

METHODS OF ANALYSIS OF COAL.

ON THE NECESSITY OF STANDARDISING A METHOD FOR THE PROXIMATE ANALYSIS OF COAL IN INDIA.

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The scientific workers in India engaged in coal research are sometimes faced with the problem as to the selection of the best method for carrying out the proximate analysis of coal. After the establishment of the Coal Grading Board in 1925 by the India Government the grading of coal on the basis of proximate analysis has been in practice and business transactions are carried out on the production of a certificate from the Coal Grading Board.

The Coal Grading Board, however, issues the certificates on getting the analytical report from the laboratory of the Alipur Test House. Almost all the coal seams in the important coalfields of Bengal, Bihar and C.P. have been graded in this way depending on the analytical results obtained from the said Test House. The coal producers and consumers are thus guided in the inland and foreign market by the certificates issued by the Coal Grading Board. The scientists working in different laboratories were always under the impression that the method followed by the Alipur Test House must have been a standard one free from inaccuracies. Later on in 1930 the method adopted by the Alipur Test House and on which the grading of coal seams is carried out was published by Brodie¹ in the *Records of the Geological Survey of India*. The method outlined by Brodie does not appear to be satisfactory and differs from the standard methods of England and America. A discussion of Brodie's method was communicated by the present author to the Geological, Mining and Metallurgical Society of India on the 18th September in the same year.²

The present author is not aware if any modification or improvement has since then been made in the Alipur Test House method. The writer therefore wants to put forward this discussion on the subject and has made an attempt in the following lines to show the necessity of standardising a method for the proximate analysis of coal in India. The attention of the scientists engaged in coal research in India should be drawn to this part of the problem and the present writer suggests that a standard method should be followed or a suitable method be evolved and standardised for use in the different laboratories of India for obtaining a much better and uniform result.

The method of proximate analysis of coal attracted the attention of the early scientists. It was also realised by them that the percentages of moisture

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and volatile matter vary considerably depending on various factors and the methods of analysis. The values obtained by proximate analyses were therefore regarded as more or less arbitrary. Hence the chemists and scientists of different countries evolved some standard methods for the analysis of coal so that people working at different centres in the same country may obtain some concordant results by following one standardised method. Thus we have got a few methods as recommended by the United States Bureau of Mines,³ by the Fuel Research Board of England,⁴ the South African Branch of the British Engineering Standard Association,⁵ and the United States Steel Corporation.⁶ But unfortunately in India we do not find any such standard method for proximate analysis of coal. With the inception of the Coal Grading Board the utility of representative samples has been realised by everybody and at the present day mine sampling and laboratory sampling are being gradually introduced everywhere. In 1910 Cunningham Hughes⁷ published an article on proximate analysis of coal. In this paper he made an attempt to put forward a method of analysing coal but as the method was not highly perfect it did not receive much recognition.

In the article dealing with the method of Brodie we find that he felt the necessity of one standard method for such analytical work. But the author of this note fails to understand why a method was adopted differing greatly from the standard methods recommended by the U.S. Bureau of Mines or the British Fuel Research Board. In that paper sufficient reasons have not been given for such deviation.

The method of determination of moisture content in a specimen of coal was discussed in the 8th International Congress of Applied Chemistry in 1912 and it appears from the report⁸ that one gram of coal should be heated in a constant temperature oven at 105°C.-107°C. for one hour, then it should be allowed to cool in a desiccator and weighed and the percentage of moisture calculated. A similar method is also recommended by the American Chemical Society⁹ and is in general practice in America and other countries.¹⁰ Shallow vessels are used in all cases for the determination of moisture.

In the Alipur Test House method about two grams of powdered coal are weighed in a weighing bottle and heated in an air oven at a temperature of 105°C. until all the moisture has been driven off and a constant weight obtained. This requires about two hours.¹¹ In the description no specification regarding the dimension of the weighing bottle has been made. This omission is regrettable. There are several types of weighing bottles, if the bottle be of narrower type a quantity of two grams will form a thick layer in the bottle and it will take a much longer time for the complete evolution of moisture. The writer of the present note has found experimentally that in the case of high moisture coals, following Brodie's method, it takes a much longer time (more than three hours) for the complete expulsion of moisture. Whereas using a pair of watch glasses of 2" diameter and taking one gram of coal, according to the method of the British Fuel Research Board, the moisture content was completely driven

off in about an hour's time. It is well known that in the determination of moisture the loss in weight is actually the sum of two opposite factors, namely, one due to the evolution of moisture causing decrease in weight and the other due to prolonged heating causing an increase in weight by the incipient oxidation of coal particles without any evolution of gas. Hence we find that in order to avoid slow oxidation the moisture determination should be finished in the shortest possible time.

Now about the receptacle for coal it may be pointed out that the vessels should be properly and carefully selected and the author suggests that the recommendation of the British Fuel Research Board in this matter should be followed.¹² Suitable vessels recommended by the Board are as follows:—

- (i) Glass petri dishes about 10 mm. high.
- (ii) Shallow silica dish.
- (iii) Shallow stoppered weighing bottles.
- (iv) Watch glasses with ground edges held together with a clip. Watch glasses with clip were also found to be the most effective drying vessel by W. F. Hillebrand.¹³

The Board points out that the weight of coal and the dimension of the dish should be arranged to give a layer of coal weighing not more than 0.3 gr. per sq. cm. of exposed surface.

A thin layer of coal on the watch glass will facilitate the almost complete evolution of moisture in about one hour's time. It has been already shown by the author that in the narrow type of weighing bottle the moisture could only be expelled by prolonged heating for several hours. And in such procedure partial slow oxidation might ensue vitiating the result for real moisture value. The author also points out that if the American method is followed, in the high moisture coals, the expulsion of moisture may not be complete in exactly one hour's time, but on the other hand some types of coal may require a little longer time. The author therefore suggests that in the determination of moisture the American method should be a little modified as given below:—

About one gram of the air-dried sample of coal (60 mesh) should be taken in a pair of watch glasses, of about 2-inch diameter fitted with clip. Any other shallow vessel may be used but the recommendation of the British Fuel Research Board to which attention has already been drawn should always be borne in mind. The watch glasses with the coal substance should be heated in a constant temperature oven for one hour at 105°C.–110°C. The pair of watch glasses is taken out of the oven and allowed to cool in a desiccator charged with conc. sulphuric acid and the first reading is thus obtained. Then every ten minutes the coal should be taken out of the oven, allowed to cool in the desiccator and weighed. The end point will be reached when a little increase in weight will be noticed showing conclusively that the slow oxidation has started in the coal substance. The previous reading should therefore be taken into account and calculation should be made accordingly.

It has been found in practice that it is generally difficult to get a constant weight in the course of an operation to find out the moisture and hence it is not easy to follow the suggestion of Brodie to determine the moisture by heating to a constant weight.

About cooling the dried coal in the desiccator one word of explanation is necessary. It is well known that powdered coal is capable of taking up a little moisture from the air but when perfectly dry or when dried at 105°C. it becomes highly hygroscopic and it has been experimentally found by the author that such dried coals, on exposure to air for even a short period, will show appreciable increase in weight. Thus powdered coal (1.15 gram) exposed to air for two days was found to absorb 0.0017 gram of moisture while an equal weight of coal from the same specimen bottle when dried and exposed to air for one hour absorbed 0.0647 gram of moisture.

It has been shown by the South African Committee¹⁴ on coal, by N. W. Lord¹⁵ and also by W. F. Hillebrand¹⁶ that coal dust after complete drying is excessively hygroscopic, probably even more so than calcium chloride. From the above consideration it is needless to point out that in the determination of moisture the desiccator should in all cases be charged with conc. sulphuric acid and not with calcium chloride. This point has been lost sight of in the method published by Brodie.

In the process of weighing a little precaution is necessary to guard against the possible sources of error due to the reabsorption of moisture by the dried coals from the atmosphere, especially in the wet season. Hence in the determination of moisture the specimen should be weighed as quickly as possible. It should be mentioned in this connection that the 'inherent' moisture of coal should always be determined and the result given everywhere should indicate the percentage of the 'inherent moisture' only. To get rid of the superficial water the sample as received should be crushed coarsely and allowed to remain exposed at room temperature for at least two days before being subjected to chemical analysis for the determination of 'inherent moisture'.

Now regarding the determination of volatile matter Brodie¹⁷ has advocated two stages of heating. The first stage of heating is done over a small bunsen flame for three minutes and in the later stage much stronger heating is applied for four minutes by subjecting the crucible to the hottest part of the burner $\frac{7}{16}$ " in internal diameter giving a flame 7" high; the crucible is then allowed to cool, the lid removed and the film of carbon adhering to the lid and a similar one on the side of the crucible are cautiously burnt off. The crucible is allowed to cool again in the desiccator and when cold it is weighed. It is quite clear that the procedure is not sufficiently definite from a scientific point of view.

We know that the volatile matter consists of gaseous and liquid products evolved from coal when it is subjected to destructive distillation and that coal is a mixture of substances possessed of different thermal stability. Volatile matter in coal therefore varies according to the temperature employed and it also depends on the degree of fineness of coal, nature of apparatus, time of

heating and the amount of moisture. It is also known that the higher the temperature the greater will be the percentage of volatile matter. Therefore the determination of volatile matter is a purely empirical procedure and concordant results can only be obtained by the adoption of a standard procedure by heating the coal at a standard temperature for a standard length of time. The dimension of the platinum crucible, the length of the flame and the position of the platinum crucible with respect to the burner should also be standardised. Brodie has given sufficient details regarding the dimension of the burner and the flame, but very unfortunately he is silent regarding the other points.

If we refer to the standard methods adopted in different countries for the determination of the volatile matter we find that the temperature at which the coal is to be heated and the period of heating are practically the same. In the American¹⁸ and the British Fuel Research Board¹⁹ method the heating is maintained at about 950°C. for exactly 7 minutes. If we are going to have concordant results of a comparable type in the determination of volatile matter it is better that we should either follow one of the standardised methods as outlined in the other countries or we should modify it to suit our own requirements. But in the report regarding the method adopted in the Alipur Test House we find that the temperature factor has been totally neglected though the measurements of the burner and the flame have been accurately given. A reference to the different standard methods will at once show that in the determination of volatile matter it is required from time to time to detect and check the temperature of the crucible by means of a thermocouple or by melting potassium chromate crystals in the crucible. Recent researches of D. F. Smith and F. A. Hartgen²⁰ of the U.S. Bureau of Mines have shown that the melting point of potassium chromate (C.P.) is about 963°C. A reference to the above work also shows that according to the older views the melting point of potassium chromate was found to vary within certain limits (between 940°C. and 975°C.). It has been pointed out in the standard methods²¹ that specimens of coal having a high percentage of moisture or occluded gases should be heated gently for two minutes or so over a small bunsen flame, in order to avoid mechanical loss by rapid escape of steam and volatile matter, before the crucible is subjected to seven minutes' full heating at 950°C. \pm 20°C. According to Brodie coal should be heated strongly for four minutes and not for seven minutes. As the temperature factor has not been taken into consideration by Brodie and as the period of heating followed by him is also different from that generally adopted, it is quite clear that the result by Brodie's method will not be comparable with those obtained by following the standard methods. Brodie does not appear to have given sufficient reasons for such deviation from the standardised methods adopted in America, England, etc. Fluctuation in the pressure of gas supply, variation in the composition and quality of the gas, etc., may have some influence in maintaining uniform temperature.

From what has been said above it is quite clear that the standard flame of 7" high as recommended by Brodie may not always give in the laboratories situated in the different parts of India the desired and definite temperature of $950^{\circ}\text{C.} \pm 20^{\circ}\text{C.}$, at which the coal is to be heated for the determination of volatile matter. The writer of this note actually found in the laboratory that with 7" flame of a bunsen burner having about $\frac{1}{2}$ " diameter, potassium chromate crystals could not be melted in a platinum crucible whereas with the same gas pressure the melting of potassium chromate crystals was effected by substituting the bunsen burner with the meker burner (No. 3 or 5). That the use of the meker in place of the bunsen burner is more advantageous has been shown clearly by F. H. Wagner²² who writes:

'The use of Meker burner is recommended by the Bureau of Mines in place of Bunsen burner owing to its superiority over the latter, especially for natural gas. The construction of the Meker burner practically eliminates the fluctuating inner cone of the ordinary Bunsen flame, and thus produces a solid flame of fairly uniform temperature, this flame completely enveloping the bottom and sides of the crucible.'

In order to overcome the fluctuating flame of the gas burner on account of excessive draught the British Fuel Research Board²³ has recommended the use of the Davies furnace, the utility of which was also pointed out by Cunningham Hughes.²⁴ The author of this note also found this little apparatus of some use and suggests that in the case of fluctuating gas flame this type of furnace or some other kind of chimney as recommended by the U.S. Bureau of Mines²⁵ may be used to secure a steady flame.

It is seen therefore that in order to maintain the definite temperature of $950^{\circ}\text{C.} \pm 20^{\circ}\text{C.}$ for a definite period of seven minutes, sufficient precaution is necessary, but if an electrical furnace is available the above-mentioned difficulties can easily be overcome. The U.S. Bureau of Mines has recommended the use of such an electric furnace for the determination of volatile matter. In the Lessing method²⁶ also we find that coal is to be heated in silica tube in an electric furnace for seven minutes at a temperature of 950°C. It is needless to point out that in the electric furnace we have got an absolute control over the temperature and there is no possibility of any fluctuating gas pressure or the loss of heat by radiation.

From what has been stated above we may expect that the percentage of volatile matter obtained by following Brodie may be a little lower than the corresponding value of volatile matter obtained by following the standard methods either American or of the British Fuel Research Board. A reference to the results obtained and given below shows that in the high moisture as well as in the low moisture coals the percentage of volatile matter after the American method was greater than that determined by Brodie's method.

| % | HIGH MOISTURE COAL (BURMA). | | | | LOW MOISTURE COAL (EKRA, JHARIA). | | | |
|----------------------------|--------------------------------|------|-----------------|------|--------------------------------------|-------|-----------------|-------|
| | Namma. | | Kalewa. | | XI Seam. | | XIV Seam. | |
| | Vola- tiles. | Ash. | Vola- tiles. | Ash. | Vola- tiles. | Ash. | Vola- tiles. | Ash. |
| American method (modified) | 39.60 | 3.70 | 42.30 | 3.00 | 19.92 | 18.82 | 20.10 | 12.80 |
| Brodie's method .. | 37.80 | 3.70 | 40.40 | 3.00 | 17.23 | 18.82 | 18.50 | 12.80 |

After the determination of volatile matter the coal was burnt to ash and from the figures in the above table we find that the ash percentage remains the same in both the cases showing conclusively that there was no loss of coal particles during the time of heating. We also find that according to Brodie²⁷ after driving off the volatile matter the lid of the crucible has to be taken out while the soot deposited on the bottom of the lid and inside the crucible is to be cautiously burnt off. This procedure of heating the crucible with the lid open in presence of air is undesirable as somebody may carry on the heating operation for a comparatively longer period and in that case the coke may be partially oxidised. In some high swelling coals the coke fills up the entire height of the crucible and sometimes touches the lid, thereby making it impossible to open the lid. Hence we find that the method introduced by Brodie cannot be universally applied with all types of coal. Moreover, it has been found that the lid contains a negligible amount of soot when the American method is followed whereas an appreciable quantity of it remains on the lid and the sides of the crucible when Brodie's method is applied, showing conclusively that the temperature was a little lower in the latter case than in the former.

From the above considerations we find that the method adopted in the Alipur Test House to determine the volatile matter is not up to the mark and differs in some respects from other standard methods. Hence we are led to conclude that the procedure of Brodie should be modified before it can be regarded as a standard method for the estimation of volatile matter.

Certain discrepancies in results due to non-adherence to any standard method have been observed in the Geological Survey of India laboratory. It was found by Dr. Fermor [*Rec. Geol. Surv. Ind.*, Vol. 62, pp. 192-194, 203 (1929)] that there was a difference of as much as 5 per cent in the volatile matter of the same coal obtained in the years 1919 and 1928 and this difference was ascribed to a change of the crucibles and the lower gas pressure in 1919 as compared with 1928. This shows that the temperature factor was not given due importance during the time of analysing coal in the Geological Survey laboratory.

The author of this note suggests the following procedure which is the American method with slight modifications:

Method :

Apparatus: Meker burner (No. 3 or 5).

Coal (60 mesh, I.M.M.).

Platinum crucible with tight-fitting lid. Capacity: 30 to 40 c.c.

Weight varying from 25 to 48 grams.

The position of the crucible should be about 2 cm. above the meker burner and the flame of the burner should be about 16 cm. enveloping the crucible so that no oxygen may have any access in the crucible. About 1 gram of coal should be heated in the full flame of the meker burner for exactly seven minutes at about $950^{\circ}\text{C.} \pm 20^{\circ}\text{C.}$ If the flame becomes unsteady, the Davies furnace or any other device should be used to overcome the draughts. In case of high moisture coals and cracking and salty coals and with those that decrepitate on heating due to large amounts of occluded gases, a preliminary gentle heating over a small flame for about two minutes (the period of heating depending on the nature of the coal) will be necessary. This preliminary heating should be followed by full seven minutes' heating on the meker burner at $950^{\circ}\text{C.} \pm 20^{\circ}\text{C.}$ If in the case of some coals it is found that some fine coal particles are actually mechanically carried away on account of the sudden evolution of a large amount of hydrocarbons that are produced at lower temperature, then a preliminary gentle heating will be necessary to avoid such a disaster. After heating for seven minutes the crucible is allowed to cool undisturbed in the desiccator charged with conc. sulphuric acid and then weighed. The loss in weight represents the volatile matter expelled plus the moisture in the coal. Then the percentage of volatile matter is calculated. The dimension of the crucible and the weight should also be standardised within certain limits, as unusually a big and heavy crucible will take away much heat before the desired temperature is obtained, whereas a smaller crucible of much lower weight will be almost immediately heated to 950°C.

About reporting the analytical results it has been the practice in some places to submit the analyses of coal on 'moisture-free' basis. In the Alipur Test House the coal is dried to a constant weight at 105°C. and then the dried coal is transferred from the weighing bottle to the platinum crucible and the volatile matter and the ash contents are determined from the dried sample. The moisture percentage is shown separately.²⁸ According to the standard methods²⁹ undried coals are analysed for the determination of volatile matter and ash.

The question whether the dried coal should be analysed has been discussed by the South African Coal Committee³⁰ and the U.S. Steel Corporation³¹ and they did not recommend the method of analysing dried coal but were of opinion that the air-dried sample should be analysed and, if necessary, the amounts of volatile matter and the fixed carbon might be calculated on the 'moisture-free' basis. It has been shown by the present writer in the foregoing pages that it is difficult to get a constant weight of coal during the time of driving off moisture and it is quite possible that on account of the highly hygroscopic

nature of the dried coal, there might be some error due to the absorption of moisture, vitiating the results for the real values of volatile matter and fixed carbon. The author is therefore of opinion that the method of analysing 'air-dried' sample and not the 'dried' sample should be standardised and introduced everywhere and the results thus obtained may be recalculated to give the figures on 'moisture-free' basis.

Regarding the sulphur determination as adopted in the Alipur Test House, Brodie³² has mentioned that the difference between the total sulphur in coal and the amount of sulphur present in the ash of the same coal is the amount of 'volatile sulphur'. A reference to literature³³ available on the detailed sulphur study will at once show that the term introduced by Brodie is rather misleading. The amount of sulphur expelled during the complete combustion of coal is known as the 'combustible sulphur' as distinct from the volatile sulphur which is the amount of sulphur that is driven off when the coal is carbonised at 950°C. for the determination of volatile matter. The 'combustible sulphur', however, includes the total amount of 'volatile sulphur'.

Regarding the determination of ash, the residue left behind in the crucible after driving off the volatile matter should be heated in the flame in free access of air until all the carbon particles are completely burnt off with occasional stirring by a platinum wire. The crucible may be heated with the lid open. After complete combustion the ash may be carefully examined if any carbon particle has been left unburnt. The end point will be reached by getting a constant weight.

The value of fixed carbon is estimated by deducting the percentage of ash from that of coke.

In conclusion the author wishes to draw the attention of the coal producers and coal consumers to the fact that the proper valuation of coal from the results of proximate analysis is only possible when such analyses are done by some standardised method, and he thinks that as there is no fixed method adopted by the coal analysts in India the time has come when one definite method for the proximate analysis of coal should be standardised and adopted everywhere. The author also draws the attention of the National Institute of Sciences of India to this important problem.

The author has made an attempt to outline in the foregoing pages one such method for the estimation of moisture and volatile matter. He also suggests that so long as there is no standardised method it is really necessary that every proximate analysis of coal published should be accompanied with a definite statement regarding the method adopted so that one may have a proper idea about the accuracy of the result.

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