue was then made alkaline and again steam-distilled. Aniline was present in the distillate. This also shows that the aniline formed a compound with the acid esters soluble in chloroform.

(3) Sulfonic acids were found to form salts with aniline which were soluble in chloroform. There is some evidence in the literature[4] that aniline reacts with neutral sulfates to form aniline sulfate. This reaction did not occur at temperatures below 140–160° C. (285–320° F.) and required at least 6 hours' heating. This the present writer has found to be true. That the reaction does not take place under the conditions of the procedure described above is shown by the following experiments: A sample of sludge was treated with aniline in boiling chloroform. The precipitated sulfate was filtered off and the filtrate allowed to stand overnight. No further precipitate appeared. It was then refluxed for 2$^3/_4$ hours. Still no precipitate was formed. The chloroform was then evaporated and the residue heated to 140° C. (285° F.) for 4 hours. A very slight amount of solid separated out, but it was too small to analyze.

(4) It was shown by the following experiment that the reaction with aniline to form a precipitate was immediate and that refluxing for a long period did not affect the results. The reaction between the neutral sulfates, if any were present, and the aniline did not form any additional precipitate under the conditions of this procedure.

	REGULAR TREATMENT 3 MINUTES' HEATING	SPECIAL TREATMENT 2 HOURS' HEATING
Weight of sludge, grams	1.549	2.01
Volume of 0.5 N $KBr.KBrO_3$ soln. required for sample taken, cc.	4.5	5.9

Calculating to free sulfuric acid shows 59.2 per cent present by the regular treatment and 59.1 per cent in the special treatment.

These experiments indicate, therefore, that, although the aniline may react with the neutral sulfates under certain conditions, the rate is so slow that it can be neglected under the conditions of the method described.

(5) The precipitate formed by the aniline on the sludge was proved to be aniline sulfate, as follows: Sludge (1.78 grams) was treated with boiling chloroform containing 10 per cent aniline and filtered through a weighed Gooch crucible. After being washed with ether until the washings were colorless, the Gooch and contents were dried at 46° C. (115° F.) The precipitate weighed 3.03 grams. One hundred fifty cubic centimeters of boiling water were poured through the Gooch in 25-cc. portions until no sulfuric acid showed in the washings and the Gooch was again dried and weighed. The insoluble matter weighed 0.045 gram. Therefore, the weight of sulfate was 2.98 grams. The washings were made up to 1 liter, an aliquot taken, and the aniline content determined by titration with 0.5 N potassium bromide–bromate solution.

	Per cent
Aniline found	65.3
Aniline calcd. (aniline sulfate)	65.5

Another aliquot of the sulfate solution was treated with barium chloride and the barium sulfate weighed.

	Per cent
Sulfuric acid found	35.0
Sulfuric acid calcd.	34.5

In view of the evidence given above, it appears that the only precipitate formed on the addition of aniline in chloro-

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[4] Heusler and Dennstedt, *Z. angew. Chem.*, **17**, 204 (1904).

Comparison of Results Obtained by Various Methods

	Method	Sludge I Per cent	Sludge II Per cent	Sludge III Per cent
A	$BaSO_4$	58.4	50.6	59.5
B	Isolation	55.1	49.0	..
C	Titration	58.6	50.0	..
D	Temperature rise	..	..	60.6
E	Aniline	58.7	50.4	59.2

form solution to light-oil sludge is pure aniline sulfate and only the free sulfuric acid in the sludge reacts.

Acknowledgment

Acknowledgment is made to the Magnolia Petroleum Company for permission to present the results of this work.

Chart of Indicators Useful for pH Measurements[1]

Clarke E. Davis and Henry M. Salisbury

National Biscuit Company, 85 Ninth Ave., New York, N. Y.

The accompanying chart of the indicators has been found to be very useful in quickly judging the pH of solutions and of spot tests on dry materials. It was compiled by noting the color produced when 4 drops of each indicator were added to 10-cc. sets of the buffer solutions recommended by Clark and Lubs.[2]

Most of the indicators are of the Clark and Lubs[3] series with the addition of a few others in common use. The one called Combination A is a 50-50 mixture of methyl red and bromothymol blue that has been found very useful because of its wide range in color changes from pink at pH 4.8 through orange, yellow, green, and finally blue at pH 7.4. Bromocresol green as suggested by Cohen[4] has been found to be very useful over its range.

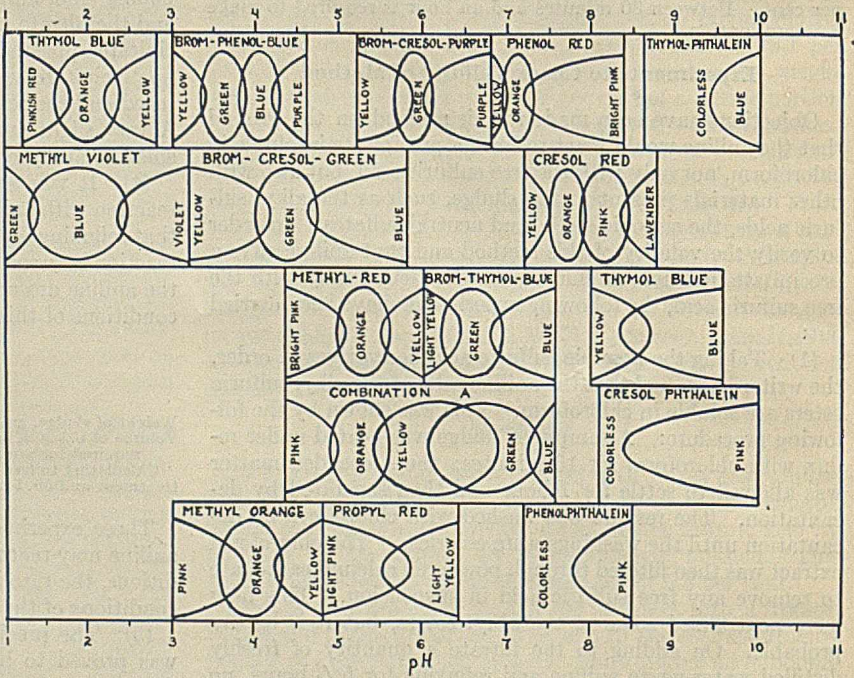
The parabolas and ellipses are used in this chart to show, by their overlapping, the blending of one color with another. Diminution or increase in color strength is shown by a decrease or increase of the vertical width of the parabola or ellipse.

The indicators were made up as shown in the table.

In using this chart to test solutions, 4 drops of the indicator are added to 10 cc. of the solution and the color is then compared with the colors noted on the chart. When used for a spot test on dry material only a very small amount of the indicator is applied directly to the material under examination and reference made to the chart after a moment or so.

Indicator	Concn. of Soln. Per cent	Solvent	pH Range
Methyl violet	0.10	1% alcohol	1.0 to 3.2
Thymol blue (acid range)	0.04	Water	1.4 to 2.8
Bromophenol blue	0.04	Water	3.0 to 4.6
Methyl orange	0.02	Water	3.0 to 4.8
Bromocresol green	0.02	Water	3.2 to 5.8
Methyl red	0.02	60% alcohol	4.4 to 6.0
Propyl red	0.02	60% alcohol	4.8 to 6.4
Bromocresol purple	0.04	Water	5.2 to 6.8
Bromothymol blue	0.04	Water	6.0 to 7.6
Phenol red	0.02	Water	6.8 to 8.4
Cresol red	0.02	Water	7.2 to 8.8
Phenolphthalein	1.00	95% alcohol	7.8 to 8.5
Thymol blue (alkaline range)	0.04	Water	8.0 to 9.6
Cresolphthalein	0.02	95% alcohol	8.4 to 10.0
Thymolphthalein	0.20	95% alcohol	9.4 to 10.0

Where possible, the use of several indicators is advised in order to give a more accurate judgment of the pH. In some parts of the pH range the pH can be judged with an accuracy of ±0.2. The operator's accuracy can also be increased by the use of buffer solutions for comparison.



Electrical measurements on unknowns followed by the use of indicators will also help the operator to judge the finer shades of color.

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[1] Received December 12, 1928. Contribution No. 11 from the Research Laboratory of the National Biscuit Company.

[2] Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

[3] Clark and Lubs, *J. Bact.*, **2**, 1, 109, 191 (1917).

[4] Cohen, U. S. Pub. Health Service, *Pub. Health Repts.*, **38**, 199 (1923); **41**, 3051 (1926).

Errors in Nitric Acid Figures

Editor of Industrial and Engineering Chemistry:

A mistake in the correct amount of fuming nitric acid to use in the Carius determination of halogens and sulfur has been carried into recent editions of analytical chemistry. This mistake renders this determination dangerous.

Corrections may have been issued on these, but a reminder to check your books, cross out the incorrect and write in the correct amount, may save time and accidents.

Fresenius, "Quantitative Chemical Analysis," Vol. II, John Wiley & Sons, 1915, on page 118 states that "to avoid explosions, 4 grams of nitric acid per 50 cc. of bomb should under no circumstance be exceeded." Three to 5 cc. of fuming nitric acid are ample for all determinations.

Scott, "Standard Methods of Chemical Analysis," 4th ed., Vol. I, p. 145, D. Van Nostrand Co., recommends 30 cc. of 96 per cent nitric acid.

Treadwell-Hall, "Quantitative Analysis," 3rd ed., Vol. II, p. 326, John Wiley & Sons, recommends 40 cc. of 1.5 sp. gr. nitric acid.

The writer has not checked other editions or books for this error.

A. W. Beshgetoor

The Dow Chemical Company
Midland, Mich.
January 4, 1929

A Utility Shaking Machine[1]

W. M. Shaw

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IN THE course of extended investigations upon the absorption properties of soils and minerals, the importance of continuous and prolonged agitation became evident. The Wagner shaking machine was the only device available for this purpose. The limited carrying capacity of this machine has proved a great hindrance to the expeditious execution of an extensive experimental program. The need for a shaker with a large carrying capacity therefore became imperative. Such a machine was designed and constructed in a local shop. This machine has now been in continuous operation for nearly two years and has given perfect satisfaction. It possesses two distinct merits in that it is adaptable to different types and sizes of containers and it is of simple, rugged, and inexpensive construction.

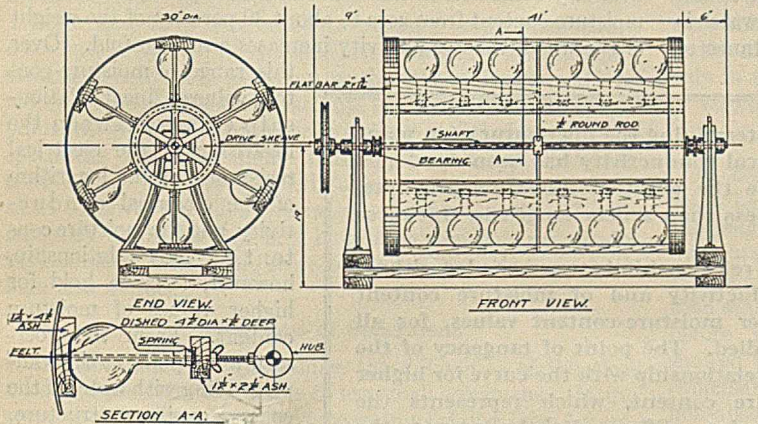

Figure 1—Diagram of Shaker

Description

The shaker (Figure 1) consists essentially of a system of trays and overhead clamps arranged radially about the shaft every 60 degrees, as shown in the end-view drawing. Each tray accommodates six containers. The six trays are held together rigidly by two outer steel bands, which are in turn connected permanently with the shaft by means of six $^1/_2$-inch rods at each end of the machine. The overhead clamps have six sockets concentric with the dished depressions on the trays. Each socket carries a 2-inch spring, one-half of which extends beyond the face of the clamp. The clamps are provided with three notches to fit over the rods and when not in use are held in place loosely by a wooden block and metal strip screwed on and fitting over the middle notch. (Figure 2) The dimensions given in the drawing are especially designed for the use of liter Florence flasks as the maximum size of container and all sizes below it. For larger containers the diameter of the machine would need be increased.

Operation

For greater convenience in loading, the trays are set each in turn at an angle of 30 degrees above the horizontal position and dipping inward. The machine is steadied in position by means of a notched break that swings out and directly under the flat bar and engages a protruding nut under each tray. (See rear end in Figure 2.) The winged nuts are run up or down to permit the proper adjustment of the overhead clamp. The preliminary adjustment of the clamp is such as to permit easy insertion of the flask and to cause about 50 per cent compression of the springs. The flask is inserted by taking hold of the neck with the right hand and placing the stopper squarely against the spring pressed sufficiently inward to permit the bottom end to swing easily into its seat, the left hand being used to steady the body of the flask. Experience has shown that this technic eliminates all chance of breakage during loading and unloading. The pressure of the spring is sufficient to hold the flasks in place only during the loading. Therefore, as soon as each tray is loaded, the outer nuts are screwed down until the stoppers just engage the sockets; the inside nuts are then screwed up tightly against the clamp. When all the trays are thus loaded, the agitation may be started and continued indefinitely. The shaker may be propelled by either a small electric or water motor with intervening countershaft to reduce the speed to about 45 revolutions per minute.

The above procedure is followed in reverse order to unload the machine. When the load is not the full capacity of the machine, it should be distributed to give proper balance. Extra overhead clamps may be provided for extreme ranges in size of neck of containers, but clamps with sockets to fit No. 7 rubber stopper have served all purposes. For containers with extra broad necks the pressure of springs and clamp is sufficient to hold them in position.

Uses

The shaker can be used:

(1) To obtain equilibrium in absorption studies with solution and solid phase systems; (2) to deflocculate soils for mechanical analysis; (3) to flocculate precipitates like ammonium phosphomolybdate; and (4) to carry out solubility studies.

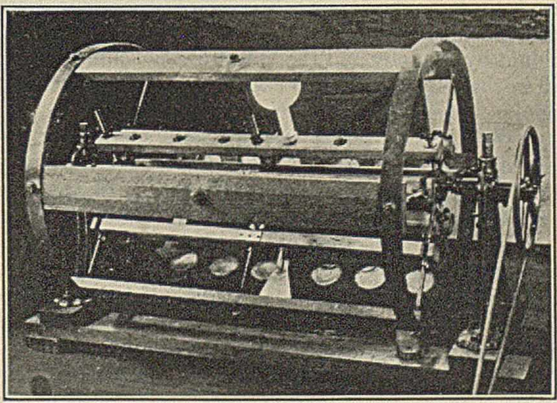

Figure 2—The Utility Shaker Partly Loaded

Acknowledgment

Acknowledgment is made of the interest shown and collaboration extended by the makers of this machine, the W. J. Savage Co., of Knoxville, Tenn.

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[1] Received October 18, 1928.

The Fiber-Saturation Point of Wood as Obtained from Electrical Conductivity Measurements[1]

Alfred J. Stamm

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A method for determining the fiber-saturation point of wood by electrical conductivity has been developed so as to minimize the effect of moisture gradients. Small specimens less than a fiber length in thickness were used.

The same linear relationship between the logarithms of electrical conductivity and of moisture content exists at the lower moisture-content values, for all of the species studied. The point of tangency of the line showing this relationship with the curve for higher values of moisture content, which represents the fiber-saturation point, differs slightly among the species, and the upper part of the curve does also.

No perceptible deviation between the results for green redwood and for resoaked redwood was observed.

Removing the extractives of redwood raises its fiber-saturation point.

Fiber-saturation values obtained by other means are given for comparison with those obtained by the electrical conductivity method.

ALTHOUGH it has long been known that variations in moisture content below a certain limit affect many important physical properties of wood, yet the determinations of this limit, called the "fiber-saturation point," have been few in number and questionable in accuracy. When it is considered that the strength of wood is greatly affected by absorbed water and not at all by free water, that the swelling and shrinking of wood are due entirely to absorbed water, and that in drying wood the absorbed water is the more difficult to evaporate, the practical importance of accurate determinations of the limit of absorption—the fiber-saturation point—is at once evident.

Fiber-Saturation Point

The term "fiber-saturation point" was first used in connection with wood to designate the moisture content below which further reduction of moisture caused changes in the strength of the wood. The absorption of water by wood belongs to the same general class of phenomena as the absorption of various liquids by different fibrous materials and elastic jellies, and it very closely resembles the absorption of water by other cellulosic fibers. In these other absorptions the terms "limit of the absorption" of the liquid by the jelly and the "limit of the solubility" of the liquid in the jelly are used to express exactly the same conception as "fiber-saturation point."

Expressed in the terms that pertain specifically to its cellular structure, the saturation point of a wood fiber may be considered as the state in which the cavity of the fiber is entirely free from moisture and its wall is saturated throughout. Shrinkage of a drying fiber begins at this point, its strength properties begin to change, and its electrical conductivity varies at different rates above and below the point. Accordingly the fiber-saturation point of a green piece of wood losing moisture may be defined provisionally as the moisture condition of the piece at which there is a break in the variation of the rates of change of its physical properties with change in moisture content of the piece. The fiber-saturation point may then be obtained by determining the point of break in such rate of change for any of the physical properties concerned. Non-uniformity in the moisture condition of a piece of wood of tangible size, which always obtains to some extent, affects the accuracy of the determination, however, and consequently different methods of determination have different degrees of accuracy.

The term "fiber-saturation point," as used throughout this discussion, will accord with the preceding provisional definition.

Relation between Conductivity and Moisture Content

The electrical resistance of wood, as the author[2] has already pointed out, changes at a tremendous rate with changes in moisture content below the fiber-saturation point. From an oven-dry condition to the fiber-saturation point, a change in moisture content from zero to about 30 per cent of the weight of the wood, the conductivity increases a million fold. Over this range of moisture-content values a linear relationship exists between the logarithm of the electrical resistance, or the logarithm of the electrical conductivity, and the moisture content.[3] This relationship, however, fails to hold for higher values of moisture content. From the fiber-saturation point to the complete filling with water of the coarser capillary structure, which in some cases is more than 200 per cent moisture content on the basis of oven-dry wood, the electrical conductivity changes less than fifty fold. The diminution of the rate of increase of electrical conductivity with an increase in the moisture content above the fiber-saturation point provides a method of determining the moisture content corresponding to this point.

Myer and Rees[4] have used this method of determining the fiber-saturation point of wood. They unfortunately used large specimens of wood, cylinders 2 inches long and 1 inch in diameter, a procedure that not only increases the difficulty involved in experimentation, but tends to decrease the accuracy of the measurements as well because of the unavoidable moisture gradients that result during the drying of the specimens. They also used a somewhat different method of obtaining from their curves the points corresponding to fiber saturation, which will be described later.

Effect of Uneven Distribution of Moisture

On account of the parabolic form of the function expressing the relationship between electrical conductivity and moisture content, it is essential that the moisture distribution of the test specimens be uniform for each measurement. If the specimens are conceived to be made up of thin laminations perpendicular to the path of the current, the electrical resistance of a specimen will be the sum of the individual resistances of the respective hypothetical laminations. Then, since the resistance of wood varies in a parabolic manner with change in moisture content, the total resistance will be at a minimum when the moisture distribution is uniform. For example, with a specimen having a 4.5 per cent moisture gradient and moisture-content values of 9.5 per cent at the center, 5.0 per cent at the surface, and an average of 8.1 per cent, the experimentally determined value of electrical resistance would be 60 per cent above the value correct for a uniform distribution of moisture; this excess in resistance corresponds to a deviation in moisture content of 0.8 per cent.[5] Such a deviation increases at a tremendous rate with increase in the slope of the moisture gradient. The nature of the gradient—that is, whether it is of the drying or the absorbing type—will also affect the results; an absorbing gradient is likely to cause more inaccuracy than a drying one of similar severity. The figures of this example thus illustrate to some extent the great importance of attaining uniform moisture-content conditions for investigative purposes.

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[1] Received December 10, 1928.

[2] Stamm, Ind. Eng. Chem., **19**, 1021 (1927).

[3] Hasselblatt, *Z. anorg. allgem. Chem.*, **154**, 375 (1926).

[4] Myer and Rees, New York State College of Forestry, *Tech. Bull.* **26**, No. 19 (1926).

Myer and Rees attempted to attain a uniform moisture distribution by holding the specimens for 2 days in sealed jars after each increment of drying, so that the moisture might be redistributed. Moisture gradients below the fiber-saturation point will gradually disappear as a result of diffusion when the specimens are held under non-drying and non-absorbing conditions. The process of diffusion, however, is extremely slow. Above the fiber-saturation point no such diffusion tendency exists, so that in a large specimen it is practically impossible to attain moisture-content values that are both high and uniform.

Dimensions of Specimens

The simplest way to minimize the difficulties of the electrical conductivity method is to use small specimens. In the research now reported, transverse sections of disk form 1.0 cm. in diameter and 0.2 to 0.35 cm. thick were used. As the thickness of these disks is less than the average fiber length, practically all of the fibers are cut across at least once, thus exposing nearly all of the fiber-cavity capillaries (lumina) to the drying conditions of the surface of the wood. Such exposure not only minimizes the gradients set up in the specimens, but also greatly reduces the time for adjustment of the moisture distribution after a period of drying that has carried the moisture content below the fiber-saturation point.

Apparatus

The apparatus used consisted of a portable suspension galvanometer (Leeds and Northrup No. 2420-C), an Ayrton shunt, a contact clamp for holding the wood sections, a key switch, and a source of direct current consisting of a single dry cell of 1.5 volts for the high-moisture-content readings, and a 90-volt battery for the low-moisture-content readings. The shunt was connected across the galvanometer and in series with the source of current, the wood contact clamp, and the key switch.

The resistance of the shunt was varied so as to allow the entire current carried by the test specimen and different fractional parts of it, as desired, to flow successively through the galvanometer; these galvanometer currents had the relative values of 1.0, 0.1, 0.01, and 0.001. The settings of the variable shunt, together with the two different applied potentials, made it possible to cover a range in conductivity of more than 100,000 times.

The clamp for holding the small wood specimens consisted essentially of a rubber-tubing screw clamp (Hofmann type) mounted on a wooden panel. A lead contact disk, 1.0 cm. in diameter and 0.2 cm. in thickness, having an appropriate electrical connection and mounted on mica insulation, was fastened over the bottom arm. The specimen was placed on this contact disk, a similar lead disk was placed on top of the specimen, and the clamp with an electrical connection on its head was then screwed down securely on the pile of lead and wood. When the pressure was sufficient to give a good contact between the disks and the specimen, a negligible deviation in the resulting current was obtained on reclamping.

Though a current flow method rather than a zero flow method was used, the effect of possible polarization was found to be negligible because of the extremely low conductivities measured, maximum values being of the order of the conductivity of distilled water.

Specimens Studied

The heartwoods of eight different softwoods and one hardwood were studied. All specimens had been previously air-dried, with the exception of the redwood. The specimens were therefore saturated by soaking in distilled water, prior to the measurements, until they sank. They were extracted only in the cases designated, and then with either hot water or alcohol.

Experimental Procedure and Results

In beginning the experimental work, after the adhering water had been shaken from the specimen under investigation, the weight of the specimen in a small sealed weighing bottle was obtained, and its electrical conductivity was determined. It was allowed to dry in the air for 5 to 10 minutes and was then sealed in the weighing bottle for 15 minutes to 18 hours before the next measurement was made. Experiments showed that for these small specimens 2 hours or so was a sufficient time to hold the specimens under non-drying and non-absorbing conditions in order to insure any possible adjustment in the distribution of the moisture taking place.

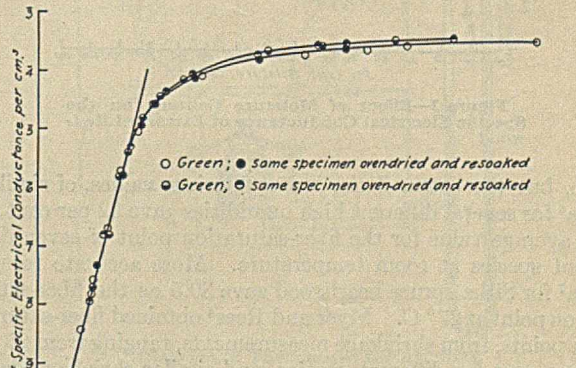

Figure 1—Effect of Moisture Content on the Specific Electrical Conductance of Non-Extracted Redwood

Figures 1 and 2 show graphically the results for redwood. The percentage moisture-content values calculated on the basis of oven-dry wood are plotted as abscissas, and the logarithms of the specific conductance of the wood are plotted as ordinates. Both curves show a linear relationship between the moisture content and the logarithm of the electrical conductivity below about 30 per cent moisture content. and above this point an increasing deviation from this relationship with increasing moisture content. All of the species studied gave practically identical lines for the linear-relationship portion. The only real variations between species were slight differences in the location of the point of tangency of the straight line and the curve, and slight differences in the nature of the curve itself.

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[5] A more extensive description of the effect of moisture gradients upon the electrical resistance is discussed in another paper by the author to appear later.

Figure 1 presents the results for two specimens of green redwood and their corresponding resoaked values after oven-drying. The data indicate slight but consistent differences between two specimens of the same kind of wood, although the differences are practically within the range of experimental error. The data also indicate that complete drying has no perceptible permanent effect upon the moisture content–electrical conductivity relationship.

Fiber-Saturation Points Determined by Different Means

The point of tangency of the curved and the straight-line portions of each graph marks the moisture-content limit for which the initial moisture content–electrical conductivity relationship is valid. This point corresponds closely with the fiber-saturation point of wood as obtained by several other means.

The moisture content of wood in equilibrium with 100 per cent relative humidity has never been accurately determined because of the tremendous effect of slight changes in temperature, but the extrapolation, to equilibrium values, of similar data[6] for several different high humidities gave 32 per cent as the average value for the fiber-saturation point of seven different species at room temperature. More accurate recent data[7] for Sitka spruce heartwood gave 30.5 as the fiber-saturation point at 27° C. Myer and Rees[4] obtained fiber-saturation points, from shrinkage measurements, ranging from 25 to 39 per cent for different species, and similar shrinkage data of the U. S. Forest Products Laboratory[8] give fiber-saturation points for Sitka spruce, by radial shrinkage, of 28 per cent and, by tangential shrinkage, of 30 per cent. Though such measurements give the correct order of magnitude of the fiber-saturation points, they are complicated by the fact that the shrinkage is not entirely transmitted to the external dimensions of a block of wood. The fact that determinations of the fiber-saturation point by the shrinkage method often give different values for radial and for tangential determinations indicates an inherent lack of accuracy in the method; for the species under discussion (Sitka spruce), however, the average of the radial and the tangential determinations (28 and 30) is exactly equal to the electrical conductivity determination (29.0). Values for the fiber-saturation point comparable to all of the preceding were obtained by Tiemann,[9] of the U. S. Forest Products Laboratory, by means of mechanical strength studies. The mechanical strength properties of wood are not affected by drying until the fiber-saturation point is reached. Below this value of moisture content most of the strength properties increase with a decrease in moisture content. Crushing strength data secured by Tiemann gave fiber-saturation points, for six species at room temperature, varying from 20 to 35 per cent moisture content. More recent data of this laboratory indicate the fiber-saturation point of Sitka spruce by means of four different strength measurements—namely, modulus of rupture, stress at elastic limit in bending, maximum crushing strength parallel to the grain, and the elastic-limit stress compression perpendicular to the grain. The fiber-saturation points thus obtained vary from 25 to 27 per cent.

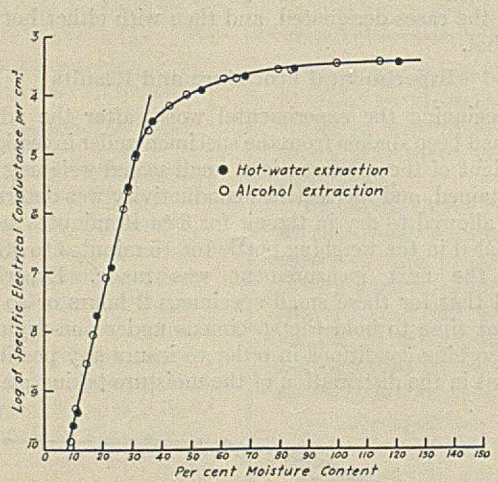

Figure 2—Effect of Moisture Content on the Specific Electrical Conductance of Extracted Redwood

Table I shows the four distinct physical properties of wood—namely, hygroscopicity (measured by relative humidity–moisture content equilibrium values), shrinkage, strength, and electrical conductivity—that are dependent upon the moisture content. The fiber-saturation values as determined by the first two are limiting values—that is, values of moisture content for 100 per cent relative humidity and 0 per cent shrinkage. The last two involve phenomena that exist on both sides of the fiber-saturation point. The values given for the fiber-saturation point represent in each case the moisture content corresponding to the limit of validity of the straight-line relationship between the amount of water imbibed by the cell wall ("bound" water) and the magnitude of the other property. The agreement of the values determined by the several methods is as good as can be expected, not only because different specimens were used in each case, but because of the effect of other incompletely controllable variables upon the properties studied.

Table I—Fiber-Saturation Point of Sitka Spruce at Room Temperature as Determined at the U. S. Forest Products Laboratory by Several Different Methods

METHOD	FIBER-SATURATION POINT
	Per cent
Relative humidity–moisture content equilibrium	30.5
Shrinkage:	
Radial	28
Tangential	30
Strength:	
Modulus of rupture	27[a]
Stress at elastic limit in bending	25[a]
Maximum crushing strength parallel to the grain	27[a]
Elastic limit stress compression perpendicular to the grain	27[a]
Electrical conductivity	29.0

[a] Indicated values.

Table II—Fiber-Saturation Points of Wood at 24° to 27° C. as Determined by Electrical Conductivity

SPECIES OF WOOD HEARTWOOD SPECIMENS	CONDITION OF WOOD	FIBER-SATURATION POINT
		Per cent
Redwood	Green	29.5
Redwood	Resoaked	29.5
Redwood	Hot-water extracted	31.0
Redwood	Alcohol extracted	31.0
Sitka spruce	Resoaked	29.0
Alaska cedar	Resoaked	28.5
Western red cedar	Resoaked	30.0
Western hemlock	Resoaked	30.5
Western yellow pine	Resoaked	30.0
Red fir	Resoaked	30.0
Douglas fir	Resoaked	30.5
Yellow poplar	Resoaked	31.5

The electrical conductivity method presented in this paper shows the least complication, by other factors, of the four methods mentioned for determining the fiber-saturation point. Table II gives the fiber-saturation point obtained by this means for several different species of wood. As might be expected, the values indicate that the extractives of redwood are less hygroscopic than the wood substance itself, for removing the extractives raises the fiber-saturation point. All of these values for the fiber-saturation point are higher than those given by Myer and Rees.[4] Part of the difference between these values and those of Myer and Rees may be due to the difference in the methods used for locating the point on the graph that represents the fiber-saturation point. Myer and Rees determined the points of maximum curvature of their graphs, whereas the present author determined in each case the point at which the straight-line portion of the logarithmic curve joins the curved portion—that is, the point where the relationship between moisture content and electrical conductivity commences to deviate from the relationship holding for water imbibed by the cell walls ("bound" water). Further differences between the sets of data may very well be due to the more nearly complete elimination of moisture gradients in this research than in that of Myer and Rees.

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[6] Hawley and Wise, "Chemistry of Wood," p. 286, Chemical Catalog Co., 1926; data of M. E. Dunlap, U. S. Forest Products Laboratory (1919).

[7] Loughborough, U. S. Forest Products Laboratory, as yet unpublished.

[8] "Manual for the Inspection of Aircraft Wood and Glue for the United States Navy," prepared by the U. S. Forest Products Laboratory, Navy Dept., Bur. Aeronautics (1928), p. 41.

[9] Tiemann, U. S. Dept. Agr., *Forest Service Bull.* **70**, 82 (1906); *Forest Service Circ.* **108** (1907).

A Heavy-Duty Thermostat[1]

D. F. Othmer[2]

University of Michigan, Ann Arbor, Mich.

A SIMPLE, rugged thermostat was desired to control at least 4000 watts of electrical energy and maintain the temperature of a small boiler constant to 0.02° C. for days at a time. The regulating force was the vapor pressure of the water boiling in the apparatus, but any of the more usual types of thermal expansion bulbs might be utilized as well as the bulb of a vapor-pressure thermometer. When the vapor pressure of the liquid may be used, it is preferable because thermal equilibrium is very quickly obtained.

Most heavy-duty electrical thermostatic circuits depend on two sets of heaters, one to deliver the largest part of the heat without change and the other to fluctuate with the relay. A single heating circuit is employed in this unit, and because of the design of the relay only one set of leads is necessary for both heating and operation of the relay.

The circuit is novel chiefly in its application of the double-slider Forsythe water-cooled rheostat (supplied by the Central Scientific Company of Chicago) and the single circuit, 220-volt, a. c. relay (supplied by Eberbach and Sons, of Ann Arbor, Mich.). Two 2000-watt General Electric immersion heaters were used in the original installation, although subsequently, when the unit was applied to glass flasks, coils of bare nichrome wire were used. Either type is satisfactory because of the very small thermal lag. To the pressure side of the manometer was attached a packing box through which passed an iron rod, nickel-plated and platinum-tipped. A suitable trap prevented liquid from entering the manometer. An ammeter to indicate the current supplied was inserted in the circuit as shown. In addition to the main switch, an auxiliary switch served to cut out the relay when desired.

On examining the diagram it will be apparent that the resistance on the rheostat between the two sliders is always short-circuited by the heavy copper rod on which they operate. When the relay is closed, that part of the resistance to the left of the left slider is also short-circuited, and the only part of the resistance that is still effective is that to the right of the right slider. By varying the positions of the sliders it is possible to obtain any desired value of the current flowing between the given limit for the open position and any higher value (below the upper limit) for the closed position. In practice, when a change was being made in the amount of heat supplied and the desired current intensity was not known, the two sliders were placed close together near the right of the rheostat. On the open position of the relay practically the whole rheostat was in circuit and only about 5 amperes flowed, while on the closed position the rheostat was almost entirely cut out and about 20 amperes flowed. The resistance of the heaters was 12.8 ohms, and the variation of the heat supplied was between 300 and 5000 watts. This large fluctuation was unnecessary, and from observation of the relative time between makes and breaks of the relay, the rheostat could be adjusted so that the variation was only 2 to 4 amperes. For smoothness of operation this was desirable, because there was a larger lag and fluctuation of temperature when the difference between the current flowing with relay open and closed was large than when it was small. Because of the two heavy contact points in the relay, sparking was not excessive even when the difference in intensity of current was as much as 15 amperes.

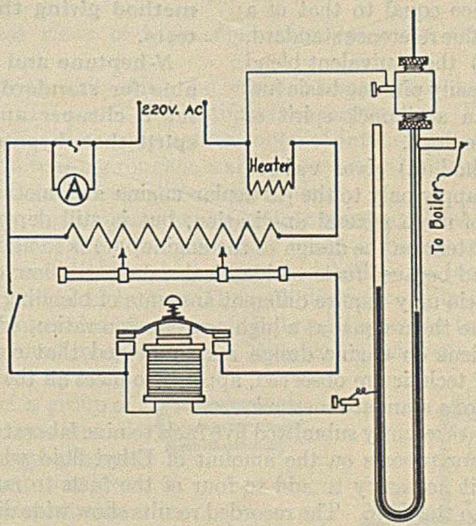

Diagram of Thermostat Connections

This type of manometer varies with change of atmospheric pressure, but the normal fluctuation of the barometer in a few hours is small compared with the vapor pressure of liquids near their atmospheric boiling point. If a very close regulation is desired over long periods of time, even this factor may be eliminated. The left arm of the manometer is connected by tubing to a bulb of a capacity large in comparison with that of the connections. This bulb (not shown in the figure) is installed in the constant-temperature boiler. A vent valve to the atmosphere is connected in the tubing to release the pressure when desired, and is opened when the thermostat is put in operation. After the desired conditions have been reached, this valve is closed and a constant pressure is maintained on the open side of the manometer, which is thus made substantially free from variations due to changes of atmospheric temperature or pressure. This auxiliary compensator is usually unnecessary, but when attached gives a manometer with a vapor-pressure thermometer on one side and a constant-volume gas thermometer on the other.

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[1] Presented as part of the paper "The Condensation of Steam" before the Division of Industrial and Engineering Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Present address, Eastman Kodak Company, Rochester, N. Y.

Standardization of Conditions for Measuring the Detonation Characteristics of Motor Fuels[1]

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Three designs of engine are described with entirely different combustion-chamber shapes and valve arrangements. Tests show that substantially equal results for antiknock value can be obtained from any of the engines if comparisons are made in terms of equivalent blends of standard spirits and provided that test conditions are suitably controlled.

The effect of each controllable variable is examined, the most important being the air-fuel ratio and, in the case of tests with the bouncing-pin indicator, the compression ratio at which comparisons are made.

The air-fuel ratio must be adjusted to give maximum pinking and, for bouncing-pin tests, the sample must be used undoped and the compression ratio adjusted to give the necessary evolution of gas in the voltameter.

Experimental errors of different methods of test have been determined and vary from ±2 to ±0.25 per cent of benzene in heptane, the bouncing-pin method giving the closest agreement between repeat tests.

***N*-heptane and pure benzene are suggested as suitable for standard reference blends, but there is need for a cheaper and more easily obtainable low-value spirit than heptane.**

Ricardo's investigations in England and the work of Midgley and Boyd in the United States have resulted, during the last seven years, in an extensive laboratory use of standard and special research engines for measuring the relative values of motor fuels.

The performance of a fuel has usually been expressed in terms of (*a*) highest useful compression ratio, (*b*) compression ratio above that of a standard spirit, (*c*) the amount of antiknock material required to make the performance equal to that of a high value reference standard, and (*d*) the equivalent blend of an easily pinking basic fuel with an antiknock spirit or metallic dope.

Method (*a*) gives values which apply only to the particular engine and method used; (*b*) is of more general application, but is still dependent to some extent on the design of the engine; (*c*) is fundamentally unsound because fuels of identical value at a low compression ratio may require different amounts of blending material to make them equal at a high compression ratio; (*d*) is least dependent on engine design and, provided that certain details of technic are observed, appears to meet all the requirements of a standard method.

Edgar[2] recently submitted five fuels to nine laboratories and asked for reports on the amount of Ethyl fluid which they found it necessary to add to four of the fuels to make each equal to the fifth. The recorded results show wide discrepancies, attributed largely to variations in the air-fuel ratio used.

MacCoull, reporting on similar tests, found equally large differences.[3] He emphasized the need for standardization of mixture strength, ignition, and other variables, and expressed the opinion that any reference scale should have some direct connection with compression ratio.

It is extremely unlikely that any one research engine, used with reasonable regard to the control of the major variables, will give contradictory values on repeat tests, but the subject has assumed such importance that further and more intensive investigation of the causes of wide divergencies between different engines is needed to enable the results from various laboratories properly to be compared.

The following account describes recent work at the Research Station of the Anglo-Persian Oil Company, and relates to the coördination of tests from three engines, two of which have compact, well-shaped combustion chambers, and the third, a combustion head designed to give as bad an arrangement as possible consistent with means for varying the compression ratio while the engine is running.

The objects of the research were fourfold:

> First, the original engine was becoming overworked and a new and smaller size had to be put into commission. It was therefore necessary to determine the relation between results of tests from the two engines.
>
> Secondly, and arising from the first, the experimental error of each method had to be carefully investigated.
>
> Thirdly, it was desired, if possible, to obtain a fairly cheap commercial engine and so to modify it that replicas could be used for fuel-testing with concordant results, irrespective of operator and geographical location.
>
> Fourthly, means had to be devised for matching new blends of fuels with known blends to a much higher degree of accuracy than seemed possible by the usual methods of test. Errors greater than 0.01 compression ratio were not permissible.

Types of Engines Used

Engine No. I was made by Messrs. J. I. Thornycroft, and has been in almost daily use since early 1924. It is in many respects similar to Ricardo's E–35 design, but has a cylinder capacity of 1025 cc. as compared with 2060 cc. The compression ratio can be varied between 3.9 and 7.6 to 1 while the engine is running, by adjusting the height of the cylinder and cylinder head in relation to the moving parts. Four overhead valves are fitted, two inlet and two exhaust, and provision is made for the use of from one to three spark plugs. One of these plugs is at one end of the cylinder diameter parallel to the axis of the gudgeon pin and the other two are placed at opposite ends of the tranverse diameter. The carburetor is a vertical modified Claudel Hobson, to which has been added a change-over device for rapidly transferring from one fuel to another. Arrangements are made for heating the inlet air to any desired temperature with an upper limit of 210° F. (99° C.). The equipment includes means for preliminary heating of the lubricating oil to insure rapid attainment of steady mechanical conditions. Water-jacket temperature, ignition advance, air-fuel ratio, and speed can all be controlled over a wide range.

Fuel consumption is measured by means of nozzle-type flowmeters feeding directly to the carburetor jet. The meters are regularly checked, and their use enables the effects of feed changes to be observed without the delay unavoidable when the time of flow of a measured volume has to be taken.

Power output and mechanical losses are determined with a floating field dynamometer.

Engine No. II was designed and manufactured by Messrs.

[1] Received December 1, 1928.

[2] Edgar, *J. Soc. Automotive Eng.*, **22**, 41 (1928).

[3] MacCoull, *Ibid.*, **22**, 457 (1928).

H. R. Ricardo and Company, and has been in use for about 12 months. It is of the single sleeve valve type with a cylinder capacity of 346 cc. The compression ratio can be varied from 5.4 to 11.9 to 1 by adjusting a $1^{3}/_{4}$-inch (4.4-cm.) diameter steel plug which slides in the combustion head. The lower end of the plug is recessed conically and the spark plug is fitted at the apex of the cone.

The carburetor is of the horizontal pattern without float chamber and is fitted with an adjustable jet. The general equipment is substantially the same as for engine No. I except that the lubricating oil heater is omitted and the water-cooling system is divided to separate the main jacket from the cylinder head.

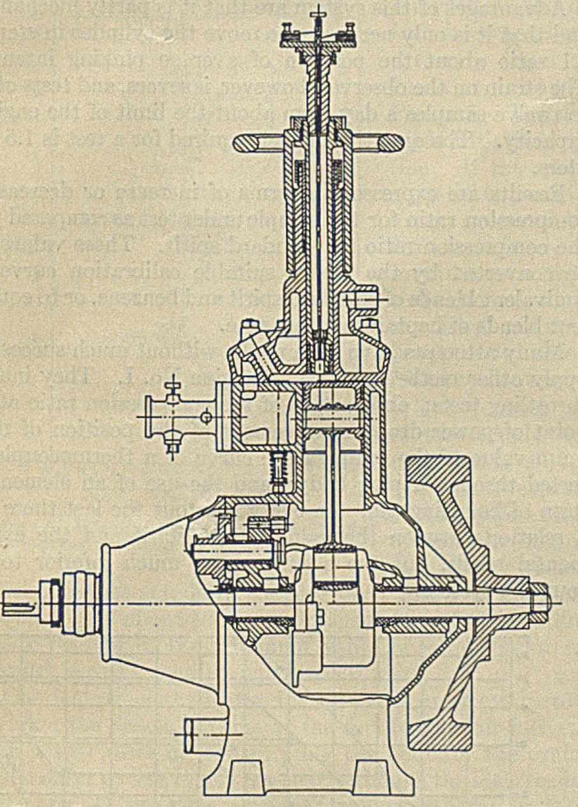

Figure 1—Armstrong Whitworth Engine with Anglo-Persian Oil Company Variable-Compression Head and Midgley Bouncing Pin

Engine No. III is a modification of a single-cylinder "B" type Armstrong Whitworth engine. Figure 1 shows a sectional arrangement. Two such units were obtained, the first being to standard design except that the crankcase venting arrangements were modified, and two extra cylinder heads were specified with compression ratios of 5.0 and 5.5 to 1 and so shaped as to avoid turbulence.

A carburetor similar to that on engine No. II was added and also the necessary air-heating, jacket-temperature control, and fuel-measuring and change-over equipment. Power output is taken by a direct-coupled dynamo, and although the absolute value is only calculable to ±2.5 per cent, changes of the order of 1 per cent can be detected. The switch gear is of standard battery-charging pattern except that a sliding rheostat has been included in the field circuit for fine control of speed. The current generated can be absorbed in a resistance or discharged to the supply mains.

It was found necessary to abandon the original magneto in favor of coil ignition, to double-key the flywheel, and to stiffen the fabric of the flexible coupling.

This engine has been in satisfactory use for routine testing of certain spirits for several months.

The second unit (engine No. III) was modified by the makers to include fixing the flywheel with nut and key on a conical-ended shaft, the flexible coupling was reënforced, and the crankshaft end play limited.

Pressure of other work made it necessary at once to run this set for a long period test of a special fuel, and during this time development work was confined to engine No. II.

Comparison between results from No. II and the first Armstrong Whitworth engine led to the belief that pinking characteristics might best be measured in an engine with a combustion space made deliberately inefficient, and with the maximum amount of flat, unsupported metal consistent with the making of a tight cylinder head to cylinder block joint.

A design was therefore prepared for a variable compression head to suit engine No. III. The sliding plug of Ricardo's design was embodied, but it was placed as far as possible from the spark plug and was reduced in diameter to $1^{1}/_{4}$ inches (3.2 cm.).

The capacities, compression ratios, and flame travel of the engines are given below.

	ENGINE No. I		ENGINE No. II		ENGINE No. III	
Capacity, cc.	1025		346		372	
Range of compression ratio	3.95 to 7.6 to 1		5.4 to 11.9 to 1		4.0 to 8.0 to 1	
	Cm.	*Inches*	*Cm.*	*Inches*	*Cm.*	*Inches*
Flame travel:						
Low ratio	11.4	4.5 (single plug)	7.24	2.85	16.5	6.5
High ratio	11.4	4.5	4.3	1.7	9.53	3.75

Sectional views of each combustion space are shown in Figure 2.

Subsequent tests with the variable-compression head on engine No. III have fully justified its construction. Pinking can be detected sharply over a range of intensities, and the mechanical running roughness always associated with pinking conditions is free from disturbing rattle.

The new head necessitated a further constructional alteration. The holding-down studs were found to be too weak to keep the joint tight at high ratios and had to be increased from $^{5}/_{16}$ to $^{7}/_{16}$ inch (8 to 11 mm.) diameter. Finally the sliding compression plug was drilled and tapped to take the diaphragm and contact unit of a Midgley bouncing pin.

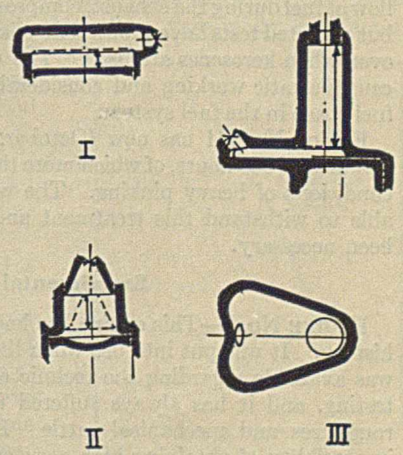

Figure 2—Combustion Spaces of Engines Nos. I, II, and III

The fuel system consists of a group of three flowmeters of special design (Figure 3) arranged to reduce to a minimum the amount of waste fuel space, the total allowance for draining a meter and clearing the pipe line after a test being only 30 cc. The cover of the fuel chamber is sealed after filling by closing the inlet and vent cocks, the only inlet for air then being through the head equalizing pipe which has an orifice close to the bottom of the meter. The spirit flows out through a measuring nozzle downwards into the carburetor feed pipe and upwards into a gage glass, the level in this glass determining the effective head on the carburetor jet and indicating the rate of flow. A flowmeter holds enough fuel for about an hour's run, and each is coupled through a needle valve to a branch pipe mounted directly under the

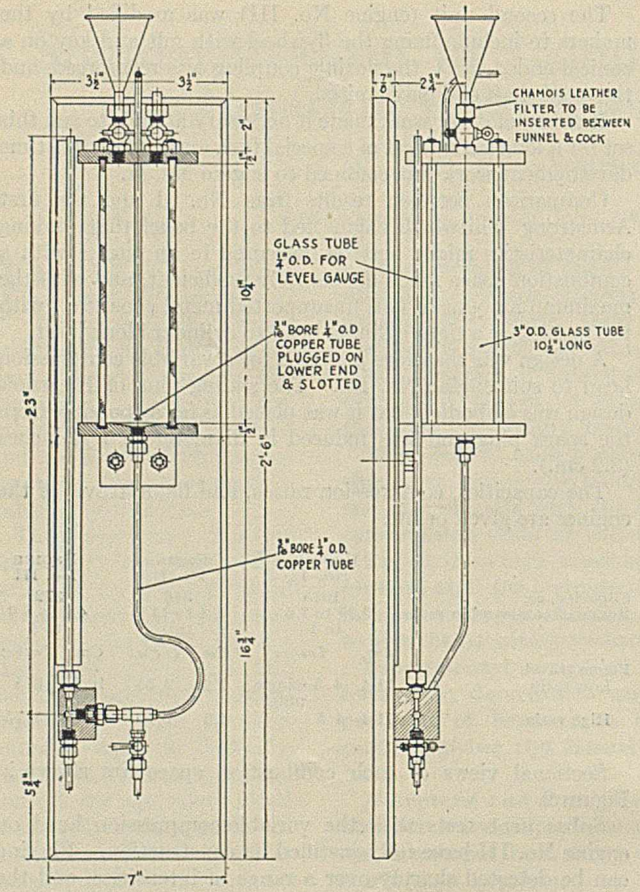
3½"
3½"
7/8"
2¼"
CHAMOIS LEATHER FILTER TO BE INSERTED BETWEEN FUNNEL & COCK
2"
1½"
GLASS TUBE ¼" O.D. FOR LEVEL GAUGE
10¼"
3/16" BORE ¼" O.D COPPER TUBE PLUGGED ON LOWER END & SLOTTED
3" O.D. GLASS TUBE 10½" LONG
23"
2'-6"
1/8" BORE ¼" O.D. COPPER TUBE
16¾"
5¾"
7"

Figure 3—Arrangement of Special Flowmeter for Armstrong Engine

carburetor jet. A fine-adjustment needle valve under the jet enables the flow to be regulated with great accuracy. Drain cocks are fitted for clearing the pipe lines and for calibration purposes. The running time required for change from one spirit to another is less than 10 seconds. Owing to the absence of a float or weir chamber, there is a slight gravity flow of fuel during the exhaust, compression, and firing strokes, but repeated tests have shown that this has no prejudicial effect even when kerosenes are used. The use of a float chamber causes erratic working and considerably increases the waste fuel space in the fuel system.

Engine No. III has now (October, 1928) been in use for upwards of 350 hours, of which more than 200 have been under conditions of heavy pinking. The working parts seem well able to withstand this treatment and no adjustments have been necessary.

Experimental

ENGINE No. I—This engine has had the most troublesome history. It was put into use when little reliable information was available regarding the technic of this branch of spirit-testing, and it has always suffered from excessive running roughness and mechanical rattle. Early tests proved the impossiblity of obtaining high accuracy merely by adjusting the head to what was judged to be a definite standard of pinking.

O. E. Mott and W. N. Hoyte, of the Research Staff of the Anglo-Persian Oil Company, conducted a long series of experiments to overcome this difficulty and finally developed what is believed to be a unique system.

When the engine is running under moderate pinking conditions a trained observer is able to detect and count the number of pinks above a certain intensity taking place in a given time. It was found that the number increased very rapidly with rise of compression ratio and that the line connecting the logarithm of the number of pinks with the corresponding compression ratios was almost straight. This line is plotted for three compression ratios (0.1 apart) at each of three ignition advances (2.5 degrees apart) with the engine running on a standard spirit, and then for two or three compression ratios and at each of the three ignition advances for the sample under test. A set of such values is shown in Figure 4. The mean value of the distances 1 to 6 in terms of compression ratio is taken as the "engine test" of the sample. Frequent repeat tests at two or three compression ratios on standard spirit are made during any series of tests.

Advantages of this system are that it is partly mechanical, and that it is only necessary to move the cylinder in steps of 0.1 ratio about the position of average pinking intensity. The strain on the observer, however, is severe, and tests of ten to twelve samples a day form about the limit of the engine's capacity. The quantity of fuel required for a test is 1.5 to 2 liters.

Results are expressed in terms of increase or decrease of compression ratio for the sample under test as compared with the compression ratio for standard spirit. These values can be converted by the use of suitable calibration curves to equivalent blends of standard spirit and benzene, or to equivalent blends of heptane and benzene.

Many attempts have been made, without much success, to apply other methods of test to engine No. I. They include throttling tests; observation of the compression ratio at the point of power drop; measurement of the position of minimum value of the temperature curve of a thermocouple inserted through a plug body; and the use of an elementary form of bouncing pin. In every case but the last there was a relation between the value of the spirit and the experimental result, but the accuracy was much inferior to the counting system.

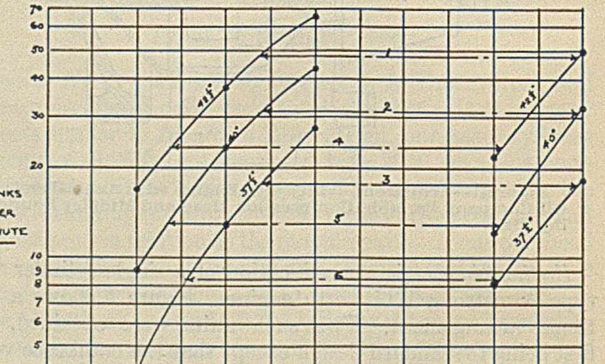

Figure 4—Counting Method of Determining Relative Value of Two Spirits

ENGINE No. II—This engine was put into service in October, 1927, and was used for some time according to the method of Ricardo. This depends on recording the compression ratios for different degrees of pinking with standard spirit and then with the sample under test. The first degree of pinking following the development of running roughness is described as "continuous slight." This is followed by "frequent moderate," "continuous moderate," "frequent heavy," etc. In a typical case the difference between two "continuous slight" positions might be 0.50 of a ratio, the difference between two "frequent moderate" 0.54, and between two "continuous moderate" 0.52. The mean, 0.52, is taken as the value of the sample in terms of compression ratios above the compression ratio for the standard spirit.

The method was satisfactory with some fuels, but disappointing with many cracked spirits owing to pronounced differences in the development of pinking from slight to heavy. It has been abandoned in favor of one standard of audibility obtained for a series of air-fuel ratios.

The fuel supply is first made weak; the compression ratio is increased to give standard audibility and the ratio noted. The mixture is then strengthened slightly and the compression ratio correspondingly reduced to keep the audibility standard. This is repeated until the minimum compression ratio position is found above which increasing values are recorded as the mixture is strengthened.

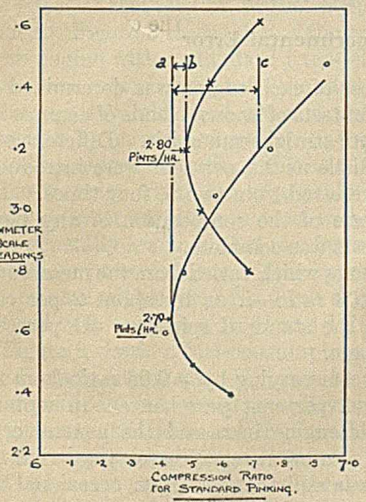

Figure 5—Effect of Feed on Highest Useful Compression Ratio for Different Spirits

Curves from two fuels are shown in Figure 5. The test is made with fixed ignition. If the spark is adjusted to give maximum power output for each feed, the minimum compression ratio point is not so marked and the experimental error is found to increase.

The "engine test" of the sample—i. e., the value of the spirit—is usually expressed as the difference between the compression ratios at *a* and *b*, *a* being for the standard reference spirit, and *b* for the sample. A quantity of about 500 cc. is sufficient for a test including a check reading of the minimum value of compression ratio against a check reading on standard spirit.

One feature of the method is that it is unnecessary to determine the absolute value of the fuel feed or air-fuel ratio. The actual rates of feed in pints per hour for the example given differ by less than 4 per cent, although the scale readings differ by 20 per cent. The change of calibration is due largely to viscosity effects.

The results, which are determined as compression-ratio differences, can be expressed in terms of equivalent blends of standard spirits if necessary.

An observer can work for longer periods without fatigue on this engine than on No. I, and there is no difficulty in testing twenty or more samples in one day.

ENGINE No. III—Three satisfactory systems have been examined on engine No. III.

An audibility method can be used as described for engine No. II and with a sample of 250 cc.

A second method is to adjust the head to give a suitable intensity of pinking on the sample fuel and to read the compression ratio. From previous calibration, this is known to correspond approximately to a certain standard blend—for example, about 10 per cent of an antiknock such as benzene in a low-value spirit. By means of the fuel change-over system already described, the engine is switched onto the 10 per cent blend and the position of correct feed—i. e., feed for maximum pinking—determined. It is then run alternately on each fuel at the feeds which give greatest pinking, and the audibilities are compared. If the blend gives a heavier intensity than the sample, a higher value blend is substituted and the test repeated until a suitable match is obtained. About 350 cc. of fuel may be needed and ten to twelve samples can be tested in a day.

The third method developed on engine No. III depends on the use of the Midgley bouncing pin in the variable-compression head.

Note—Results of tests with a variable-compression engine and a bouncing-pin indicator by Campbell, Lovell, and Boyd, IND. ENG. CHEM., **20**, 1045 (1928), emphasize the importance of making tests at the air-fuel ratio which gives maximum pinking and at a compression ratio adjusted to suit the sample under test.

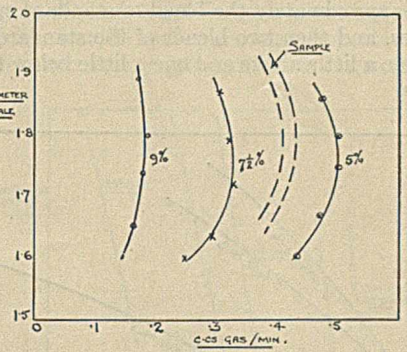

Figure 6—Bouncing Pin Tests: Relation between Gas Liberated and Fuel Feed for Various Commercial Benzene Blends and a Test Sample

It is essentially a system of matching blends. The technic is identical with that previously described as regards adjustment of feed, but the amount of gas collected in the bouncing-pin voltameter is used to indicate the position of maximum pinking and to show when a blend of standards has been obtained equivalent in value to the sample under test.

The instrument is of the latest type in which the piston originally used has been replaced by a thin steel diaphragm. A new bouncing pin had to be made to suit the length of the variable-compression plug of the engine and the weight of this pin has been kept identical with the original.

For several weeks results were negative. In some cases there appeared to be more bounce with a high-value than with a slightly lower value fuel. Several contact-gap settings and operating voltages were tried, but while changes of blend equivalent to 0.75 to 1 per cent benzene were detected, results were not always duplicable. The first really satisfactory comparisons were obtained when it was realized that it was essential to run the engine with pinking considerably heavier than that adopted for audibility tests.

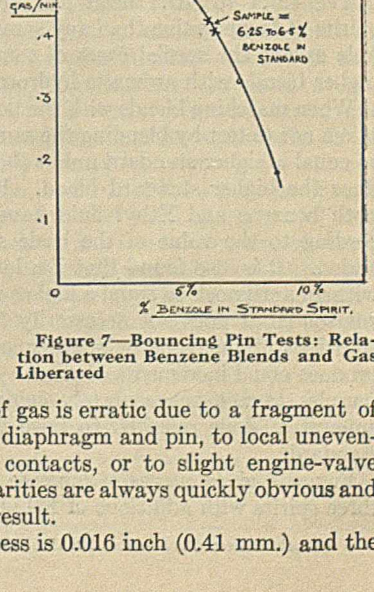

Figure 7—Bouncing Pin Tests: Relation between Benzene Blends and Gas Liberated

Some erratic results were traced to the splitting of a diaphragm, and when this was replaced the body of the variable-compression plug above it was filled with kerosene for cooling purposes. This arrangement has since run without any trouble, except that occasionally the quantity of gas is erratic due to a fragment of dirt getting between the diaphragm and pin, to local unevenness developing on the contacts, or to slight engine-valve stickiness. Such irregularities are always quickly obvious and have no effect on a test result.

The diaphragm thickness is 0.016 inch (0.41 mm.) and the exposed diameter $^{7}/_{16}$ inch (11.1 mm.). The pin weighs 31.5 grams and the contact gap is set to between 0.007 and 0.008 inch (0.18 and 0.20 mm.). The voltage across the contact gaps is 55 and the current is limited to a maximum steady value of 2.5 amperes by a series resistance. The contact gap is shunted with a 0.1 microfarad condenser. Dilute sulfuric acid of specific gravity 1.24 is used in the voltameter and a little alcohol is added to prevent the bubbles of gas from sticking to the walls of the measuring tube.

The sample to be evaluated is first tested by audibility to determine approximately the blend of standard spirits which it resembles, and then two blends of the standard spirits are made up one a little above and one a little below the value of the sample.

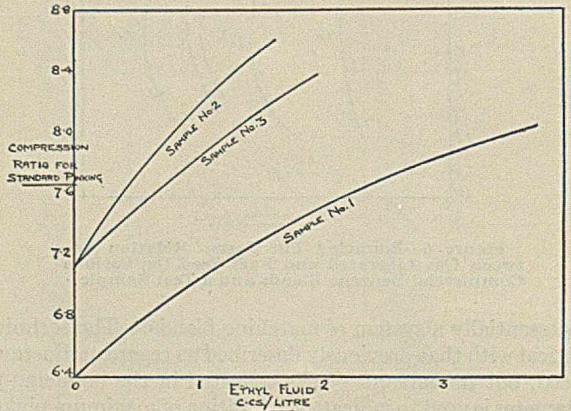

Figure 8—Effect of Ethyl Fluid on Samples of Spirit from Different Sources

The engine is then run on the lower blend and the compression ratio increased until about 0.4 to 0.5 cc. of gas is collected per minute at the fuel feed which gives the maximum volume. Figure 6 shows gas collected plotted against flowmeter reading. The mean of at least three consecutive minute readings is taken for each fuel setting.

The sample and the second blend are tested in the same way and finally check tests are made on each fuel at the feeds giving maximum gas collection. Figure 7 shows a typical test result expressed as equivalent percentage of antiknock spirit in low-value standard spirit. About a 0.5-liter sample is needed for this method and a single test may occupy an hour or more. If a number of similar samples are to be tested, the average time for a test is considerably reduced.

The 4.0:1 to 8.0:1 head has sufficient range to include spirits of higher value than any sample commercially obtainable except the special cases of some racing spirits and the higher blends with aromatic hydrocarbons or dopes.

When matching blends with the bouncing pin, care must be taken not to test by blending the sample itself with antiknock to equal a higher standard unless the object is merely to produce the higher standard blend. Ricardo[4] has shown that both benzene and Ethyl fluid have effects which vary according to the value of the basic spirit to which they are added. It is also found that if a low-value spirit is blended with an antiknock to equal a higher value spirit from a different source, it does not necessarily follow that equal further additions of the same or another antiknock to the two will produce equal increments of value. It is for this reason that samples cannot be accurately compared by measuring the amount of dope required to raise them to a common high standard.

Figure 8 gives curves of increase of compression ratio for three spirits with additions of Ethyl fluid. One cubic centimeter per liter in sample 1 raises the value by 0.63 of a compression ratio, in sample 2 by 1.04, and in sample 3 by 0.70. Sample 3 was made initially equal to sample 2 by adding commercial benzene to sample 1. If these three spirits are tested by measuring the amount of ethyl fluid required to make them match at a compression ratio of 8:1, they will be placed in the order 2, 3, 1, the required additions being 0.82, 1.28, and 3.65 cc. per liter, respectively. At 7.12:1, samples 2 and 3 are equal and are better than sample 1 by 1.2 cc. of Ethyl fluid per liter.

The same effect is noticed with proknock substances. Thus the addition of 0.1 per cent of amyl nitrite reduces the value of sample 1 by 0.3 of a compression ratio and the value of sample 2 by 0.4 of a compression ratio.

Experimental Error

The experimental error of each engine was determined by making a large number of tests of known blends of commercial benzene and a standard straight-run spirit. Differences in benzene content of as little as 2.5 per cent were introduced and every sample was retested from two to four times. The observers were not aware of the composition of any blend until the entire set of tests was complete.

Engine No. I gave results which varied from the mean curve by not more than ±0.03 ratio—i. e., by about 2 per cent commercial benzene in the standard spirit, or ±1 per cent pure benzene in *n*-heptane.

Engine No. II gave tests varying by ±0.06 ratio from the mean—i. e., by about ±2 per cent pure benzene in heptane. As experience with this engine increased the general error became much less and is now rarely greater than that for engine No. I, but there is still the risk of an occasional abnormal result due to the pinking being taken to too high a degree as compared with the comparison standard.

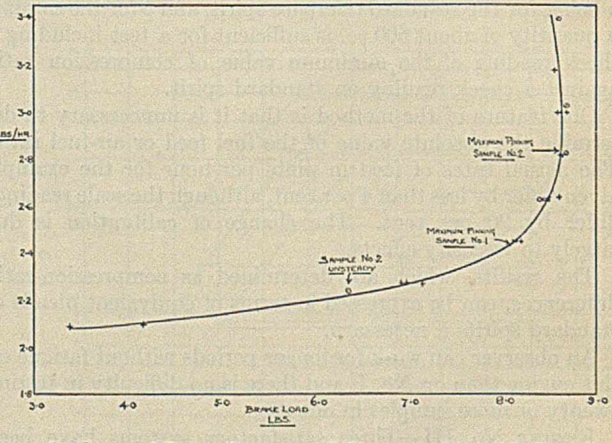

Figure 9—Curve of Power Output and Consumption with Straight-Run and Cracked Spirits, Showing Positions of Maximum Pinking

Engine No. III gave the same error as No. II in terms of compression ratio but only ±1.5 per cent in terms of benzene in heptane. This difference is due to the progressive increase of compression ratio reducing the pocket under the variable compression plug and thus improving the shape of the combustion space at the higher ratios and reducing the length of flame travel. This increase of sensitivity is also noticed on engine No. II as compared with No. I, but only to a marked extent beyond 1.0 compression ratio above the useful limit for the straight-run standard spirit (Figure 12).

The error of the matching method by audibility is of the same order as the method of counting used on engine No. I—i. e., about ±0.03 compression ratio.

It is, of course, obvious that an average of duplicate tests will give greater accuracy by any method, but, apart from considerations of time, there are many cases where the supply of fuel is insufficient for more than a single test or a test of each of a series of blends.

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[4] World Power Conference, London, 1928.

Determinations with the bouncing pin with identical samples on several different runs show that the maximum error for a single test by this method is less than ±0.01 ratio or about ±0.25 per cent benzene in heptane. This accuracy is obtainable either for normal spirits, cracked spirits, or for kerosenes without any difficulty.

Influence of Controllable Variables

Fuel Feed—Among the controllable variables of an engine, the effect of fuel feed or air-fuel ratio has already been mentioned. Figure 5 shows that if the two fuels had been tested in an engine with a standard fixed-jet carbureter adjusted to give maximum pinking with the sample fuel, then the higher value spirit would have given a test result lower than the standard by an amount *a–c*—i. e., the error would be as high as 0.28 compression ratio. Errors of this sort are particularly liable to arise when non-adjustable jets are fitted or when multi-cylinder engines are used with the throttling method. It is generally assumed that maximum pinking coincides with maximum power output. This appears almost invariably to be the case with engine No. I but slight differences have been noticed with engines Nos. II and III.

Figure 9 shows a fuel-consumption power output curve for the Ricardo engine (No. II) given by a straight-run spirit and by a cracked spirit of less volatility and high end point. The power output is identical from each fuel, but the points of maximum pinking differ and vary not only with the fuels used but with the intake air temperature. Consistent results can, however, always be obtained from any of the engines if the feed is adjusted to give maximum audibility, and irregularities arise if the air-fuel ratio is adjusted to give maximum output.

Spark Plugs—The selection of a suitable spark plug may be of considerable importance. Engine No. I works well with a K. L. G. type E. L. T. plug. This is a long-reach design and gives no trouble for ratios up to about 5.5 to 1. At higher compression ratios a special plug with greater heat-resisting properties is needed.

Engine No. III has run throughout on a standard Lodge CB3 plug which is in a completely jacketed pocket.

Engine No. II was originally fitted with a K. L. G. type 210 plug and failures of both this and the 214 type were frequent. After several months it was noticed that pre-ignition with non-pinking fuels always occurred at or below 10:1 compression ratio and that irregular running was frequent between 8:1 and 10:1.

During a series of tests on blends of pure benzene and paraffin hydrocarbons it was noted that at a ratio of 9:1 the engine continued to run at 1700 r. p. m. even if the ignition was switched off, it being difficult to decide that the combustion noise was not continuous moderate pinking. The essential difference between pinking and pre-ignition was that the former disappeared as speed increased whereas the latter grew worse. At 1800 r. p. m. the pre-ignition was so bad as repeatedly to reduce the speed violently by 200 to 300 r. p. m. When the speed was adjusted to 1600 r. p. m., the engine ran quite steadily with normal ignition. The compression plug was then drilled out to take a plug with 18-mm. thread diameter and the K. L. G. Company coöperated in a series of tests with their range of special racing plugs. The first two failed owing to carbon deposit on the electrodes. They were overcooled for the engine. The third plug (K. L. G. 464) allowed the head, for the first time, to be taken up to 11.9:1 (the maximum compression ratio) without the least sign of pre-ignition on commercial benzene and other non-pinking fuels. The speed could then be increased from 1700 r. p. m., and at 2400 r. p. m. the running was still quite smooth.

This plug gave trouble with carbon at low ratios and was replaced by K. L. G. 396 which is a detachable model. It can be used at the maximum ratio on benzene without trouble at 1700 r. p. m. but pre-ignition develops at 2200 r. p. m. It has now been in regular use for several weeks without a single misfire and withstands prolonged testing of racing spirits at extremely high ratios.

The selection of plugs is not likely to affect test results from average spirits, but it is of particular importance at high ratios and for fuels where auto-ignition is suspected.

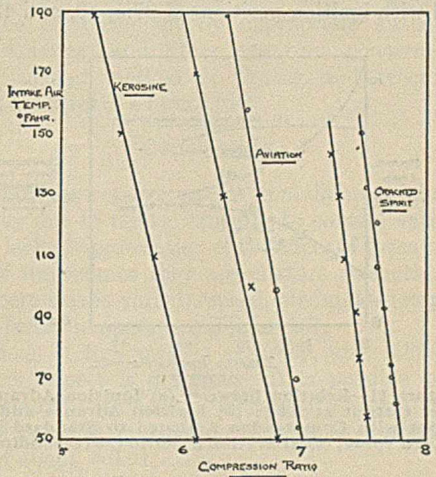

Figure 10—Effect of Alteration to Inlet Air Temperature on Highest Useful Compression Ratio

Engine Speed—Engine speeds have been chosen in each case with regard to torque characteristics and general mechanical noise.

Engines Nos. I and III are run at 1200 and 750 r. p. m., respectively. These speeds give approximately maximum pinking, there being a decrease of audibility with both rising and falling speed. Neither engine is affected appreciably by small changes of speed.

Engine No. II is run at 1700 r. p. m. and pinking increases steadily to 1300 r. p. m., the lowest speed at which tests have been made. A change of 100 r. p. m. alters the compression ratio for standard audibility by about 0.1.

Air Intake and Water Temperatures—Ricardo[5] has emphasized the need for air-intake heating to obtain consistent results. The addition of a standard number of heat units to the air entering the carburetor has been found to make as much as 30° F. (17° C.) difference between morning and afternoon intake temperatures in summer, and nearly 50° F. (28° C.) between extreme winter and summer conditions. The effect of this variation, as far as it has been examined, is to increase the difference between the highest useful compression ratios of two fuels as the intake air temperature is increased. Figure 10 shows the relation between compression ratio and intake temperature for a series of fuels including typical aviation spirit, No. 1 spirit, cracked spirit of poor volatility, and kerosene. The actual value of intake-air temperature is not nearly so important if tests are made by matching the samples with equivalent standard blends provided that the temperature is maintained at a constant value.

Note—Recent tests have shown that spirits which are equal as regards antiknock value at a low water-jacket and inlet-air temperature may differ slightly at high jacket and air temperatures. The difference is unimportant and is most marked when comparisons are made between blends of low-value spirit and benzene and equivalent blends of low-value spirit and metallic dopes.

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[5] Empire Motor Fuels Committee Report, Institution of Automobile Engineers, 1924.

The standard intake temperature which has been adopted for all routine tests of spirit is 120° F. (48.9° C.) and is measured by a thermometer shielded from heater radiation and from carburetor blowback. Kerosenes are tested at 180° F. (82.2° C.). Water jacket and head temperatures are maintained at 120° F. for spirits and 180° F. for kerosenes.

Change of water-jacket temperature has a similar, but much less marked effect to that caused by alteration of air inlet temperature.

IGNITION SETTING—For routine tests engine No. I is operated with ignition positions of 37.5, 40, and 42.5 degrees before top center, 40 degrees being approximately the setting for optimum output on standard spirit at its highest useful compression ratio. Engine No. II is run with a setting of 30 degrees and No. III with 20 degree advance, these also being values for highest output on standard reference spirit at the highest useful compression ratio.

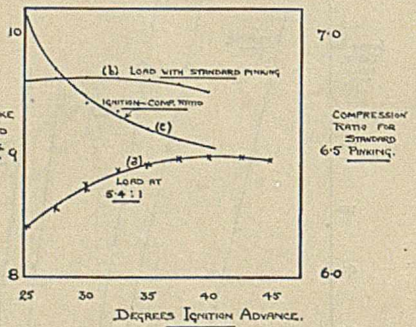

Figure 11—Relation between (*a*) Ignition Advance and Power Output at 5.4:1; (*b*) Ignition Advance and Power Output with Compression Adjusted to Standard Pinking for Each Value; (*c*) Alteration in Ratio Corresponding to (*b*)

The settings are kept constant at all other ratios, for two reasons: First, although a more retarded spark will increase output at high ratios, it also reduces pinking. Each engine will run without either pinking or pre-ignition on suitable fuel at its maximum ratio and standard ignition setting, and retardation to obtain maximum power output reduces the available range of the engines.

Secondly, the ignition setting for maximum power output at standard audibility is not very sharply defined, although the sharpness varies with the engine. In cases such as engines Nos. II and III where the power output is small, it is impossible to determine the maximum value to nearer than ±2 degrees, but an error of 4 degrees makes 0.17 of compression-ratio difference (by the audibility method). There is therefore less risk of error if a fixed ignition setting is used (or a fixed series of settings for the counting method used on engine No. I).

Figure 11 shows the relation between ignition setting and power output of engine No. II running on standard spirit with the head adjusted to (*a*) a non-pinking position, and (*b*) to standard pinking audibility for each ignition setting. The same diagram also shows the change in compression ratio necessary to compensate for alteration of ignition if constant pinking is maintained.

The difference between the best ignition advance for one fuel and another at the mixture strength for maximum pinking is not considered sufficient to justify any deviation from a standard setting, since the increase of experimental error with variable ignition more than offsets any possible gain in accuracy of comparison.

Figure 12 shows the relation between increase of compression ratio and percentage of commercial benzene in standard spirit for each engine. It indicates that there is no direct method of comparing compression ratio figures from one engine with those from another.

Given a standard air-intake temperature to the carburetors, constant speeds, fixed ignition, and operation at an air-fuel ratio giving maximum pinking under these conditions, then there is no difference between test results from any of the three engines when values are expressed in terms of the proportions of standard reference hydrocarbons required to make a blend to match the sample under test. This statement is based on a large number of tests and repeat tests with spirits, kerosenes, and doped spirits. The only observed exception is a slight difference between results from the counting method on engine No. I and the audibility or bouncing-pin tests on the other engines, when testing blends of certain classes of cracked spirit. In this case the difference does not exceed 1.25 per cent of benzene in heptane (0.04 ratio on engine No. I).

Road Tests for Pinking

Road tests on different cars are particularly liable to give contradictory results. Rough approximations to values from research engines may be obtained with a car fitted with an engine having a well-designed induction system if the carburetor is set to give the weakest stable running mixture at full throttle and provided that tests are only made when temperature conditions have become steady.

A skilled observer can generally detect a change equivalent to an addition of 5 per cent benzene by noting the highest speed at which sudden opening of the throttle causes a definite degree of pinking.

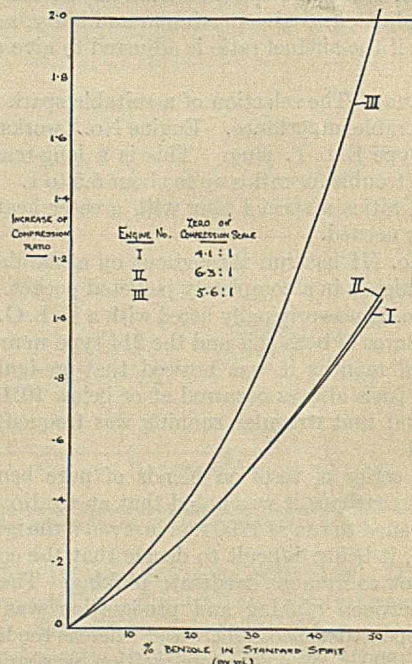

Figure 12—Relation between Added Commercial Benzene and Increase of Highest Useful Compression Ratio for Engines I, II, and III

Fundamental Standard Fuels

Hitherto it has been customary for investigators to use as their standard reference fuel some spirit readily available to them in consistent quality; this has generally taken the form of a definite refinery cut from a definite crude oil—preferably one which pinks at a low compression ratio. For experimental purposes it is then blended with controlled proportions of an antiknock material such as benzene or lead tetraethyl.

The serious disadvantage of this procedure is obvious. It implies that even if the standard fuel really remains consistent, it is not available in different parts of the world and is therefore an arbitrary and unscientific standard. The valuable contribution of Edgar[6] to this problem—namely, that *n*-heptane (a low-value hydrocarbon obtainable in a high state of purity from the Jefferson pine) and 2,4,4-trimethylpentane (an octane which can be prepared synthetically and which resembles benzene in its antiknock qualities) should be used as the fundamental standards, is well known, but owing to the considerable cost and difficulty of obtaining these materials, especially the octane, the proposal has not yet been widely adopted. It would seem much more advantageous to use, instead of the costly octane, the hydrocarbon benzene, which can be obtained cheaply in a high state of purity, which can be readily checked by testing the freezing point of the material.

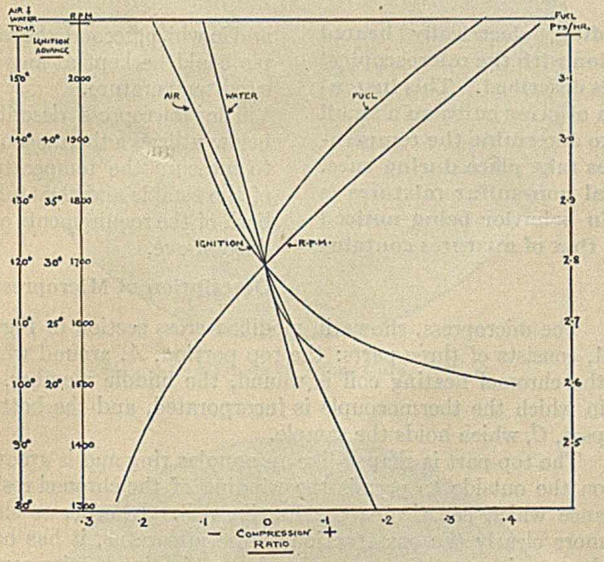

Figure 13—Effect on Highest Useful Compression Ratio of Alteration of Controllable Variables

Whatever fundamental standards are ultimately adopted, the following considerations hold:

(*a*) The standards when suitably blended should cover the entire range of motor fuels liable to pinking.

(*b*) They should be reliable (this implies that they should be pure chemical substances) and cheap. If low cost is not possible, a suitable sub-standard range should be available. *N*-heptane and pure benzene are suggested as suitable hydrocarbons by which the complete range of fuels can be matched.

(*c*) A standard method of stating the effect of blends of antiknock substances should be universally adopted.

For general work substandards prepared from any locally available spirit of average quality, with benzene or a proknock (such as amyl nitrite) should suffice. Each fresh supply of substandard material should be tested against the fundamental heptane-benzene blends over a suitable range, all test results being expressed in terms of heptane-benzene.

It is frequently necessary to determine the effect of different percentages of blending material on a basic spirit. For commercial work such tests will naturally be made on the spirits in which an individual refinery is especially interested, but for research purposes when high accuracy and consistency are necessary, the blends should be made with a pure hydrocarbon. If this is not done, inconsistencies will arise owing to differences in the chemical constitution of the basic spirits, even though these have the same antiknock value, for equal amounts of antiknock substances may have different effects on two spirits of different chemical nature. Results should be expressed in terms of equivalent blends of heptane-benzene, but should include reference both to the substance under test and the material used for blending.

There still remains urgent need both for the development of a manufacturing method for producing a pure and pinking hydrocarbon in abundant quantity at a reasonable cost (in view of the relative scarcity and high price of heptane) and also for the establishment by appropriate authorities in England, America, and other countries concerned, of a universally agreed method of testing and recording the detonating qualities of a motor fuel.

Conclusions

1—Divergencies between results from different laboratories are probably due to failure properly to control variables on account of lack of appreciation of the effect of these variables. In order of importance they are mixture strength, ignition setting (where this is varied), speed, air-intake temperature, and water-jacket temperature (Figure 13).

2—Methods of test vary in accuracy, and calibration of each in this respect is desirable. It is possible to obtain consistent results with a sensitivity equal at least to ±0.25 per cent of benzene in heptane—i. e., a compression ratio variation of about ±0.01.

3—Values expressed in terms of compression ratio or differences between compression ratios apply strictly only to the engines on which the tests are made.

4—Matching of a sample against standard blends by audibility or bouncing-pin methods should be at a compression ratio giving pinking with the sample. Large errors may arise if the antiknock values of two spirits from different sources are compared by determining the amount of an antiknock required to bring each to a much higher standard.

5—The bouncing pin, operated from a diaphragm, appears to be the most accurate apparatus for evaluating samples in terms of standard hydrocarbon blends. It can be used without fatigue, it is independent of engine noise, and it needs very little attention to secure consistent results. Faulty operation is immediately obvious and can generally be traced to its source (engine or pin) at once.

6—If it is desired to express the pinking tendencies of a fuel in terms of a scale of compression ratios, the scale should be determined on an engine with a well-designed head and results should be expressed in compression-ratio differences between samples rather than in absolute values. This system lacks the accuracy of the matching method but gives fairly close agreement for normal designs of variable compression head.

Acknowledgment

The authors desire to record their thanks to the directors of the Anglo-Persian Oil Company for permission to publish these researches, which have been conducted in the Engine Research Department of the company.

The director of a large research and control organization has found two items of considerable utility. In the work of this laboratory gold-plated weights have not been entirely satisfactory but chromium-plated weights for analytical and other balances are proving very satisfactory. For drying, either solids or liquids, Pyrex-glass pie plates have proved very successful.

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[6] Presented before the Division of Petroleum Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

A Temperature-Recording Micropress for Studying the Course of Vulcanization[1]

James C. Walton

Boston Woven Hose and Rubber Company, Cambridge, Mass.

A new temperature-recording, electrically heated micropress for use in connection with the microscopical observation of vulcanization is described. This instrument permits the duplication of press cures on a small scale and renders it possible to determine the temperature at which various changes take place during cure.

The vulcanization of several non-sulfur mixtures is studied, certain differences in behavior being noticed between this type of cure and that of mixtures containing sulfur.

A SURVEY of the extensive literature on the nature of vulcanization reveals the fact that, almost without exception, work on this problem has been confined to purely analytical methods of attack. This classical chemical procedure shows only the final result of vulcanization—that is, the sum of all changes that have taken place—and thus ignores changes in the degree of dispersion, an inversion of phases, and other changes which may be of fundamental importance but which cannot be detected by the older chemical methods.

Microscopic investigation, on the other hand, offers a new method of attack, with many possibilities, inasmuch as it permits observation of the progressive changes that take place throughout the vulcanizing process and leads to a better knowledge of colloidal changes, which may in themselves be sufficient to explain vulcanization. Weber[2] was the first to recognize the insufficiency of analytical methods, and he introduced the microscope in the study of the blooming of sulfur. This technic was later utilized by Breuil,[3] Loewen,[4] and Regnaud.[5] All these investigators first heated their samples in an oven and then subjected them to microscopical examination; hence no simultaneous curing and microscopical observation was possible.

It was only during the past year or so that further work was done along this line by Hauser and by Dannenberg. The micropress developed by Hauser[6] employs steam as the heating medium. In this equipment the temperature of the sample is found from the temperature-pressure relation of saturated steam, and accordingly this apparatus can only be used for work above 100° C. Since the press was designed for curing at one definite temperature, it is not adaptable to temperature measurement where the temperature is rapidly changed. Dannenberg[7] devised an electrically heated micropress which permits the examination of the sample throughout the curing operation. With this equipment the temperature of the sample is found by inserting a thermometer in a small hole in the apparatus midway between the heating coil and the sample. Because of the location of the thermometer and because no account is taken of such factors as rate of heating and radiation and convection losses, this method of measurement does not give the true temperature of the sample.

The ideal equipment for microscopic vulcanization would be one which, first, would permit the accurate recording of the temperature of the sample over a range of 30° to 170° C., and in which, second, the sample could be kept at any desired temperature.

The micropress described below utilizes a thermocouple to measure the temperature of the sample and thus fulfils both of the requirements outlined above.

Description of Micropress

The micropress, shown in modified cross section in Figure 1, consists of three parts: the top portion, *A*, around which the chromel heating coil is wound, the middle member, *B*, in which the thermocouple is incorporated, and the bottom part, *C*, which holds the sample.

The top part is shaped like an annular ring and is grooved on the outside to permit the winding of the chromel resistance which constitutes the heating coil. In order to show more clearly the construction of the apparatus, it has been drawn without the asbestos lagging, which in practice covers the top and side of the member *A* in order to confine the heat and to protect the objective of the microscope.

The middle member, *B*, is cup-shaped to permit the focusing of the microscope on the sample. A thermocouple is incorporated in this member by inserting an iron and a constantan wire in this member so that their ends are just flush with the metal surface which fits over the sample.

The bottom section, *C*, is recessed to receive the sample, which is placed between a circular slide and cover glass. A small hole is bored through both bottom and middle members in order to allow the light from the condenser to pass through the sample and up into the microscope.

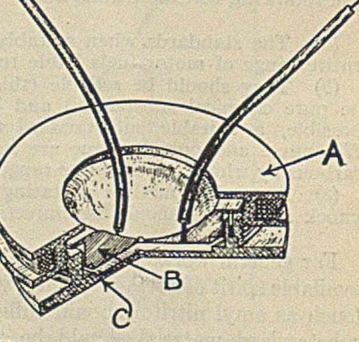

Figure 1—Cross Section of Micropress

It is evident that the middle member, which is made of mild steel and has inserted in it an iron and a constantan wire, acts as the hot junction of the thermocouple. Both wires are insulated and attached to the terminals of a millivoltmeter, 0 to 10 millivolts range, which act as the cold junction of the couple.

The thermocouple as constructed records the temperature of only that part of the hot junction exposed to the air, and since this is far from the temperature of the sample it was necessary to calibrate it. This was done by placing organic crystals of known melting point between a slide and cover glass in the same position as the rubber sample. Current was applied to the heating coil and the melting of the crystals was observed microscopically, the millivoltmeter reading being taken at the time the crystals melted. A number of crystals of wide melting range were used in the calibration.

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[1] Presented under the title "Microscopical Observations on the Vulcanization of Sulfur-Free Rubber Compounds" before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Weber, "Chemistry of India Rubber," p. 110, London, 1919.

[3] Breuil, *Caoutchouc*, **2**, 82, 118, 158, 197 (1905).

[4] Loewen, *Gummi-Ztg.*, **27**, 1301 (1913).

[5] Regnaud, *Chimie et industrie*, **18**, 93T (1927).

[6] Hauser, "Colloid Symposium Monograph," Vol. VI, p. 207 (1928).

[7] Dannenberg, *Kautschuk*, **3**, 104, 128 (1927).

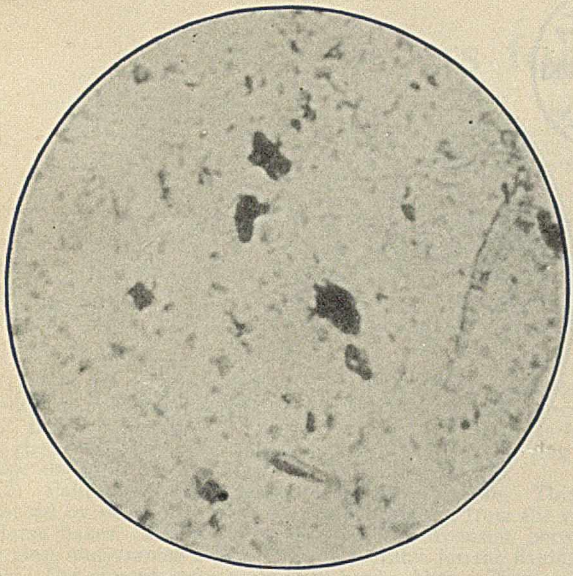

Figure 2—Mixture II before Cure. 750 ×

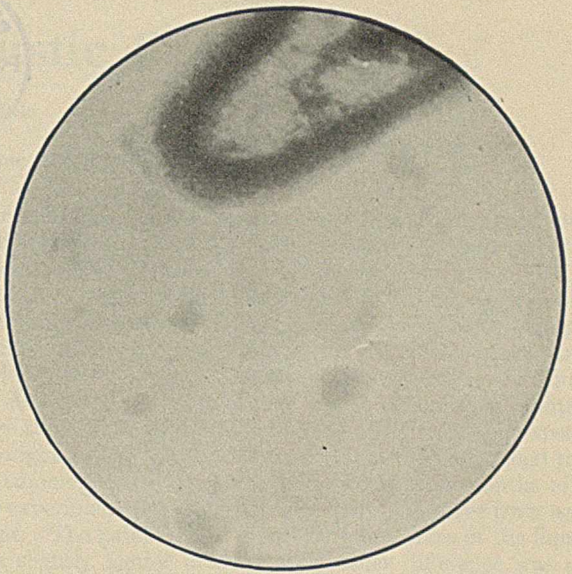

Figure 3—Mixture II Heated. 750 ×

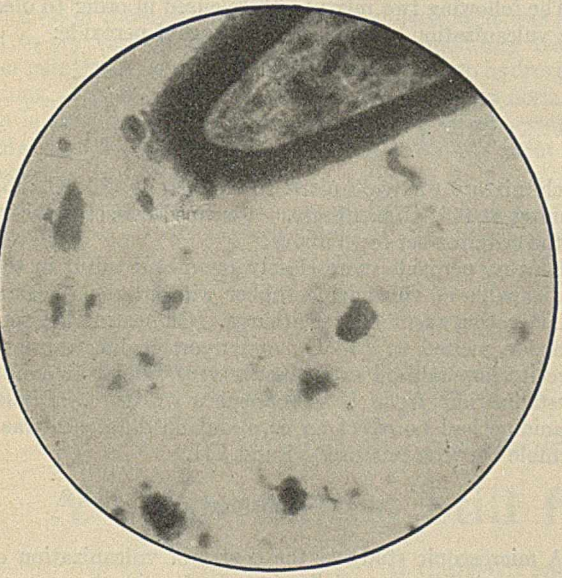

Figure 4—Mixture II after Cooling Following Cure. 750 ×

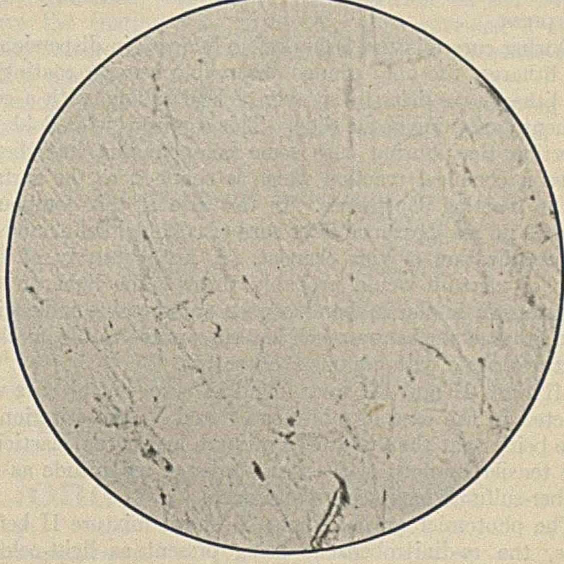

Figure 5—Mixture IV before Cure. 750 ×

and a curve was determined for the temperature range usually encountered in vulcanization—viz., 30° to 170° C.

In using the apparatus, the sample is placed between a circular slide and cover glass and is placed in the recess in the bottom member. The middle portion is next put in position over the sample and the bottom screwed into the top member. These parts are screwed together until the sample is compressed or squeezed out sufficiently thin to permit light from the condenser to pass through the sample.

Curing Agent

Most of the work done in the study of vulcanization has been carried out with sulfur as the curing agent. Ostromuislenskii,[8] Stevens,[9] and Fisher and Gray[10] have shown, however, that it is possible to vulcanize rubber with non-sulfur compounds such as *m*-dinitrobenzene and benzoyl peroxide, the physical properties of the cured rubber being similar to those of rubber vulcanized with sulfur.

Experimental

The following experimental work is by no means complete, but was performed in an endeavor to demonstrate the possibilities of micro-vulcanization in the equipment described. Incidentally, it shows the effect of non-sulfur compounds as curing agents.

Five mixtures were cured, mixture I being a control to judge the state of vulcanization of those mixtures cured with non-sulfur agents.

	I	II	III	IV	V
Smoked sheets	100	100	100	100	100
Sulfur	3	..	..	..	..
Litharge	10	10	10	..	..
m-Dinitrobenzene	..	3	3	3	3
Diphenylguanidine	..	..	1	..	1

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[8] Ostromuislenskii, *J. Soc. Chem. Ind.*, **35**, 59, 369 (1916).

[9] Stevens, *Ibid.*, **36**, 107 (1917).

[10] Fisher and Gray, Ind. Eng. Chem., **20**, 294 (1928).

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

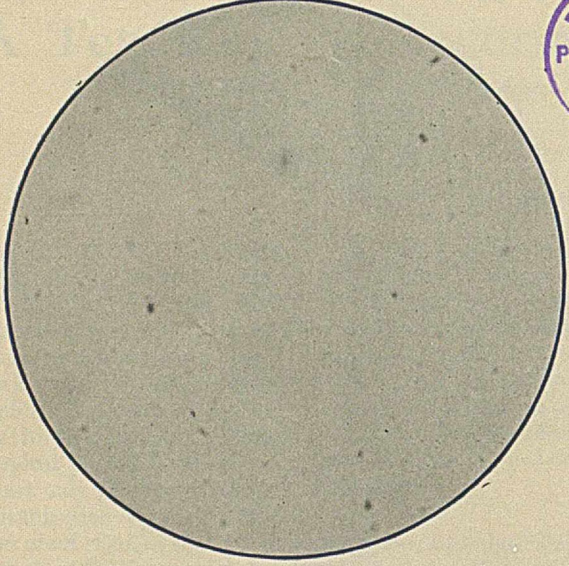

Figure 6—Mixture IV Heated. 750 ×

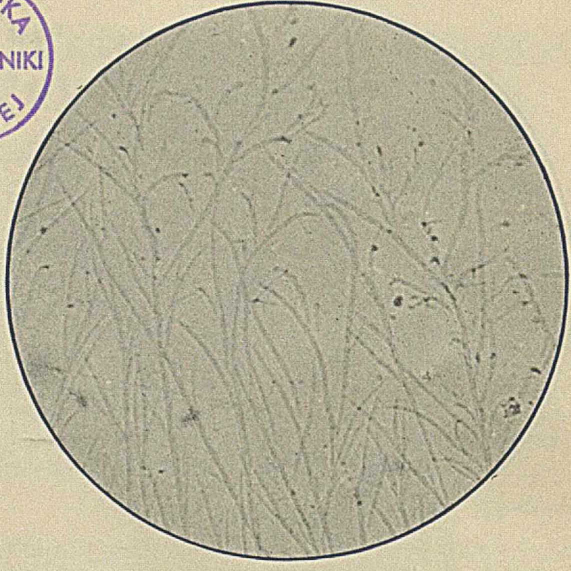

Figure 7—Mixture IV on Cooling Following Cure. 750 ×

These mixtures were cured 60, 90, and 120 minutes at 145° C. in a press.

During cure mixture I showed no increase in dispersion of the litharge, the only change observable being a coating of the litharge particles by a layer of lead sulfide, with a consequent darkening of the slide. This conforms with Pohle's[11] assertion that during cure some compounding ingredients cause a chemical reaction which is confined to the surface of the reacting substances. In the case of this compound there is no reappearance after cure of colloidal sulfur and no recrystallization of this element. A further study of this type of mixture would probably throw some light on the fact, known in the rubber footwear and topping industries, that litharge stocks are much less susceptible to bloom than mixtures cured with organic accelerators.

Mixtures II and III were found to cure, but no cure was effected in the case of mixtures IV and V, the criterion of cure being that the vulcanized mixture had nerve, elasticity, and tensile strength of the same order of magnitude as the rubber-sulfur-litharge control mixture.

The photomicrograph (Figure 2) shows mixture II before cure, the *m*-dinitrobenzene being present as light-colored needles, while the dark particles are litharge. When the mixture is heated (Figure 3) the *m*-dinitrobenzene melts at 40° C. and a flow similar to that observed with sulfur cures takes place. No change in the degree of dispersion is discernible. When the mixture cools down after cure (Figure 4) minute colloidal droplets appear, but no recrystallization of the *m*-dinitrobenzene takes place.

Figure 5 shows mixture IV, rubber and *m*-dinitrobenzene, before cure. When this mixture is heated at 145° C. for 2 hours, the *m*-dinitrobenzene melts and an optically empty picture is obtained (Figure 6). No vulcanization takes place, and on cooling an immediate reappearance of *m*-dinitrobenzene crystals is observed (Figure 7).

Mixture V acts in the same manner, no cure taking place and the *m*-dinitrobenzene recrystallizing when the mixture cools.

It would appear that an activator such as a metallic oxide—e. g., litharge—is necessary to secure a cure with *m*-dinitrobenzene, and that diphenylguanidine, a substance which accelerates vulcanization with sulfur, has no appreciable effect with the compound above.

The following two mixtures were cured in order to observe the vulcanization of rubber with benzoyl peroxide:

	VI	VII
Smoked sheets	100	100
Benzoyl peroxide	$6^2/_3$	$6^2/_3$
Diphenylguanidine	....	1

Each mixture was vulcanized 15 minutes at 130° C., and 15 minutes at 145° C. in a press. A cure was effected according to the criterion set forth above.

Benzoyl peroxide more closely resembled sulfur in that it was capable of vulcanizing rubber without the necessity of an activating agent such as litharge. On heating the benzoyl peroxide melted at 54° C., and upon cooling down after cure it recrystallized in a manner very similar to sulfur recrystallization from a rubber-sulfur mixture. Diphenylguanidine had no effect on cure and no difference was discernible between mixtures VI and VII.

Conclusions

A microscopic study of the course of vulcanization offers many possibilities, especially since, by its aid, the progressive changes which take place during vulcanization can be followed. Using the micropress described above, it is possible to observe these changes and to record the temperature at which they take place.

A rubber-sulfur-litharge mixture after cure exhibits no recrystallization of sulfur even when cured for a very short time. A further microscopical study of the vulcanization of this type of rubber mixture may yield an explanation of the bloom-preventing properties of litharge.

m-Dinitrobenzene and benzoyl peroxide both vulcanize rubber in the absence of sulfur. The former requires an activator such as litharge and does not recrystallize from the mixture when a cure is effected, whereas the latter does not require an activator and recrystallizes after cure in a manner very similar to sulfur.

Acknowledgment

The writer wishes to take this occasion to express his thanks to E. A. Hauser for the interest he has taken in this work and for the helpful suggestions he has given.

---

[11] Pohle, *Z. wiss. Mikroskop.*, **44**, 183 (1927).

Containers for Caustic Solutions[1]

Byron A. Soule

University of Michigan, Ann Arbor, Mich.

CAUSTIC soda stored in an unprotected glass bottle attacks the glass. The liquid, becoming saturated with silicate, soon is unsatisfactory for use, especially in analytical work. Various expedients have been suggested to eliminate this difficulty. Among them may be mentioned the following:

(1) Coating the inside of the container with paraffin or ceresin. While either is easily applied, both are open to the objection that, unless in a relatively thick layer, they soon separate from the glass and float to the surface of the liquid, thus leaving the bottle unprotected.

(2) Painting the bottle with Bakelite varnish. This is attacked by caustic solutions and soon separates from the glass in large flakes. Difference in coefficient of expansion between the glass and varnish may also be responsible for the flaking.

(3) Use of containers made from hard rubber. These, while effective, are opaque and somewhat costly.

(4) Use of ceresin bottles. These are obtainable only in smaller sizes and tend to soften during hot weather.

Since all of these devices are open to objection, it was decided to try various others. After some exploratory tests, rubber paint[2] was found to be unaffected by sodium hydroxide solutions, at least up to a concentration of about 5 normal, which is the highest ordinarily encountered in a laboratory. On March 1 five bottles were coated with rubber paint as indicated in Table I.

Table I—Coats of Paint and Strength of Alkali Solutions

SOLUTION	NUMBER OF COATS	NaOH NORMALITY
1	1	1
2	1	3
3	1	5
4	3	0.1
5	3	3

The next day the first three bottles were filled slightly over half full with sodium hydroxide solutions of the concentrations specified (Table I) and then placed in a dark cupboard. On March 7 the last two bottles were filled and placed beside the others. When next examined, on March 14, all samples seemed to be in good condition except No. 3, which apparently had lost some of its coating above the surface of the liquid. On May 12, no notable change having occurred, the bottles were transferred to the top of a laboratory desk and exposed to bright daylight, but not direct sunlight. They stood thus all summer. On October 6, approximately 7 months after the experiment was started, every sample was free from sediment. The paint in No. 5, beneath the surface of the liquid, was slightly lighter in color. No other difference was observed.

A portion of the 5 normal solution was removed and acidified to test for silicate. After standing more than 1 hour a slight cloudiness was noted. Examination of the bottle where the coating was apparently gone revealed a thin, tightly adherent film of rubber, evidently of adequate protective thickness.

Standardization of solution 4 at various times during the test period has given a practically constant value for the normality (Table II).

Table II—Standardization of Solution 4

DATE	NORMALITY
April 9	0.0876
May 12	0.0873
October 6	0.0873

Note—The use of rubber paint for protection of glass bottles against the action of hydrofluoric acid has proved unsatisfactory. Gaseous hydrogen fluoride passes through the coating fairly readily and attacks the glass. This ultimately results in a separation of the rubber from the glass.

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[1] Received November 17, 1928.

[2] Thermoprene, Acid Seal Paint No. 1023, obtained from The B. F. Goodrich Co., Akron, Ohio. *See* Gray, IND. ENG. CHEM., **20**, 156 (1928).

A Continuous Still for Conductivity Water[1]

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Department of Chemical Engineering, University of Michigan, Ann Arbor, Mich.

A CONTINUOUS, practically automatic fractionating column for producing very pure, or conductivity, water has been constructed which has proved so satisfactory that other laboratories may be interested in its construction.

Construction

The equipment consists essentially of two block-tin bodies, 1 and 6, equipped with block-tin coils and connected to the bottom of two columns, 4 and 2, interconnected at the top, and two condensers, 3 and 5, one at the top of each column.

All parts of the still coming in contact with water or vapor are made of block tin.

The still body containers are made of two 8-inch wrought-iron pipe nipples 18 inches long, provided at each end with an 8-inch flange screwed flush with the nipple end, as indicated by the heavy lines in the figure. The block-tin lining for the still is prepared by rolling a sheet of block tin $24^1/_2$ by $18^1/_2$ inches to form a cylinder $24^1/_2$ inches high. The edges are butted and burned together both inside and out with a hydrogen-air torch flame. An annular flat ring of block tin $11^1/_2$ inches outside diameter by $7^7/_8$ inside is burned on one end of each cylinder to form a block-tin flange. The cylinders are then placed flanged ends down on a flat support and the 8-inch pipe nipples and flanges slipped over the tin stills. The block-tin cylinders are located centrally within the nipples and the space between the cylinders and the nipples is packed with insulating material lightly tamped into place. Similar tin rings of the same dimensions are slipped over the top of the tin still bodies, pressed against the flat faces of the nipple flanges, the projecting rim of the cylinders peened over the edge of the flat annular tin rings, and the joints welded with the torch. The block tin used in building these stills is $^1/_{10}$ inch thick.

The bottoms of the still are made integral with the steam coils as indicated in the figure. The steam coils are made by winding 24 feet of block-tin pipe, $^{11}/_{16}$ inch outside diameter

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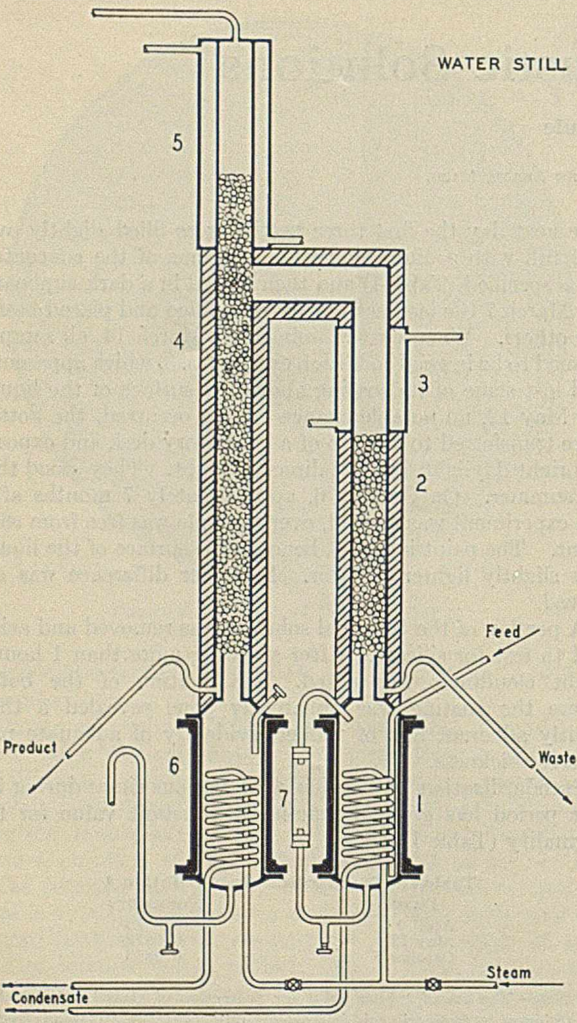
[1] Received November 26, 1928.



and $^{3}/_{8}$ inch inside diameter, around a 6-inch cylindrical form, spacing the turns $^{1}/_{2}$ inch as shown. Disks of block tin $8^{1}/_{2}$ inches in diameter, slightly coned toward the center, serve as bottoms of the stills and are pierced with $^{3}/_{4}$-inch holes so as to locate the steam coil centrally within the still. A hole is burned through the centers of the bottom pieces into which is welded the end of a block-tin pipe to serve as a drain for the still. To this tin pipe is burned a nipple threaded internally at the other end with a $^{1}/_{8}$-inch pipe thread and provided with a plug of block tin threaded with a similar thread about 8 inches from the still bottom.

The metal is built up around the connections to the bottom of the still and to the steam coils so that no ordinary strain will crack off the block-tin pipe. The ends of the inlets and outlets to the steam coils are threaded with a $^{3}/_{8}$-inch pipe thread, on which are turned brass couplings. These couplings connect to a $^{3}/_{8}$-inch navy-type union for connection to the steam line. The bottoms and coils so completed are welded on the base of the tin cylinder in the final assembly.

The small inner cylinders on the tops of the stills act as traps to catch the liquid returning to the still. As it is desirable to discard practically all of the liquid flowing down the first column, this cylinder is made small. These small cylinders are 7 inches high by 3 and 3 $^{1}/_{2}$ inches outside diameter, respectively.

The two condensers are constructed from 4-inch outside diameter block-tin tubing as the center core, and 6-inch outside diameter tubing as the outer core. The condenser on the top of the first column is 12 inches high and that on the top of the second column, 3 feet high.

The first column, 2, is 25 inches and the second column, 4, 44 inches from the top of the still to the bottom of the condenser. In preparing these columns and condensers, it is necessary to form them from sheet block tin which has been burned both inside and outside at all joints.

For connecting the two columns a 4-inch elbow, one leg 12 inches and the other 7 inches in length, is welded into the long column in the position shown in the figure. The columns, after being welded together with the condensers, are scrubbed thoroughly on the inside with hot distilled water, and washed first with 1:1 hydrochloric acid and water and then with distilled water. The tops of the stills are similarly cleaned and welded onto the bottom of the columns, the still top with the smaller inner cylinder being attached to the base of the column carrying the smaller condenser.

The columns are packed with Raschig rings made of tin $^{1}/_{40}$ inch thick formed into rings $^{3}/_{4}$ inch wide and $^{3}/_{4}$ inch in diameter. The larger condenser at the top of the taller column is packed with these rings for about one-half its height. The rings are thoroughly cleaned in the manner described before the columns are packed.

The still bodies and coils are similarly cleaned and the still bottoms welded in place. The columns and condensers are set on a wooden framework above the still bodies previously placed in position below the columns. The still bodies are then adjusted to the proper height so that the top of the still bodies and the bottoms of the columns are in proper contact. Then the two flanges are burned to the tops of the still bodies making a continuous block-tin fractionating equipment with all joints welded or burned.

A gage glass, 7, is provided for the first still body. This is the only place where any material other than block tin comes into contact with the water, and, being in contact only with the impure distilled water supplied to the first still, introduces no impurities into the product.

The condensers at the top of the columns are cooled with tap water; or if it is desired, might serve as preheaters to the simple distilled water fed to the first still as raw material.

The steam coils are connected to low pressure (35 pounds maximum) steam supply through navy-type unions and valves.

The distilled water fed to the first still is controlled by a $^{1}/_{4}$-inch tin-lined valve or cock welded into the line, and secured firmly to a 2 by 4 upright nailed to the framework supporting the still. From this valve the distilled water flows through a piece of $^{1}/_{4}$- by $^{3}/_{8}$-inch tin pipe through the top of the still down to the bottom of the first still shown as the feed line to the first still.

Operation

The general plan of operation of this equipment is as follows: The water is vaporized in the first still body, 1. The water vapor travels upward through the packing of the first column, 2. A portion of the vapor is condensed by the reflux condenser, 3, and flows down the column removing the less volatile impurities in the water according to the principles of fractional distillation. This water is discarded through a trap at the bottom of the first column as shown in the figure. The uncondensed vapor which passes through the reflux condenser, 3, at the top of the first column, travels across to the second column, 4, where it is condensed by the reflux condenser, 5, at the top of the second column, flows down through the column packing, meeting an upward current of steam generated from pure distilled water in the second still body, 6. The function of this second column is to remove the more volatile impurities from the impure vapors leaving the first column. Part of the water vapor is vented through the top of the reflux condenser, 5, on the top of the second column carrying with it the more volatile impurities in the water. At the base of the second column some of the water is trapped off and collected as product, the balance flowing into the second still body, 6, to be revaporized in order to furnish the steam for scrubbing the water coming down the second column of the more volatile impurities and dissolved gases.

The operation of the still is controlled by proper manipulation of a number of valves, which, when once adjusted, need no further attention provided the steam pressure and the temperature of the cooling water remain constant.

The first still is charged with a permanganate solution and filled about two-thirds with distilled water. The steam is then turned on the first still until the water begins to vaporize. The supply of the distilled water is then turned on proportionately. Cooling water flows into the condenser at the top of the first column at such a rate that the water in the condenser jacket operates almost at the boiling point, as usually only a small reflux ratio is required to produce water of a high degree of purity. The cooling water in the second condenser at the top of the second column is so adjusted that most of the water is refluxed by this condenser.

There should be a small amount of steam passing out of the pipe at the top of the second column to insure the removal of the more volatile impurities in the water, just as there should be a small amount of water wasted from the bottom of the first column to insure the removal of the less volatile impurities in the water.

Product is removed from the inverted U-tube at the base of the second column. It is necessary to pinch the end of this tin pipe so as to form a small orifice allowing about 4 or 5 liters of product to be removed per hour when the still is operating properly. As soon as water begins to flow out of the product pipe, steam is turned into the coils in the second still at such a rate as to cause a small but constant flow of steam through the tin pipe at the top of the large condenser on the second column.

Before using the water from the second still it was allowed to run for 1 week, during which time the still bodies were drained twice daily by taking the plugs out of the pipes at the bottom of the stills. At the end of 1 week the water obtained from the still was found to have a pH value of substantially 7 as measured by bromothymol blue hydrogen-ion indicator.

A Receiver for Vacuum Distillation[1]

Edgar J. Poth[2]

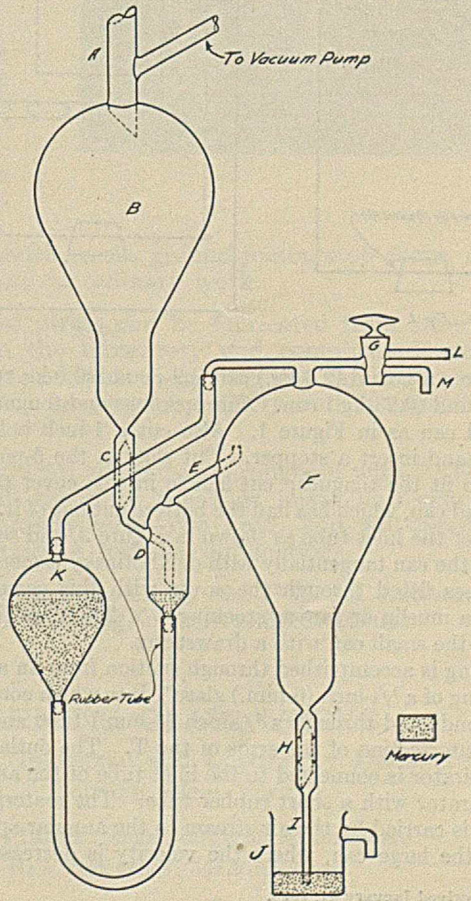
UNIVERSITY OF TEXAS, AUSTIN, TEXAS

IN CONNECTION with an investigation being carried out in the Texas laboratory on nitrogen bases occurring in California kerosene stock, a vacuum distillation receiver has been designed that entirely eliminates stopcocks in the distillation train and any possible contamination of the distillate from tap grease. This innovation not only obviates contamination of the distillate, but dispenses with a stopcock, present in all other types of receivers, that may give trouble either from leakage or sticking.

The device is illustrated in the accompanying figure. It is made of Pyrex glass. *A* is sealed onto any form of condenser (not shown in figure) and leads into receiver *B*, which may be of a different type and graduated if desired. *B* and *F* are conveniently made of Kjeldahl flasks, because the design of these vessels is well adapted to either large or small fractions and insures good drainage. *C* and *H* are ordinary float check valves sealed against mercury. *G* is a three-way stopcock.

During distillation the leveling bulb *K* is so adjusted that container *D* fills with mercury, thus causing valve *C* to become mercury-sealed. Bulb *F* serves a double purpose: first, any leakage at *C* can be stopped by evacuating at *L*; and second, when the capacity of *B* is not great enough for a particular cut, *F* also can be used for storage, although with this apparatus the distillate can be drawn at any time without interfering with the distillation.

When it is desired to make a cut, half fill *D* with mercury and, with *I* dipping under mercury, evacuate the system through *L* of stopcock *G*. With the fall of pressure in *F*, *C* opens automatically when, by the proper adjustment of the leveling bulb *K*, the contents of *B* are transferred to *F*. It is evident that any liquid remaining in *D* can be forced over and, since *E* is directed upward, the distillate can be com-



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[1] Received November 15, 1928. This paper is the outgrowth of distillation experiments being carried out at the Chemical Laboratory of the University of Texas in an investigation on "The Nitrogen Compounds in Petroleum," listed as Project 20 of American Petroleum Institute research. Financial assistance in this work has been received from a fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Fellow; J. R. Bailey, Director, Project 20.

pletely displaced by mercury. After adjustment of the mercury so as to fill *D*, the vacuum in *F* can be broken. Then *C* closes, *H* opens, and the distillate drains into *J* overflowing into an appropriate receiver. To hasten the emptying of *F*, pressure may be applied at *M*.

This method of cutting fractions is being used on several stills, varying from a micro-apparatus of 10 cc. capacity to one handling 5 liters, in which about 50 liters of bases from California kerosene stock are undergoing exhaustive fractional distillation.

Air Separator for the Laboratory[1]

R. E. Zinn

Victor Chemical Works, Chicago, Ill.

In experimental work with finely ground solids it is often necessary to obtain a physical separation which is not readily done with the regular 100- to 200-mesh sieves. This is particularly true in cases where the material does not screen easily because it is too light or because the particles adhere to one another; also, it may be desired to effect a separation of material finer than 200 mesh. Under these conditions the desired result is most readily obtained by means of air separation.

A convenient air separator suitable for qualitative separation has been successfully built and used by the writer. Such a device may be easily and quickly made from materials that are generally available about a laboratory. Its construction will be evident from the accompanying sketches and the description which follows.

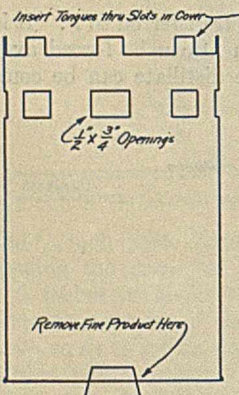
Insert Tongues thru Slots in Cover
$\frac{1}{2}$" x $\frac{3}{4}$" Openings
Remove Fine Product Here

Fig. 1.

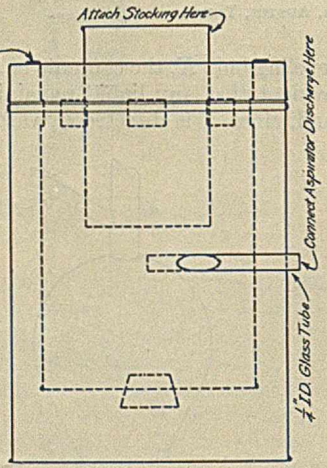
Attach Stocking Here
Connect Aspirator Discharge Here
$\frac{1}{4}$" I.D. Glass Tube

Fig. 2.

Secure a 5-pound (2.3-kg.) can, a 2-pound (0.9-kg.) can, and a $^{1}/_{2}$-pound (0.23-kg.) can. Cut openings and tongues in the 2-pound can as in Figure 1. Also cut a 1-inch hole in the bottom and insert a stopper. Cut slots in the 5-pound can cover to fit the tongues; cut a hole in this cover to fit the $^{1}/_{2}$-pound can, which has had the bottom cut out of it. Make a hole for the inlet tube as shown in Figure 2, and secure the tube to the can tangentially with deKhotinsky cement. Seal the pieces fitted through the cover with this cement also. Attach a muslin or canvas stocking 4 × 24 inches (10 × 60 cm.) to the small can with a drawstring.

Feeding is accomplished through suction from an aspirator consisting of a $^{1}/_{4}$-inch (6-mm.) glass T into which compressed air is conducted through a $^{1}/_{8}$-inch (3-mm.) tube and nozzle to the intersection of the arms of the T. The outlet end of this aspirator is connected to the inlet tube of the assembled air separator with a short rubber tube. The material to be treated is carried by the air stream to the annular space just within the large can, where the velocity is decreased sufficiently to drop out the coarser material. The finer particles are further carried by the air current through the openings just below the cover and into the central space, where they are deposited. They may be recovered, without removing the stocking, through the hole which is closed with the stopper. Any material which is carried past this chamber is arrested in the stocking filter. With a little experience an operator can control the degree of separation as desired by changing the amount of compressed air to the aspirator.

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[1] Received January 31, 1929.

Self-Emptying Suction Flask for Sugar Determinations[1]

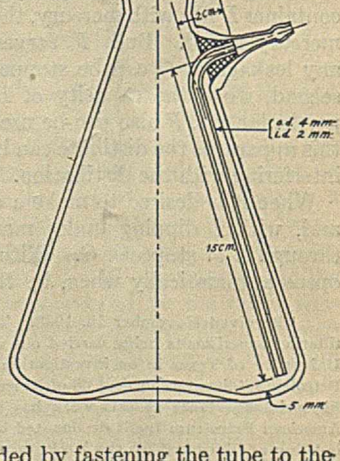
Gilbert Pitman

Fruit Products Laboratory, University of California, Berkeley, Calif.

In the Munson and Walker method of determining sugar difficulty is often experienced in washing the precipitated copper oxide with alcohol and ether. Ordinarily the ether washings volatilize so rapidly when striking the hot wash water in the flask that they form a pressure great enough to dislodge the asbestos mat in the Gooch crucible.

The following modification in the suction flask has been found useful in overcoming this difficulty. It also permits rapid washing and makes frequent emptying of the flask unnecessary. The principle involved is merely that of drawing the hot wash water from the flask by suction through a glass tube extending to the bottom of the flask.

A piece of glass tubing of approximately 4 mm. outside diameter and 2 mm. inside diameter is bent at an angle of slightly more than 90 degrees and cut so that one end is about 2 cm. and the other about 15 cm. from the bend. It is cut to fit the flask so that its final position is as shown in the illustration, with the bottom end about 5 mm. from the bottom of the flask. The short end of the tube is fastened to the suction outlet by means of a small rubber stopper that has been previously shaped to make a tight fit and sealed to the flask with clear Duco. The stopper is held in place with fine copper wires during drying. These may be dissolved later with nitric acid.



Instead of the arrangement described above, an Erlenmeyer flask may be fitted with a two-hole rubber stopper through which a funnel and a suction tube extend to the bottom of the flask. Or the use of the small rubber stopper for the side connection may be avoided by fastening the tube to the suction outlet by means of a glass ring seal.

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[1] Received January 29, 1929.

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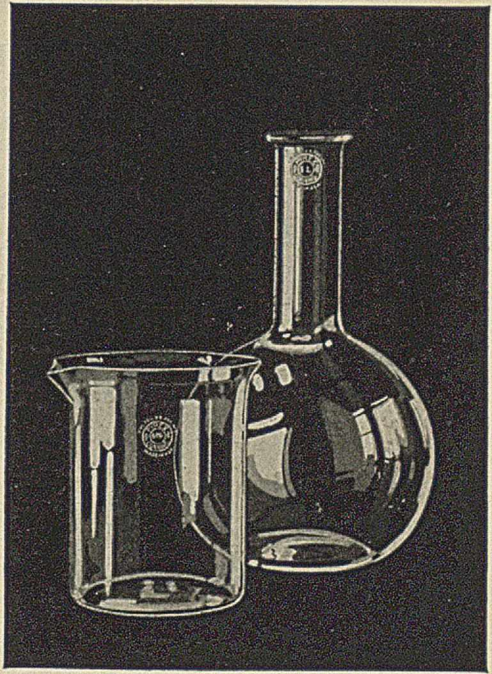

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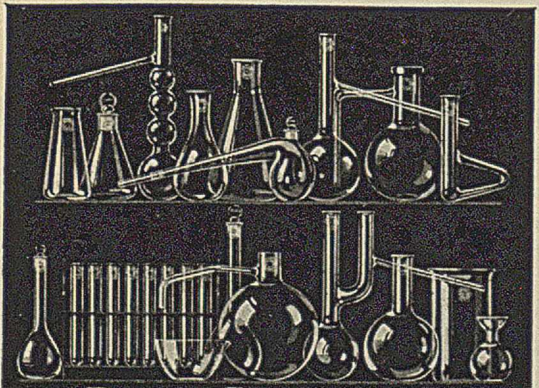

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By JOHN E. TEEPLE, PH.D

CONSULTING CHEMIST AND CHEMICAL ENGINEER AND ASSOCIATES
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The story of the raising of a "war baby," by the application of research, technology and common sense, to a great industry, able to meet in competition two great foreign monopolies (potash and borax) reads like a tale from the Arabian Nights. It is no fantasy however, for we find here the record of scientific research and engineering skill, diagrams and data, whereby this was brought about, and (what is more rare) that courage and team work never so resplendent as when engaged in desperate enterprises.

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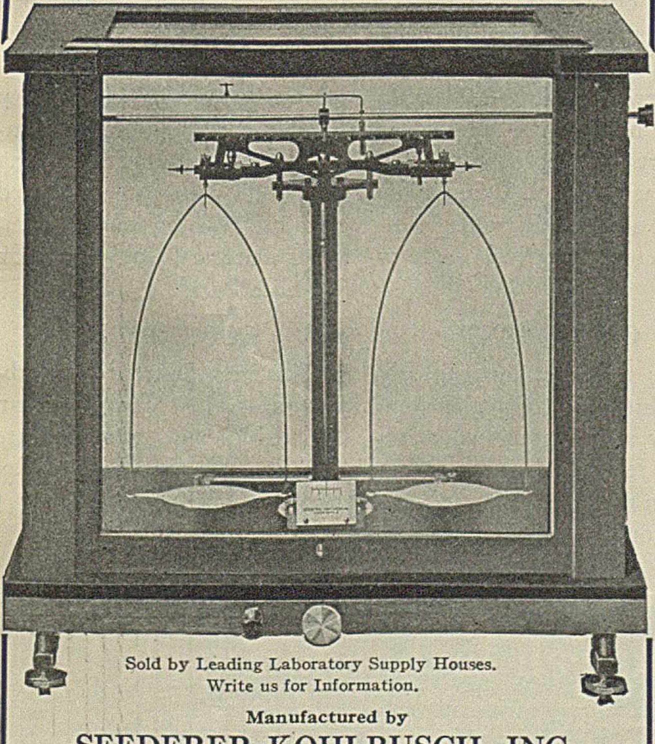

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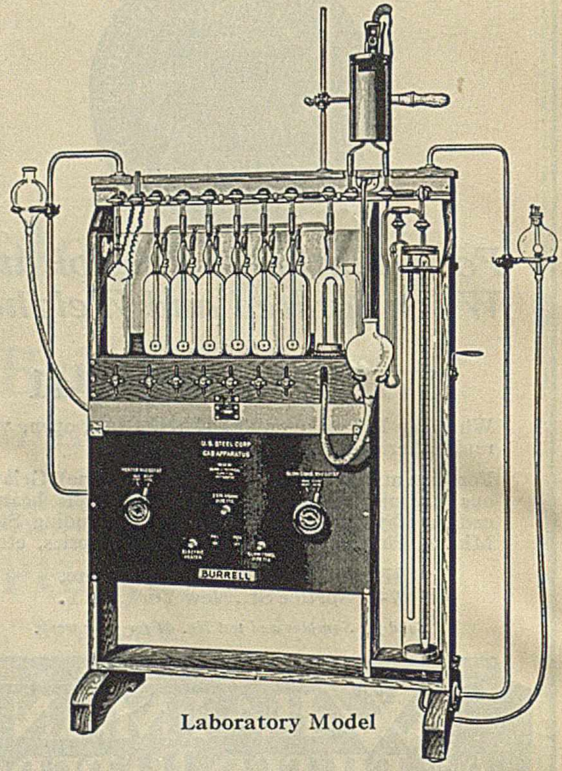

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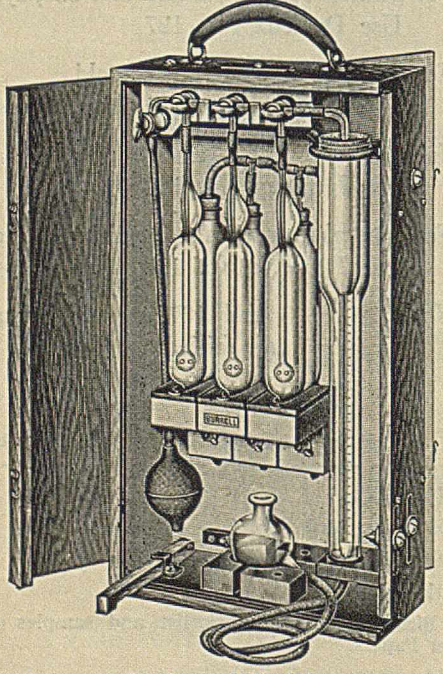

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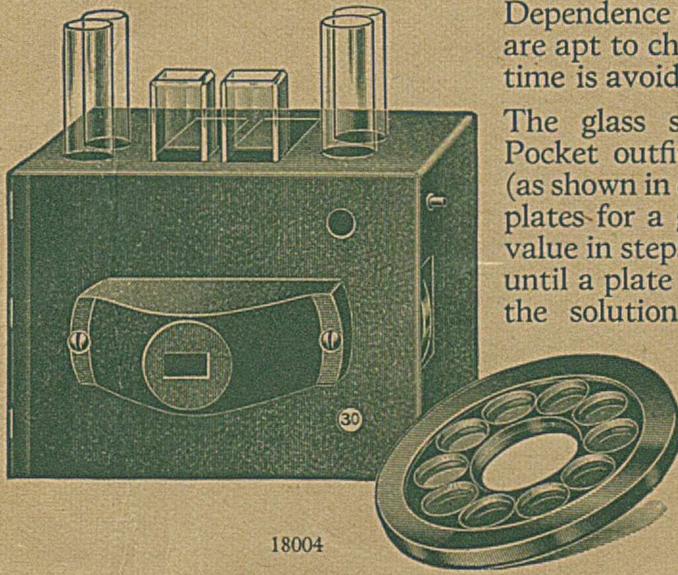

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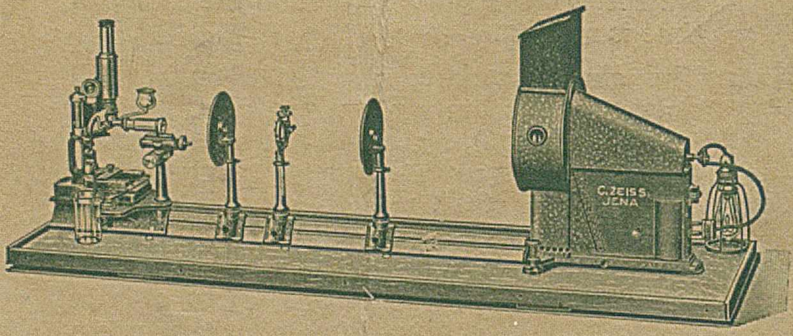

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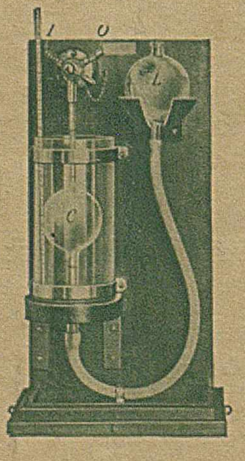

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