Faster, easier and more accurate emissions calculations

by Lou Janke, delegate to ISO/TC 27, Solid mineral fuels, *and Ken Riley, member of ISO/TC 27/SC 5,* Methods of analysis

International concern with carbon emissions and their impact on climate change has drawn attention to the combustion of fossil fuels, and of coal in particular. Traditionally, the commercial world has been more interested in the energy content of coal and its efficiency in a power station. Consequently, thermal coal has been traded according to its calorific value. With more focus on carbon emissions and their impact on the environment, the market value of specific coals today may well depend on their carbon content.

The least bad choice

To objectively evaluate the impact of carbon dioxide emissions from coal combustion, it is necessary to accurately determine its level of carbon. Although ISO standards [1] are available for the determination of carbon and hydrogen in coal, these gravimetric techniques are time-consuming, labour-intensive and require the skills of the practiced analytical chemist.

The procedures in these ISO standards had their origins (at least in part) in the work conducted by the German chemist, Justus Liebig[2]. Interestingly, Liebig was not very impressed with his own method, which was also used to determine nitrogen, and reputedly stated "Ich glaube nur, dass sie unter den schlechten die am wenigsten schlechte ist" ("I only believe that among bad choices, it is the least bad").

Thus, it is not surprising that, over 150 years later, newer and more rapid instrumental methods are preferred. However, the wide-spread use of these rapid instrumental methods has generated conflicting results and disagreements between laboratories. It was therefore clear to ISO technical committee ISO/TC 27, *Solid mineral fuels*, subcommittee SC 5, *Methods of analysis,* that this move occurred without sufficient effort to conduct controlled testing and assessments, and had not complied with the basic principles of standardization.

Rescued by pedantic unimaginative little judges

In general, the conservative adoption of new methods entails considerable debate. As Primo Levi states in his

1) ISO 625:1996, *Solid mineral fuels – Determination of carbon and hydrogen – Liebig method*, and ISO 609, *Solid mineral fuels – Determination of carbon and hydrogen – High temperature combustion method*.

2) Annalen der Physik und Chemie, 1831, 21, 1-43.

book, *"The Periodic Table"*,[3] the analyst's virtues are "as an incorruptible guardian, a severe, pedantic, unimaginative little judge, a stick poked in the wheels of production." Levi's description is harsh, but does capture the fundamental essence of conservatism in analytical chemistry. This conservationism or carefulness arises from the need to demonstrate that a method or procedure provides the correct results. Moreover, the results must be reproducible from one laboratory to another, anywhere in the world, regardless of the source and location. As a result, ISO/TC 27/SC 5 began work on ISO 29541, *Solid mineral fuels – Determination of total carbon, hydrogen and nitrogen content – Instrumental method*, to determine whether it was possible to achieve this for the new rapid instrumental methods.

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Initially, questionnaires were distributed worldwide to establish the frequency of use, as well as the procedures employed for the calibration of these modern instruments. The results confirmed that different laboratories were using different instruments, calibration procedures and materials for calibration. Some calibrants, including in-house coal samples or certified reference material (CRM) coal – not actually certified for their carbon, hydrogen or nitrogen content – were being used inappropriately.

In addition, data from original papers on the analysis of coal using ISO 609, *Solid mineral fuels – Determination of carbon and hydrogen – High temperature combustion method*, and ISO 625, *Solid mineral fuels – Determination of carbon and hydrogen – Liebig method*, were examined, together with the data from CRM coal certificate documentation and interlaboratory test results for the American Society for Testing and Materials (ASTM) Method D 5373 – an instrumental method for the determination of carbon, hydrogen and nitrogen. This statistical analysis indicated that calibration bias accounted for as much as 50 % of the difference in the results generated by various laboratories.

Eureka !

As a result, ISO/TC 27/SC 5 proceeded with care and attention to detail, to select laboratories from around the world and prepare coals for testing. Detailed instructions for the calibration of instrumental methods were developed to produce a method that would achieve consensus of results, of a level equivalent to ISO 609 and ISO 625. The effort was successfully completed over four years.

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ISO 29541 has now been trialled in 14 laboratories around the world. The statistics from the interlaboratory study demonstrate that the standard will improve the accuracy and reduce the variability of the rapid instrumental methods for the determination of carbon, hydrogen and nitrogen in coal – in the same laboratory and between different laboratories. This method will also provide more reliable calculations of carbon dioxide emissions from coal combustion.

Originally, the methods on which the procedures described in ISO 609, ISO 625 and ISO 333:1996, *Coal – Determination of nitrogen – Semi-micro Kjeldahl method* are based were completed in the 19th century in a number of countries, i.e. by Liebig of Germany, Kjeldahl of Denmark, Dumas of France and Stas of Belgium. Thus, it is fitting that the development of ISO 29541 was also achieved internationally through the participation of ISO member countries.

ISO 29541 is a reminder that good analytical chemistry is required to guarantee accurate data. It can then be used not only in the world of trade, but in the continued evaluation of scientific theories that are relevant to us all. ■

3) First published in Italian in 1975.

About the authors

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Lou Janke is President of Quality Associates International Ltd., Canada. He has been a delegate to ISO/TC 27, and a member of the American Society for Testing and Materials (ASTM) committee D05 on Coal and Coke for over 25 years. He has served as chairman of ASTM committee D05 on Coal and Coke, on the Board of Directors of ASTM, as Convenor of various working groups within ISO/TC 27, and represented Canada at meetings of the United Nations Economic Commission for Europe. He has designed or participated in 40 validation studies for ISO and ASTM coal and coke standards.

A morning's ploughing

Preoccupations with climate change and greenhouse gas emissions dominate today's world agenda. However, already 150 years ago, Justus Liebig was applying his work to calculate carbon uptake in plants. This information can help us estimate the role of plants as carbon sinks – their ability to absorb and temporarily store carbon dioxide. To quote Liebig:

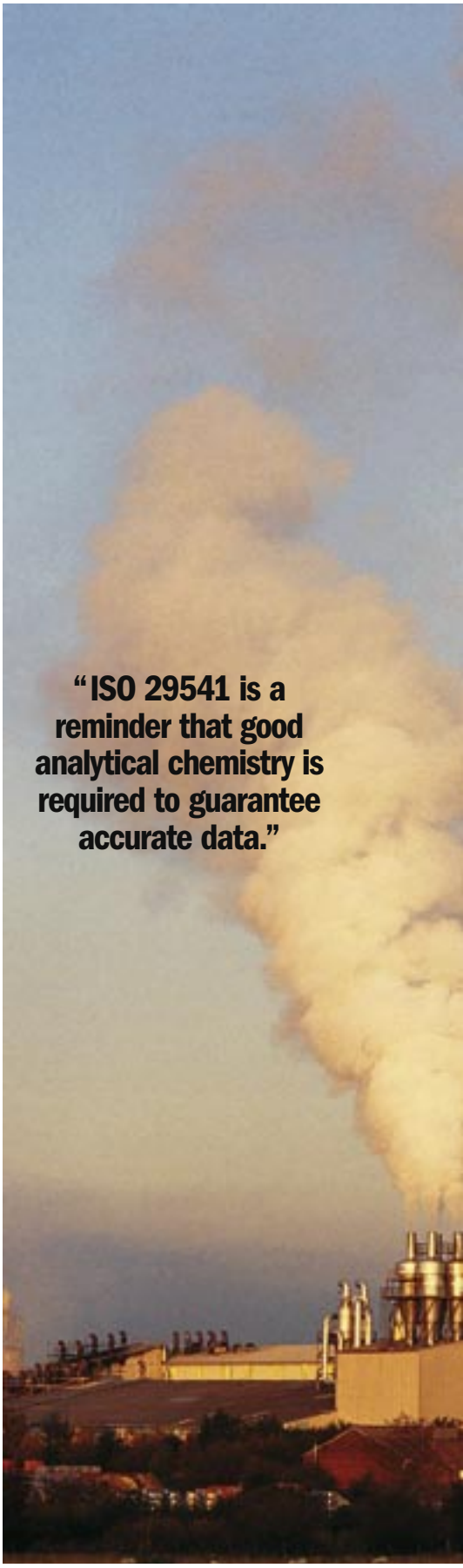
"From a morgen of good meadow land, 2 500 pounds weight of hay, according to the best agriculturists, are obtained on an average. This amount is furnished without any supply of organic substances, without manure containing carbon or nitrogen. By irrigation, and the application of ashes or gypsum, double that amount may be grown.

But assuming 2 500 pounds weight of hay to be the maximum, we may calculate the amount of carbon and nitrogen derived from the atmosphere by the plants of meadows.

According to elementary analysis, hay, dried at a temperature of 100ø Reaumur, contains 45.8 % of carbon and 1.5 % of nitrogen. 14 % of water retained by the hay, dried at common temperatures, is driven off at 100ø. 2 500 pounds weight of hay, therefore, corresponds to 2 150 pounds, dried at 100ø. This shows us, that 984 pounds of carbon, and 32,2 pounds weight of nitrogen, have been obtained in the produce of one morgen of meadow land." [4)]

It is interesting to note that the term "morgen" allegedly derives from the German and Dutch word for "morning". Thus, the area of a morgen is equal to that covered by a morning's ploughing, a measurement that clearly varies from country to country. This example therefore provides another indication of the importance of standardization for analytical chemistry. Just imagine if we still measured a land's area by a morning's ploughing !

4) Temperature in this quote uses the Reaumur scale : 100ø on the Reaumur scale is equivalent to 125°C.
The text is extracted from Letter XV of Liebig's Volume of Chemical Letters written in Giessen, August 1843 (http://www.ul.ie/~childsp/liebig/)



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