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SUBJECT: THE USE OF THE CALORIMETRIC BOMB FOR THE DETERMINATION OF CARBON IN COAL

AFDELING:
DIVISION: CHEMISTRY

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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

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THE USE OF THE CALORIMETRIC BOMB FOR THE DETERMINATION OF CARBON IN COAL

The method normally employed in determining the amount of carbon present in a combustible material is to combust in a stream of oxygen. The products of combustion are passed over heated copper oxide, lead chromate and finally over silver gauze, the carbon dioxide being absorbed in potassium hydroxide solution or sofnolite and weighed.

This method, though in general use, is tedious and requires considerable care and experience to ensure reliable results, more especially with volatile substances.

Carbon compounds may be oxidised very rapidly when burnt with a large excess of oxygen in the calorimetric bomb and various methods have been proposed for determining the amount of carbon dioxide so formed and thus the carbon content of the combusted material.

Goutal (Fuel, 1923, p.344) describes a means of estimating the carbon content of a fuel by a volumetric method. He uses a bomb of his own design in which he ignites the fuel under a pressure of 25 atmospheres of oxygen. The gases from the bomb are passed through a special tall absorbing tower containing 150 ccs. of $\frac{N}{6}$ sodium hydroxide solution which absorbs the carbon dioxide. This solution is then treated with 50 ccs. $\frac{N}{1}$ barium chloride, which precipitates barium carbonate. The remaining sodium hydroxide is then titrated with $\frac{N}{6}$ hydrochloric acid using phenol phthalein as indicator.

According to Whitaker (Fuel, 1928, p.63) certain difficulties have been experienced in the use of this method, mainly with regard to the adjustment of the rate of discharge of the gases from the bomb, the complete absorption of the carbon dioxide and the avoidance of contamination with carbon dioxide from the air and the washing water.

Whitaker, in this same paper, describes a method which, he claims, is more rapid than that of Goutal and gives results of equal accuracy. It has the added advantage that no standard solutions are required. He uses the type of bomb designed by Goutal and burns about 0.2 - 0.3 gms. of substance under a pressure of 25-30 atmospheres of oxygen. The carbon dioxide, after drying, is passed through a 100 ccs. gas sampling tube and the volume of gas produced during the combustion is measured by a flow meter, also in series with the train. The amount of carbon dioxide in the 100 ccs. sample is determined by analysis in a Haldane gas analysis apparatus. The carbon content of the fuel is calculated from this value and from the total volume of the dry gas, i.e. the corrected meter reading plus the volume of residual gas in the bomb. This volume has to be reduced to a dry gas value at N.T.P. which, of course, requires accurate readings of the barometric pressure and the metering temperature. Uncontrolled temperature and pressure fluctuations in the gas are sources of error and another possible source of error lies in the fact that the composition of the gases is determined on a 100 ccs. sample. Since the total volume of the gases at normal pressure is approximately 2 litres any error in the determination of the carbon dioxide percentage in the 100 ccs. sample will be increased twenty fold in the final result. Whitaker admits a further source of error in the flowmeter and specifies that this must be standardised frequently and that the gases must be discharged very slowly.

In this method the advantage of requiring no standard solutions is offset by the fact that the apparatus required is elaborate and, at least superficially, it seems unattractive.

In view of the disadvantages inherent in all the rapid methods of carbon estimation so far proposed, a more simple and expeditious method of estimating the carbon dioxide formed by combustion in the calorimetric bomb was sought.

Barium hydroxide has been extensively used as a quantitative absorbent for carbon dioxide and the titrimetric estimation of barium carbonate, barium hydroxide mixtures is experimentally simpler than that of the corresponding mixture of sodium compounds. Barium hydroxide was therefore selected as the absorbent. To overcome the difficulty of absorbing the gas after its release from the bomb it was decided to introduce an excess of barium hydroxide into the bomb before the combustion and to estimate the carbonate formed after combustion by titration.

The bomb used was of the Berthelot-Mahler-Kroeker type with a capacity of approximately 250 ccs. fitted for use with a silica cup. In order to accommodate sufficient barium hydroxide solution for the absorption of the carbon dioxide formed, it was found necessary to modify the internal fittings of the bomb as follows:-

(a) The oxygen inlet tube was cut off to a length of approximately 5 cms., which ensured that the end was well above the level of the liquid in the bomb.

(b) In order to keep the silica coal cup above the liquid level, the cup-holder had to be similarly shortened. Since, with the normal type of ring cup holder, this would prevent the insertion of the silica cup into the ring from above, the closed ring was replaced by a split ring of spring steel into which the cup could be inserted from below by prising open the ring.

The general arrangement of the bomb as modified is shown in section in Figure 2.

With these modifications, 125 ccs. of solution could be run into the bomb without interfering with the ignition and combustion of the coal.

The absorbent used was approximately $\frac{N}{5}$ barium hydroxide (about 35 grms. $Ba(OH)_2.8H_2O/L$) which was made up and allowed to stand until the carbonate had settled, when the supernatant liquid was siphoned off into a carbon dioxide-free container provided with a guard-tube filled with sofnolite. (See fig.I).

For the purpose of testing the proposed method as applied to the determination of the carbon content of coals, the following experimental procedure was adopted.

About 0.15 gms. of coal was accurately weighed into a silica combustion cup and approximately 100 ccs. of barium hydroxide run into the bomb. The coal was ignited under a pressure of 25-30 atmospheres of oxygen, the carbon dioxide formed being absorbed by the barium hydroxide. The excess of oxygen was then blown off and the precipitate of barium carbonate together with the excess barium hydroxide washed into a 1 l. flask. Using phenol phthalein as indicator, the excess of barium hydroxide was neutralised with $\frac{N}{5}$ hydrochloric acid and the amount of barium carbonate was then determined by titration with $\frac{N}{5}$ hydrochloric acid using methyl red as indicator.

A preliminary series of experiments were conducted to determine the effect of variations in the experimental technique.

(a) Shaking of the bomb was found to be essential. Apparently a scum of barium carbonate forms on the surface of the liquid which hampers the absorption of carbon dioxide.

The effect of varying periods of shaking is shewn in Table I. From this it will be seen that a period of 5 minutes is sufficient for the complete absorption of the carbon dioxide.

(b) The direct titration of barium carbonate with hydrochloric acid was found to be impracticable owing to the slow rate of reaction between the acid and the solid carbonate. A rapid and accurate determination of the carbonate is accomplished by adding a measured excess colume of $\frac{N}{5}$ hydrochloric acid, boiling off the carbon dioxide and titrating the excess of acid with $\frac{N}{10}$ sodium hydroxide using methyl red as indicator.

(c) In order to avoid the need for completely washing out the bomb, a measured volume of sodium hydroxide solution was tried as the absorbing medium, aliquots of the soluble product being subsequently titrated. Due, however, to the effervescence of dissolved gases during the measurement of the aliquots, no advantage was derived from this modification. An added disadvantage of this modification was that the bomb had to be dried before each determination.

(d) The Blank Value

A series of tests were carried out on a number of coal samples both by the standard combustion method (ultimate analysis) and by the method under investigation. Comparative figures for the carbon contents on the moisture-free basis are recorded in Table II. It will be seen that the carbon percentage as determined by the bomb method is consistently 0.5 to 0.6 units higher than that given by the standard method.

A blank determination made with the bomb using no coal but otherwise reproducing the experimental procedure gave a result equivalent to 0.6 units of carbon. This is in agreement with the comparative tests referred to above.

(e) The tests described under (d) were carried out using ordinary distilled water. If CO_2 -free water is used, the values for both the blank determination and the coals are reduced by 0.4 units of carbon, the blank value being 0.2 carbon units and the carbon contents of the coals 0.2 units higher than the standard values. This difference may be accounted for by the difference in the acid concentrations at which phenolphthalein and methyl red change colour. The volume of solution which is titrated in these determinations is about 300 ccs. and it was found that 300 ccs. of CO_2-free distilled water required 0.15 cc of $\frac{N}{5}$ Hydrochloric acid to change its acidity from that of the colour change of phenol phthalein (pH=8) to that of methyl red (pH=5). This acid volume corresponds to 0.12 carbon units. Practically the whole of the blank value of 0.6 carbon units is thus accounted for showing that no appreciable absorption of carbon dioxide from the air occurs during the test procedure.

The use of CO_2-free water in the test introduces a complication in the procedure which is not considered necessary for routine tests as the blank value obtained when ordinary distilled water is used is constant. To prevent undue contamination of the distilled water in the wash bottle by carbon dioxide, the air space above the water should be kept as small as conveniently possible by frequent replenishment of the water. Under such conditions the carbon dioxide concentration in the wash water remains practically constant.

The method finally adopted for the determination of carbon in coals and similar substances is as follows:-

Weigh out accurately about .14 to .15 gms. of the coal previously ground, to pass a No. 52 B.S. Sieve , into a silica combustion cup. If the carbon content of the coal is likely to exceed 80%, approximate to the lower weight, to ensure that the quantities of reagent used are sufficient. Connect up the fuse wire in the usual way.

Into the bomb run about 100 ccs. of barium hydroxide. Exact measurement is unnecessary provided only that sufficient is added to absorb all the carbon dioxide likely to be formed during the combustion of the coal. Screw up the bomb immediately and blow in oxygen slowly to avoid violent splashing of the liquid inside until the pressure is about 25 atmospheres. The coal is ignited in the usual manner and the bomb placed on a shaker for about 5 minutes. This ensures the complete absorption of the carbon dioxide formed in the hydroxide.

Blow off the oxygen relatively slowly, so as to empty the bomb in about half a minute. Close the valves to prevent the solution and precipitate being washed into the valve seatings. Open the bomb and transfer the precipitate of barium carbonate completely to a 1 l. flask using a minimum of wash water. The wash bottle should be kept filled as previously described.

Add a few drops of phenol phthalein and titrate the excess of barium hydroxide with $\frac{N}{5}$ hydrochloric acid. The end point is obscured somewhat by the white precipitate of carbonate, so titrate until a stage is reached such that, on the addition of a further drop of indicator, no pink colouration is produced. With practice the end point can easily be recognised and, in any case, if the same point is taken for each determination and also for the blank determination, any error is eliminated. In this manner the excess of hydroxide is neutralised while the carbonate remains unaffected.

Now add to the solution 100 ccs. of approximately $\frac{N}{5}$ hydrochloric acid by means of a pipette and boil for a few minutes to expel carbon dioxide. This quantity of acid should be more than sufficient to dissolve all the carbonate; if it is not (as will be seen on the addition of methyl red) a further measured quantity (say 5 ccs.) must be added. The excess of acid is titrated with standard $\frac{N}{10}$ sodium hydroxide using methyl red as indicator. This end point is sharp.

With each batch of determinations a blank value is determined by duplicating the experimental procedure in every respect except that no coal is burnt in the bomb.

The method of calculating the percentage of carbon in the coal is as follows:-

If:-

Weight of coal used = W gms.

Moisture content of coal = M %

Normality of sodium hydroxide solution = N.

Volume of N normal sodium hydroxide required to neutralise 100 cc. of the hydrochloric acid solution = U ccs.

Volume of N normal sodium hydroxide required to neutralise the hydrochloric acid in the blank determination = V ccs.

Volume of N normal sodium hydroxide required to neutralise the hydrochloric acid in the actual test = v ccs.

Then:-

The gross weight of carbon absorbed by the barium hydroxide solution is

$$\frac{12\,(U - v)\,N}{1000} \text{ gms.}$$

and the gross percentage of carbon in the dry coal is

$$\frac{120\ (U - v)\ N}{W\ (100 - M)}\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

This is the percentage recorded in the second column of Table II. The nett weight of carbon absorbed by the barium hydroxide, (carbon derived from the coal only) is

$$\frac{12(V - v)\ N}{1000}\ \text{gms.}$$

and the nett percentage of carbon in the dry coal is

$$\frac{120\ (V - v)\ N}{W\ (100 - M)}\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

This is the actual carbon content of the dry coal as determined by this method.

The weight of carbon represented by the blank determination is

$$\frac{12\ (U - V)N}{1000}\ \text{gms.}$$

This quantity may be expressed as a percentage of carbon in the form

$$\frac{120\ (U - V)N}{W\ (100 - M)}\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots\ (1) - (2)$$

or, assuming W(100 - M) to be 15 gms, the expression becomes

$$8\ (U - V)N\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

and represents the amount by which the gross percentage of carbon should be reduced to give the nett percentage.

For the series of experiments recorded in Table II, the correction calculated from equation (3) was found to be 0.6 units. If this correction be applied to these results, the carbon contents obtained by the bomb method approximate closely to the values obtained by the standard method.

ADVANTAGES OF THE BOMB METHOD

The determination of carbon in coal by the bomb method is much more rapid than by the standard combustion method. A duplicate determination can be done in one hour as compared with four hours by the latter method. At the same time the accuracy of the bomb method is sufficient for all practical purposes.

The apparatus required by the bomb method is, exclusive of the bomb itself, inexpensive and simple to construct, and no great manipulative skill or experience is required in its use.

Furthermore, only two standard solutions are required which can be easily standardised with pure calcite.1)

This method has been in use in the Fuel Research Institute for some considerable time and has been found to be of especial value for the analysis of coals and oil shales of high ash content. The carbon content of such materials is difficult to determine accurately by the standard method whereas by the bomb method the estimation presents no difficulties even when the ash content is as high as 50%.

J. Adams

ASSISTANT

8th April, 1938

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1) Text book of Quantitative Chemical Analysis. Cumming and Kay. 4th edition. p. 53.

TABLE I

Period of Shaking.	5 minutes	10 minutes	30 minutes
Carbon %	71.30	71.34	71.20

TABLE II

Sample	Percentage Carbon			Difference
	By Bomb Method		By Ultimate Analysis	
	Single Tests.	Mean		
Coal A	75.34	75.50	74.9	.6
	75.46			
	75.50			
	75.53			
	75.54			
	75.57			
	75.58			
Coal B	78.25	78.48	77.8	.7
	78.42			
	78.44			
	78.49			
	78.63			
	78.63			
Coal C	66.77	66.83	66.3	.5
	66.88			
Coal D	69.07	69.18	68.7	.5
	69.28			
Coal E	72.44	72.48	71.9	.6
	72.51			
Coal F	76.60	76.62	76.1	.5
	76.64			
Coal G	73.32	73.31	72.8	.5
	73.30			
Coal H	78.60	78.6	78.1	.5

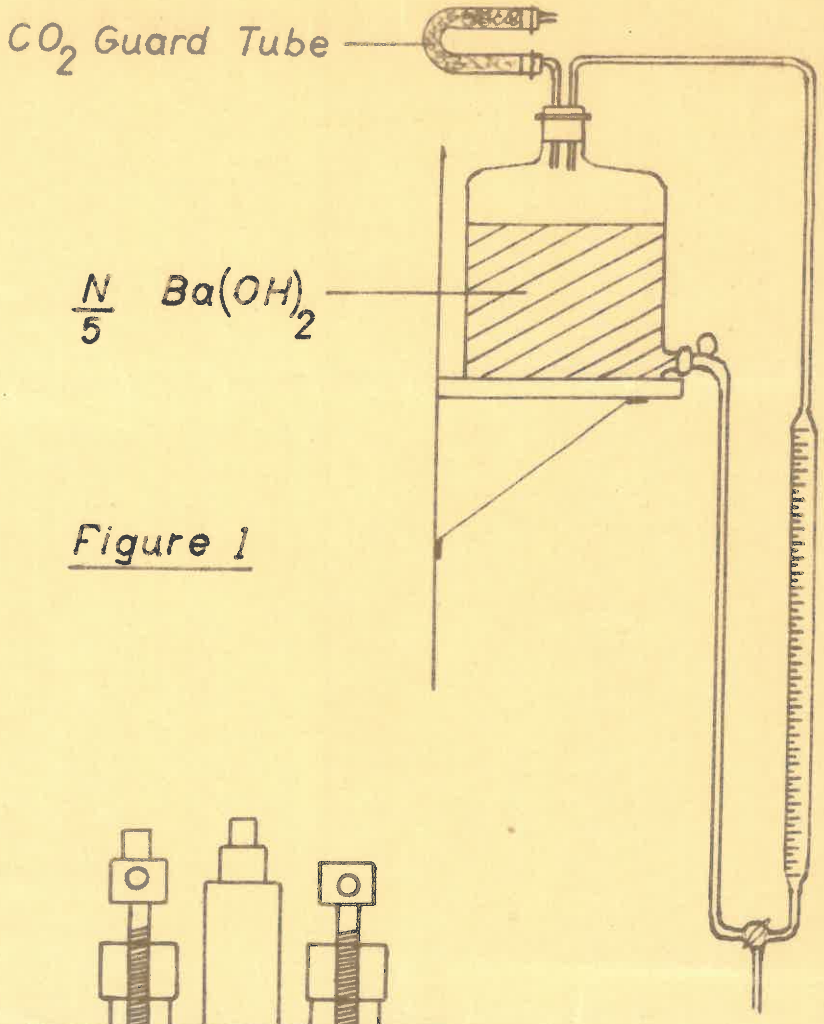

Figure 1

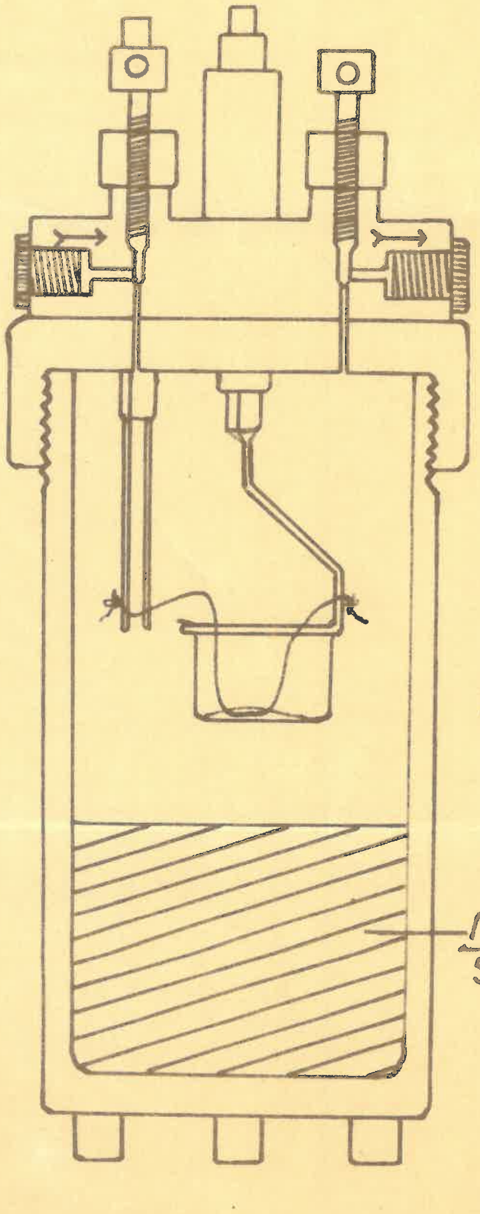

Figure 2