



A Review on Steam Coal Analysis -Calorific Value

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Abstract: Many test methods are available for estimating the calorific value of coal either by direct testing with Standard Test methods or with the help of statistical equations. A comprehensive compilation of most available methods of analysis for calorific value of steam coal have been done. Particular emphasis has been given on the precautions to be taken while conducting the test and necessary improvements in documentation and preparation to address the understanding of possible errors for a better quality management.

Key Words: Coal, Calorific Value, XRF, DTA, DSC, Bomb Calorimeter, Indian Standards (IS), ISO, ASTM

I. Introduction

Coal includes chemical energy that is converted at a power plant into electric energy with determined efficiency. The efficiency is dependent, among others, on coal quality parameters, since the efficiency of the boiler is a function of gross calorific value and content of ballast in coal. The energy value of coal, or the fuel content, is the amount of potential energy in coal that can be converted into actual heating ability. It indicates the amount of heat that is released when the coal is burned. The Calorific Value varies on the geographical age, formation, ranking and location of the coal mines. It is expressed as kJ/kg, Kcal/kg or BTU/lb. in the SI unit system. Coal contains moisture. The calorific value is expressed in two different ways on account the moisture in the coal. When coal burns the moisture in coal evaporates taking away some heat of combustion which is not available for our use. Gross Calorific Value or Higher Heating Value it is the total heat released when burning the coal. The quantity known as higher heating value (HHV) (or gross calorific value or gross energy or upper heating value) is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced. This is the same as the thermodynamic heat of combustion since the enthalpy change for the reaction assumes a common temperature of the compounds before and after combustion, in which case the water produced by combustion is liquid. Net Calorific Value or Lower Heating Value it is the heat energy available after reducing the loss due to moisture. The Heating Value determines how much fuel is required in the power plant. The quantity known as lower heating value (LHV) (or net calorific value) is determined by subtracting the heat of vaporization of the water vapor from the higher heating value. This treats any H₂O formed as a vapor. The energy required to vaporize the water therefore is not realized as heat. Gross heating value (GHV) accounts for water in the exhaust leaving as vapor, and includes liquid water in the fuel prior to combustion. This value is important for fuels like coal, which will usually contain some amount of water prior to burning.

Higher the Calorific Value lesser the amount of the coal required per unit of electricity. Higher calorific value also means the cost of the coal is higher but is offset by the lower cost of logistics, storage and ash disposal. The calorific value of coal is the heat liberated by its complete combustion with oxygen. Most applications which burn fuel produce water vapor which is not used, and thus wasting its heat content. In such applications, the lower heating value is the applicable measure. This is particularly relevant for natural gas, whose high hydrogen content produces much water. The gross calorific value is relevant for gas burnt in condensing boilers which condense the water vapor produced by combustion, recovering heat which would otherwise be wasted. Calorific value is a complex function of the elemental composition of the coal and can be determined experimentally using calorimeters. This is the most important parameter that determines the economics of the power plant operation.

There are many available literatures available covering methods of estimation calorific value of coal either by equipment test or from the statistical analysis. Also National and International Standard institutions like IS, ASTM, ISO etc. have published the test methods. The objective of this paper is to make a rapid review of all the test methods (with limited applicability to Indian laboratory conditions) and look for any opportunity of perfection on the existing understanding of the test methods. It is an independent review without any bias in mind and don't have any intentions finding mistakes in the system rather recommending precisely cautionary steps in doing the test more accurately by the lab.

II. Review of Test Methods for Calorific value of Coal

A. Estimation of CV by regression

During the 1980s a new technique of genetic algorithms (GAs) based on stochastic optimization techniques have been applied to a number of engineering problems [1].

Regression analysis has been done on the data from 775 USA coals (with less than 30% dry ash) to develop an empirical equation by Mason and Gandhi [2] that estimates the calorific value of coal from C, H, S and ash (all on dry basis); expressed in SI unit their equation is:

$$Q = 0.472C + 1.48H + 0.193S + 0.107A - 12.29 \text{ (MJ/kg)}$$

Given et al. [3] used theoretical physical constants to develop a relation to determine the gross calorific value from elemental composition based on data from US coals (expressed in SI units):

$$Q = 0.3278C + 1.419H + 0.09257S - 0.1379O + 0.637 \text{ (MJ/kg)}$$

where, C, H, S, and O are on a dry, mineral-matter free basis, mineral matter is from the modified Parr formula, O is by difference, C is adjusted to a carbonate-free basis, and H is adjusted to exclude hydrogen in bound water present in clay minerals.

Cordero et al. [4] have given the correlation between HHV, VM and ASH as follows:

$$\text{HHV} = 35.43 - 0.1835\text{VM} - 0.3543 \text{ ASH (MJ/kg)}$$

Majumder et al. [5] have developed a new proximate analysis based correlation:

$$\text{HHV} = -0.03 \text{ A} - 0.11\text{M} + 0.33 \text{ VM} + 0.35 \text{ FC (MJ/kg)}$$

CANFIS stands for coactive neuro-fuzzy inference systems. The CANFIS model integrates fuzzy inputs with a neural network to speedily solve poorly defined problems. A total of 4540 set of coal sample from U.S. Geological Survey Coal Quality database, [6] are analyzed, shows the regression analysis of proximate and ultimate analysis of coal samples. The R^2 value of 0.99 shows that there is an overall good fit of data with 95% confidence level. Hence, the best-correlated multivariable equations, between the various mentioned parameters and GCV can be presented as following equations: [7]

$$\text{GCV (MJ/kg)} = 91.4621 - 0.0556 \text{ M} + 0.02800 \text{ V} - 0.9039 \text{ A} - 0.5687 \text{ C} - 0.6972 \text{ N} - 1.1252 \text{ O} - 0.8775 \text{ S}$$

The identification of GCV for coals by this method demonstrated that CANFIS optimized by genetic algorithm is the better alternative.

B. Measurement of CV by DSC

The most widely used methods for determining coal heat content are the ASTM accepted adiabatic and isothermal jacket bomb calorimeters. However, these methods suffer from the disadvantages of being time consuming and requiring fairly complicated operator technique. Thermal analysis techniques, particularly differential scanning calorimetry (DSC), offer a viable alternative to the other standard methods, because DSC does provide the ability to quantify heats of reaction, and enables the user to directly determine the heat content of coal.

The value of the specific heat capacity of any substance depends mainly on temperature [8]. In the case of coal, its carbon content, the moisture content, volatile matter, and the composition and content of ash have great influence on the specific heat capacity value. The values of specific heat capacity, calculated from Richardson's function [9] for temperature range to 600 K are much higher than those calculated on the basis of other functions. In the case of functions proposed by Kirov [10] and Postrzednik [11], it can also be noted that the volatile matter has a greater impact on specific heat than the carbon content. While in the case of the function proposed by Merrick [12], carbon content has greater impact than volatile matter. It was assumed that, in this temperature the decomposition of coal material occurs and is connected with the change of the volatile matter content. Because of dissimilarity, Richardson's function is not included in these charts. For the determination of change taking place in the coal, the simulation calculations using the model of pyrolysis developed by Ściążko [13] were made. This model allows to calculate the change of the efficiency of each evolved volatile matter component for any coal and for any arbitrary heating rate. The efficiency of a particular component is proportional to the amount of volatile matter, and the closing model equations is the mass balance of elements [14]. Definitively, the generalized model of pyrolysis allows to calculate kinetic parameters of the overall volatile matter and its components and to determine the amount of exuded volatile matter and its component at a given temperature. As a result of simulations, the properties of chars obtained from each coals in the temperature range from 500 to 1300 K were obtained.

C. Calculation of CV from XRF data

Study of rapid determination of coal quality, namely, determination of the ash content and caloric value in the coal samples of the mine and electric power station laboratories, has turned out more important in the last years. The calorific value of coal has a linear dependence on the ash content in coal. Results of determination of the calorific value by the correlation method fitted well at the medium moisture samples [15]. But the error was bigger in the case of smaller moisture and bigger than medium moisture samples [16].

D. Measurement of CV by DTA

In some instances, an adiabatic and isothermal jacket bomb calorimeter is not available or the sample even be too small for accurate use. To combat such problems, there is evidence that Differential Thermal Analysis (DTA) is applicable to the determination of the calorific value of coal. [17-19].

The furnace temperature is ramped to 110°C and held isothermally. This ensures that any weight loss experienced is a direct effect of the moisture of the coal. The temperature is then ramped to 900°C and held isothermally. Any weight loss occurring in this isotherm region is a direct result of the loss of volatiles. The previous two steps are performed in a nitrogen atmosphere. For the third part, the atmosphere is changed to oxygen. This creates an environment suitable for combustion. Once the coal is completely combusted, the residue is taken as the ash. The ignition rate is very important when discussing the combustion of coal. High heating rates will cause simultaneous evolution and ignition of volatiles, whereas with low heating rates devolatilization will occur prior to ignition and combustion. The burning profile of coal can be an instrumental analysis in distinguishing between different coals.

E. Computerized coal analyzer using a pulsed neutron beam

Computerized coal analyzer using a pulsed neutron beam: Desham Gu et.al. [20]. In his work, the pulsed neutron beam bombards the elements in coal samples and interacts with the nuclei of its different atoms. This bombardment induces several different reactions. Among those reactions, the thermal neutron capture reaction $[n, \gamma]$ and the inelastic scattering reaction $[n, n', \gamma]$ will induce instantaneous γ -rays. The elemental analysis of coal, including the coal industrial value analysis, shows that the inelastic reaction cross section of carbon and oxygen are relatively larger, whereas the other elements have larger capture cross sections. The instrument uses the pulsed neutron generator to control the emitting period of pulsed neutron beam to separate the inelastic spectrum induced by fast neutrons and capture spectrum induced by thermal neutrons. After the spectrum separation, we analyze the spectrum data to produce the elemental analysis of the coal samples. The direct measurement of C and O means that calorific values can be measured without recalibrating for each particular seam analyzed can be done by Vourvopoulos et. al. [21] & also can produce substantial financial savings to a coal-fired power plant.

F. IS: 1350 (Part II) – 1971 [22]

1. **Analysis sample** of about 300 g of air-dried coal, ground to pass 212-micron IS Sieve (see IS:460-1962[23]) if already ground to pass 212-micron IS Sieve, shall be re-sieved to verify that all the material passes this sieve, and then air-dried for 24 hours and mixed and bottled as above. The normal method of mixing coal in the laboratory is to roll it on a sheet of rubber cloth and turn it over at interval with a large spatula or flat spoon. A laboratory mechanical mixer is, however, preferable.
2. **Special moisture sample** of 1 kg of coal or 2-5 kg of coal crushed to pass 12-5-mm square-mesh screen {see IS: 460-1962), to be sent in duplicate.
3. Where air-drying has been adopted in the preparation of the samples, the percentage loss of moisture in this operation shall be required to be recorded on the label together with the method of sampling used.

Two methods have been described to determine the calorific value of coal and the calorific value as determined in these methods is the gross calorific value of coal at constant volume expressed in calories per gram. They are:

- a) making use of calorimetric bomb immersed in a static or isothermal water jacket
- b) making use of calorimetric bomb immersed in an adiabatic jacket

When any part of the system is changed, the mean effective heat capacity is redetermined at intervals not longer than six months, the redetermined mean should be within 5 cal/ °C of that previously determined. If the difference is greater than 5 cal/°C experimental procedures should be examined and carefully checked.

The results of duplicate determinations in one laboratory should agree to within ± 25 cal/g, and those between different laboratory to within ± 50 cal/g.

This method is applicable to all bituminous coals and anthracites provided sufficient excess of oxygen is present to ensure complete combustion. How about the applicability of this method to lignite coal which are mostly steam coal is not clear when the testing range of calorific value is not specific?

F. ASTM D2015-00 [24]

ASTM D2015-00, Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter (Withdrawn 2000 and no replacement)

G. ASTM D3286-96 [25]

Standard Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter (Withdrawn 2000 replaced by D5865)

H. ASTM D5865-13 [26]

ASTM D5865-13 Standard Test Method for Gross Calorific Value of Coal and Coke, can be used to compute the total calorific content of the quantity of coal represented by the sample for commercial purposes, regulatory

requirements, evaluate the effectiveness of beneficiation processes and to classify coals [27]. The analysis sample is the material pulverized to pass 250- μm (No. 60) sieve, prepared in accordance with Method D2013 [28] for coal.

The important aspects of ASTM D5865 are:

- The precision requirement as expressed in 10.8.1. The precision of ten acceptable calibration test runs shall have a relative standard deviation (RSD) no greater than 0.17%. If after considering the possibility of outliers using criteria established in Practice E178 [29], this limit is not met, one should review operation of the calorimeter for any assignable cause. Operating deficiencies should be corrected before performing additional calibration measurements as required.
- It is not good practice to report extrapolated data obtained outside the range of calibration. The range of reliable calibration can be considered as the range of reliable measurement and vice versa. The working limits for the instrument calibration shall be determined and defined in terms of the corrected temperature rise. All subsequent measurements shall be kept within these limits.
- At least three reference samples should be measured during any of these periods when the periods are considered to be potentially significant.
- Results are expected to scatter with a normal distribution within the limits. Systematic trends or patterns in the data plots may be early warning of incipient problems and are cause for concern; hence techniques to identify such should be practiced by using Control Chart Method for Calibration Verification and Rolling Average Method.
- Large differences in the rates of combustion between the calibrant (benzoic acid) and the unknown (lignite) or significant differences in combustion chemistries may give rise to systematic errors that are difficult to detect. The use of test substances in such check experiments can help demonstrate that the techniques and procedures used in determining heats of combustion of unknown materials are reasonably free of persistent errors.
- Use of Laboratory Control Materials:
 - the heat of combustion of LCMs are not certified
 - issues such as stability, homogenization techniques to be considered
 - proper conditions for storage must be addressed
- At least one CRM or LCM must be analyzed along with each batch of 20 or fewer samples. If the laboratory fails to meet either the precision or accuracy control limit criteria for a given analysis of the CRM or LCM, the data for the entire batch of samples is suspect.
- Carry out a moisture determination in accordance with Test Method D3173 [30] or Test Methods D7582 [19] on a separate portion of the analysis sample preferably on the same day but not more than 24 h apart from the calorific value determination so that reliable corrections to other bases can be made.
- Report the calorific value as Q_{vad} (gross) along with the moisture of the sample as determined M_{ad} .
- The repeatability and reproducibility limits are shown below

Table 1: Ranges and Limits of Repeatability & Reproducibility for the Gross Calorific Value of Coal

Coal Type	Range	Repeatability	Reproducibility
Manual Adiabatic Calorimeter, 2.36 mm coal			
Bituminous	29 535 to 33 720 J/g	± 160 J/g	± 249 J/g
Subbituminous-Lignite	20 442 to 29 651 J/g	± 140 J/g	± 346 J/g
Microprocessor Controlled Calorimeter, 250 μm coal			
Bituminous	26 280 to 34 190 J/g	± 149 J/g	± 256 J/g
Subbituminous-Lignite	21 860 to 27 680 J/g	± 193 J/g	± 381 J/g

- Exposure to air at ambient temperature causes deterioration to the extent that various properties of coal are affected, including the heating value. With the exception of the anthracite sample, the heating values diminished anywhere from 250 to 950 J/g. The average monthly degradation is in the range of 6 to 23 J/g. Sufficient care to be taken for sample storage and complete analysis at the earliest.

I. ISO 1928:2009 [31]

The salient points ISO 1928 [31] are as below:

- The coal and coke used for the determination of the calorific value shall be the analysis sample ground to pass a test sieve with an aperture of 212 μm . In some circumstances, it has been shown that a maximum particle size of 250 μm is acceptable for low- and medium-rank coals.
- Either the moisture content shall be determined on samples weighed within a few hours of the time that samples are weighed for the determination of calorific value, or the sample shall be kept in a small, effectively closed container until moisture analyses are performed, to allow appropriate corrections for moisture in the analysis sample.
- For coals having ash values exceeding approximately 35 %, there is a possibility of incomplete combustion, and a sufficient, known mass of auxiliary material should be added to ensure a temperature rise similar to that obtained in benzoic acid calibrations.
- When a mercury-in-glass thermometer is used, the corrections specified in the certificate issued with the thermometer shall be applied to the observed initial temperature and the final temperature.
- Systematic errors can arise, for example, from evaporation of calorimeter water, from uncontrolled heat exchange along various paths and/or imperfections, and lag in an adiabatic temperature control system during the reaction period. Cancellation of this type of error depends largely on the similarity between the calibration tests and the combustion of the fuel samples with respect to time-temperature profile and total change in temperature of the calorimeter.
- As long as the initial pressure of oxygen and the reference temperature are kept within $(3,0 \pm 0,3)$ MPa and (25 ± 2) °C, respectively, the departure from certification conditions caused by pressure and/or temperature deviations is within ± 3 J/g and it is not necessary to account for it.
- A convenient way of checking a system already calibrated by combustion of, for example, 1,0 g samples is to use the benzoic acid as an unknown.
- For the ordinary series of calibrations, five satisfactory combustions on benzoic acid shall be carried out. The standard deviation shall not exceed 0,20 %. If the precision requirement is not met, the cause for the unsatisfactory results shall be identified and corrected, and a new series of calibration tests shall be performed.
- Where a change to the system is not involved, the new mean value of ϵ shall be within 0,25 % of the previous value. If the difference is greater than 0,25 %, the test procedures shall be examined and the cause of the problem identified and dealt with.
- Repeatability ± 120 J/g and reproducibility ± 300 J/g.

III. Precautions

Each of these following criteria will cause an error in an experimental result, either directly during the course of the experiment or later during the data reduction procedure. Furthermore, every time the experiment is repeated, these errors will continue to enter, usually to about the same extent and with the same positive or negative sign. Detection and elimination of systematic error is very difficult because one is rarely certain of its origin or, for that matter, its existence. One might, for example, rely on comparison measurements between different laboratories of the quantity in question, especially if the measurements are intended to be highly accurate. More routinely, the use of blank determinations or the use of certified standards (e.g., the use of a NBS standard Benzoic Acid sample for the calibration of a bomb calorimeter) are obvious strategies to reduce systematic error but no procedure, however extreme, will guarantee an error free measurement. In fact, it is impossible to ever know for certain that all systematic error has been eliminated from an experiment! However, errors can be minimized when the lab adopts certain precautions as briefed below-

Wire

- Preferably use NIST Certified Nichrome wire with known calorific value (valid supporting document should be generated or available with lab)
- Fasten the wire tightly under the sleeves
- Arrange the wire in such a way that it is just above the sample
- The energy released by the combustion of fuse wire should be considered to get more accuracy. For this the weight of fuse wire to be fastened to the poles and the weight of fuse wire left as residue after combustion should be measured. The net weight of wire which burns out will be the difference between the two. This net weight should be multiplied by the calorific value of the wire to obtain the net heat generated due to combustion of the wire which should be included in the calculation to obtain more accurate result.

Combustion Bomb

- the bomb will be capable of (a) burning completely one gram of coal using an initial oxygen pressure of 30 atmospheres and (b) withstanding, with an adequate safety factor but without excessive mass, the maximum pressure likely to be produced.
- 250 to 350 ml capacity (existing bombs of up to 500 ml capacity, if resistant to intragranular corrosion,

- not more than 3.25 kg weight
- capable of withstanding under test, for ten minutes and without permanent deformation, an internal pressure of 210 kg/cm² (request supplier to produce certificate for bomb)
- When more than one bomb of the same design is used, it is imperative to use each bomb as a complete unit. Colour coding is recommended. Swapping of parts can lead to a serious accident.

Oxygen

- Purity of Oxygen, it should 99.9% and certified by supplier. Keep supporting certificates each time buy the oxygen cylinder. (valid supporting document should be generated or available with lab). Never use commercial grade of oxygen because of presence other gases will impact the results and combustion may not be complete with the available oxygen.
- Adjust the pressure of the oxygen cylinder to fill the bomb vessel slowly up to 35 atm or as per specification. Don't over pressurize, may create safety hazards.
- Final Oxygen pressure in bomb measured to 0.01 atm on a calibrated pressure gauge. (calibration document)
- The temperature of the oxygen inside the bomb measured to 0.1°C with a calibrated mercury thermometer (valid supporting calibration document should be generated or available with lab)

Weight

- Care should be taken while the crucible with sample to avoid spillage of the sample and also limit the sample weight so that bomb should not liberate more energy than specified by the manufacturer. This may lead to erroneous results as well as create safety hazards.
- The absence of a buoyancy correction to the weight of the water placed in the calorimeter can. The uncertainty due to the absence of the buoyancy correction in the calorimeter weight was estimated from the known variation in air density during the benzoic and experiments (12 mg/l) and the approximate volume of the calorimeter can plus water (2.59 l). The resulting percentage error was arbitrarily multiplied by two because it is quite evident from the method used to adjust the weight of water in the can [32].
- Convection currents, may also make a substantial contribution to the weighing error
- Defective meter zero in reading in balance.
- Use of a calibrated balance in the range of the weighment of sample (valid supporting document should be generated or available with lab)
- Linearity and Stability check for balance (valid supporting document should be generated or available with lab) with a primary calibrated weights.
- Application of uncertainty errors in the weighing range of the test.

Water

- Maintain correct water level in the pipette tank (how to ensure this?)
- The calorie, or gram calorie, is the quantity of heat required to raise the temperature of 1 gram of pure water by 1 °C. The heat energy of pure water is 1 cal/g-°C and 1 btu/1b-°F. How pure is the testing water is important? Usually triple distilled water serves the purpose.
- Never forget to put fresh triple glass distilled water of 1-2 ml inside the body of the bomb in each experiment (or follow manufacturers recommendation) (valid supporting document should be generated or available with lab like date of preparation, volume and consumption for triple distilled water)
- Distilled in low grade stainless is not the same as distilled in good glass distillation unit. This can be verified with conductance and keep record.
- Exposure to air will allow carbon dioxide to dissolve in the water which will raise the conductivity, i.e., pass slightly more electricity. Prefer freshly prepared.
- Instead of using hand to put the bomb in bucket water, if a provision is made to insert the bomb without making any contact of bucket-water to the hand, error in measurement may be decreased. This will avoid loss of bucket water because of wetting of the hand.

Temperature

- All the parts of calorimeter if not in thermal equilibrium, find out the effect of a temperature gradient on calorimetric measurements. It was observed that the lid of the jacket was about 0.006 °C colder than the rest of the jacket presumably due to poor water circulation in the lid.
- The stirrer motor should not change the water temperature by ± 0.1 °C even in 30 minutes of operation (valid supporting document should be generated or available with lab)

- The sensitivity of the temperature control system is such that the temperature drift of the calorimeter vessel, when in balance at 20°C, does not exceed ± 0.0005 °C
- It was found that there is a difference between the temperatures of the calorimeter surface and the water in the vicinity of the resistance thermometer and that this difference varies with time in the electrical calibrations in a different way than in the benzoic acid experiments. Need to address this issue in uncertainty budget.
- The isothermal jacket should be provided with means of keeping its temperature constant throughout the determination to within ± 0.1 °C. (conduct blank experiments to confirm)
- Galvanometer sensitivity should be $\pm 1 \mu\Omega$ (valid supporting document should be generated or available with lab).
- The thermistor should calibrate in situ with a small size Pt100, class 1/10 using an 8½ digits precision ohmmeter and Pt100 should be calibrated against a SPRT (25 X; Tinsley, 5187A) temperature, in accordance to the International Temperature Scale of 1990, ITS-90 [33]
- Identify the stem correction for thermometer or the temperature.
- An uncertainty in the corrected temperature rise should be considered (valid supporting document should be generated or available with lab).
- Check the linearity and calibration in the experiment operating range of thermometer periodically with a calibrated and certified thermometer (stand by). (valid supporting document should be generated or available with lab).
- The thermometer shall be of 6-degrec range and duly certified by the National Physical Laboratory or any other primary national or international body with traceability.
- It shall be graduated to 0.01 °C and used with certified corrections which shall be given to within 0.002 °C at intervals of not more than 0-5 °C.
- The thermometer shall be tapped before each reading in order to prevent the mercury thread from sticking.
- If a thermometer of the Beckmann type is used, and the certificate of testing does not show the changing value of the degree, due to the variable amount of mercury in the bulb, determinations of the water equivalent shall be done to various temperatures, say, when the zero of the thermometer corresponds to 10°C, 15°C, 20°C (about), etc., and the appropriate value, found by interpolation, shall be used when calorimetric determinations are made. A solid stem thermometer is preferable.
- A magnified viewer without parallax error and with a minimum magnification X5 shall be used to permit the reading of temperatures by estimation to 0.001 °C, if manual recording.
- Instead of using a normal 0.01 °C resolution mercury in glass thermometer, if we use a more sensitive temperature sensor like RTD or thermocouple, with a data acquisition system, we shall be able to plot a graph of rise in temperature of bucket water with time. And by using this graph we will be able to perform the cooling correction programmatically. This correction factor, if considered and included in the calculation, will compensate for the heat loss from bucket-water to the jacket-water and the assumption of ideal adiabatic condition will no longer be required.

Pressure

- Confirm the pressure is maintained for a period of 30 minutes without any sign of leakage inside the bomb at 300 kg/cm² hydraulic pressure (valid supporting document should be generated or available with lab).
- correction for the metal scale when using a barometer.
- Check for leakages by submerging in water or with soap solution.
- Apply the calibration error

Sample crucible

- Before use in the calorimeter, heat treat base metal crucibles for a minimum of 4 h at 500°C to ensure the crucible surface is completely oxidized.
- Base metal alloy crucibles are acceptable (platinum preferable), if after three preliminary firings, the weight does not change by more than ± 0.0001 g.
- Corrosion reaction from ash to be checked visually as well from consistency of weight of crucible.

Calibration

- Calibration and calibration check of the instrument should be done regularly to avoid errors.
- The calibration of the bomb should be made with NIST certified benzoic acid and not the commercially available benzoic acids of high purity as the calorie content is not certified by the manufacturer with national and/or international traceability. Certified Reference Material (CRM) - Reference material

characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability. NIST Standard Reference Material® (SRM) - A CRM issued by NIST that also meets additional NIST-specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material (NIST SP 260-136). Note: An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs. The terms "Standard Reference Material" and the diamond-shaped logo which contains the term "SRM," are registered with the United States Patent and Trademark Office.

- The uncertainty budget for benzoic acid in joules per gram of sample was found to be 2.2 to 4.0 [34,35]. It would be preferable, in spite of the difficulty of measuring it, to evaluate the correction experimentally in absolute calorimetric measurements unless the calorimeter has been specifically designed to eliminate the error.
- Considering the cost part, in addition to NIST SRM, a laboratory developed CRM can be developed for short-term verification initiative but not calibration purpose (valid supporting document should be generated or available with lab).
- Particle size pass through 60 mesh screen is important as combustion process inside bomb is very short time. Bigger particles likely to have incomplete combustion, hence low calorie result.
- At least three reference samples should be measured during any of these periods when the periods are considered to be potentially significant.
- The compound to be pressed into a pellet form and the surface cleaned with a stream of oxygen. The apparent mass of the sample and auxiliary substance is determined with a micro-balance, with a sensitivity of $\pm 10^{-7}$ g.
- Be sure to make an estimate of the uncertainty of resonance energy (valid supporting document should be generated or available with lab).

Routine Calibration/verification Check

- We should understand the difference between routine calibration check and routine energy equivalent check with Benzoic Acid CRM. Consider a standardization test in which 0.9914 grams of standard benzoic acid (heat of combustion 6318.4 cal/g) produced a temperature rise of 2.639 °C. The energy equivalent of the calorimeter is then calculated as 2374 Cal/°C (not considered the corrections usually applied for heats introduced by the fuse and by acid formation).
- It is important to note that the energy equivalent for any calorimeter is dependent upon a set of operating conditions, and these conditions must be reproduced when the fuel sample is tested if the energy equivalent is to remain valid. For instance, the addition of one gram of water in the calorimeter will alter the energy equivalent value by one calorie per degree Celsius. Less obvious but equally important are the changes resulting from different bombs or buckets with unequal masses, different operating temperatures, different thermometers, or even the biases imposed by different operators. So by checking the energy equivalent (W) the bomb calorimeter is not calibrated but the fitness of the equipment is validated. After the energy equivalent has been determined, the calorimeter is operationally fit for testing fuel samples.
- In addition to the above, the lab must do at least one calibration check to ascertain the functionality of the equipment in the calorific value range of the test of the day. In simple word, the lab should at least test two coal samples (either SRM/CRM/LRM or lab developed control samples) of known range of calorific value for identifying the stability of the equipment for the testing range of the samples of the day.
- For example, low volatile bituminous coal of 6700 cal/g and a lignite of 3800 cal/g should not be tested with single point calibration with Benzoic acid of 6318 cal/g. The linearity of the range is not acceptable with single point calibration and functionality of bomb calorimeter cannot be proved with both the ranges. Linearity is determined by the analysis of samples with analytic concentrations spanning the claimed range of the method or the calibration limit of lab. The results are used to calculate a regression line against analytic calculation using the least squares method. It is convenient if a method is linear over a particular range but it is not an absolute requirement. Where linearity is unattainable for a particular procedure, a suitable algorithm for calculations should be determined. [36].
- The following figure (fig 1) is a theoretical plot of different standard coal samples for their calorific values. It can be seen very good linear correlation ($r^2=0.92$) along with the Benzoic acid.

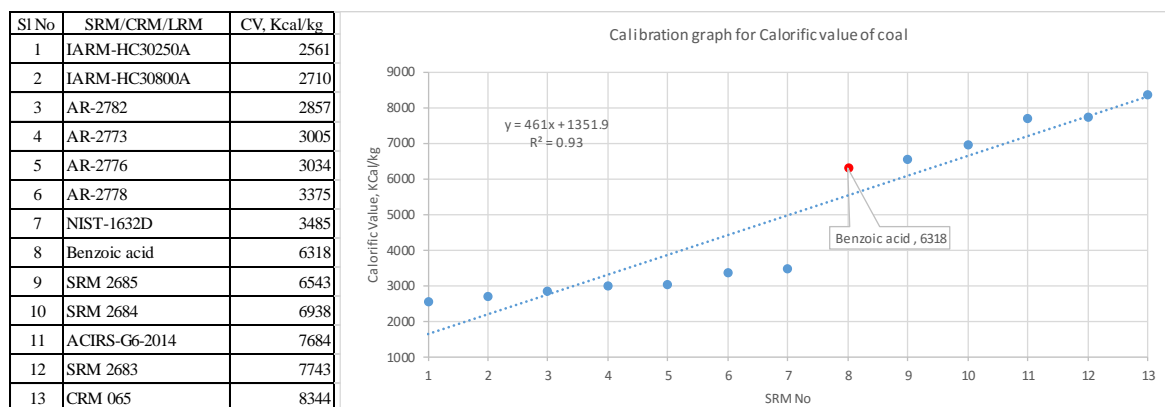


Fig 1 Calibration graph of calorific value of coal

But when we separate the high calorie coal from the graph and plot the low calories standard samples along with Benzoic acid, (fig 2) the linear correlation is very poor ($r^2=0.58$). However, after removing the Benzoic acid (fig 3) the regression coefficient found to be excellent ($r^2=0.96$). This clearly supports, a single point calibration with Benzoic acid for the steam coal calorific value estimation is not accurate, however, for the functionality check of the bomb calorimeter is acceptable.

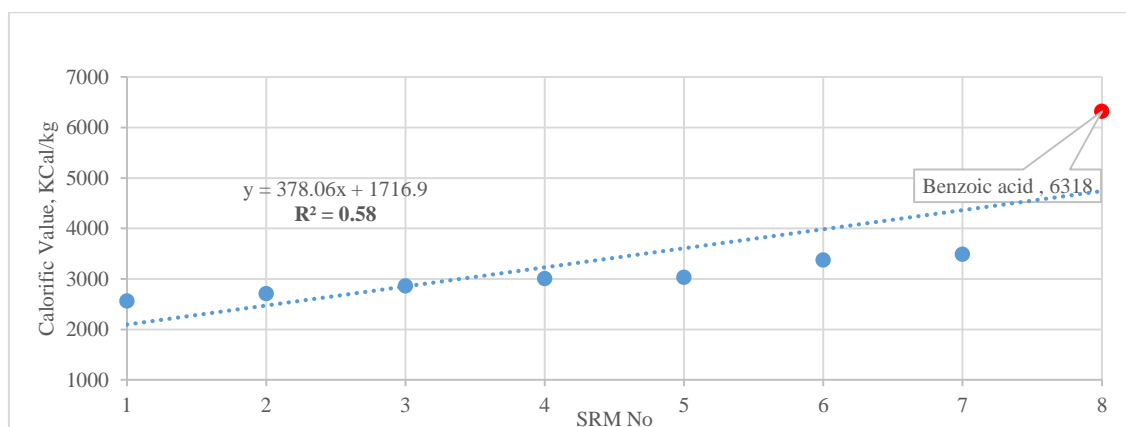


Fig 2 Calibration graph of calorific value of low calorie coal with Benzoic acid

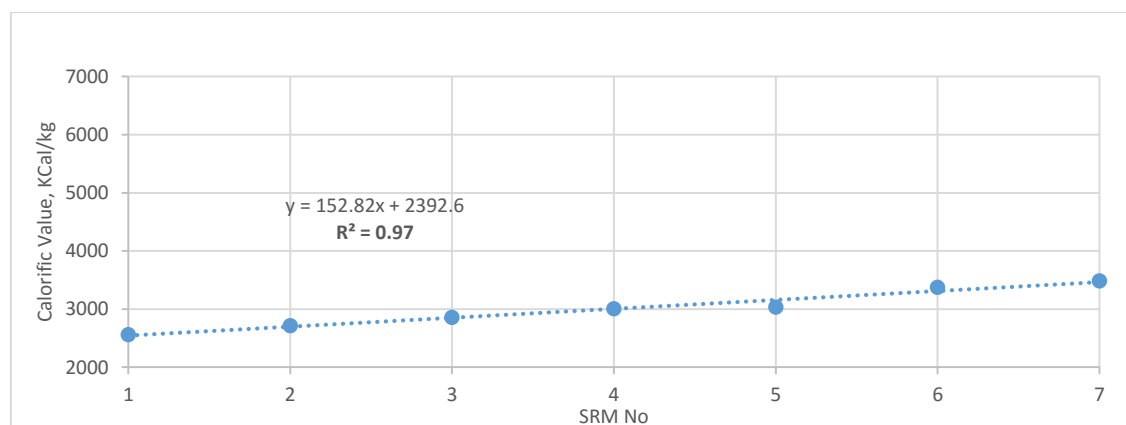


Fig 3 Calibration graph of calorific value of low calorie coal without Benzoic acid

- We can take the example of an analogue or digital stop watch with minute function as least count cannot be used in Olympic Games, as it needs resolution of milliseconds. So the calibration has to be in microseconds and minutes to prove its fitness for use in the range of its test, for which the laboratory must determine its own precision data based on test data, to declare its fit for use for the specified test.

- For high calorie coal sample, the CRM samples like CRM 065: Calorific Value $34.915 \text{ kJ/g} \pm 0.070 \text{ kJ/g}$ (uncertainty) [37], SRM 2683, 2684 and 2685 [38,39]. A higher rank bituminous coal, ACIRS-G6-2014 with calorific value $32.150 \pm 0.0092 \text{ MJ/kg}$ can also be included in calibration.
- Low calorie coal CRM sample like AR 2773, 2776, 2778, 2782 [40] give a choice of calibration of bomb calorimeter for lignite steam coal sample analysis. Also SARM 18 is a high-volatile, low-rank bituminous coal with a rank in the vitrinite category V7., SARM 19 is a subbituminous to bituminous coal and is of generally very low rank (average V4) [41] can be included for calibration check purpose of bomb calorimeter. Standard samples like IARM-HC30025C, IARM-HC30250A, IARM-HC30075C, NIST-2685b [42] can also be considered.

General

- Expel the gas slowly while diffusing the bomb vessel after analysis.
- At the end of the experiment, the gases in the bomb are released and the bomb is then opened to check for the presence of any traces of carbon or other signs of incomplete combustion. Check it under focused light for a better visibility.
- Repeat the analysis if any un burnt sample is found in the crucible after analysis.
- Boil the bomb calorimeter extracts to expel carbon dioxide before titration.
- While still hot, titrate with standard barium hydroxide
- If equipment is attached with a temperature recorder or plotter, optimize the speed, resolution and baseline.
- Keep copies of relevant standard test method which should be up to date.
- Routinely conduct internal procedural audit with associated chemists to keep cognizant as human mind has tendency to overlook or adopt convenience.
- Conduct Gage R&R for associated measuring instruments and chemists.
- Follow ISO 17025 guidelines even the lab is not accredited.
- Periodically, verify the uncertainty budget for calorific value.
- Always plot the standard CRM/SRM/lab internal control sample values in control chart with upper limit and lower limit in a trend line chart and display, so variations or trend can be visualized to take corrective action than observing single value of the day.
- While selecting CRM or SRM keep in mind the matrix of the sample to be tested for better accuracy like ash content, TM levels, volatile matter, sulphur and calorific value.
- Pressure, mechanical, and dimensional tests on bombs (first at least once in three years 3 years or 1000 firings (depending on use) then every 500 firings).
- Checks on calorimeter dimensions and for thread slackness.
- Replace O-rings and valve seats in accordance with manufacturer's instruction.
- The period given between successive calibrations is a maximum period. More frequent calibrations may be required if the equipment is repaired, moved, is in constant use or a change in operating circumstances occurs.
- Coal laboratories must maintain adequate quality control in supervision of equipment performance by the use of appropriate reference materials on a regular basis.
- Whenever possible, unless otherwise stated in the relevant standard, equipment should contain all items of apparatus specified in the test method when being calibrated.
- The calibration requirements for other general items of equipment used in coal testing (e.g. balances, thermometers, thermocouples, volumetric glassware, etc.) are found in the General and Reference Equipment Tables available from the NATA website Reference Equipment Tables available from the NATA website [43].
- Oxidation reduces the calorific value of coal. Low rank coals will lose about 190 Btu-per-pound for each 1% increase in oxygen content while high rank coals will lose about 240 Btu-per-pound for each 1% increase in oxygen content [44]. Preservation of all gross as well as laboratory samples are very important.
- Keep an alternate verification system like regression check, DTA or DSC etc. for having a conformance of result.
- Do the duplicate sample check for same lot sample collected from another sampling point like cross belt in a power plant.
- At least yearly once participate in a round robin test program or else cross check samples in other reputed labs or with customer or supplier labs.
- ***In results, include the mean value from the repeated experiments as well as the simple error analysis for both the standard benzoic acid or CRM reference and the real sample along with the residual***

moisture in test sample as determined during simultaneous check of calorific value and residual moisture.

IV. Conclusion

Fossil fuels still power the vast majority of automation and electricity production for industry and knowing the correct fuel to air ratio is of vital importance in the modern day world of carbon emissions. It is essential to know the exact amount of fuel so as not to have too much waste or uncombusted product at the end. It in turn is also to have the correct amount of oxygen so as to burn off the fuel sufficiently. Insufficient oxygen for the mass of fuel also leads to leftover fuel and the full calorific value of the fuel is not obtained. In industry these ratios become very important as cost saving and cost effectiveness are at the heart of any business and when you are purchasing vast quantities of coal you need them to be cost effective in their operation. The right fuel also is a very important factor when applied to industry and heat generation. This emphasize the importance of estimation of calorific value in coal.

An error of 1 ml in making the acid titration will change the thermal value of coal 1.0 calorie, an error of 1 cm in measuring the amount of fuse wire will change the thermal value by 2.3 calorie, an error of 1gm in measuring he the 2kgs of water will change the thermal value by 2.8 calorie, an error of 1 mg in weighing the sample will change

The thermal value 6.7 calorie, an error of 0.002 °C in measuring the temperature rise will change the thermal vale by 4.8 calorie. If all those errors are in same direction, the total error would be 17.6 calorie. Therefore, laboratories are required to estimate uncertainty of measurement for the CV tests being carried out [45] and compare with the repeatability expressed with the standard test method. This should be on the basis of EURACHEM and GUM where standard methods include uncertainty factors, laboratories may use them for the estimates [46].

Systematic error is the limiting factor in determining accuracy. Thus systematic error, which is always present to some extent, will ultimately determine the accuracy of a measurement. Repeated measurements of GCV (either CRM/SRM or lab control sample) will always exhibit fluctuations of the measured values about some mean value. Indeed, it is a fundamental assumption (sometimes called the Postulate of Measurement) that, as the number of measurements tend to infinity, the running mean will eventually settle down to some fixed quantity called the 'limiting mean'. These fluctuations are assumed to arise because of a number of small inherently uncontrollable processes, each of whose effect is individually small. These errors are thus called Random Errors and can be reckoned as the difference between the value of the n^{th} measurement and the mean value. Because random error is amenable to statistical analysis, it is possible to derive a measure of its influence. The most common measures of the precision in the original data points are the sample variance and the corresponding standard deviation.

Repeating the experiments reduces the standard error by the factor. Thus while the standard deviation (for the infinite experiment) is a characteristic of a particular apparatus and therefore can be reduced only either by redesign of the apparatus or the standard error can be reduced by repetition of experiments. When dealing with the mean of a series of experiments, the standard error is actually the best estimate of random error so experimental repetition is often well worthwhile. On the other hand, the reduction in the standard error is not linear with respect to n so at some point it may be more economical to look at improving the apparatus instead of just making more measurements. Random error is the limiting factor in determining precision. Precision reflects how close our measurements are to one another. If we make a series of measurements and then calculate the standard deviation for these results we will find that the smaller the standard deviation the better our notion of precision, whereas conversely, the more spread out the results, the larger the standard deviation and hence the poorer the precision.

In summary then, accuracy measures how close the mean value is to the true value whereas precision measures the closeness of the individual results. Repetition will increase precision by reducing the standard error, but will have no effect on accuracy. The lab personnel must understand this and produce the results.

V. References

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