| cm. | Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$. | cm. | Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$. | C111. X. | Per cent. of iron. $y = \frac{0.03027}{x - 0.28}.$ |
|--|--|-----|--|--------------|---|
| 7.4 | 0.00425 | 8.6 | 0.00363 | 9.8 | 0.00318 |
| 7.5 | 0.00419 | 8.7 | 0.00359 | 9.9 | 0.00314 |
| 7.6 | 0.00414 | 8.8 | 0.00355 | 10,0 | 0.00311 |
| 7.7 | 0.00408 | 8.9 | 0.00351 | IO. I | 0.00308 |
| 7.8 | 0.00402 | 9.0 | 0.00347 | 10. 2 | 0.00305 |
| 7 .9 | 0.00397 | 9.1 | 0.00343 | 10.3 | 0.00302 |
| 8.0 | 0.00392 | 9.2 | 0.00339 | 10.4 | 0.00 299 |
| 8.1 | 0.00387 | 9.3 | 0.00335 | 10.5 | 0.00 296 |
| 8.2 | 0.00382 | 9.4 | 0.00331 | 10 6 | 0.00293 |
| 8.3 | 0.00377 | 9.5 | 0.00328 | 10.7 | 0.00290 |
| 8.4 | 0.00372 | 9.6 | 0.00324 | 10.8 | 0.00288 |
| 8.5 | 0.00368 | 9.7 | 0.00321 | 10.9 | 0.00285 |
| UNIVERSITY OF NASHVILLE. Nashville, Trnn. | | | | | |

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNI-VERSITY, No. 68.]

ON THE DETERMINATION OF SULPHUR IN COAL.¹

BY CHARLES W. STODDART. Received May 26, 1907.

THE Committee on Coal Analysis, appointed by the American Chemical Society in 1895, failed to select one standard method for the estimation of sulphur in coal. The following work was undertaken with reference to this fact, and to decide, if possible, which of the many rapid determinations is the most accurate.

COALS EMPLOYED.

The coals used were selected from a large number of samples, and represent a wide range of composition and locality. The following analyses of these coals are arranged in order of hardness, from coke to lignite, with sulphur content as first found by the ordinary Eschka method:

| | HH. Per cent. | FF. Per cent. | X. Per cent. | T. Per cent. |
|-----------------------------|------------------|------------------|-----------------|-----------------|
| Moisture | 0.00 | 1.93 | 2.22 | Ι.ΙΟ |
| Volatile combustible matter | 0.70 | 2.55 | 3.78 | 4.87 |
| Ash | 10.78 | 1.97 | 6.91 | 16.25 |
| Sulphur | 1.03 | 0.73 | 0.80 | 2.02 |
| Carbon | 87.49 | 92.82 | 86.29 | 75.76 |

¹ Read at the May meeting of the New York Section of the American Chemical Society.

SULPHUR IN COAL.

| | AA. Per cent. | A. Per cent. | I. Per cent. | K. Per cent. |
|-----------------------------|------------------|-----------------|-----------------|------------------|
| Moisture | 2.25 | 2.22 | 0.48 | 0.34 |
| Volatile combustible matter | 4.94 | 7.55 | 15.82 | 17.72 |
| Ash | 3.13 | 14.93 | 3.83 | 6.95 |
| Sulphur | 0.58 | 0.91 | 0.61 | 1.20 |
| Carbon | 89.10 | 74.39 | 79.26 | 73.79 |
| | H. Per cent. | P. Per cent. | L. Per cent. | N. Per cent. |
| Moisture | • •.40 | 0.44 | 0.53 | 0. 89 |
| Volatile combustible matter | 18.40 | 20.40 | 28,89 | 32.15 |
| Ash | 3.21 | 6.32 | 12,22 | 4.40 |
| Sulphur | 0.70 | 1.71 | 2.93 | 0.65 |
| Carbon | • 77.29 | 71.13 | 55.43 | 61.91 |
| | E. Per cent. | D. Per cent. | B. Per cent. | GG. Per cent. |
| Moisture | · 0.99 | 0.77 | 0.87 | 17.77 |
| Volatile combustible matter | r 34.36 | 40.76 | 72.86 | 43.76 |
| Ash | · 10.56 | 6.72 | 6.15 | 7.60 |
| Sulphur | 2,20 | 1.12 | 1.85 | 0.51 |
| Carbon | • 51.89 | 50.63 | 18.27 | 30.36 |

HH is a Connellsville coke, Pennsylvania.

FF, broken coal from Luzerne County, Pennsylvania.

X, anthracite coal from Pittston, Pennsylvania.

T, egg coal from the Scranton District, Pennsylvania.

AA, from Kingston, Pennsylvania.

A, Ontario and Western coal.

I, from Somerset County, Pennsylvania.

K, West Virginia steam coal.

H, Pocahontas coal.

P, steam coal from the Beech Creek region, Pennsylvania.

L, steam coal from West Virginia.

N, high-grade steam coal from the Buffalo, Rochester, and Pittsburgh region, Pennsylvania.

E, gas coal from West Virginia.

D, gas coal from West Virginia.

B, cannel coal from Grayson, Kentucky.

GG, lignite, from Bismarck, North Dakota.

SELECTION OF METHODS.

In going over the various methods employed for the determination of sulphur in coal, it was found that the number was too great to admit of all being applied to each sample; therefore certain methods were selected as typical ones for comparison on the sixteen coals. If only two or three coals had been chosen, it would have been feasible to apply all or most of the methods; but it was thought far better to use the few important methods on many coals which varied widely in composition and sulphur content.

Carius' decomposition of the substance with fuming nitric acid in a sealed tube is accurate, and might be applied in this case, but in using coals with a high percentage of volatile combustible matter, the pressure produced would probably shatter the tube. A modification as given by Hodgson¹ permits the tube containing 0.5 gram of sample and 15 cc. of fuming nitric acid to remain open for six hours, while being heated on a water-bath at 80°-90° C.: 5 cc. more acid is then added, the tube sealed, heated at 150° C. for from four to five hours in a furnace, opened to relieve the pressure, and reheated at 180°-200° C. for from two to four hours. The residue is filtered off and treated separately for sulphur. The filtrate is evaporated down with sodium hydroxide, the nitric acid driven out by hydrochloric acid, and dehydrated. The dry mass is taken up with water, acidified slightly with hydrochloric acid, and barium chloride added. This modification is long and tedious. and no better than other methods.

The best standard means for obtaining the sulphur content of a coal is combustion in an atmosphere of oxygen, passing the products of decomposition through some absorbent solution, and testing the residue for sulphur. Sauer's combustion method² is probably as well known as any, but elaborate apparatus is required, and complete decomposition of the tarry products is not easy. Other modifications, notably that of Drown,³ are not much better.

At Columbia University there is an Atwater-Blakeslee bomb calorimeter in which coal can be burned in oxygen under any pressure up to 50 atmospheres. This gives complete combustion, and as there are appliances for passing the products of combustion through absorbent solutions, all volatile sulphur compounds, if any, can be readily recovered. The combustion is almost instantaneous, the operation very simple, and all troublesome apparatus avoided. Under these circumstances the calorimeter was selected as the means of obtaining standard figures for sulphur. The method of procedure is as follows:

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¹ This Journal. **20**, 883.

² Ztschr. anal. Chem., 12, 32.

³ Am. Chem. J., 2, 404: 4, 11.

Standard Method.-About 0.5 gram of coal is forced into a pellet by means of the special press which accompanies the calorimeter. The pellet is carefully weighed in a tared platinum capsule, and placed in the support which consists of a wire ring fastened to a straight rod. The latter projects through the cover of the bomb. A second rod passes through the cover, parallel to the first, but not touching it. A fine iron wire, coiled spirally in the center, is attached at each end to the parallel rods, and is in contact with the pellet of coal. The cover is now placed on the bomb which is of heavy steel, platinum-lined throughout. A heavy steel flange is set over the cover and screwed down tightly by means of a lever and clamp. A lead gasket in the cover fits over the top of the bomb so that the apparatus is hermetically sealed. In the cover is a valve with a connection for the oxygen tank, in order that the gas under a pressure of 25 atmospheres can be forced into the bomb. After closing the valve and disconnecting from the tank, the bomb is attached by the projecting rods to a row of four 16 candle-power lamps in parallel, giving a current of 2 amperes. When the circuit is closed the lamps flash for an instant. The wire is of course oxidized at once when it becomes incandescent from the current, and its melting breaks the circuit. The combustion of the coal is completed. The bomb is disconnected, and a delivery tube of fine bore is introduced into the valve. The other end of the tube is fastened to a U-tube containing hydrochloric acid and bromine water. The valve is opened slightly and the compressed oxygen bubbles through the absorbent solution. If any sulphur dioxide is present, it is thus recovered. Combustion under pressure, however, in all probability converts the sulphur all to sulphur trioxide which is condensed with the moisture on the interior of the bomb. After the gas has been exhausted, the cover is removed, and the latter, as well as the inside of the bomb, thoroughly washed out into a beaker. The residue is filtered off, washed, dried, and fused with sodium potassium Then it is leached with water, filtered, acidified, carbonate. evaporated to dryness, and dehydrated, taken up with 1.5 cc. of hydrochloric acid and 200 cc. of water, filtered, 10 cc. of barium chloride added to the warm solution, and allowed to stand over night. There is usually iron present, so precipitation should be completed in the cold, and the solution not boiled at first. The original filtrate from the bomb washings is boiled to expel bromine, 10 cc. of barium chloride added, and the sulphur determined as barium sulphate. The sum of the sulphur obtained in the filtrate and residue is the total sulphur in the coal. With an average of 580 mg. of coal taken, the barium sulphate in the residue averaged 4.2 mg.

The soft coals press very readily into pellets, but the hard coals do not. The latter were therefore packed into the capsule as tightly as possible, and a small piece of ashless filter-paper fitted over the top to prevent scattering. The coil of wire was sunk in the coal and the ends pierced the paper. In this way complete combustion of the hard coals was obtained.

Although in some cases, especially with coke, mechanical difficulties have been encountered in getting complete combustion, this method is chemically most perfect. The oxidizable sulphur is oxidized under the most favorable possible conditions, and the residual sulphur converted to sodium sulphate by fusion; now if the precaution is taken to dehydrate the silica and to precipitate the barium sulphate under the best conditions, this seems to be the most reliable method for standard results, though perhaps too long for technical work.

Other Methods.—To compare with the standard method, Eschka's was of course chosen as being the best known method for estimating sulphur in coal. A method recommended by Stolba,¹ and unlike Eschka's, was also selected. Antony and Lucchesi² proposed a method that, they claimed, gave better results than Eschka's. It was apparently worth trying. Their original article proposed the precipitation of barium sulphate in a nitric acid solution. This is, of course, impracticable. Dubois³ copies their method exactly, but substitutes hydrochloric for nitric acid. As an example of fusion methods Thomson's⁴ was chosen. Hodgson⁵ used sodium peroxide as an oxidizing agent, and it was decided to try his method.

The details of the various methods as used in this work are as follows:

- * Bull. Assoc. Belge des Chim., 15, [6], 225.
- 4 J. Soc. Chem. Ind., 8, 526.
- * This Journal, 20, 886.

¹ Listy Chemické, 12, 20;.

² Gazz. chim. ital., 29, 181.

Eschka's Method.—Heath's modification, slightly changed:¹ I gram of finely powdered coal is mixed with I gram of magnesium oxide and 0.5 gram of sodium carbonate in a platinum dish having a capacity of 75-100 cc. A crucible may be used. The magnesium oxide should be light and porous. The dish is heated on a triangle over an alcohol lamp. The mixture is frequently stirred with a platinum wire or glass rod, and the heat applied very gradually. especially with soft coals. Towards the end, the bottom of the dish should be at a low red heat. When the carbon is all consumed, the mass is transferred to a beaker and the dish rinsed about 50 cc. of water being used. Fifteen cc. of saturated bromine water are added and the solution boiled for five minutes. The residue is allowed to settle and the clear liquid decanted through a filter; it is boiled a second and third time with 30 cc. of water, and washed very thoroughly. The residue was not further examined. The volume of the filtrate should be about 200 cc. One and a half cc. of concentrated hydrochloric acid are added and the solution is boiled until the bromine is expelled. Now 10 cc. of 10 per cent, barium chloride solution are added to the hot solution drop by drop, and with constant stirring. It is next digested over a low flame, with occasional stirring, until the precipitate settles clear. The barium sulphate is filtered and washed, using a small ashless filter-paper, ignited and weighed.

Stolba's Method.—I gram of finely ground coal is mixed with I gram of silver powder and I gram of potassium acid carbonate, and the whole carefully heated with frequent stirring until no dark particles remain. The mass is then transferred to a beaker with about 50 cc. of water and boiled, allowed to settle, and the clear liquid decanted through a filter. Two more portions of water, 30 cc. each, are added and the solution boiled as before. The residue is now transferred to the filter and thoroughly washed. The filtrate is acidified with 1.5 cc. of hydrochloric acid and the carbon dioxide boiled out. Ten cc. of barium chloride are added, and barium sulphate is precipitated as in Eschka's method. In most cases it is found advisable to add a few drops of ammonium acetate solution to prevent a slimy brown residue from running through the filter. It is also frequently necessary to filter the

¹ This Journal. 21, 1127.

solution more than once to obtain a clear filtrate for the precipitation of barium sulphate.

Antony and Lucchesi's Method.-I gram of finely powdered coal, mixed with 4 grams of manganese dioxide. I gram of potassium permanganate, and 2 grams of sodium carbonate, is placed in a platinum crucible and covered with a layer of the same oxidizing mixture. Heat is applied very gradually at first to prevent deflagration of the contents, and is finally raised until the bottom of the crucible is just reddened. After half an hour of such heating the mass is allowed to cool and is then transferred to a beaker with about 50 cc. of water and boiled. It is now allowed to settle and the clear liquid decanted through a filter. Two more additions of 30 cc. of water each are made, and the mixture is boiled as before. The mass is finally all transferred to the filter and thoroughly washed. The filtrate is acidified, and barium sulphate precipitated. In this case two filtrations are always necessary to obtain a clear solution. The addition of ammonium acetate solution helps to a great extent. Manganese dioxide is the cause of the trouble.

Thompson's Method.—I gram of the coal is mixed with 2 grams of sodium carbonate and gently heated until all the carbon is burned away. The mass is then fused and a little potassium nitrate added to complete the oxidation to sulphate. After the mass has cooled it is leached with water, filtered, the filtrate acidified with hydrochloric acid, and evaporated to dryness. The silica is dehydrated, the mass taken up with 1.5 cc. of hydrochloric acid and about 50 cc. of water, and filtered. The filtrate is diluted to 200 cc., and barium sulphate precipitated as usual.

Hodgson's Method.—1 gram of the coal is placed in a nickel crucible and covered with 4 grams of sodium potassium carbonate and I gram of solid sodium hydroxide. The crucible is covered and heat applied gently until gases are driven off. Then the heat is raised and small amounts of sodium peroxide are added until no further action occurs. Perfect fusion is now obtained with the blast-lamp. The mass is allowed to cool and is then leached thoroughly with water,—about 50 cc. It is then filtered, washed with hot water, the filtrate acidified with hydrochloric acid, evaporated to dryness, the silica dehydrated, and the dry mass taken up with hydrochloric acid and water. After filtering, the sulphur is determined as usual. Only two samples were tried by

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this method. The results were low, and the method unsatisfactory.

GENERAL PRECAUTIONS.

To avoid possible contamination from gas, alcohol lamps were used throughout these experiments.

All the chemicals were carefully tested for sulphur, and the necessary correction applied, if needed. Sodium carbonate, potassium acid carbonate, hydrochloric acid, and bromine contained no sulphur. Magnesium oxide contained 0.002 per cent.; manganese dioxide, 0.004 per cent.; potassium permanganate, 0.028 per cent.; sodium hydroxide 0.015 per cent.; and sodium peroxide, 0.002 per cent.

Constant acidity was maintained in all the analyses for the precipitation of barium sulphate; namely, 1.5 cc. of concentrated hydrochloric acid to 200 cc. of solution.

It was found convenient to add the barium chloride solution from a burette. After the 200 cc. of acidified solution had been heated to boiling on an asbestos disk, the burette was brought over the beaker and 10 cc. of 10 per cent. barium chloride solution were added drop by drop, stirring all the time. The stirring was continued at intervals after the barium chloride had been added, until the barium sulphate settled clear.

RESULTS.

The results as obtained by these methods are as follows:

| Coal. | Combustion method, Per cent. | Eschka's method. I Per cent. | "Eschka's Dehydrated." Per cent. | Stolba's method. Per cent. | Manganese dioxide method, Per cent, | Thomson' method. Per cent. |
|-------------------------|------------------------------------|------------------------------------|--|----------------------------------|--|----------------------------------|
| HH | 0.67 | 1.03 | 1.01 | 0.89 | 0.67 | |
| FF | 0.70 | 0.73 | ••• | 0.65 | 0.58 | 0.59 |
| x | | 0.80 | | 0.81 | 0.79 | |
| т | 1.65 | 2.02 | 1.67 | 1.64 | ••• | |
| AA | 0.51 | 0.58 | 0.56 | 0.51 | 0.52 | |
| A | 0.67 | 0.91 | 0.70 | 0.62 | | |
| I | ·· 0.64 | 0,61 | | 0.60 | o. 6 0 | 0.55 |
| к | 1.21 | 1.20 | | 1.15 | | |
| н | •• 0.70 | 0.70 | | 0.62 | ••• | |
| P | • | 1.71 | ••• | 1.75 | ••• | |
| L | . 3.09 | 2.93 | ••• | 3.08 | ••• | 3.08 |
| N | 0.65 | 0.65 | ••• | 0.65 | 0.64 | 0.67 |
| E | 2,23 | 2.20 | ••• | 2.05 | | |
| D | 1.21 | 1.12 | ••• | 1.07 | | |
| B | ·· 1.35 | 1.85 | 1.35 | 1.34 | ••• | |
| GG | | 0.51 | | 0.38 | 0.50 | ••• |
| ¹ See follow | ving paragrap | oh. | | | | |

DEHYDRATION OF SILICA IN ESCHKA'S METHOD.

In examining these results it is seen that HH, T, AA, A, and B are lower by the combustion method than by Eschka's. It was thought that the higher results might be due to silica coming down with barium sulphate. To remedy this, dehydration was tried after acidification of the filtrate. The percentages thus obtained are given in the column marked "Eschka's Dehydrated." Evidently in the case of HH it was not silica that caused a high result. The trouble seems to have been in the combustion method. HH, being a coke, had practically no moisture or volatile combustible matter, and was consequently so dry that it would not pack at all in the capsule. Complete combustion was in no trial obtained, and the sulphur was not obtained on fusing the residue.

AA was lowered only a little, but T, A, and B show that dehydration of silica is necessary in order to get accurate results. T had 16 per cent. of ash, A 15 per cent., B only 6 per cent., and AA 3 per cent. Although a high percentage of ash would be expected to give more silica to contaminate the barium sulphate, this contamination is not always confined to high ash coals. The temperature to which the substance is subjected must have something to do with the interference of silica, and as it is very difficult to keep the same temperature for all the experiments, it is better in all cases to dehydrate the silica.

BARIUM, STRONTIUM, AND CALCIUM SULPHATES IN ESCHKA'S METHOD.

P, by Eschka's method, is lower than by the combustion method. The residue was tested for barium to see if sulphur as barium sulphate might have been present, and not obtained by this treatment. None was found. Nevertheless it is interesting to know whether or not Eschka's mixture obtains sulphur contained in the coal as barium sulphate, strontium sulphate, and calcium sulphate. H was selected and separate additions of 10, 20, 30 and 40 mg. of pure barium sulphate were made. The sample thus obtained was subjected to exactly the same treatment as at first. In every case the silica was dehydrated to avoid any possible contamination.

Barium sulphate in H as first analyzed = 0.0510 gram.

SULPHUR IN COAL.

| Theo | oretical results. Gram. | Actual results. Gram. |
|-------------------------|----------------------------|--------------------------|
| +10 mg. barium sulphate | 0.0610 | 0.0510 |
| +20 mg. barium sulphate | 0.0710 | 0.0551 |
| +30 mg. barium sulphate | 0.0810 | 0.0559 |
| +40 mg. barium sulphate | 0.0910 | 0,0622 |

The same additions were made again and the mass was treated at a very much higher temperature (bright red) for about an hour after the carbon was all burned off.

| Result | s with high heat. Gram. |
|-------------------------|----------------------------|
| +10 mg. barium sulphate | 0.0613 |
| +20 mg. barium sulphate | 0.0682 |
| +30 mg. barium sulphate | 0.0667 |
| +40 mg. barium sulphate | 0.0901 |

These results are irregular, but indicate that, as usually carried out, the method gives a fraction of the sulphur present as barium sulphate, and that the conversion of larger amounts is entirely dependent on the increased temperature.

Using the same sample, 10 and 40 mg. of strontium sulphate were added.

| | retical results. um sulphate. Gram. 0.0637 | Actual results. Barium sulphate. Gram. 0.0620 |
|-------------------------------|---|--|
| +40 mg. strontium sulphate | 0,1018 | 0.0943 |
| Also 10 and 40 mg. of calcium | sulphate were a | dded. |
| Bar | oretical results. ium sulphate. Gram. | Actual results. Barium sulphate. Gram. |
| +10 mg. calcium sulphate | 0.0681 | o .o68o |
| +40 mg. calcium sulphate | 0.1196 | 0.1179 |

Silica was dehydrated in these experiments as in the case of barium sulphate.

It is a well-known fact that when strontium sulphate and calcum sulphate are boiled with sodium carbonate they are converted to strontium carbonate, calcium carbonate, and sodium sulphate. This fact alone was depended upon to get the sulphur so combined, and therefore high heating was not employed. The results indicate that such is the case. But as only 0.5 gram of sodium carbonate is used in the Eschka method, not quite all of the strontium and calcium sulphates were converted to sodium sulphate. If a larger quantity of sodium carbonate had been added, all the sulphur would have been obtained.

CHARLES W. STODDART.

SILVER POWDER IN STOLBA'S METHOD.

The presence of silver powder in Stolba's method seemed unnecessary. It certainly was not needed for the purpose of carrying sulphur in solution as silver sulphate, since no precipitate of silver chloride formed on acidifying the filtrate with hydrochloric acid. To test the necessity of its use four samples (AA, L, N, and B) were chosen and the method repeated, omitting the silver powder. The results are as follows:

| Without silv Per c | er powder. First results. ent. Per cent. |
|-----------------------|---|
| AA o., | 53 0.51 |
| L 3. | 33 3.08 |
| N o. | 60 0.65 |
| B I.; | 38 1.34 |

With the silver powder the results agree almost exactly with the standard method; without it they do not. The silver powder is evidently very useful, but what its function is we do not know.

MANGANESE DIOXIDE IN ANTONY AND LUCCHESI'S METHOD.

Results from Antony and Lucchesi's method are very good, but its fault as a rapid means of estimating sulphur is the action of the manganese dioxide. It runs through the filter very badly, requiring at least two, and usually three, filtrations to obtain a clear solution. Even then the precipitate of barium sulphate is contaminated with manganese dioxide. The addition of a few drops of ammonium acetate solution checks, to a certain extent, the running through. Great care has to be observed in heating up the mass, else deflagration will cause loss by spattering.

DEHYDRATION IN THOMSON'S METHOD.

Thomson's method seems simple and gives fair results, but dehydration of the silica is absolutely necessary after the fusion with carbonate.

SODIUM PEROXIDE IN HODGSON'S METHOD.

Hodgson's use of sodium peroxide is no improvement over the old deflagration method of fusion with carbonate and nitrate. Sodium hydroxide contains sulphur and is hard to weigh accurately. Sodium peroxide also is impure to a slight extent, and since it is added in small portions at a time, and quickly becomes sticky, it is extremely difficult to know just how much has been put in. Worst of all, the mass glows and spits violently when the sodium peroxide is added to the fused mixture, and great care must be exercised to prevent loss. Only two samples were tried with this method. Complete combustion was in no case obtained, constant attention was required, and the use of the blast-lamp needed at the end, thus allowing contamination from the gas flame. All in all this method is exceedingly impractical.

GENERAL COMPARISON.

Comparing all these methods of estimating sulphur with the standard, it appears that Eschka's method is the best. In order to get accurate results, however, the silica must be dehvdrated. For commercial purposes the method without dehvdration is satisfactory. As to ease of manipulation, Eschka's method is much better than the others. There is no deflagration or sputtering of the dry mass, providing, of course, that high heat is not applied at once, and moderate care is observed. In the manganese dioxide method the mass will splutter unless extreme care is taken. Stolba's method is almost as bad. The sodium peroxide method is worst of all. As regards ease of filtration, Eschka's method is again the best. There is no running through of the residue. Manganese dioxide always runs through, and the Stolba method gives trouble. The Eschka method gives sulphur combined as strontium sulphate and calcium sulphate, and if heated to a bright red heat will get small amounts of sulphur existing as barium sulphate.

CONCLUSION.

Attention is called to the fact that a large number of coals were selected from many samples received, in order to get the widest possible range both of composition and locality. Hence the methods were tried under all conditions in which sulphur might exist. If only a few samples had been used, and very thoroughly worked over, definite conclusions would have been quickly reached —conclusions that would hold only for those few coals. Where many and varied samples are tried, the conclusions may not be quite as definite, but such as they are they apply to all coals.

The comparison of results strongly confirms the accuracy of the standard method on all the samples of coal.

Eschka's method with the silica dehydrated is the best of the existing practical methods.

The remaining methods, though capable of accuracy in many cases, and particularly adapted to certain coals, do not by the reliability of the results or the ease of manipulation rival either the standard method or that of Eschka.

The preceding work was undertaken at the suggestion of Professor Edmund H. Miller, and for his advice and assistance throughout the course of these experiments the writer owes his most grateful thanks.

QUANTITATIVE LABORATORY, May 20, 1902.

ON A METHOD FOR THE DETERMINATION OF VERY SMALL VAPOR-TENSIONS IN CERTAIN CIRCUMSTANCES.

BY LAUNCELOT W. ANDREWS. Received june 7, 1902.

WHILE much has been done in recent years on the vaportensions of solvents, there has been but little work upon the tension of volatile substances in solution. It can not be doubted, however, that an investigation of phenomena of the class alluded to, promises interesting results if the experimental difficulties can be overcome. The method to which I would invite attention is based on a comparison of the tension of the solvent, assumed as known. with that of the substance dissolved.

If a substance, whose vapor-tension is S and molecular weight is M, evaporates freely into a volume V of air until the latter is saturated, we have for the weight of the substance evaporated, W, at constant volume,

$$W = MSV \text{ const.}, \tag{1}$$

in which the constant depends upon the units chosen. If a second substance with vapor-tension s, molecular weight m, evaporates simultaneously into the same volume of air to saturation, its weight, w, will be

$$w = msV$$
 const. (2)

Combining equations (1) and (2) and assuming all quantities as known, except s and V, we have

$$s = \frac{wMS}{mW}.$$
 (3)