Every joule counts

Dr Georg F. Szczendzina, DCC-GmbH, Germany, and Kai-Oliver Linde, IKA-Werke GmbH & Co. KG, Germany, discuss laboratory analysis of net and gross calorific value of coal and other fuels.

The exact determination of calorific value is not just important for those on a diet: it is also of major importance for the fuel business. This article discusses the key factors behind accurate laboratory analysis of calorific value of coal and other fuels.

IKA's modern calorimeters enable the exact calorific value to be determined with the required degree of precision and in accordance with international standards.[1] The IKA C 5000 calorimeter includes adiabatic and isoperibolic operation, a high level of automation and a further rapid (dynamic) mode. At the end of the test, this calorimeter can also automatically vent the decomposition vessel: automated oxygen flushing of the decomposition vessel, as required for example under the German standard DIN 51900, is thus possible.[2]

Figure 1. The energy content of solid fuels.

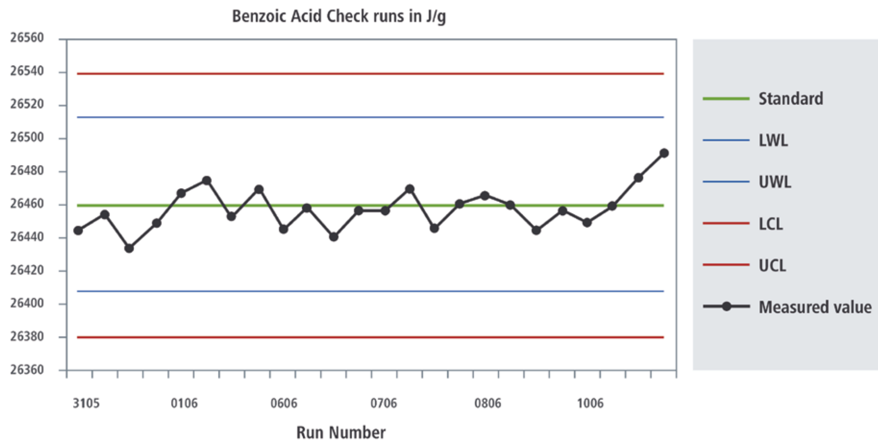

Figure 2. Example of x chart for check sample runs.

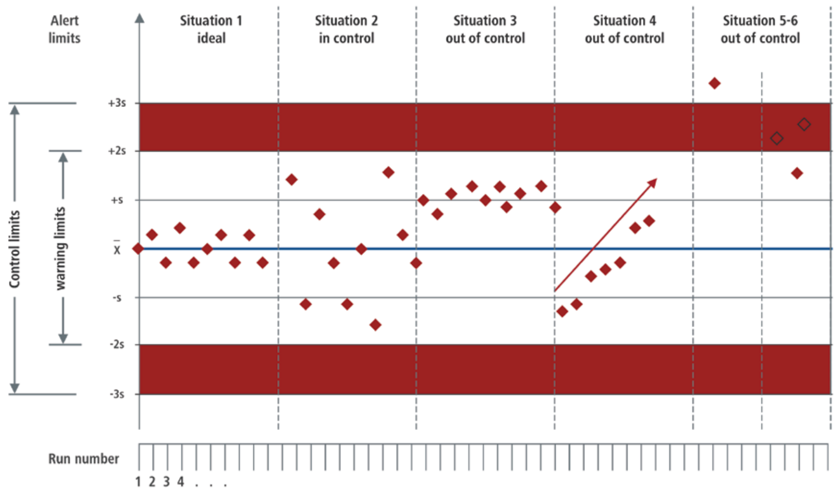

Figure 3. Control charting: mean value control chart.

In addition to complete automation of the water handling system, the unit operates independently of any further external connections, with the exception of the power supply and oxygen connection. IKA supplies four different models of calorimeters with different levels of automation as options. This enables selection of the correct unit for the regulation or standard in question and for each application and number of samples.

The performance of the IKA C 5000 has been demonstrated using the Shewhart control chart for the Benzoic acid check sample x chart (Figure 2).

Laboratory testing

The ability of IKA calorimeters to determine the relevant parameter required for invoicing purposes, namely calorific value, has been proven, in that they meet the stringent requirements of the various national and international standards. This is particularly important for ISO/IEC 17025 accredited fuel testing laboratories.[3] Such laboratories prove their competence by participation in round robin tests (also referred to as interlaboratory comparison or proficiency-testing programmes). With the advent of ISO/IEC 17025, laboratories must have procedures that enable them to assess their individual measurement uncertainty.

Quality control measures

Internal quality control using control charts

The use of so-called control charts to check precision and trueness shows visually whether a test process is under control. Figure 3 shows a sample mean value control chart for six situations. The warning limits (LWL: lower warning limit; UWL: upper warning limit) are defined as a mean value $\bar{x} \pm 2s$ (s: standard deviation). A test process is out of control if the control limits (LCL: lower control limit; UCL: upper control limit), mean value $\bar{x} \pm 3s$, are exceeded (Situation 5). Situation 1 is the ideal case. All measurements are close to the mean.

Situation 2 is under control, as the measurements are in a normal distribution within the warning limits, but are less precise. Situations 3 to 6 are out of control. In Situation 3, 10 consecutive values are on one side of the central line. In Situation 4, seven consecutive values show an upward trend. Situation 6 shows two out of three consecutive values outside the warning limit.

External quality control by DCC round robin tests

Round robin tests are the most important element in a laboratory's external quality control. Accredited fuel testing laboratories must participate regularly and successfully in round robin tests in order to prove their competence e.g. in the determination of the calorific value. DCC Delta Coal Control GmbH is an international provider of round robin tests for solid fuels. Numerous substances can be analysed annually by fuel testing laboratories. IKA's laboratory has also participated successfully in the DCC solid fuel round robin tests.

Generally, solid recovered fuels and renewable fuels are increasing in importance. Renewable fuels are produced from renewable resources, wood pellets, wood chips, olive kernels, palm kernels, coffee grounds, torrified fuels and Cfossred©. These fuels are also burned in power plants, mixed with hard coal and lignite.

Biofuels are alternative fuels for extending fossil fuels, which can now be incorporated seamlessly. The combustion of biogenic carbon is climate neutral. The trade in CO_2 emission certificates enables a financial benefit to be obtained by replacing fossil CO_2 with biogenic CO_2. As biomass (biogenic carbon) is a renewable fuel, fuels such as e.g. Cfossred, a carbon fuel with reduced fossil carbon content, can contribute to a saving of resources and increase supply security through diversification. These "new" fuels do, however, place high demands on the skill of the analytical laboratories and the equipment used.

Precision and trueness

Precision and trueness are vital in the determination of parameters (Figure 4). To ensure the quality of analysis results, it is necessary to assess the accuracy of the methods and monitor this on a routine basis. The accuracy can be assessed as the sum of random errors (precision) and systematic errors (trueness) using various means.

By using validated methods, precise measurement equipment, certified reference material and participation in round robin tests as external control measures, and using control charts, Q-samples and check-samples as internal control

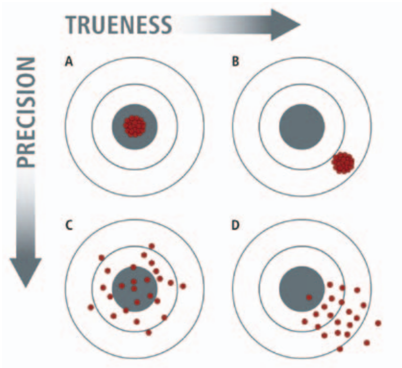

Figure 4. Precision and trueness. A: Precise and true (with one outlier); B: Precise but not true (the chemist's nightmare); C: True but not precise; D: Not true and not precise.

Table 1. Measuring protocal example.	
Sample	1070301
Sample properties	DCC coal sample
Test date	20 June 2011
Start time	14:08
Operator	IKA Application Laboratory
Calorimeter	C2000, vessel 1
C-value	8940 J/K
Mode	Isoperibolic 25°C
Weight-in quantity	1.0394 g
Temperature rise	3.6044 K
Extraneous energy 1	50 J
Extraneous energy 2	0 J
Ignition energy	70 J
Hov (an)	**30,886 J/g**
Net calorific value acc.	**DIN 51900-1 : 2000 (6)+(7)**
Air dry loss (ar)	7.78 %
Total water (ar)	10.19%
Analytical moisture (ad)	2.61%
Residual moisture (DIN 51718)	2.61%
Ash (ad)	7.98%
H (ad) (DIN 51718)	4.61%
Carbon (ad)	75.09%
Sulfur (ad)	0.62%
Hup (an)	**29,838 J/g**
Huv (an)	**29,877 J/g (DIN 51900-1 : 2000, (A.1)**
Reference states	
Hov (ar)	28,482 J/g
Hov (waf)	34,545 J/g
Hov (wf)	31,714 J/g
Hup (ar)	27,326 J/g
Hup (waf)	33,443 J/g
Hup (wf)	30,703 J/g

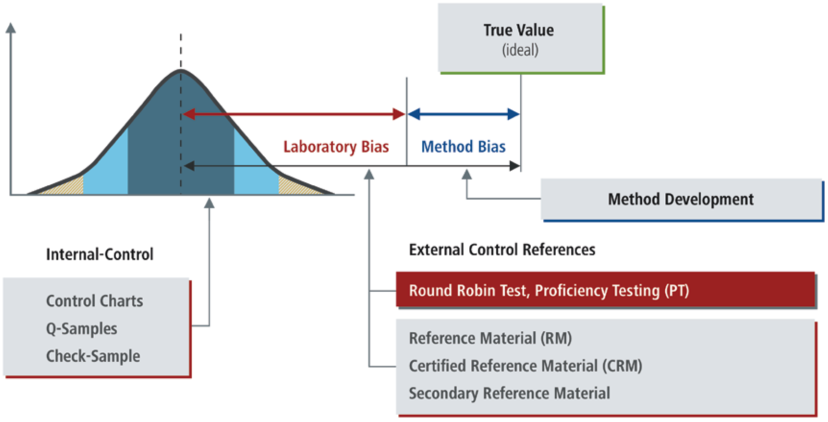

Figure 5. Internal and external control measure for quality assurance in analysis.

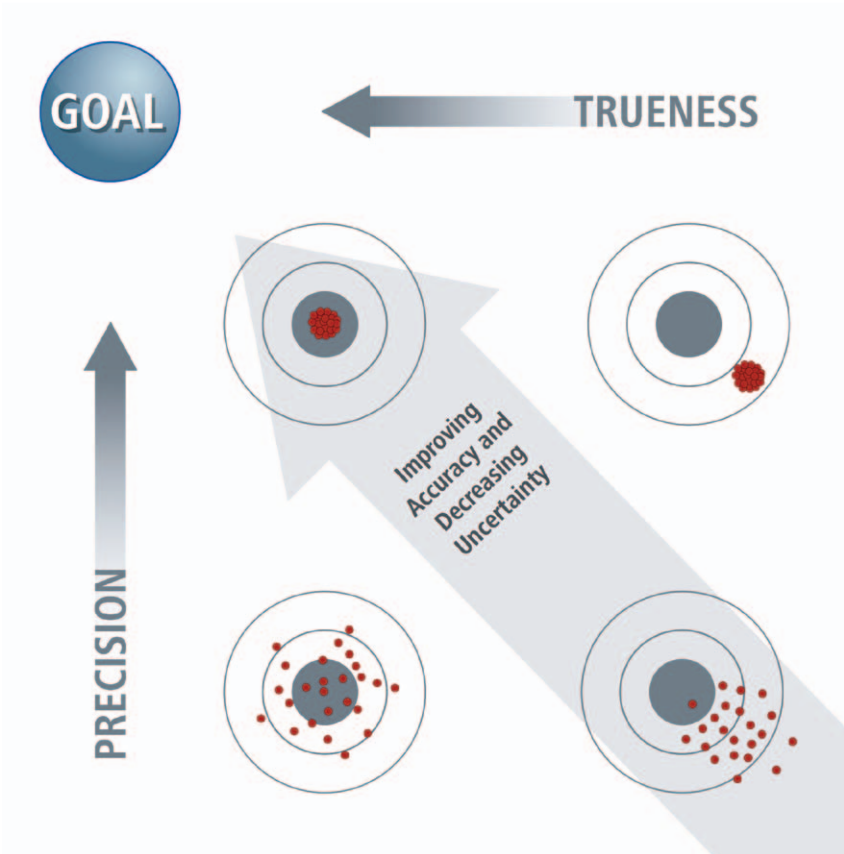

Figure 6. The analyst's goal.

measures, the laboratory is able to minimise errors and so come very close to the “true” value (Figure 5).

Gross and net calorific value

The gross calorific value of the DCC round robin test sample used here is determined in the isoperibol mode. The C5040 Calwin calorimeter software, for example, can be used to calculate the net calorific value in accordance with DIN 51900.
The same applies to many other common calorimeter standards.
The software also enables the results to be directly transferred to Microsoft Excel and correction calculations to be carried out quickly and easily. The report of the results shown in Table 1, provides an overview of all measured, input and calculated parameters. The different states of the coal that can be calculated are also taken into account.

The gross calorific value (Hov) is measured in the calorimeter under constant volume conditions. Using the CALWIN software, the net calorific value (Hu) – which is important in the fuel industry – can both be calculated at constant pressure (which is closer to reality) as the Hup, and also shown as the net calorific value at constant volume (Huv). Both values are used in the international fuel trade. Other values shown below are determined using the relevant analysis equipment (drying cabinet to determine water content, TGA thermogravimetric analysis to determine e.g. ash, volatile matter, sulfur analyser, CHN [carbon, hydrogen, nitrogen] analyser etc.).

Summary

Legal principles and increasing quality requirements mean that analysis laboratories must be able to demonstrate that they have an effective quality management system in place. The aim of each rule of good laboratory practice is to minimise errors (random errors) and bias (systematic errors or asymmetrical errors) and maximise trueness and precision. The sum of trueness and precision gives the accuracy (Figure 6). The basis for obtaining correct measurements is the use of suitable, validated analysis methods, reliable and properly calibrated equipment with a high level of accuracy and regular participation in round robin tests and laboratory comparisons. WC

References

1. For example, DIN 51900, ASTM D 5865, ISO 1928, GB 213, GOST etc.
2. DIN 51900 is the German standard for testing of solid and liquid fuels – determination of gross calorific value by the bomb calorimeter and calculation of net calorific value.
3. ISO/IEC 17025 is the general requirements for the competence of testing and calibration laboratories.