connected with the one cylinder hanging in the beaker, containing the liquid, on a water-bath over a Bunsen burner.

When the liquid in the beaker has about the desired temperature, the lamp is extinguished and the weight of the cylinder ascertained.

Now the thermometer is read off again and the weight again ascertained. If the temperature has risen in the meantime the operation is repeated, till the weight is less than at the first reading. The averages of all temperatures and of all weights are taken and used for the computation.

A SHORT STUDY OF METHODS FOR THE ESTIMATION OF SULPHUR IN COAL.[1]

By G. L. Heath.

Received June 15, 1898.

As manufacturer's requirements with regard to certain metallurgical processes become more exacting from year to year, the determination of sulphur in the fuel must become more important. The interest taken in this subject is evidenced by the appointment of the committee from the society who have just made their preliminary report. The writer has been led, as a matter of interest, to communicate some experimental work upon the determination of sulphur.

There has been a little controversy, or doubt, as to the relative accuracy of the two "sintering" or "ignition" methods in general use as compared with each other, or with the old method of fusion with sodium carbonate and potassium nitrate. It must be assumed and understood that the following work was done rather to study methods and show precautions necessary, than to obtain close check results. This remark explains a discrepancy in results on one coal of very high sulphur content, since the methods which will now be described as used by the writer, were purposely not modified to suit that special case.

1. THE "FUSION" METHOD.

This is so well given in the text-books with so little variation that full description is unnecessary.[2] Blair's modifications used.

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[1] Read at the meeting of the New York Section, June 3, 1898.

[2] Blair's Analysis of Iron, *1888*, p. 245.

In our experience, much care must be taken to dehydrate, by evaporation with acid, the silicic acid which dissolves in the solution of the fused alkali. This renders the process too slow for technical work.

2. ESCHKA'S METHOD.[1]

a. One gram of powdered coal is intimately mixed with one gram of pure magnesium oxide and one-half gram sodium carbonate, and heated with the flame of a large (eight-ounce) alcohol lamp in a platinum dish of about 100 cc. capacity. A dish is much to be preferred to a narrow crucible, since it offers a better exposure of the coal to the air, and prevents excessive heat and dry distillation in the interior of the mass.

The mixture is frequently stirred with a platinum wire and the heat is raised very slowly, especially so with very soft coals. The flame, which is kept in motion and barely touches the dish at first until strong glowing has ceased, is increased gradually until, in fifteen minutes, the bottom of the dish is at a low red heat. When the carbon has burned away the mass is transferred to a No. 2 Griffin beaker and boiled five minutes with 100 cc. of distilled water and some oxidizing agent.

Fifteen cc. of saturated bromine water, as recommended by Mack and by Handy, is the purest and most efficient reagent to use, safer than the plan of adding ammonium nitrate during ignition. The hot liquid is then passed through a washed filter and the residue washed with hot water until the total volume is approximately 200 cc. The filtrate is then acidified strongly with hydrochloric acid, boiled until the free bromine is driven off, and sufficient hot solution of barium chloride added to insure the precipitation of all the sulphuric acid as barium sulphate, which is settled, filtered, and ignited.

b. Fresenius recommends that the ignited mixture be boiled directly in bromohydrochloric acid, which will dissolve all the sulphur in high coals, but loads the solution with salts and possibly silica.

c. The modification, recently published, involving the use of silver oxide, does not seem to offer any advantage whatever

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[1] *Chem. News*, **21**, 261 ; *J. Anal. Appl. Chem.*, **6**, 611.

over the other methods using inexpensive material, and is not included in the table.

3. HUNDESHAGEN'S METHOD.[1]

It is a familiar fact that this modification differs from Eschka's only in the substitution of potassium carbonate for sodium carbonate. The advocate of the first salt claimed that sodium carbonate did not retain all the organic sulphur from certain Bohemian brown coals.

J. O. Handy,[2] of Pittsburg, presented tests from which he deduced a conclusion in opposition to that of Hundeshagen, but he does not appear to have tested the particular class of coals specified by the latter chemist. The writer has, accordingly, experimented with a variety of samples, including Bohemian brown coal, and has experimented also with a few variations in the details of procedure. Part of the foreign samples were procured from the Michigan College of Mines, and a fine specimen of the Bohemian article from Prof. Lattimore, of the University of Rochester.

The proximate analyses were carried out as usual with the author, according to Blair's[3] modification of Heinrich's method. Blank analyses for the sulphur in reagents were also carried through. This is the more necessary, as I have sometimes met with goods labelled by importers "strictly C. P.," which were rather impure.

An inquiry, in one case, elicited the statement from a clerk that his house labelled articles C. P. to fill orders for the highest grade, even if they were only a common grade on the market at the time. The American firm of Baker & Adamson, it is but just to state, has furnished the purest chemicals for fuel analysis that we could obtain anywhere.

4 AND 5. WILEY'S AND CARIUS' METHODS.

I have had no experience with the Wiley and Carius methods, which are not so much used, as such, in America.

6. WET METHOD OF CALVERT.

The "wet method" of Calvert[4] is useful for the scientific inves-

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[1] *Chem. Ztg.*, 16, 1070; also *J. Anal. Appl. Chem.*, 6, 385.

[2] *J. Anal. Appl. Chem.*, 6, 116.

[3] Blair's Analysis of Iron, *1888*, p. 243.

[4] *Chem. News*, 24, 26; also Watts' Dictionary of Chemistry.

TABLE I.

PROXIMATE ANALYSES OF THE DOMESTIC AND FOREIGN COALS. SULPHUR INCLUDED IN FIGURES—NOT DEDUCTED FROM CARBON.

No.	Variety.	Special characteristics.	Locality.	Per cent. moisture at 105° C.	Per cent. volatile and combustible matter.	Per cent. fixed carbon.	Per cent. of ash.
1	Bituminous	clean lump	Ohio, U. S.	0.72	37.15	57.01	5.12
2	"	fine slack of	" "	0.78	30.72	54.92	13.58
3	Anthracite	clean lump	Penna., U. S.	2.47	3.00	88.80	5.73
4	"	" "	" "	2.95	3.23	86.95	6.87
5	Bituminous	" "	W. Va., U. S.	0.62	31.28	62.07	6.03
6	"	fine slack of	" "	0.75	29.64	62.75	6.86
7	Gray, soft	friable	Rhenish Prussia	2.72	23.03	6.41	67.84
8	Bituminous, soft	a little shaly	Pleasant Hill, Iowa, U. S.	1.26	43.72	45.65	9.37
8B	" "	weathered shaly sample	" " " "	1.85	42.90	45.97	9.28
9	Black, jet	lustrous, vitreous	Spain or Bohemia	2.83	38.70	49.46	9.01
10	Kerosene shale	grayish brown, woody pieces	N. S. Wales	0.07	82.05	5.81	2.07
11	Carmel	grayish	Hartley Vale, Blue Mts., N.S. Wales	0.07	81.37	5.32	13.24
12	Lignite	brown lump	Kosten, Bohemia	8.17	44.14	39.14	8.55

tigation of the forms in which the sulphur exists in fuel, but is unsuitable for technical work.

7. FAHLBERG-ILES PROCESS.[1]

The modified Fahlberg-Iles process of fusion with caustic potash in a silver crucible is correct, but is open to a strong objection, which does not affect either Eschka's or Hundeshagen's methods. It is necessary to heat slowly over an alcohol lamp to complete fusion, and the silica is thereby rendered soluble, but must be subsequently dehydrated by tedious evaporation. Accordingly, I have confined this work to the two most rapid technical methods, including a few results by complete fusion for comparison.

TABLE II.

EXPERIMENTAL SULPHUR DETERMINATIONS. PER CENT. OF SULPHUR FOUND.

		Oxidized by bromine water.			
No. of sample.	Treated in 100 cc. platinum dish.	Eschka's method.	Hundeshagen's method.	Oxidized with hydrogen peroxide. Eschka's method.	Fusion method with sodium carbonate and potassium nitrate in crucible.
1	Ignited..........	1.375	1.364	1.372	....
2	"	2.203	2.197	....	....
3	"	0.529	0.551	0.545	....
4	"	....	0.530	0.521[2]	....
5	"	1.063	1.068	....	....
6	"	1.637	1.635	....	....
7	"	1.480	1.540	1.760(*c*)[3]	....
	"			1.690(*d*)	
8A	"	4.95	4.99	....	4.97(*e*)
	"		4.74		
8B[4]	"	4.76	4.69(*g*)	....	....
	"	(*h*)4.80	4.88(*m*)	....	4.89(*f*)
9	"	0.201	0.203	....	....
10	"	0.364	0.375	....	....
11A	"	0.43	0.41	....	....
11B	"	0.30	0.33	....	....
12	"	0.966	0.967	0.923	0.968
	"	(*h*)0.907		0.983(*d*)[3]	

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[1] Furman's Manual of Assaying, *1895*, p. 88.

[2] Hundeshagen's method used in this case.

[3] Oxidized with sodium peroxide.

[4] This is sample 8A weathered by two years' exposure of the powder to air.

7(*c*). Two grams sodium peroxide added during the ignition.

7(*d*) and 12(*d*). Two grams of sodium peroxide added to the aqueous solution of the ignited residue, and boiled. The 7(*c*)(*d*) results are too high owing to dissolved silica.

8(*e*). The fused mass was directly dissolved in dilute acid, and then evaporated to dryness, taken up again with dilute hydrochloric acid, and filtered.

8(*f*). The fused mass was boiled with water only, and the solution filtered, then acidified with hydrochloric acid, and evaporated to dryness in order to dehydrate silica. (*g*). Ignited very quickly at strong heat in dish. (*h*). Ignited this quickly in crucible. See No. 8B, Hundeshagen's method, also No. 12. 8B, 11, and 12 were made with a compact variety of magnesium oxide, and in analysis 8B not quite all the sulphates could be extracted in five minutes boiling with water.

8(*m*). Ignited mass dissolved directly in bromohydrochloric acid.

From the foregoing experimental analyses in addition to regular work, considerable information has been secured concerning the effect of variation in the small details of the standard methods, and the precautions to be observed in their use, which might be summed up for discussion, as follows:

1. I cannot confirm the statement of Hundeshagen that Eschka's mixture does not retain all the sulphur from certain coals, and as far as my experience goes must agree with Handy's opinion with one qualification.

2. Rapid heating with magnesium oxide and alkaline carbonate in a deep crucible may be made to give a little lower results than slow heating in a shallow dish with such a coal as No. 12 (brown coal), but with coal No. 11 (jet) it was necessary to heat very slowly, even in a dish, so as to avoid too great a heat, which might allow dry distillation of combined sulphur without complete oxidation.

Hundeshagen's loss, which he attributed to the inability of sodium carbonate to retain all the sulphur of brown coals, may be due to rapid heating in a crucible of the sodium carbonate mixture, which is also more dusty than one of coal, magnesia, and potassium carbonate.

3. The "sintering" methods, when performed with good

judgment, agree closely with the results obtained by fusion of the coal with sodium carbonate and potassium nitrate.

4. If the "fusion method" is used, or sodium peroxide employed as an oxidizing agent, great care must be taken to dehydrate all silica by evaporation with hydrochloric acid.

Some chemists direct that the fused mass should be boiled with water and filtered before acidification with hydrochloric acid.[1] Other authorities state that the fused mass is to be dissolved directly in dilute acid.

The first procedure is to be preferred as the iron oxide and insoluble matters are removed at once by the filtration of an aqueous solution of the fusion.

5. The purest and most efficient reagent to complete the oxidation of sulphur compounds in the aqueous solution of the ignited residue of the "ignition" methods is a saturated solution of bromine in water. The use of hydrogen peroxide involves the testing of every bottle of the reagent for the very variable quantity of sulphuric acid it always contains. If this impurity is determined by a blank analysis and the amount deducted in the proper manner, the results obtained by its use are quite satisfactory (see 1, 3, 4, 12).

If sodium peroxide is added at first to a mixture of coal and magnesium oxide, the action is too violent. If added when the coal is nearly burned, the mass, nevertheless, balls on heating and some soluble sodium silicate appears to be formed by the heating or during subsequent aqueous extraction, and the barium sulphate will be a little impure unless silica is dehydrated by evaporation. Refer to coal analysis No. 7 (*c*) and (*d*).

In the writer's experience, no reagent gives as good results as the bromine water.

6. The five minutes' boiling of the ignited residue of coal ash, magnesium oxide, and carbonates with water (as generally prescribed by the authors) is sufficient to convert all the insoluble sulphates of lime, iron, etc., unless these substances are present in considerable quantity, or unless the magnesium oxide is a compact, heavy sample, as employed with No. 8B and No. 12. Under these circumstances the boiling and extraction of the ignited residue with water should be prolonged

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[1] Blair's Iron Analysis; see also Stillman's Engineering Chemistry, p. 20.

for, say, an additional period of ten minutes—a precaution not alluded to by chemical authors, but a necessary one.

The two following experiments were made in order to show that this precaution must be taken with fuels, especially weathered coals, carrying a large amount of either iron or calcium sulphates.

TABLE III.

Sample No. 13.	Barium sulphate. Gram.
Taken, 1+ grams coal, yielding	0.0295
Added 0.1869 gram C. P. calcium sulphate, yielding	0.3202
Total	0.3507
Result of ignition, boiling five minutes with 100 cc. water + 15 cc. bromine and washing (blank allowed for)	0.2615
Deficiency =	0.0882

Sample No. 14.	Barium sulphate. Gram.
Taken, 1+ grams coal, yielding	0.0325
Added 0.4070 gram weathered ferrous sulphate containing the equivalent of	0.3490
Total	0.3815
Result of ignition, boiling five minutes with 100 cc. water + 15 cc. bromine and washing (blank allowed for)	0.3509
Deficiency =	0.0306

As far as my experience goes, the methods, irrespectively of Eschka and Hundeshagen, which involve a simple ignition, at low temperature, with a sulphur absorbent, are far preferable as rapid operations, suitable for technical work, to any plan necessitating a complete fusion with a consequent solution of silica. The two preferred methods will uniformly furnish accurate results, within usual limits of error in sampling, if the operator will only exercise a little judgment in certain cases.

With anthracite coal and coke there is no liability to error. With softer fuels, especially lignites, the materials should be especially well ground, well mixed, and stirred during the ignition in an open dish and if the proximate analysis and the appearance of the ash, indicates that the coal contains a large percentage (over three per cent.) of sulphur as pyrites (or calcium sulphate in the ash), the boiling and washing should be continued for a longer time, and the washed residue finally dissolved in acid, and qualitatively tested by itself.