

possible by rotating the block-tin condensing tube to raise the distillation flask completely from its support. It may then be easily removed without danger of breaking. The apparatus costs but a third as much as when made with copper condensing tank, and is practically indestructible; the materials employed in its construction can be obtained of any plumber or gas fitter and put together with a pipe wrench. Under ordinary conditions the labor and material for a ten-tube still will not cost more than \$35.00.

STATE LABORATORY OF HYGIENE,  
INDIANAPOLIS, IND.

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## SOME EXPERIMENTS ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COALS AND LIGNITES.<sup>1</sup>

By E. E. SOMERMEIER.

Received May 23, 1906.

THE method in general use in this country for the determination of volatile combustible matter is that recommended by the Committee on Coal Analysis appointed by the American Chemical Society.<sup>2</sup> The directions given are as follows:

"Place 1 gram of fresh, undried, powdered coal in a platinum crucible, weighing 20 or 30 grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear but the under surface should remain covered with carbon. To find 'Volatile Combustible Matter' subtract the per cent. of moisture from the loss found here."

This is the method used in the volatile determinations made in the Chemical Laboratory of the United States Geological Survey Fuel Testing Plant, the only modification being that the flame is protected from air currents by enclosing in a cylindrical

<sup>1</sup> Published by permission of the Director of the United States Geological Survey. Read before the Columbus Section of the American Chemical Society, May 23, 1906.

<sup>2</sup> This Journal, 21, 1122-1126.

asbestos shield 15 cm. long and 7 cm. in diameter, the platinum triangle being located 3 cm. below the top of the shield. The use of the shield gives more uniformity in the heat treatment with a corresponding greater uniformity of results. It is well recognized that variations in the size of the crucible, tightness of the lid, strength of the flame, etc., affect the process noticeably. Under uniform conditions the same operator usually has no great trouble with duplicates but it is quite probable that different operators working even under only slightly different conditions would have considerable trouble in duplicating results.

In most coals the routine results obtained in the laboratory have checked to within less than 0.3 or 0.4 per cent.; occasionally a sample has given trouble and the variation between duplicates without any apparent reason was as great as 1 per cent. On some lignites it has been found impossible to obtain close duplicates and on a few samples the carrying out of the official method gives very inaccurate results. This may be shown by the results obtained in the laboratory upon two different samples of the same lignite, which samples differed from one another only in the amount of moisture remaining in the air-dried sample and perhaps in the fineness of the grinding. The results on Sample No. 1 are as follows:

Moisture.....	9.88
Volatile matter.....	36.17
Fixed carbon.....	43.65
Ash.....	10.30
Sulphur.....	1.30

Sample No. 2.

Moisture.....	20.24
Volatile matter.....	58.48
Fixed carbon.....	10.85
Ash.....	10.43
Sulphur.....	1.03

This great difference in the fixed carbon results could not be accidental as all of the results on both samples were duplicated. A series of determinations was begun to determine, if possible, the cause of this great variation. Two causes were suspected and both were found to be partly responsible for the difference. (1) Mechanical loss due to the throwing out of solid particles by the too rapid expulsion of the volatile matter. The pos-

sibility of loss from this source is mentioned in the report of the committee but the results of their experiments are negative. (2) A different breaking down of the hydrocarbon compounds when expelled under different conditions and in the presence of variable amounts of moisture.

The results of Mr. N. M. Austin as published in the committee's report show that a preliminary treatment of the sample at a low heat and then the application of the full flame of the Bunsen burner gives higher results in fixed carbon than where the full flame of the Bunsen burner is applied from the beginning.

The proximate analysis of the sample of lignite giving the unusual results was finally reported by the laboratory as follows:

Moisture.....	20.24
Volatile matter.....	35.42
Fixed carbon.....	33.91
Ash.....	10.43
Sulphur.....	1.03

A series of seven results by the official method gave for volatile matter on this sample an average of 62.5 per cent. with a variation between high and low results of over 12 per cent. Three results of volatile matter on this sample made after previous expulsion of the moisture at 105° gave average volatile matter 39.6 per cent. with a variation between high and low results of 5.9 per cent. Preliminary treatment by driving off the moisture and most of the volatile matter at a low heat was then tried, the flame of the Bunsen burner being turned down to 10 cm. and the crucible gradually heated. The application of the heat was regulated by holding the burner in the hand and heating in such a way as to expel the moisture slowly and gradually smoke off most of the volatile matter, the volatile matter escaping freely enough during the last minute of this preliminary heating to burn with a small flame around the edge of the crucible cover. Two results with five minutes of preliminary heating and then seven minutes over the full flame of the Bunsen burner gave an average in volatile matter of 35.08 per cent., the variation between the two results being 0.23 per cent. Two results with three minutes' preliminary heating and seven minutes over the full flame of the Bunsen burner gave an average of 35.6 per cent. with a variation of 0.75 per cent. between results. A result

obtained by four minutes of preliminary heating and then seven minutes over the full flame gave 35.42 per cent. The difference in results obtained by the three, four and five minute preliminary treatment is small and in all subsequent experimental tests the time of the preliminary heating was four minutes. To determine the mechanical losses and difference in volatile compounds given off, a number of ash determinations were made after the driving off of the volatile matter by the official method and after driving off the volatile matter in connection with the preliminary heating. The results of volatile matter and ash on three determinations by the official method are as follows:

Volatile matter.....	66.72	67.47	54.82
Ash.....	4.30	4.38	7.25 <sup>1</sup>

Two determinations with four minutes of preliminary heating and then seven minutes over the full flame gave:

Volatile matter.....	36.06	36.65
Ash.....	11.16	11.15

That mechanical losses occurred during the rapid evolution of the volatile matter by the official method was also indicated by the shower of solid carbon particles driven off as sparks during the first few minutes, while with the preliminary heating these sparks were nearly or entirely absent. The average volatile matter on the first two determinations was 67.1 per cent., the average ash 4.34 per cent. The average volatile matter on the two results by the modified method was 36.35 per cent., ash 11.15 per cent. The moisture in the sample determined at this time was 19.78, giving fixed carbon 32.72 per cent. The difference in the ash results on the two pairs is 6.81 per cent., or the amount of sample driven off mechanically by the regular method is 6.81 ÷ 11.15, or 61 per cent. Taking this portion of the fixed carbon result by the modified method gives 20 per cent. as the amount of fixed carbon expelled mechanically in the first determinations. The results on the official process after making this correction and also taking the correct ash value are as follows:

<sup>1</sup> This result is possibly explained by the fact that this sample stood for two hours in the crucible after weighing out and a considerable amount of the moisture content may have escaped before the sample was treated for the determination of the volatile matter.

Moisture.....	19.78
Volatile matter.....	47.10
Fixed carbon.....	21.97
Ash.....	11.15

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100.00

After making this correction for mechanical losses the difference in the fixed carbon by the two processes is still 10.75 per cent., which difference must be due to the difference in the breaking down of the hydrocarbon compounds by the different heat treatment. The ash from the third result by the official method was 7.25 per cent. or the loss of ash 3.9 per cent. Correction for fixed carbon mechanically carried off is accordingly  $3.9/11.15$  or 11.4 per cent. The result, after making the fixed carbon and ash corrections, figures as follows:

Moisture.....	19.78
Volatile matter.....	43.42
Fixed carbon.....	25.65
Ash.....	11.15

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100.00

The difference in this case in fixed carbon by the two methods due to the different heat treatment is 7.07 per cent.

*Effect of Fineness of Sample.*—This particular sample was very finely ground. To find out how much this difference in result was due to the fineness of grinding, a duplicate portion of the same sample was ground down till it passed a 40-mesh sieve. The results of duplicates by the official method and the modified method obtained are as follows:

	Official method.	Preliminary heating.
Volatile matter.....	42.07	35.72
Ash.....	10.25	11.20

Or loss in ash 0.95 per cent. The proximate analysis of the sample by the modified method is as follows:

Moisture.....	19.35
Volatile matter.....	35.72
Fixed carbon.....	33.73
Ash.....	11.20

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100.00

The correction for fixed carbon to be applied to the result of the official method is  $0.95/11.20$  or 8.5 per cent. of the fixed

carbon result of the modified method, which is 2.9 per cent. The results by the official method after correcting for mechanical loss of fixed carbon and ash are as follows:

Moisture.....	19.35
Volatile matter.....	39.17
Fixed carbon.....	30.28
Ash.....	11.20
	100.00

The difference in fixed carbon between the two methods due to different heat treatment is 3.45 per cent. These results show, at least, for lignites that the fineness of the sample has an important effect upon the result. Upon another sample of lignite similar to the one already tested, except that it contained more moisture (30.45 per cent.), the results obtained are as follows:

Average of results by the modified process:

Moisture.....	30.45
Volatile matter.....	30.97
Fixed carbon.....	27.75
Ash.....	10.83
	100.00

The results in volatile matter and ash by the official method:

Volatile matter.....	44.40
Ash.....	8.12

Hence, the correction to be applied to the fixed carbon and ash for mechanical loss is 2.71/10.83. Applying these corrections, the results by the official method are:

Moisture.....	30.45
Volatile matter.....	37.43
Fixed carbon.....	21.29
Ash.....	10.83
	100.00

The difference in the fixed carbon results between the two samples due to different heat treatment is 6.46 per cent.

To test the effect of the fineness of grinding upon the determination of the volatile matter in ordinary bituminous coal a sample of Kentucky coal containing 2 per cent. moisture, 5.7 per cent. ash and 0.9 per cent. sulphur was still further reduced in ash content by floating on a calcium chloride solution, sp. gr.

1.32. The lighter portion was then thoroughly air-dried and separated by sifting into the following sizes: 1/4 to 1/10, 1/10 to 1/20, 1/20 to 1/40, 1/40 to 1/80 and 1/80 and finer. The proximate analyses of the samples by the official method are as follows:

	Moisture.	Volatile matter.	Fixed carbon.	Ash.
1/4-1/10.....	1.15	39.05	58.20	1.60
1/10-1/20.....	1.45	38.80	58.55	1.20
1/20-1/40.....	1.70	38.55	58.35	1.40
1/40-1/80.....	1.90	38.05	58.40	1.65
1/80 and finer....	2.05	35.54	59.66	2.75

By the modified process with four minutes of preliminary heating the result in volatile matter on the 1/20 to 1/40 size was 33.75 per cent. and on the 1/80 and finer 32.85 per cent.

The results in volatile matter on these different sizes are somewhat higher on the coarse samples. However, the different ash contents of the different sizes indicate that the sizing had to a degree separated the coal into somewhat different varieties, as the higher ash content of the finer sample would not in itself be sufficient to account for the lower volatile results. In order to see whether the difference was due to the fineness of grinding or difference in the coals, a portion of the 1/20-1/40 sample was ground down in an agate mortar and the volatile matter determined on this fine portion. The average of several results was 37.6 per cent. as against 38.55 per cent. on the coarse sample.

From this series of results it appears, at least in low moisture bituminous coals, that the finer ground samples give somewhat lower volatile matter than the coarser samples, probably due to the more complete sintering together of the fine samples upon heating, with the consequent effect upon the giving off of the volatile matter.

*Effect of Different Heat Treatment.*—In order to find out how much effect different heat treatment has on different coals, a series of samples was selected ranging from anthracite to peat, most of the samples used in the tests having been previously more or less completely air-dried so as to permit of better handling in the laboratory. Determinations for volatile matter were made in duplicate by the regular official method and by the four-minute preliminary heating method. The proximate analysis of the samples with the volatile matter determined by the official method is tabulated in the first five columns; the results for volatile matter by the preliminary heating are given in the sixth column; the

differences in volatile matter by the two methods are given in the seventh column. The determinations for moisture were all made in accordance with the official method by weighing out a separate sample. The same is true of the determinations for ash with the exception that upon two or three of the lignite samples and one of the Pennsylvania samples the results for ash are those obtained after the determination of the volatile matter by the modified process. These particular samples and results are all specifically mentioned elsewhere in this paper.

Source of coal.	Moisture.	Official method. Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Volatile matter with four min- utes' preliminary heating.	Difference.
Colorado anthracite...	2.80	5.05	77.55	14.60	0.60	4.90	0.15
Arkansas.....	0.83	12.47	72.05	14.65	2.14	12.37	0.10
Pennsylvania.....	0.90	17.35	74.92	6.83	0.97	16.07	1.28
Pennsylvania.....	1.05	33.10	53.30	12.55	1.76	30.35	2.75
Kentucky.....	2.99	37.51	56.68	2.82	0.58	34.78	2.73
Indiana.....	4.20	37.70	45.65	12.45	4.13	34.67	3.03
Washington.....	6.65	35.87	44.57	12.91	0.68	34.25	1.62
Indiana.....	8.40	34.40	48.72	8.48	1.47	32.00	2.40
North Dakota (lignite).....	11.65	45.58	32.97	9.80	1.04	40.17	5.41
Illinois.....	12.40	32.18	42.82	12.60	1.30	30.12	2.06
Texas lignite (fine) ...	19.78	62.50	6.57	11.15	1.03	35.42 <sup>1</sup>	27.08
Texas lignite (40- mesh duplicate)....	19.35	42.07	27.38	11.20	....	35.72	6.35
Texas lignite (not air-dried).....	30.45	44.40	15.42	9.73	....	30.97	13.43
Massachusetts peat ...	13.25	49.80	16.21	20.74	0.58	47.92	1.88

With the exception of the anthracite and semi-anthracite samples, the results by the preliminary heating as compared with the official method all show a considerably less amount of volatile matter and a correspondingly greater amount of fixed carbon. In the case of the lignites, the greater volatile matter by the official method, as has been shown, is partly due to mechanical losses.

<sup>1</sup> Two determinations upon the fine sample of Texas lignite made by heating for four minutes over a flame 5 cm. high and then seven minutes over the full flame (25 cm.) gave 35.47 per cent. volatile matter. Almost an exact check upon the result obtained by the four-minute preliminary heating with a 10 cm. flame regulated by holding burner in the hand.



In order to see if mechanical losses might account for the differences on the bituminous coals, determinations for the ash after the determination of the volatile matter were made on one of the Pennsylvania samples. The average results for ash on the samples by the two methods are as follows:

	Ash.
Official method.....	12.56
Preliminary heating.....	12.53

These results indicate no mechanical loss whatever and in none of the samples except the lignites were visible solid carbon particles driven off in the form of sparks, and the differences must be ascribed to the different breaking down of the hydrocarbon compounds by the difference in heat treatment.

*Effect of the Presence of Moisture.*—Comparisons of the results of volatile matter on a great number of samples differing from one another in moisture content indicate that the presence of loosely held moisture in the sample causes a higher volatile result. In order to obtain more definite data on this question three samples low in moisture and representing widely different kinds of coal were selected for a series of determinations. The effect of loosely held moisture upon the determinations for volatile matter in each of these samples was determined by adding to the sample after weighing out definite amounts of water, which was thoroughly mixed with the sample by means of a fine platinum wire and the volatile determination then made in the usual manner according to the official method. The first sample selected was a sample of Pennsylvania coal. The proximate analysis of the air-dried sample is as follows:

Moisture.....	1.05
Volatile matter.....	33.00
Fixed carbon.....	53.30
Ash.....	12.55
Sulphur.....	1.75

The results for volatile matter in this sample determined in the presence of additional moisture are as follows:

	Volatile matter.
With 0.05 gram additional moisture.....	33.60
With 0.1 gram additional moisture.....	33.70
With 0.15 gram additional moisture.....	33.80
With 0.2 gram additional moisture.....	34.10
With 0.3 gram additional moisture.....	33.90

The second sample was an air-dried sample of Illinois coal, the proximate analysis of which by the regular official method is as follows:

Moisture.....	2.35
Volatile matter.....	39.35
Fixed carbon.....	44.65
Ash.....	13.65

The results of volatile matter with the additional moisture added to the sample are as follows:

	Volatile matter.
With 0.03 gram additional moisture.....	39.60
With 0.05 gram additional moisture.....	39.30
With 0.10 gram additional moisture.....	40.00
With 0.15 gram additional moisture.....	40.05
With 0.2 gram additional moisture.....	39.75

The third sample was an air-dried sample of Arkansas lignite, the proximate analysis of which by the official method is as follows:

Moisture.....	10.85
Volatile matter.....	38.50
Fixed carbon.....	31.40
Ash.....	19.25
Sulphur.....	0.83

The results for volatile matter with the additional moisture are as follows:

	Volatile matter.
With 0.05 gram additional moisture.....	40.35
With 0.10 gram additional moisture.....	41.20
With 0.15 gram additional moisture.....	40.90
With 0.20 gram additional moisture.....	44.90

Without exception all of these results show that the presence of loosely held moisture in the sample increases the value obtained for the volatile combustible matter. The average increase for the Pennsylvania sample is about 0.7 per cent. On the Illinois sample the increase for volatile matter is 0.4 per cent. On the Arkansas lignite the increase is 3.3 per cent.

To see what effect this loosely held moisture might have on the volatile determinations where the sample was first subjected to four minutes of preliminary heating over a low flame determinations were made upon these samples with and without additional moisture. The results are as follows:

Pennsylvania sample with no moisture added, volatile matter 30.35. With 0.3 gram added, the volatile matter 31.65.

The Illinois sample with no moisture added, volatile matter 34.85. With 0.15 gram moisture added, volatile matter 36.10.

The lignite sample with no moisture added, volatile matter 36.90. With 0.2 gram moisture added, 37.40.

These results show that even with a gradual preliminary heating the presence of loosely held moisture increases the value of the volatile determinations, the difference in some of the samples being as great as the difference by the official method, from which it appears that the rapid application of heat sufficient to drive off this moisture results in a reaction between the water vapor and the carbon or hydrocarbons in the coal.

*Conclusions.*—The results of the foregoing experiments and tests show that the value obtained for volatile matter in coal is affected to an important degree by the method of heating the sample, by the fineness of pulverization and by the amount of loosely held moisture present. In bituminous coals these differences do not exceed 3 or 4 per cent. and appear to be entirely due to a different breaking up of the hydrocarbon compounds under the different conditions of heat treatment, fineness of sample and amount of moisture present. In the case of lignites where the difference may be as high as 25 per cent. this difference is largely due to the mechanical loss in the sample during the rapid expulsion of the volatile matter.

*Correctness of Results.*—Since the determination of the volatile matter is a purely arbitrary one unless mechanical loss can be shown, as in the case of lignites, it appears that any results obtained by following out the regulation method should be considered as correct, any difference in results due to differences in fineness of pulverization or to the amount of moisture present having no effect upon the correctness of the value actually obtained. The differences due to difference in pulverization or moisture content do, however, have a very important effect when it comes to the question of different chemists obtaining concordant results upon different samples of the same coal.

In regard to the difference in results obtained due to a different heat treatment, while the method of heating as given by the official method may be considered as giving the correct result it does not necessarily give us a result approximating very closely

the volatile matter as given off when the coal is fired under a steam boiler or especially when coked in a coke oven, as under these conditions the volatile matter is driven off gradually and during a considerable interval of time, and it appears that the slower driving off of the volatile matter from the sample in the laboratory gives results more in accordance with these conditions than does the official method. This latter fact is, however, a matter of minor importance, for so long as all volatile determinations are done in the same way it makes very little difference what that way is.

In the case of lignites where the application of the official method causes mechanical losses it appears desirable and necessary that the committee so modify the official method for volatile matter in lignites as to prevent this loss, and the results of these foregoing determinations and experiments are published at this time with a view of bringing this matter before the committee and the public.

U. S. GEOLOGICAL SURVEY,  
FUEL TESTING LABORATORY.

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## THE RELATION OF SODIUM TO POTASSIUM IN SOIL AND SOLUTION CULTURES.<sup>1</sup>

BY J. F. BREAZEALE.

Received May 12, 1906.

THE determination of the exact amount of salt absorbed from solution by plants during the process of growth has been the subject of many experiments in former years. The ordinary gravimetric or volumetric methods which have usually been employed in such investigations have been on the whole inadequate for such work. The soil solution or the nutrient solution best suited to the requirements of most plants is usually of such a low total salt content that slight changes in its concentration cannot be detected by ordinary analytical means without the expenditure of an amount of time which is almost prohibitive. In the same way the amount of salt a seedling will absorb from solution in the course of a short period of its growth is usually too small to be detected by such methods.

For several years past the Bureau of Soils has been devising and adapting analytical methods which are well suited to such

<sup>1</sup> Published by permission of the Secretary of Agriculture.