

tation  $23.1^{\circ}$ , equal to six and seven-tenths per cent. oil; color, lemon peel only.

4. "Ten Cent Lemon:" Alcohol, 71.7 per cent.; rotation  $21.5^{\circ}$ , equal to six and three-tenths per cent. oil; precipitation with correction showed five and six-tenths per cent. oil; difference due to presence of cane-sugar; color, tropæolin.

5. "Monarch Lemon Extract:" Alcohol, 94.66 per cent.; rotation  $25.7^{\circ}$ , equal to seven and a half per cent. oil; precipitation gave seven and three-tenths per cent. oil of lemon, having a refraction of  $65^{\circ}$ - $69^{\circ}$ .

6. "Bon-ton Extract of Lemon:" Alcohol, 22.85 per cent.; rotation  $0.1^{\circ}$  (trace of oil); coloring-matter, dinitrocresol.

7. "Extract of Lemon:" Alcohol, 89.9 per cent.; rotation  $20.8^{\circ}$ , equal to six and one-tenth per cent. oil; precipitation yielded six and two-tenths per cent. oil of lemon, of refraction  $63^{\circ}$ - $68^{\circ}$ .

8. "Double Strength Lemon Extract:" Alcohol, 54.4 per cent.; rotation  $1.8^{\circ}$ , equal to one-half per cent. oil; color, dinitrocresol.

9. "Lemon Extract from druggist:" Alcohol, 92.0 per cent.; rotation  $15.9^{\circ}$ , equal to four and nine-tenths per cent. oil; precipitation showed five per cent. oil, of refraction  $64^{\circ}$ - $68^{\circ}$ .

Only such extracts as fail to precipitate with water occasionally show a slight laevorotation.

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## ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COKE AND ANTHRACITE COAL.

BY RICHARD K. MEADE AND JAMES C. ATTIX.

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SOME years ago a discussion arose between the consumer and the manufacturer of a coke as to its value. The user objected to the high ash and in support of his claim gave the analysis of his chemist, in which the ash was reported at eighteen per cent. The maker replied that the analysis was worthless as the chemist who made the analysis was probably incompetent, since he had reported nearly three per cent. of volatile combustible matter and that in a seventy-two hour coke the volatile combustible matter could not be nearly so high. The question was referred to a well-known analytical chemist. His analysis, while agreeing with that of the consumer's chemists in the percentage of ash, gave the volatile combustible matter as six-

tenths per cent. The consumer's chemists then checked their work and still found over three per cent. of volatile combustible matter. They used the method of heating a one-gram sample for three and a half minutes over a Bunsen burner and then for the same length of time over a blast-lamp, reporting the loss after deducting the percentage of moisture (found on another sample) as volatile combustible matter. A letter to the referee brought out the fact that he used a ten-gram sample and heated for the same length of time. The only excuse the consumer's chemists could give their employers was, that they used the method published in Blair's standard work on the analysis of furnace materials and products and that this was the method usually published in works on metallurgical analysis.

Of the commonly published methods for the determination of volatile combustible matter in coke and anthracite coal, none reach anywhere near even approximation. The method of Hinrichs<sup>1</sup> which, by the way, he recommends for soft coal and says nothing about coke or anthracite, gives far from true results; nor is the method even comparative. Heating first over a Bunsen burner and then over a blast-lamp drives off volatile matter and traces of moisture and *burns some carbon*. The loss occasioned by the latter in many cases amounts to several times that by the two former occurrences. This burning may be prevented by heating the sample in a non-oxidizing atmosphere, such as nitrogen. The loss after such a heating will represent the volatile products driven off by a high temperature. What these products are it is not our purpose to discuss. Probably even when the sample has been thoroughly dried moisture is among them.

The determination of volatile combustible matter in coke is worth doing well or worth doing not at all. If the determination of volatile combustible matter is used for checking the coking of the coal, it is an important determination of itself, and so long as the determination of the fixed carbon depends upon a knowledge of the volatile combustible matter, it is a necessary one indirectly. For, if the volatile combustible matter is one or two per cent. above what it should be, by just so much will the fixed carbon fall short of the true percentage.

The following investigation, looking toward a more satisfactory

<sup>1</sup>*Chem. News*, 18, 33.

method of determining volatile combustible matter, in coke and anthracite, was undertaken by the writers over two years ago and was the outcome of the incident mentioned in the opening paragraph of this paper. The first step was to heat samples of coke in nitrogen, determine the loss and call such loss "volatile combustible matter" after subtracting the moisture, driven off by one hour's heating at  $110^{\circ}$  C. The method of procedure consisted in weighing samples of from three to four grams of coke into a small platinum dish, placing this in the crucible of the carbon apparatus described by Dr. Porter W. Shimer in the July number of this Journal<sup>1</sup> and passing a slow current of nitrogen through the apparatus until the air had been driven out. The nitrogen used was prepared by heating together, saturated solutions of potassium nitrite and ammonium chloride. The gas was kept in glass gas-holders, and freed from oxygen by passing through cuprous chloride dissolved in hydrochloric acid. The gas was dried just before use by passing through calcium chloride tubes, dipped in front of the crucible. The exit tube from the crucible dipped into strong sulphuric acid, keeping any moisture or air from getting back into the crucible. After passing through the crucible for half an hour the current of nitrogen was slackened, a low flame placed under the crucible, the water-cooling apparatus started and the heat then carefully raised. After heating the coke for a few minutes over the full Bunsen flame, the blast-lamp was made to replace the latter and a high temperature maintained for ten or fifteen minutes. The sample was cooled in the current of nitrogen, removed, and weighed. Below are a few results upon a sample of coke which had been dried for one hour at a temperature of  $110^{\circ}$  C.

After heating three grams over a blast-lamp for fifteen minutes, the loss was found to be 0.31 per cent. After again heating, an additional loss of 0.0003 gram or 0.01 per cent. occurred.

After heating three grams for ten minutes over a blast-lamp, the loss was 0.0090 gram or 0.30 per cent. After again heating, an increase of 0.0001 gram or 0.003 per cent. occurred.

After heating three grams over a blast-lamp for six minutes, the loss was 0.0095 gram or 0.32 per cent. On again heating, the sample lost 0.0002 or 0.007 per cent.

<sup>1</sup> This Journal, 21, 557 (1899).

Heating in hydrogen was also tried and gave practically the same result. The losses from four determinations were 0.31, 0.31, 0.29, and 0.30 per cent.

At the time these investigations were undertaken, we supposed the idea of heating in nitrogen was original with us. A letter from Mr. W. H. Blauvelt, of the Semet Solvay Co., of Syracuse, N. Y., however, informed us that the method essentially as worked out by us was used in his laboratory and also in various technical and commercial laboratories in England and in Germany. Hydrogen, answering apparently as well as nitrogen, replaced the latter in most of these laboratories.

Samples of coke and anthracite were carefully standardized by heating in nitrogen and the volatile combustible matter then determined by various methods in common use.

The method commonly published of heating one gram for three and a half minutes over a Bunsen burner and then for the same length of time over a blast-lamp was first investigated. A sample of Pocahontas (West Virginia) coke losing, on heating in nitrogen, 0.61, 0.62, and 0.60 per cent. was used in the experiments.

We noted the following points :

Different operators get widely varying results as these determinations will show.

Operator.	Per cent of volatile combustible matter.	True per cent of volatile combustible matter.
A .....	3.01	0.61
B .....	2.51	0.61
C .....	2.36	0.61
D .....	2.25	0.61

This variation is due to the size of the crucible, the tightness of the joint between the crucible and its lid, the height at which the crucible is placed above the flame and the size of both the Bunsen burner and blast-lamp flames. A large crucible will give a higher result than a small one because the larger the crucible the more air will be present and consequently the more coke will be burned and the greater the loss will be on ignition. Below are some results on this.

Size of the crucible. cc.	Per cent. volatile combustible matter.
12	1.96
12	1.90
16	2.10
16	2.21
21	2.56
21	2.58
30	3.19
30	3.42

Since the burning takes place only on the surface of the sample, the shape of the crucible would also effect the result. In a narrow crucible the loss due to burning of the carbon would be less than in a wide one. In all of the above experiments crucibles of the usual forms were used. Of course the fit of the lid makes a great difference. Dr. Porter W. Shimer, in order to effect a close joint between the crucible and the lid, uses a thin piece of wet asbestos paper. This lessens considerably the quantity of carbon burned.

Ignition over different burners or blast-lamps gives varying results. A large flame, other things being equal, will burn more carbon than a small one. A few results will show the variation one may expect.

Burner. No.	Blast. No.	Loss on ignition. Per cent.
1	1	2.12
1	1	2.20
2	1	2.31
2	1	2.39
1	2	2.91
1	2	2.80
2	2	3.00
2	2	3.11

The results by this method are not even comparative, because some cokes burn more readily than others. A soft coke burns more readily than a hard one. A sample of Connelsville coke containing 0.65 per cent. of volatile combustible matter as determined by heating in nitrogen, gave 2.31 per cent. by heating in a covered crucible. Another sample of Connelsville coke gave 0.21 per cent. of volatile combustible matter on heating in nitrogen and 2.66 per cent. on heating in the same covered crucible, over the same burner and blast-lamp and under as nearly the

same conditions as it was possible to obtain. In this instance a coke containing only one third as much volatile combustible matter as another gave by this method 0.35 per cent. more.

The fineness to which the sample is reduced and the percentage of ash in the coke also probably affect the result.

As the size of the sample increases, a proportionately smaller loss is incurred by burning; there is a limit, however, to which the size of the sample may be carried, for, as the sample increases, the time required to heat the mass of coke to the proper temperature increases also, and a point is reached when the seven-minute heating fails to drive off all the volatile combustible matter. Below is a table showing the effect of the size of the sample on the result.

No. of the sample.	Loss on heating a dried sample in nitrogen.	Loss on heating dried samples of the weight indicated in a covered crucible, for seven minutes.				
		One gram.	Three grams.	Five grams.	Ten grams.	Fifteen grams.
1. Pocahontas coke ....	1.24	3.01	2.10	1.61	1.21	0.96
2. New River coke.....	0.32	1.69	0.93	0.69	0.55	0.47
3. Connelsville coke....	0.37	1.49	1.03	0.81	0.52	0.42
4. By-product coke.....	0.54	1.61	1.08	0.87	0.60	0.41
5. Pocahontas coke ....	0.28	1.52	0.90	0.69	0.40	0.38
6. Piedmont (W. Va.)...	0.31	2.87	2.00	1.31	0.96	0.54
7. Anthracite coal.....	2.85	5.10	4.19	3.01	1.87	1.03

The use of a large sample in some cases apparently reaches the same result as heating in nitrogen, but even here the result is chance. A change of burners or crucible will affect a large sample less than a small one but still quite enough to change the loss considerably. In sample No. 3, Connelsville coke, the use of a large sample in the determination shown in the table gives nearly the same result as is obtained by heating in nitrogen. But on taking a sample from the crucible and reheating in nitrogen an additional loss of 0.17 per cent. or nearly one-half of the total volatile matter was experienced, or in other words of the 0.42 per cent. of volatile combustible matter found by heating a fifteen-gram sample first for three and a half minutes over a Bunsen burner and then for the same length of time over a blast-

lamp, 0.20 per cent. was due to volatile matter expelled and 0.22 per cent. to carbon burned.

The Committee on Coal Analysis of the American Chemical Society recommend heating the sample of coal over a Bunsen burner for seven minutes. For soft coals this heating may be sufficient but for anthracite or coke the blast must be used in order to drive off all the volatile combustible matter. The committee, of course, did not recommend their method for coke analysis, or at least failed to say so, in their preliminary report.

A sample of coke containing 0.61 per cent of volatile combustible matter was heated for seven minutes over a Bunsen burner then cooled and weighed. The loss was 0.78 per cent. On heating in nitrogen an additional loss of 0.48 per cent. was experienced. The heating over a Bunsen burner in this case was only sufficient to drive off 0.13 per cent. of volatile matter.

A sample of anthracite containing 2.85 per cent. of volatile combustible matter was heated for seven minutes over a Bunsen burner and then cooled and weighed. The loss was 2.26 per cent. On heating in nitrogen an additional loss of 1.02 per cent. was experienced. The heating over a Bunsen burner in this case drove off 1.83 per cent. of volatile combustible matter.

It is regretted that the larger portion of the work involved by this investigation had been completed before the preliminary report of the Committee on Coal Analysis was published; consequently the authors were not able to apply this method upon as many samples as they would have liked.

If after heating a sample of coke or anthracite over a blast-lamp and burner for say seven minutes and weighing we again heat over the same burners and for the same length of time, the second heating will give us an approximation of the amount of carbon burned in the first. If the loss, therefore, from the second heating is deducted from that of the first the difference will agree fairly closely with the loss obtained by heating in nitrogen or hydrogen. The results, theoretically, should fall a little below the results obtained by the latter method since the volatile matter which is present in the first heating only, displaces some of the air and consequently there will be more oxygen present in the crucible during the first heating than during the second, and more carbon will be burned. To offset this, there will be

slightly less carbon in the crucible upon the second heating, and the coke will be protected somewhat by a slight film of ash formed by the burning during the first. When the sample is small this does not seem to introduce any considerable error and the results are as apt to be higher as they are to be lower than those obtained by heating in nitrogen. Care must be taken to have the conditions of the second heating similar to those of the first. The same burner and blast-lamp must be used; the position of the crucible in the flame and the size of the flames themselves must be the same for each heating.

The timing of the heats must be done with the second hand of the watch or clock and the flames must be protected from air currents and draughts. To show how closely these blanks agree and the range of accuracy of the methods some results follow.

Three gram samples heated for three and one half minutes  
over a burner and then for three and a half minutes over a  
blast give per cent. loss.

Sample. No.	1st. Heat.	2nd. Heat.	3rd. Heat.	4th. Heat.
1	2.01	0.86	0.84	0.88
2	0.93	0.65	0.61	0.62
3	0.94	0.51	0.56	0.50
5	0.90	0.62	0.67	0.66
6	1.03	0.67	0.66	0.72
7	3.47	0.85	0.89	0.83

By subtracting the second loss from the first we have the results in the first column below.

Sample. No.	By subtracting the second loss from the first.	By heating in nitrogen, per cent. loss.
1	1.15	1.24
2	0.28	0.32
3	0.43	0.37
5	0.28	0.28
6	0.36	0.31
7	2.62	2.85

This is the only simple method we have tried which gives results that approach anywhere near those obtained by heating in nitrogen and hydrogen. The use of asbestos paper to make a close joint between the crucible and its lid is to be recommended where this method is used. The writers have tried placing a weighed sample of coke in a crucible and covering this with a weighed amount of freshly ignited sand. While the blank



from burning does not run quite so high, it does not seem to be any more constant and the results do not seem to justify the extra weighing. It is possible that in a coke laboratory analyzing a fairly even product, a constant blank might be found and deduced, saving the extra heating and weighing.

The writers wish to acknowledge the valuable suggestions of Dr. P. W. Shimer, of Lafayette College, Easton, Pa., and to thank for their kindness Mr. W. H. Blauvelt, of the Semet Solvay Co., of Syracuse, N. Y. and Mr. G. H. Caperton, of the Fire Creek Coal and Coke Co., West Virginia.

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## REVIEW.

### SOME RECORDS OF PROGRESS IN APPLIED CHEMISTRY.<sup>1</sup>

The year just passed has been remarkable for the extension which the industry has undergone rather than for the development of new processes or products. Everywhere demand for products has grown and production has responded to meet it. In the United States this is particularly marked, and it is illustrated in the statistics of the imports and exports of raw materials used in the chemical arts, and of the finished product. Materials needed in the industry in this country, but not produced, or capable of production here, have been brought here in increased quantities, while the finished products have been exported in much the same ratio. We may select for illustration a few products representing the larger industries, and therefore, most widely affecting the general welfare, quoting aggregate values of the various imports.

	1897.	1898.	1899.
Alizarine products.....	\$1,022,970	\$ 886,332	\$ 700,485
Coal-tar colors and dyes ....	3,196,478	3,689,214	3,799,353
Glycerine .....	1,182,099	774,709	1,024,131
Calcium chloride.....	1,375,560	1,422,920	1,159,271
Potassium chlorate .....	458,095	308,458	173,488
Caustic soda.....	1,147,763	476,032	252,291
Sal soda.....	82,695	40,266	20,905
Soda-ash .....	1,241,321	589,714	310,742

If on the other hand we consider the products exported, we find a like favorable state of affairs:

<sup>1</sup> Read before the New York Section, October 6, and November 10, 1899.