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CONFERENCE CONTRIBUTION

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Reference materials for long-term environmental programs

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Abstract The application of reference materials (RMs) for quality control in analytical chemistry within long-term environmental monitoring and banking programs is described. The profitable use of different levels of RMs, in particular the introduction of problem-designed internal control materials and internal reference materials at the German Environmental Specimen Bank is demonstrated. Moreover, further demands from biosphere-oriented programs for future developments of certified reference materials (CRMs) are discussed.

Introduction

After years of expansion in environmental related monitoring activities, the aspect of scientific quality seems to attract more attention in corresponding programs. This is of particular importance in the field of environmental analysis because the production of huge amounts of data for many years did not contribute enough to the creation of systematic, scientifically sound information about the state of our environment and the processes occurring therein. Moreover, the public concern about environmental issues demands reliable data for the preparation of political decisions with social and economic consequences.

At present environmental analysis is often only directed to the monitoring of abiotic matrices such as air, water, soil and sediment. But the biosphere offering many pathways of pollution transfer to mankind is attracting now more interest. Therefore, biomonitoring programs require chemical analyses of a broad range of plant or animal materials. Several tendencies can be identified at present: The number of chemical compounds of environmental concern, showing already at low concentrations besides carcinogenic or toxic activity phenomena such as allergic reactions or endocrinic effects, is increasing. Therefore, analytical activities have to be more directed to characterize patterns of substances in complex environmental samples rather than analyzing single compounds of interest. Environmental pollution is now widely accepted as a global problem with the consequence that observation programs have to take into account not only local, but also regional and international scales at a comparable high level of quality. At the same time monitoring is extended from heavily polluted sites and anthropogenic emission sources to other regions even including background areas which are important for data assessment. Processes within the environment are occurring at very different time scales and many of them should not only be controlled temporarily but rather permanently.

Long-term environmental monitoring programs have to be based on particularly high levels of analytical quality. Otherwise, comparison of data between different areas, identification of temporal trends and prediction of future developments become ridiculous. A modern approach of environmental observation includes environmental specimen banking (ESB), which is performed in several countries as a combination of environmental monitoring and documentation by means of representative samples in their original chemical composition at low temperatures [1]. One of the most advanced ESB programs is performed in Germany where representative environmental specimens from marine, limnic and terrestrial ecosystems throughout Germany are systematically sampled, homogenized, freshly stored and partially characterized since 1985. Details of these ESB procedures and conditions were reported elsewhere [2–4]. This paper is focussed on experiences to develop and use reference materials (RMs) for the environmental analysis within such a long-term environmental program.

ESB experiences with CRMs

The development of new analytical procedures as well as the permanent performance of internal quality control are requiring appropriate well-characterized reference materi-

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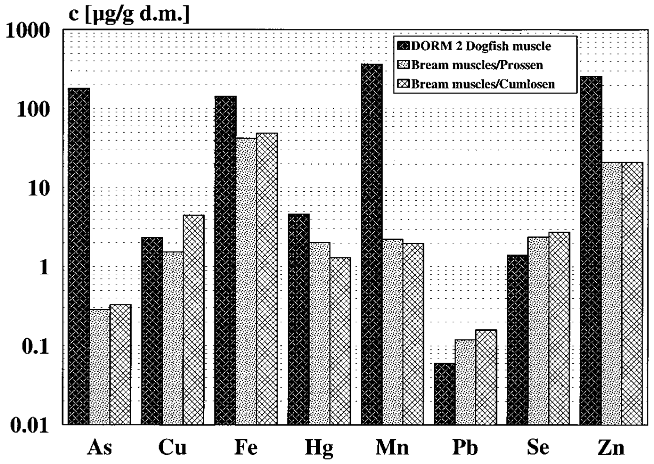

Fig. 1 Comparison of element concentrations (related to dry mass) in the CRM DORM 2 and matrix related ESB samples from the River Elbe

als. Therefore, the laboratories of the German ESB are using corresponding commercially available certified reference materials (CRMs). It turned out, however, that necessary boundary conditions for the selection of appropriate biological RMs for quality control of day-to-day analysis such as matrix comparable biological specimens and organs as well as comparable concentration patterns are seldom fulfilled by certified reference materials (CRM). This is demonstrated in Fig. 1 by the comparison of partial element patterns of a CRM “Fish Tissue” and two ESB materials representing fish muscles from the River Elbe. Turning from the analysis of a CRM to the characterization of ESB samples creates often additional analytical problems during various steps of the analytical procedure. Alterations in procedures for sample preparation (extraction, digestion, etc.) and instrumental determination of analyte concentrations can be necessary. This can arise from the ESB use of non-sieved powders with different particle size distribution in comparison to CRMs, different concentration ratios of interfering substances in ESB samples and for less stable compounds even from chemical transformations during processes normally applied by CRM producers such as freeze-drying [5].

A comparison of current CRMs [6] and the range of ESB matrices (Table 1) shows that from the point of view of matrix matching with ESB specimens only various sediments, mussel tissues, tree needles or leaves and fish tissues are presently available. Environmental observation programs directed also to other specimens should stimulate the production of new reference materials. On the other hand, the experience of ESB laboratories from the large sample throughput of real environmental samples contributes significantly to their qualified participation in certification campaigns. The need for own RMs within ESB programs is obvious because no CRM producer can cover the range of environmental matrices from differently polluted ecosystems necessary for quality control in ESB analysis.

ESB reference materials

For the purpose of high analytical quality and economic efficiency three groups of materials for internal quality control are used within the ESB program at the Research Center of Jülich (Table 2). So-called internal control materials (ICM) are produced simply by mixing of surplus material from subsamples which have to be analyzed regularly. That means, an ICM can be composed of identical matrices from various locations or sampling campaigns. ICM samples are often already in the freeze-dried state. They are only used for measuring the repeatability of a specific, routinely applied analytical procedure over an extended period of time. Moreover, ICMs represent useful and relatively inexpensive test materials for the initial stage of analytical developments.

The next level is called internal reference materials (IRMs). These are natural matrices, comparable to the ESB specimens and collected once in large amounts (about 5–50 kg) in selected ecosystems of the long-term environmental observation program. IRMs are processed in the same manner as the ESB samples, that means in an uninterrupted cryo-chain at liquid nitrogen temperature [3, 7]. The resulting homogenized, fresh powder material is used for many years as matrix identical IRM for the purpose of developing new analytical procedures, for optimizing existing procedures, for controlling the quality of the digestion step during total element determinations and for stability checks (see below). Therefore, IRMs are characterized internally with respect to their particle size distribution after grinding [7], the homogeneity of selected elemental distributions at the milligram level [8] and the concentrations of as many analytes as possible (see e.g. [9]). The determination of elements in such IRMs is performed with different independent analytical procedures for assuring the trueness of the results. Examples for such intermethod comparisons are shown in Fig. 2, where optical (AAS with electrothermal atomization: ET-

Table 1 Environmental matrices of the German ESB

Terrestrial Ecosystems	Limnic Ecosystems	Marine Ecosystems
Spruce/pine shoots	Bream (muscles, liver)	Bladderwrack
Poplar/beech leaves	Zebra mussels (tissue)	Common mussels (tissue)
Pigeon eggs	Sediments	Eelpout (muscles, liver)
Earthworms		Herring gull eggs
Deer livers		
Soils		

Table 2 Classification of materials for quality control used within the ESB analysis

Term	Examples
Internal control material (ICM)	Bream liver
	Bream muscles
	Pigeon eggs
	Pine shoots
	Beech leaves
	Eelpout muscles
Internal reference material (IRM)	Spruce shoots
	Poplar leaves
	Common mussel tissue
	Herring gull eggs
	Bladderwrack
Certified reference material (CRM)	BCR Mussel tissue
	BCR Tuna fish
	NIES Sargasso
	NIST Pine needles
	NIST Citrus leaves
	NIST Oyster tissue
	NIST Mussel tissue
	NRCC Dogfish liver

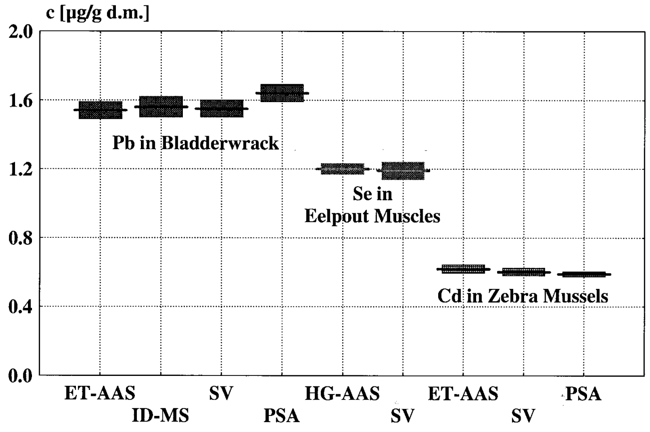

Fig. 2 Intermethodic comparison for element determinations in ESB samples; mean concentrations and standard deviations, from 24 (36 for ID-MS) repetitions, related to dry mass (ET-AAS: electrothermal AAS with graphite furnace, ID-MS: isotope dilution MS with thermal ionization, SV: stripping voltammetry, PSA: potentiometric stripping analysis, HG-AAS: hydride generation AAS)

AAS; hydride generation AAS: HG-AAS), mass spectrometric (isotope dilution MS with thermal ionization: ID-MS) and electrochemical (stripping voltammetry: SV; potentiometric stripping analysis: PSA) principles were applied in parallel for the determination of Pb, Se and Cd, respectively, in ESB matrices. In addition, interlaboratory comparisons are organized for the external control of analyte concentrations in such IRMs [10].

Despite the in-house production and use of ICMs and IRMs certified reference materials (CRMs) are indispensible for long-term environmental programs of sufficient analytical reliability. They are used at longer intervals for controlling routinely applied procedures, but also for the final training step of new analytical personnel and performance tests of new instruments introduced into the program. Analytical developments are checked with the analysis of well-known CRMs and these materials are always included in intermethod and interlaboratory comparisons organized by the ESB. For certain analytical approaches such as the determination of elements in soils and sediments by X-ray fluorescence, CRMs are needed for calibration purposes.

An important prerequisite for the long-term use of reference materials consists in their chemical stability. This is of particular significance for natural, non-manipulated environmental material of biological origin. Until now, only freeze-dried CRMs are investigated during the certification process for the stability of a few selected substances under certain conditions (see e.g. [11]). Recently, a comparison between methylmercury concentrations in freshly stored mussel tissue and freeze-dried material from the same homogenized batch, both stored at –80° C for years, did not show significant differences for this analyte [12]. But it is important to consider a fundamental problem of long-term stability checks of reference materials: There are two possibilities of changes over time, firstly a variation of the chemical composition of the material and secondly differences – hopefully only improvements – in the analytical performance over many years can happen. It is difficult to separate both influences, if concentration changes in stored materials are detected after long times. Therefore, it is recommended to characterize concentration patterns of the RM rather than only a few constituents. If analytes with different physicochemical properties (volatility, degradation kinetics, etc.) are properly selected, repetitive identical patterns after long time of storage point to chemically stable material. Naturally, it is extremely important to perform the initial RM characterization under a strict quality control regime. This includes (in the case of IRM analysis within the ESB) statistically sound checks of repeatability and reproducibility, intermethod comparisons and, if possible, also the application of analytical methods with a high degree of traceability, such as isotope dilution MS [13]. From the point of view of long-term stability it is advantageous that the IRMs are stored at the Research Center of Jülich under the same conditions as the ecological ESB material, i.e. as fresh material at liquid nitrogen temperature. Therefore, future comparative investigations are possible.

Future demands

Modern environmental analysis has to contribute to the effect-oriented investigation of analytes in samples from different ecosystems. The current transition from determinations of total metal concentrations to “forms of elements” (defined operationally by the use of extraction schemes) [14] or better to “chemical species” (e.g. organometallic compounds, metals with different oxidation states, metal complexes) represents a major step forward. But it implies also significant challenges for analytical chemistry and an increasing demand for appropriate reference materials. At present there are only a few environmental reference materials available with certified contents of metal species such as methylmercury or organotin compounds [15]. In general, broader spectra of certified analytes in environmental matrices are necessary including less stable compounds of ecological and toxicological concern such as organometallic compounds of Pb or Sb, complexes of Al or Cu, and different oxidation states of metals/metaloids such as Cr or As. This can only be realized by different preparation processes for reference materials in comparison to the presently applied techniques. Certainly, demands from users and legislation has to stimulate this development.

Moreover, environmental analysis needs more reference materials of biological origin at different trophic levels because studies of distribution and fate of anthropogenic pollutants within the environment will be focussed in the next years to a larger extent on the investigation of food webs. Corresponding analytical developments and quality control have to be based on materials with natural concentration levels and chemical patterns (including RMs from environmental background areas) and not on artificially spiked materials. This is of particular importance for analytical methods which have limited selectivity for analytes of environmental concern and/or which are sensitive to so-called matrix effects, that means to interferences from non-target constituents of the real sample. Moreover, different recoveries can be obtained with spiked RMs as a result of analytical procedures which include separation steps such as extraction because of the non-naturally bound analytes.

The increasing application of reference materials for calibration purposes (for techniques such as XRF) and the rigorous validation of complete analytical procedures are asking for CRMs of systematically varying composition with precisely known concentration values. From our point of view the analytical quality parameter “precision” should be improved for most of the data on environmental CRMs available at present. Hence, also the aspect of material homogeneity related to analytically relevant sample weight-in will also play an important role in the future [16].

Overall long-term experiences from permanent environmental observation and ESB programs can contribute to the detection of shortcomings, future needs and necessary developments in the field of environmental reference materials.

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