for a standard curve. The decrease in number of drops is very soon apparent, the solution becomes cloudy, and, in a few days, nearly all of the oleate appears to be precipitated, while the filtrates, no matter what the original strength, show a strong tendency to the same minimum drop number.

LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY OF WISCONSIN,
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A RAPID METHOD FOR THE DETERMINATION OF SULPHUR IN COAL AND COKE.

BY J. D. PENNOCK AND D. A. MORTON.

Received October 5, 1903.

As is well known, foundrymen require coke containing a minimum percentage of sulphur. It has been found necessary to be able to quickly determine the percentage of sulphur in the coal to be used for coke-making in order that a selection of those cars containing coal low in sulphur, may be made, for the railroad companies charge demurrage on all cars not emptied in twenty-four hours. By the method described in this paper, one chemist has been able to make twenty determinations of sulphur in six hours.

The determination of sulphur in coals and cokes, as described in this paper, is, in its essential features, a combination of parts of two methods already in use. These parts are, first, the process used by Sundstrom[1] for the complete oxidation of coals by means of sodium peroxide; second, the method of Andrews[2] for the volumetric estimation of the sulphur thus formed.

In carrying out these processes, however, various modifications have been introduced in order to accomplish, as perfectly as possible, the end in view; namely, the accurate, rapid, and convenient estimation of sulphur in coals and cokes. This object is satisfactorily accomplished by following the method as outlined below.

APPARATUS AND SOLUTIONS.

Crucible.—A soft steel crucible of about 40 cc. capacity, the lid being perforated with a small hole for the introduction of the igniting wire.

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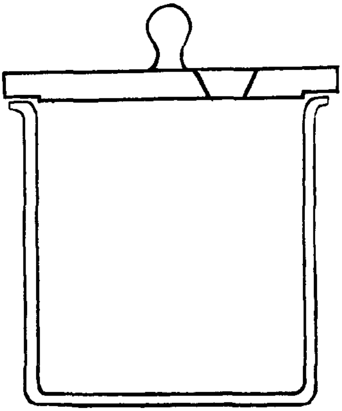
[1] This Journal, February, 1903.

[2] *Am. Chem. J.*, **11**, 567; *J. Anal. Chem.*, **4**, 73 (1890).

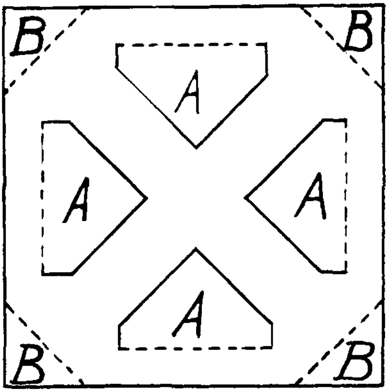
Crucible Stand.—Any arrangement suitable for holding the crucible firmly in place and out of contact with the beaker during the peroxide combustion.

The following diagrams show the form of crucible and stand used in this laboratory:



Crucible.

Thickness of walls and bottom of crucible, $^1/_{32}$ inch.
Hole in cover, diameter at top, $^1/_4$ inch.
Hole in cover, diameter at bottom, $^3/_{32}$ inch.
Other dimensions as shown in diagram. The crucible and lid are nickel-plated.



Stand.

The stand is made from a sheet of aluminum, 2 inches by 2 inches, cutting as indicated by the heavy lines, then bending upward at right angles the four points marked "A," and downward at right angles the four points marked "B," making the bends along the dotted lines.

Barium Chromate Solution.—A solution of 23 grams pure barium chromate in a mixture of 80 cc. concentrated hydrochloric acid and 920 cc. water. With the use of commercial C. P. barium chromate, much trouble has been experienced because of its impurity. A suitably pure barium chromate may be prepared by adding a dilute potassium chromate solution to the theoretical quantity of barium chloride, also in dilute solution, and then washing the precipitate thoroughly.

Sodium Thiosulphate Solution (tenth-normal).—24.8 grams of the pure crystallized salt dissolved in water and the solution diluted to 1 liter.

Iodine Solution (tenth-normal).—12.69 grams iodine dissolved in a solution of 18 grams potassium iodide in 50 cc. water and the mixture diluted to 1 liter.

Starch Solution.

THE DETERMINATION.

Introduce into the crucible 16 grams sodium peroxide and 0.7 gram coal (or 11½ grams sodium peroxide and 0.7 gram coke), and mix thoroughly by means of a small spatula. Cover, and place the crucible on its stand in a 20-ounce beaker of water, in such a way that the lower half only is immersed and the base of the crucible is slightly raised from the bottom of the beaker. Ignite the contents by thrusting a red-hot wire through the hole in the cover into the mixture. Complete fusion and combustion take place almost instantaneously. After three minutes or more, remove the stand and tip the crucible over on its side in the water. The fusion dissolves in a few moments and the crucible is then rinsed and removed. Add hydrochloric acid to the solution until distinctly acid, and boil. To the boiling liquid add ammonia until a few drops in excess, let boil vigorously a minute or two, then add 15 cc. of barium chromate solution and boil another minute. Add sufficient water to the boiling solution to make its volume 200 cc., then ammonia until several drops in excess, and continue boiling vigorously for one or two minutes longer. Allow to settle a few moments, filter and wash the precipitate twice thoroughly, using from 20 cc. to 30 cc. of hot water for each washing.

Add about 1 gram potassium iodide crystals to the filtrate, cool to 30° C., add 5 cc. hydrochloric acid, then run in the thiosulphate solution until the end-point is reached. The presence of a few cubic centimeters of starch solution renders the end-point more distinct. Titrate back, if necessary, with the iodine solution.

$$\text{cc. } N/10\ Na_2S_2O_3 \times 0.153 = \text{per cent. S.}$$

The determination depends, of course, on the fact that the precipitation of barium sulphate liberates an equivalent amount of chromic acid, which remains in solution as ammonium chromate when the excess of barium chromate is precipitated by ammonia.

REMARKS.

The directions for the peroxide combustion should be followed with especial care, for, if less sodium peroxide is used than the directions require, the reaction may be explosively violent; and, on the other hand, if too much sodium peroxide is used, the combustion will be incomplete. Also, the thorough mixing of the fuel with the peroxide must not be neglected or an explosive and incomplete reaction will result.

After each addition of ammonia, the solution is boiled to remove most of the excess, but it should still remain slightly ammoniacal. The addition of the barium chromate does not always precipitate the sulphate immediately, but the subsequent boiling for one or two minutes insures complete precipitation. The final washing of the precipitates, if carried too far, will dissolve precipitated chromate and thus introduce an error. It has been found that two washings, using a small amount of hot water for each, produces the desired effect of thoroughly removing the chromate in solution without decomposing the precipitate.

RESULTS.

Up to the present time more than 1000 determinations by this method have been made in this laboratory. The accuracy of the results has been tested by comparison with the Sundstrom method, with the Eschka method, and by tests on solutions of known sulphate content. A number of the results thus obtained are cited below. The determinations on coal sample No. I were made independently by three analysts, each making two tests by the volumetric and two by the Eschka method. The four volumetric determinations of coke sample No. I required exactly one hour's time, showing the extreme rapidity as well as the accuracy of the method.

	Soft coal samples.				Coke samples.	
	I.	II.	III.	IV.	I.	II.
Per cent. S, volumetric method.	1.95 2.03 1.97 1.98 2.01 2.04	1.26 1.26 1.30	1.16 1.16	1.06 1.06 1.02	0.71 0.70 0.70 0.75	1.43 1.41
Per cent. S, Eschka method.	2.03 2.06 2.04 2.06 2.04 2.00	1.30	1.20	1.05 1.07	0.75 0.68 0.70 0.70	
Per cent. S, Sundstrom method.						1.47 1.42

Solutions, each containing 23 grams sodium chloride, a little iron, and a known quantity of sulphate (hence practically of the same composition as the solution obtained by the peroxide fusion of a coal) gave the following results:

Per cent. S present	0.46	0.914	1.37	2.29	0.98	1.96
Per cent. S found	0.45	0.91 0.90 0.92	1.35	2.33 2.36	0.96 1.02 0.99 0.99	1.93

CONCLUSION.

The results of all tests show that the method carried out in accordance with the above directions, is accurate to within a few hundredths of a per cent., and is so rapid that an average of two or even three complete determinations per hour can be accomplished. It can be used with especial advantage where large numbers of sulphur determinations are required, since in such a case its saving in time and in the use of platinum becomes an important item.

The method can be successfully employed not only for the determination of sulphur in coals, but also, with suitable modifications, for the determination of small percentages of sulphur in a large number of organic and inorganic substances.

LABORATORY OF THE SOLVAY PROCESS CO.,
SYRACUSE, N. Y.

ON TRIPHENYLMETHYL ACETATE.

BY M. GOMBERG AND G. T. DAVIS.

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HEMILIAN,[1] the discoverer of triphenylcarbinol, observed that the carbinol reacts with acetyl chloride, giving rise to hydrochloric acid and a crystalline mass which, on exposure to moist air, loses acetic acid and changes back to the carbinol. With acetic anhydride and with benzoyl chloride he obtained unstable esters, which were readily decomposed by water and by alcohol. Later, Allen and Kölliker[2] described a method for the preparation of triphenylmethyl acetate, which consisted in the action of acetyl chloride upon triphenylcarbinol ethyl ether,

$$(C_6H_5)_3C - O - C_2H_5 + CH_3COCl = (C_6H_5)_3C - O - OCCH_3 + C_2H_5Cl.$$

They claim to have identified the escaping gas as ethyl chloride, and give the melting-point and the solubilities, as well as the

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[1] *Ber. d. chem. Ges.*, **7**, 1207 (1874).

[2] *Ann. Chem.* (Liebig), **227**, 116 (1885).