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Traceability in Chemical Analysis – What Does that Mean?

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Abstract. Today, many results of chemical analyses show a poor comparability as can be shown by interlaboratory comparisons. This is partly due to the fact that a widely accepted metrological measurement basis is not yet existing for chemical analysis. Also, in many cases the uncertainty of the whole analytical procedure is not known. However, due to increasing globalisation, the mutual recognition and thus the reliability and comparability of measurement results is an important issue. Chemists and metrologist worldwide have been working on a concept to achieve comparable results. The present activities in order to improve comparability of results are described and a concept to achieve traceability to the SI (Système International d'Unités) is presented.

1. The Importance of Chemical Analysis for Life and Economy

The results of chemical analyses are often the basis for important decisions, for instance in trade (conformity to specifications or legal limits), in environmental management (sorting of waste, renovations), in production (process control), in health care (diagnosis, treatment) and in many other fields. It is evident that a reliable data basis is required in order to permit correct decisions to be made. Due to increasing globalisation, the lowering of trade barriers and the associated mutual recognition of test results are becoming vital issues. However, mutual recognition requires confidence in the analyst's competence to produce correct and comparable results.

2. The Current Situation of Comparability of Measurement Results

Every chemist engaged in analytical work knows how difficult it is to guarantee the accuracy of results. There are so many uncertainty factors that cannot be quantified but which affect the results of an analysis. Analysts do their utmost to prevent or correct systematic deviations, but 100% certainty is never possible. We would be in a far better position if we knew at least how far we are from 100% certainty or, in other words, if we know the real uncertainty of our results. Many interlaboratory comparisons have regularly shown how uncertain the results of chemical analyses can be and how poor comparability is. *Fig. 1* shows the poor comparability of chemical results in an inter-laboratory study on ashes from wood combustion which we organised 1998 for Swiss laboratories. Many other inter-laboratory studies reveal a similar result. How can this situation be improved with justifiable expenses? In the past, organisations such as the WTO (World Trade Organisation), ISO (International Organisation for Standardisation), BIPM (Bureau International des Poids et Mesures), Eurachem, EUROMET, CITAC (Co-Operation on International Traceability in Analytical Chemistry) and others have started to draw up concepts with the aim of promoting the mutual recognition of test results and thus simplifying international trade. If comparability of the results of chemical analysis can be proven, repetitions of measurements can be avoided and savings in time and staff resources are achieved.

3. What is the Problem in Chemical Analysis?

Modern chemical analysis is carried out using instruments which are quick, automatic, highly sensitive and mostly specific for a particular substance. However, the measurement is often carried out in a 'black box' in which a number of processes run which are neither fully under control, nor fully understood (like absorption phenomena in a hot flame). In addition, the whole analytical procedure has a relatively high level of uncertainty caused by the large number of steps in the procedure, unexpected interactions and poor stability of many substances. Furthermore, most analytical procedures are relative measurements which require reference materials to which the measurement results can be traced. But unfortunately, in many cases the specified amount of a reference substance has not correctly been determined. All of these factors have a decisive impact on the overall uncertainty. Many of them cause systematic deviations which are not easy to detect. Therefore, the uncertainty of a complete analytical procedure is mostly unknown. However, without knowledge of the real uncertainty, no result is comparable to a result from another laboratory.

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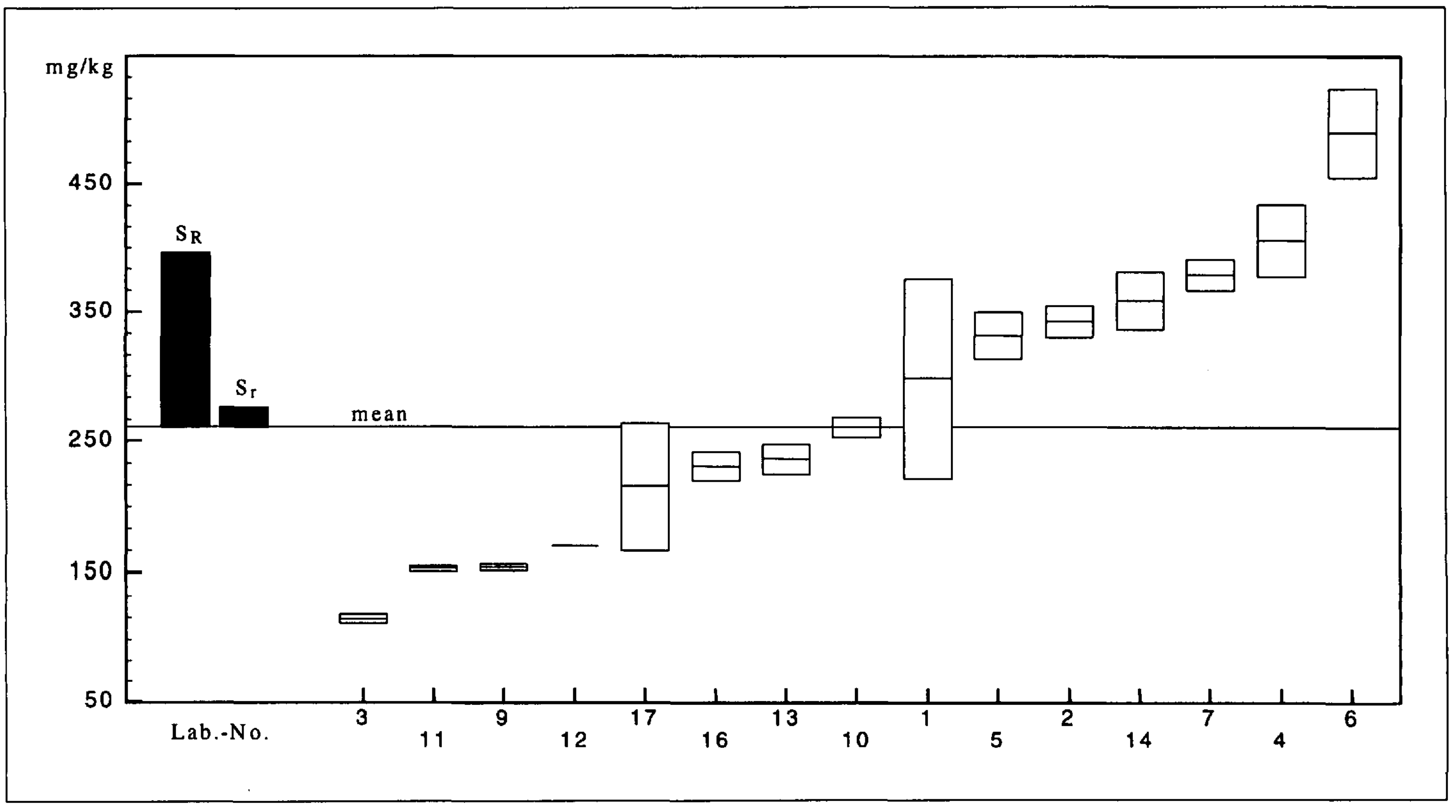

Fig. 1. *Determination of chromium in a cyclon ash from wood combustion in an intercomparison.* Ten elements were analysed in three samples (wood, bottom ash and cyclon ash) by 15 laboratories. The overall homogeneity of the distributed cyclon-ash samples was found to be better than 5% rel. For chromium in cyclon ash, the obtained relative reproducibility (rel. s_R) was 52%, the relative repeatability (rel. s_r) was 6%.

4. Metrology – the Science of Measurement

In the field of physical measurements for length, mass, time, current strength, temperature and light intensity, an internationally accepted metrology system has been built up based on the International Meter Convention of 1875. By this system, measurement data are traced to a common measurement basis and thus to the SI. By applying this system, the correctness of results can be easily verified and an overall comparability is achieved. Chemical analysis, which is the measurement of the amount of substance, was not taken into account for a long time. Only since 1971 the mole has been defined and included into the SI as the unit of the amount of substance. However, the metrological system for the physical units cannot be directly used in the field of chemistry. Neither a defined basic substance with unchangeable characteristics, nor a single basic measurement principle applicable for any kind of analysis exists which could form the end of a traceability chain. The SI traceable measurement of the amount of substance demands a more complex solution due to the large number of substances and their possible combinations. Since the end of the 80s, chemists and metrologists world-wide have been working on a concept for the traceability of the measurement of the amount of substance, but even today a clear measurement basis is not yet existing. In particular, the practical application of available concepts has yet to be implemented. Easy-to-use tools are urgently required. EMPA St. Gallen is about to establish a measurement basis for a part of chemical analysis in close co-operation with OFMET (Swiss Federal Office of Metrology in Wabern) and other metrological institutes all over the world.

5. Concept and Tools for Implementing Traceability to the SI

The set-up of a metrological basis is the major task of a metrological institute. This implies the development and application of directly SI-traceable measurement techniques and principles (so-called primary methods of measurement and primary materials). Also, a metrological institute has to provide a practical link to the SI which can be used by a service laboratory in order to achieve traceability of its results. A most practicable link is the reference material which is used for calibration of the measurement instrument. This material can be regarded as a carrier of the SI-traceable value or, in other words, as a transfer standard. However, it is strictly required that this reference material itself is traceable as far as possible to the SI employing all the knowledge and technology available. This shall be the case for reference materials which are seriously produced and certified according to ISO Guides 30 to 35 [1–5]. The other important aspect is the knowledge of the whole analytical procedure. Of course, the laboratory must know the total uncertainty. A certified matrix reference material can help to validate the procedure. It also gives some indications for the uncertainty. A possible path to achieve traceability is shown in *Fig. 2*.

5.1. *Primary Methods and Primary Materials*

By definition, primary methods are described fully mathematically and their uncertainty can be completely calculated. This means that a quantitatively functional link between the measurement signal and the amount of substance or its concentration is known in all details without the use of empirical factors. Empirical corrections of systematic deviations are not permitted. From the current situation, the following methods are identified by the CCQM (Comité Consultatif de Quantité de Matière) to have the potential to be 'primary' in a metrological sense: gravimetry, ti-

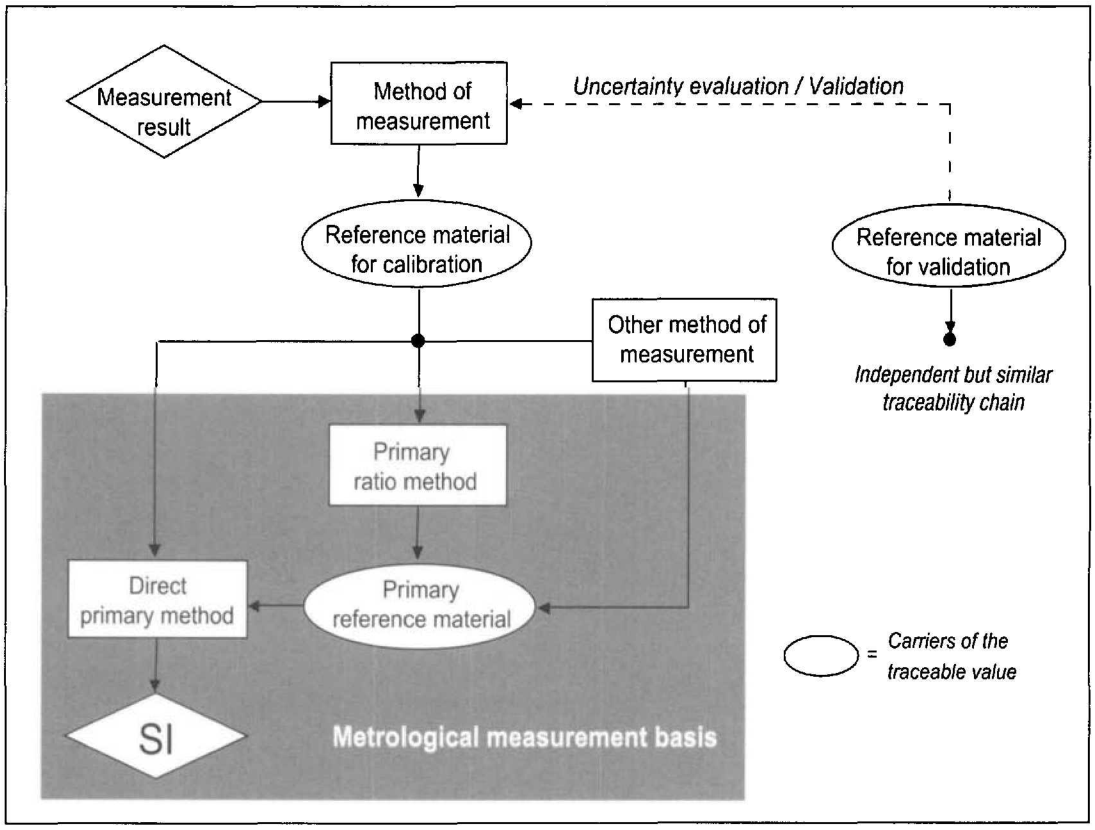

Fig. 2. *General path to achieve traceability for an analytical measurement.* The traceable value is transferred to the laboratory performing the analysis by the different types of reference materials which have to be linked to the SI by means of primary methods of measurement.

trimetry, coulometry, isotopic dilution mass spectrometry (IDMS) and some colligative methods. 'Potential' in this sense means that these methods can only be designated as primary when all criteria mentioned above are fulfilled. It is obvious that this involves enormous costs and can hardly be implemented within given standard laboratory routines. Therefore, it is a main task of metrological institutes to operate these methods in a primary sense and to develop, produce and provide primary materials as part of a measurement basis in order to create the ultimative link to the SI.

5.2. *Reference Material*

Reference materials for the calibration of instruments are an important link in the traceability chain as the measured value of the sample is directly calculated from the concentration of the analyte in the calibration solution. But there is no doubt that also so-called matrix reference materials are a decisive factor in chemical analysis when they are used for the validation of complex analysis processes. Currently, many different reference materials are available on the market. Unfortunately, in many cases their declared contents have a level of uncertainty which is either falsely declared or not declared at all. It is important that there are reference materials available whose content, purity and level of uncertainty are correctly determined and fully documented in a certificate as specified in ISO regulations [1–5].

5.3. *Determining Measurement Uncertainty*

According to the new ISO regulations [8], measurement uncertainty is an integral part of a test result. The result is no longer considered to be a single value and its error is no longer regarded as the difference between this value and the true value. The result is rather considered to be a range consisting of a value and its uncertainty. In order to promote the implementation of these regulations, Eurachem has published a guide which shows how a complete uncertainty budget can be calculated for an analytical process [9]. Nevertheless, experience has shown that the implementation of this ISO regulation remains difficult and time-consuming. The tools must be made even more transparent and user-friendly. Therefore, EMPA has initiated the development of a software system consisting of the program and an extensive database which shall allow a quick evaluation of the measurement uncertainty (Eureka project E! 1910 MUSAC).

5.4. *Inter-Laboratory Comparisons*

Although traceability of results cannot be achieved by inter-laboratory comparisons, *e.g.*, proficiency tests, they are a suitable means for evaluating comparability. But even then, such comparisons are only useful when they are seriously organised and evaluated. ISO and EA (European Co-operation for Accreditation of Laboratories, formerly WELAC) have drawn up guidelines for this purpose [6][7]. For instance, the aim of an inter-laboratory comparison must be clear from the beginning and the requirements must be specified. The test samples must be homogeneous, sufficiently stable and, if possible, traceable to the SI. It is absolutely vital that inter-laboratory comparisons are properly co-ordinated in order to achieve mutual acceptance and thus permitting a laboratory's outlay to be optimised.

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