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Accuracy and Traceability Concepts Applied to Environmental Speciation Analysis

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Traceability issues are of increasing concern in all fields where chemical measurements form the basis for decisions. The concepts of accuracy and traceability as applied to environmental analysis, however, are still prone to misunderstandings. Some years ago, Horwitz stated that "considerable evidence exists in the literature that few analytical chemists pay attention to the question of the reliability of the analytical results they produce. These chemists believe that a natural law exists in measurement science and that, if the directions for conducting a measurement are followed, the true value necessarily results" [1]. This corresponds to the long-term debate about precision or reproducibility over accuracy [2], which is now relayed by on-going discussions on accuracy and traceability: While accuracy refers to the closeness of analytical values to 'true values' (trueness) and among various repetitions (precision), the term traceability implies a link of data obtained to established references through an unbroken chain of comparisons all with stated uncertainties. Recent controversial discussions have illustrated the misunderstanding, which may occur among the analytical community with respect to accuracy and traceability issues in the area of speciation analysis, with possible consequences on environmental data interpretation.

Speciation analysis is not anymore a new feature. The IUPAC defines this term as 'the analytical activity of identifying and measuring the quantity of one or more individual chemical species in a sample' [3]. The speciation of an element is defined as 'the distribution of defined chemical species of an element in a system' [3]. Chemical species of some elements (e.g. organotin, organic mercury) are now included in the list of substances to be determined in the frame of international environmental programmes, requiring an increasing knowledge and care with respect to quality control (including traceability issues) at all monitoring steps (from sampling to reporting data) [4].

Analytical techniques used for the determination of chemical species are generally based on a succession of steps (e.g. extraction, derivatisation, separation, detection) which are all prone to various sources of systematic errors. Within the last decade, international collaborative efforts (through interlaboratory studies and the certification of reference materials) have enabled one to systematically study hyphen-

ated techniques used for the determination of chemical species of, for example, arsenic, chromium, mercury, lead, tin and selenium in environmental matrices (water, fish or mussel tissues, sediments) [5-7]. The determination of operationally-defined element fractions (extractable forms of trace elements) in sediment and soil matrices has also been collaboratively studied, mainly to harmonise and standardise extraction schemes in order to improve the comparability of data (stressing that, strictly speaking, this type of determination should not be covered by the term 'speciation') [8]. In this context, all these collaborative efforts have been understood as being directed towards a strive for accuracy (trueness and precision). It has been recognised recently that the achievements actually enabled mostly to establish reference points (e.g. certified values in reference materials) which does not necessarily correspond to 'true values' but rather offers a mean for laboratories to compare their data internationally and, hence, achieve traceability. This ambiguity still generates confusion and misunderstandings among the scientific community. This communication discusses this issue, focusing on analytical measurements only. Extending discussions on general traceability issues would imply an examination of steps prior to laboratory work (sampling, storage, etc.) which is beyond the scope of this contribution.

References

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