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FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA.

BRANDSTOF-NAVORSINGS-INSTITUUT

VAN SUID-AFRIKA.

SUBJECT:
ONDERWERP: ROUTINE METHODS OF COAL ANALYSIS. THE DETERMINATION OF THE CALORIFIC VALUE OF A COAL.

DIVISION:
AFDELING: CHEMISTRY.

NAME OF OFFICER:
NAAM VAN AMPTENAAR: S. D. COETZEE.

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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

REPORT NO. 21 OF 1950.

ROUTINE METHODS OF COAL ANALYSIS.

THE DETERMINATION OF THE CALORIFIC VALUE OF A COAL.

The method adopted at the Institute is that laid down by the S.A. Standards Specification c.f. "The Determination of the Comparative Calorific Values of Coals in South Africa." S.A. No. 5 - 1940. Further reference can be made to "Calorimetry" by Dr. Quass, F.R.I. Bulletin No. 13.

CARE AND MAINTENANCE OF APPARATUS:

1. The balance must be kept clean and should be checked before each weighing and if necessary, adjusted.

2. The fine adjustment valve, fitted to the oxygen cylinder, must be adjusted to give a steady rate of oxygen flow whenever a full oxygen cylinder is taken into use, thereafter only the valve on the cylinder must be manipulated whilst filling the bombs with oxygen.

3. Before each determination the outside of the bomb (after assembly) must be dried with a towel.

4. After each determination the bomb must be rinsed out with water and the threads must be cleaned with the brass-hair brush. Furthermore, ash accumulating on the terminals must also be removed with this brush.

5. After the last experiment for the day the bombs must be cleaned as in 3 and 4 and in addition the bomb top must be brushed inside (large camel-hair brush) to remove ash that may accumulate on the inside. The top is then dried and placed on the shelf next to the base which

after/.....2.

after cleansing is also thoroughly dried inside and outside.

6. The rubber sealing-washer functions best when thoroughly moist. When not in use it must be immersed in water in a beaker and kept next to the rest of the bomb.

7. On no account should sand be used as a covering to prevent blowing out of coal during combustion.

8. Never exhaust the bomb gases through the oxygen inlet valve.

9. If oxygen leaks from the bomb from either the valve or the threads a new valve or rubber washer must be inserted. If the outlet valve leaks then a piece of rubber is cut from a rubber stopper and inserted in the outlet valve.

10. On no account use a tool to open or close the bomb or its valves. A defectless bomb does not need tools to be manipulated.

11. Every Friday, immediately after lunch, one of the bombs must be taken to the engineers for inspection. This must be done by the officer in charge of survey.

12. On no account may parts of one apparatus, including the bomb, vessel or thermometer be interchanged with another apparatus.

13. The water-jacket and calorimeter-vessel must be cleaned and polished every Friday afternoon by the officer who worked with the apparatus during the week.

14. The thermometers are accurate within very narrow ranges, which are different for different thermometers. The thermometers are standardised within these limits

and/.....3.

and all determinations must be carried out within these limits. (See later).

15. The temperature of the water in the calorimeter-vessel must be from 0.5 to 1.0°C lower than the water in the bath. (see later).

16. The room temperature must be kept as constant as possible, i.e. the door must be kept closed during the day and night. On no account can the door be left open for any length of time. (See later).

17. If any part of an apparatus is not functioning properly it must be reported to the officer in charge of survey who will see that the necessary repairs are effected. All repairs must be done by the engineering staff except replacement of the Schröder valves and rubber sealing ring.

18. The determination is a difficult one and it is essential that during a calorific value determination, great care is exercised when weighing, assembling and carrying out tests.

19. Greatest care must be exercised in handling the Beckmann thermometers. A written report must be handed to the Deputy Director stating reasons whenever a thermometer is broken.

20. The bath must be kept at 30°C ± 0.1°C.

21. Readings must be taken every minute including the readings immediately after firing. (See later).

SETTING OF THERMOMETERS:

Determinations are carried out between fixed limits on the thermometer. These limits are fixed by:

(a)/.....4.

(a) The accuracy of the capillary of the thermometer,

(b) The endeavour to keep the cooling correction as small as possible.

The thermometer is immersed in the water in the bath at $\pm 30^{\circ}C$ and the reading taken (care must be taken that this reading is well within the range fixed by (a)). The limits between which the preliminary readings may be taken is now finally fixed in the range and on a range of not less than $0.5^{\circ}C$ and not more than $1.0^{\circ}C$ <u>below</u> the reading obtained by immersion in the bath. At the commencement of a determination the water in the calorimeter will then be between 0.5 and $1.0^{\circ}C$ below the temperature of the bath and will also comply with (b). in that after firing the temperature will rise to between 0.5 and $1.0^{\circ}C$ above the bath temperature and in this way give the smallest cooling correction.

<u>METHOD:</u>

Weigh into a cup 1 gram of air dried coal. Attach a length of firing-wire between the poles of the bomb-base, in such a manner that a loop is made which will dip into the coal when the cup is in position. Always use approximately the same length of firing-wire.

Into the base pour 10 ccs. of water and then screw the top on tight with the hands. Do not use too much force as the bomb must again be opened by hand.

Connect the bomb to the outlet tube on the oxygen cylinder and by opening <u>only the main</u> cylinder valve a little, slowly admit oxygen to the bomb until a pressure of approximately 30 atmospheres is registered (when the cylinder is nearly empty, a lower pressure than 25 atmospheres is not permissible as it will cause incomplete combustion).

Close the/.....5.

Close the valve and disconnect the bomb. Immerse the bomb into a bucket of water or the bath to ascertain any leakage of oxygen from the bomb. Dry the bomb on the outside.

Weigh into the calorimeter-vessel 3000 grams of water taken from the bath tap, i.e. at a temperature of 30°C. Dry the outside of the vessel. Transfer the calorimeter-vessel into the calorimeter-jacket placing it in the centre. The bomb is now put into the water in the vessel so that the three supports as well as the contact point at the bottom of the bomb-base are in their corresponding positions on the connecting compressed fibre plate in the bottom of the calorimeter-vessel. Attach the terminals of the electric circuit.

The stirrer is now inserted and connected. By slightly turning the pulley ascertain whether the stirrer is moving freely about the bomb, adjust the calorimeter-vessel if necessary. Place the Beckmann thermometer and covers in position and start the stirring. The rate of stirring is 120 strokes per minute.

If the mercury thread top is below the range fixed for the thermometer the water in the calorimeter-vessel can be warmed by means of inserting the hot iron therein, if, on the other hand, the mercury thread top is above the fixed range the apparatus must be dismantled and colder water put into the calorimeter-vessel.

Only after a lapse of not less than 7 minutes during which the apparatus reaches a state of equilibrium, the readings can commence. The room temperature is always below, and during winter time well below, the bath temperature, it is therefore necessary to allow for the air in the space between the calorimeter-vessel and the bath to warm up to a

temperature/.....6.

temperature between the temperatures of the bath and the calorimeter-vessel i.e. approximately 29.5°C. For this reason it is also necessary that the door to the Cal.Val. room be kept closed during the day as well as at night. The windows may be kept open.

Read the temperature registered on the thermometer to the nearest .001°C. The reading can be taken accurately and parallax avoided if care is taken that the graduation line, on the thermometer, nearest the mercury top is a straight line i.e. the line is not curved upwards or downwards through refraction by the capillary tube immediately in front of the graduated plate. Continue the readings for 5 successive minutes. At the end of the 5th minute fire the coal by closing the electric circuit.

During the chief period which extends from the instant of firing until the minute during which the temperature reaches a maximum, take the first two readings to the nearest 0.01°C and the later readings as accurately as possible. Usually after 4 to 6 minutes the temperature reaches a maximum and the thermometer must continually be watched to ascertain the maximum temperature reached and the time taken and recorded (see example at end). Take five successive readings (at minute intervals) after the maximum temperature was reached.

Stop the stirrer and dismantle the apparatus. Do not use tools to release the gas from the bomb or to unscrew the bomb-top. Inspect the inside of the bomb for any unburnt coal. If unburnt coal is found, the determination must be repeated.

Empty the calorimeter-vessel into the bath, then rinse and clean the bomb with the brushes provided.

/.....7.

DETERMINATION OF THE WATER EQUIVALENT OF THE CALORIFIC VALUE APPARATUS.

Warning: The greatest care and attention must be paid to this determination since on this result depends the accuracy of all calorific values subsequently determined.

The determination of the water equivalent must be written into the standardisation book and all the readings, weights and calculations clearly shown. Determinations carried out on paraffin must also be written in this book.

Apparatus: The apparatus used is exactly similar to that used in the determination of the calorific value.

Method: The acid must be dry and must be kept in a desiccator when not being used.

The method adopted is to burn under exactly similar conditions as the coal a known weight of standard benzoic acid. Weigh a 4 inch length of cotton and insert it into the pellet press which was previously thoroughly cleaned. Weigh out 1.0 to 1.1 grams of benzoic acid and pour it into the pellet chamber. Compress into a pellet and weigh the pellet in a calorific value cup of known weight. All these weights must be correct to 0.0001 gram.

The apparatus is assembled and the experiment conducted as described for a coal. The only difference is that the length of firing wire which must be the same as that used for coal, must be in contact with the benzoic acid and the cotton thread tied onto the wire. Care must be taken to ensure that all the cotton thread is in the cup, if an end hangs over the side of the cup it might fall into the water before being completely burnt.

Accuracy:/.....8.

Accuracy: Four or more determinations should be made and the average taken. Results should not differ by more than 12 grams, i.e. 3412 - 3418 - 3424 and not 3406 - 3418 - 3430.

The water equivalent must be determined for different points in the fixed range on the thermometer viz. if the range is between 0.8°C and 1.3°C then the commencing temperatures for the water in the calorimeter-vessel must read 0.8; 0.95; 1.1 and 1.3°C approximately.

CALCULATION OF RESULTS.

When a quantity of fuel is ignited in the bomb calorimeter, the heat liberated during combustion causes a rise in temperature of the calorimeter-vessel and its contents. Owing to heat transferance, due to factors such as radiation and conduction the observed rise in temperature correponds to a heat liberation slightly different from that evolved by the fuel. It is necessary therefore, to apply a correction, preferably as small as possible, to the observed rise in temperature which will give the actual rise in the temperature caused by the combustion of the fuel.

The cooling correction used at the F.R.I. is obtained through calculation by an abridged formula and is not very accurate. The formula used is that of Moser:

$$C = mf - (f + 1)$$

where C = the cooling correction in °C.

M = the number of minutes of the chief or combustion period (if the maximum temperature is reached between two full minutes then the minute after the maximum is taken).

f =/.....9.

f = the average fall of temperature per minute in the after period.

i = the average rise of temperature per minute in the preliminary period (when the temperature falls, then i becomes negative).

The corrected rise = the difference between the time of the first reading after the maximum temperature is attained and the time of firing plus the corrected rise

= t max. - t firing + C.

Example:

Preliminary Period.		Chief Period.		After Period.	
0.	1.762	6.	2.35	11.	3.704 .003
1.	1.760 +-.002	7.	3.38	12.	3.700 .004
2.	1.757 -.003	8.	3.689	13.	3.695 .005
3.	1.755 -.002	9.	3.706	14.	3.690 .005
4.	1.752 -.003	9½.	3.708	15.	3.684 .006
5.	1.750 -.002	10.	3.707		

$T = t_{max} - t_{firing} + C$

$C = mf - (f + 1)$

$m = 5$; $f = .0046$: $i = -.0024$

$C = 5 \times .0046 - (.0046 - .0024)$

$= .0208$

$T = 3.707 - 1.750 + .0208$

$= 1.957 + .0208$

$= 1.9778.$

The calorific value or evaporative power of a coal, expressed in pounds of water evaporated at boiling point by one pound of coal, is the water equivalent of the calorimeter multiplied by the corrected rise in temperature and divided by the latent heat of steam at 100°C. i.e. 539 cals./gram.

/.....10.

$$\text{Cal.Val.} = \frac{\text{W.E. x corrected rise}}{539} \quad \text{lbs./lb.}$$

$$= \frac{3460 \times 1.9778}{539} \quad \text{lbs./lb.}$$

$$= 12.70 \text{ lbs./lb.}$$

CALCULATION OF THE WATER EQUIVALENT OF A CALORIMETRIC APPARATUS.

The water equivalent of the calorimeter is equal to the weight of the benzoic acid used, multiplied by its heat of combustion per gram plus the weight of the cotton thread used and multiplied by its heat of combustion per gram and the total divided by the corrected rise in temperature.

The corrected rise in temperature is calculated in exactly the same manner as described for a coal.

$$\text{W.E.} = \frac{(\text{wt. benzoic acid} \times 6324) + (\text{wt. cotton} \times 4180)}{\text{Corrected Rise.}}$$

(Sgd.) S. D. COETZEE
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PRETORIA.

3rd August, 1951.
