Anal Bioanal Chem (2006) 386: 1121–1136
DOI 10.1007/s00216-006-0660-6

REVIEW

Franz Ulberth

Certified reference materials for inorganic and organic contaminants in environmental matrices

Received: 9 June 2006 / Revised: 27 June 2006 / Accepted: 28 June 2006 / Published online: 5 September 2006

Abstract Chemical measurements often constitute the basis for informed decision-making at different levels in society; sound decision-making is possible only if the quality of the data used is uncompromised. To guarantee the reliability and comparability of analytical data an intricate system of quality-assurance measures has to be put into effect in a laboratory. Reference materials and, in particular, certified reference materials (CRMs) are essential for achieving traceability and comparability of measurement results between laboratories and over time. As in any other domain of analytical chemistry, techniques used to monitor the levels and fate of contaminants in the environment must be calibrated using appropriate calibration materials, and the methods must be properly validated using fit-for-purpose matrix-matched CRMs, to ensure confidence in the data produced. A sufficiently large number of matrix CRMs are available for analysis of most elements, and the group of chemicals known as persistent organic pollutants, in environmental compartments and biota. The wide variety of analyte/level/matrix/matrix property combinations available from several suppliers enables analysts to select CRMs which sufficiently match the properties of the samples they analyse routinely. Materials value-assigned for the so-called emerging pollutants are scarce at the moment, though an objective of current development programmes of CRM suppliers is to overcome this problem.

Keywords Certified reference materials · CRM · Environmental chemistry · Quality assurance · Quality control · Uncertainty · Traceability

F. Ulberth (✉)
European Commission, DG Joint Research Centre,
Institute for Reference Materials and Measurements,
Retieseweg 111,
2440 Geel, Belgium
e-mail: franz.ulberth@ec.europa.eu

Introduction

International and national programmes require the monitoring of levels of contamination in environmental compartments to preserve the natural habitat we live in and to support life and the functioning of society now and in the future. The European Union adopted a comprehensive system of control to protect the environment from pollution and to improve the quality of Europe's nature as a whole. Under this system monitoring requirements and quality objectives are stipulated, obliging Member States to monitor and assess the quality of air, water, soil, etc., and to identify and reverse trends in environmental pollution. The data produced by monitoring programmes constitute the foundations for decision making. Because such decisions might drastically affect individuals, communities, enterprises, or society as a whole in different ways, the quality of such data must be ensured by subjecting the measurement systems used to vigorous quality-assurance and quality control (QA/QC) procedures. Such procedures must ensure that the analytical techniques used in monitoring programmes remain temporally and spatially stable. An integrated and internationally accepted set of measures, which must be deployed as a concerted effort, has been developed over the years for QA/QC of analytical data. ISO/IEC 17025 [1] describes, in essence, the requirements necessary for setting up and operating such a system. Factors contributing to the reliability and comparability of measurement results are summarised in Fig. 1. Reference materials (RMs) and, in particular, certified reference materials (CRMs) play a key role in this ensemble of tools for ensuring confidence in measurement data.

This article will review basic concepts of matrix-matched CRMs, their production, selection, and use, with special emphasis on environmental measurements. The topic has been much more thoroughly treated in other monographs [4–7] and in more specialised review articles [7–13]. Pure elements and compounds, elements and compounds in solution, and gases and gas mixtures, although the basis of instrumental analysis via calibration, are deemed beyond the scope of this review.

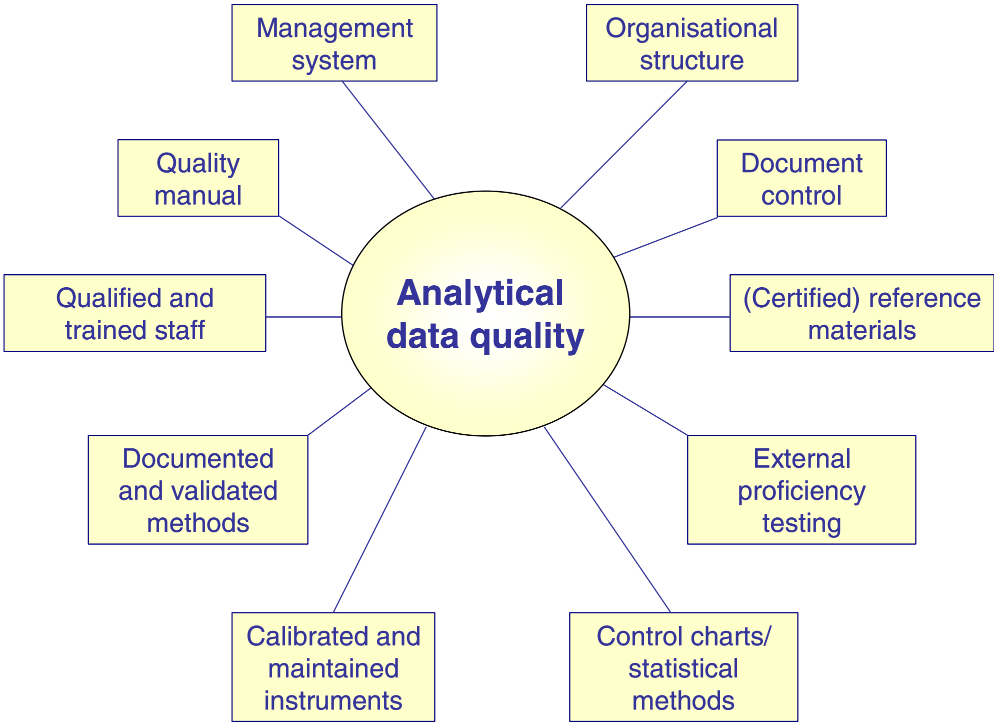

Fig. 1 Aspects of quality-control or quality-assurance systems for testing laboratories

Reference material-formal definitions

A variety of terms have been used in the literature to describe the nature of these materials: reference materials, certified reference materials, reference standards, quality-control materials, etc. Correct usage, and common misconceptions in the terminology of RMs, have recently been critically discussed [14].

The current version of the International Vocabulary of Basic and General Terms in Metrology (VIM) [15] defines RM as:

Material or substance one or more of whose property values are sufficiently homogenous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, and for assigning values to materials and CRMs as:

Reference material, accompanied by a certificate, which has one or more properties whose value is certified by a procedure that establishes traceability to the accurate realisation of the unit in which the values of the properties are expressed, and for which each certified value is accompanied by a stated uncertainty with a given level of confidence.

Thus, the three distinctive main features of CRMs are:

- certified property value
- uncertainty statement
- traceability statement

The VIM is currently under revision; in the meantime ISO REMCO (the Committee on Reference Materials of the International Organization for Standardization) has suggested modification of these definitions to make them more meaningful for end-users and to avoid confusion about the underlying concepts [16]. One objective of these modifications is to make it clear that the term “reference material” is generic and should be understood as sort of a “family name”, and that this family comprises CRMs and non-certified RMs. The most notable clarifications relate to the nature of the certified property, which could be quantitative or qualitative (e.g. identity of substance or species), and to normative references related to RM preparation and certification (e.g. ISO Guides 34 and 35). Another salient feature of the ISO REMCO definitions is the specific reference to the homogeneity and stability of (C)RMs.

Types of certified reference material

CRMs are a key element of analytical data quality assurance and are used for four main purposes:

- instrument calibration;
- method validation, in particular for assessment of the trueness of a method;
- ensuring the traceability of measurement results; and
- statistical quality control (charting).

Other main uses include verification of the performance of a measurement instrument and training and/or qualification of operators.

Pure substances certified for their purity and stoichiometry, or pure substances dissolved in a suitable solvent, are pivotal, because in many instances they are the anchor point for building up a metrological traceability chain. They are used for calibration of a measurement instrument and this traceable calibration is a principal component in achieving traceability in chemistry. Some analytical techniques (X-ray fluorescence, spark-source emission spectrometry, solid-sampling atomic-absorption spectrometry, etc.) cannot be calibrated by use of pure substances or solutions, because it is essential the analytes of interest are contained in a matrix as similar as possible to the real samples.

Traceability is a relatively new concept in analytical chemistry and requires analytical chemists to link measurement results to stated references through an unbroken chain of comparisons, all having stated uncertainties. CRMs are such stated references with known uncertainties; linking measurement results to CRMs, or to the quantity values embodied in the CRMs [17], ties them to a reference, and if the CRMs themselves are traceable, e.g. to the International System of Units (SI), the measurement results obtained would be traceable to the same reference system.

Because chemical measurement processes for real-world materials include several sample pretreatment steps before the actual measurement, certified matrix materials are necessary for assessing the validity of the whole analytical process. In particular, a matrix CRM will enable straightforward assessment of the trueness of the applied method; if no suitable CRM is available this pivotal characteristic can only be approximated by using alternative approaches, for example spiking and recovery experiments. Matrix CRMs should be similar in composition (level of analyte, matrix type, interferences), format (liquid, semi-solid, solid), and physical processing history (fresh, frozen, sterilised, dried) to the samples regularly analysed.

Matrix CRMs are by far the QA/QC tools most often requested by practitioners. Certified calibration materials (pure substances and solutions) are regarded as less important, presumably because they can be obtained as non-certified chemicals with relative ease from specialised supply houses. Because of the prominent role of certified calibration materials in establishing traceability through calibration, however, the awareness of analysts should be directed toward use of these materials and the benefit gained when they are properly applied.

Preparation and value assignment of certified reference materials

Because preparing and value-assigning a reference material is a sophisticated and resource-intensive process in terms of knowledge, equipment, and man power, a rather limited number of institutions, either public or private, offer such services. A non-exhaustive list of producers and/or distributors of (C)RMs is given in Table 1; this compilation is intended to inform the reader and not to order the quality of the services offered. A very informative tool is the COMAR data base (http://www.comar.bam.de), which is free of charge and lists thousands of CRMs produced world-wide by approximately 200 producers in 27 countries. Another specialised web-site dealing with different aspects of CRMs, including a searchable catalogue, can be found at http://www.virm.org.

Preparation of CRMs requires the certifying body to implement a highly integrated process-planning and quality-assurance scheme to realise the physical production and value assignment of CRMs (Fig. 2). To make the whole process transparent and to inform producers and users of CRMs about organisational and metrological requirements of CRM preparation and value-assignment, ISO has issued several guidelines, in particular ISO Guides 34 [18] and 35 [19]. Third-party accreditation of CRM production on the

Table 1 Producers and distributors of (certified) reference materials for environmental studies

Producer/certifying organisation	Country	Web site
Czech Metrological Institute (CMI)	Czech Republic	http://www.cmi.cz/
Federal Institute for Materials Research and Testing (BAM)	Germany	http://www.bam.de
Institute for Reference Materials and Measurements (IRMM)	EU	http://www.irmm.jrc.be
International Atomic Energy Agency (IAEA)	International	http://www-naweb.iaea.org/nahu/nmrm/nmrm2003/descript.htm
Korea Research Institute of Standards and Science (KRISS)	Korea	http://www.kriss.re.kr/
LGC Ltd	UK	http://www.lgc.co.uk/
National Center of Metrology (CENAM)	Mexico	http://www.cenam.mx/
National Institute for Standards and Technology (NIST)	USA	http://www.nist.gov/
National Institute for Environmental Studiesn (NIES)	Japan	http://www.nies.go.jp/
National Measurement Institute Australia (NMIA)	Australia	http://www.measurement.gov.au/
National Metrology Institute of Japan (NMIJ)	Japan	http://www.nmij.jp/
National Research Centre for Certified Reference Materials (NRCCRM)	PR China	http://www.nrccrm.org.cn/
National Research Council of Canada, Institute for National Measurement Standards (NRC-INMS)	Canada	http://www.inms-ienm.nrc-cnrc.gc.ca/
National Water Research Institute	Canada	http://www.nwri.ca/nlet/crm-e.html
Distributors of CRMs		
LGC Promochem	UK	http://www.lgcpromochem.com/
RTC	USA	http://www.rt-corp.com/
Sigma-Aldrich	USA	http://www.sigmaaldrich.com/

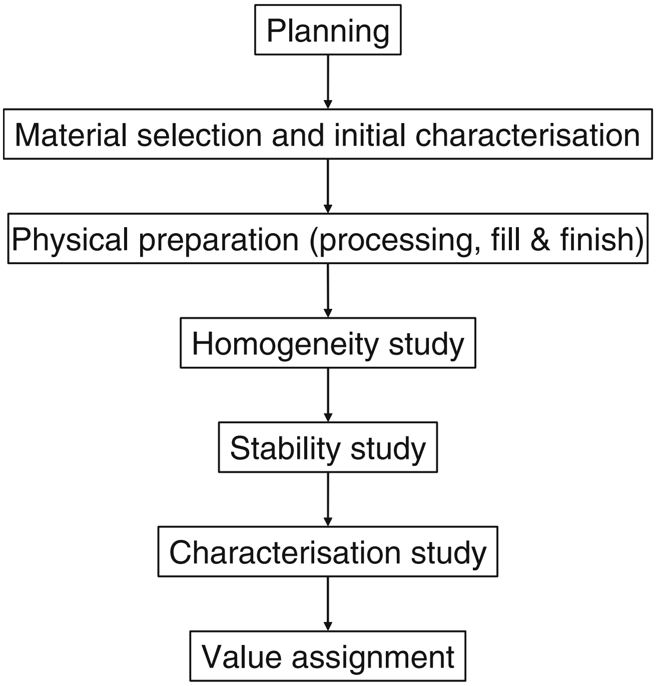

Fig. 2 ISO Guide 34-compliant preparation and value-assignment scheme (simplified) for CRMs

basis of the combined application of ISO Guide 34 and ISO/IEC 17025 is currently seen by many CRM producers as the best means of demonstrating competence and of complying with the stringent CRM quality requirements expressed by ISO/IEC17025-accredited calibration and testing laboratories.

From the principal layout of a certification procedure as given in Fig. 2 it follows that the three main contributors to the uncertainty of the certified value, i.e. the homogeneity and the stability of the material and the measurements leading to characterisation of the property value, must be taken into account when stating the expanded uncertainty (U) of the certified property value in a way compliant with the Guide to the Expression of Uncertainty in Measurements (GUM) and ISO Guide 35 [19]:

$$U = k \times \sqrt{u_{\mathrm{homo}} + u_{\mathrm{stab}} + u_{\mathrm{char}}}$$

where U is the expanded uncertainty, k the coverage factor (usually set to k=2, which approximates a 95% confidence level), u_{homo} the uncertainty due to the inhomogeneity of the material, u_{stab} the uncertainty due to the instability of the material, and u_{char} the uncertainty in the characterisation of the property value.

The underlying principles, the organisational aspects, and statistical evaluation of homogeneity and stability studies have been summarised in several review articles [20–23]; the reader is referred to these for in-depth information. In this context it is important to realise that, contrary to previous CRM guidelines, the inhomogeneity and instability of a CRM must be quantified and an allowance for these contributions must be made in the uncertainty budget for the certified property value.

Characterisation measurements may be performed by one or more laboratories using a primary method, whose measurement results are, by definition, traceable to the SI [24], a method for which all possible sources of bias are known, or several independent methods [25]. How the results of such certification measurements are combined for assignment of the certified property value would lead beyond the scope of this review, but can be found in ISO Guide 35 [19] and other related publications [26–28].

Many environmental and biological CRMs may degrade over time, even when stored under favourable conditions (at low temperature, in the absence of irradiation and oxygen), necessitating periodic monitoring to check whether the certified values are still valid. If not, the certified property values and the associated uncertainties must be revised or the material withdrawn from the market.

Selection of certified reference materials

Ideally, CRMs should be as similar as possible to the sample being routinely analysed. In reality, the physical form of any RM is always a compromise between the "as close to reality as possible" sample requested by the end user and the "as stable and homogeneous as possible" sample required for certification with the lowest possible uncertainty. Many environmental candidate (C)RMs are therefore transformed into dry, finely ground powders using techniques such as ball-milling, jet-milling, cryo-grinding, etc., in combination with oven-drying or freeze-drying. Other reasons for choosing such technology are the low cost of storage and transport of powder samples and their excellent stability under extreme transport conditions in comparison to frozen wet materials. With the increasing development of RMs for clinical analysis, however, producers became aware that insufficient matrix matching with real samples might make a CRM quite useless because of lack of "commutability", i.e. the inter-assay properties of the CRM are not comparable with those of routine samples. Although exact CRM matrix format-matching is an issue in clinical chemistry, measurements on traditional environmental matrices, for example soil, sediment, and sludge, are not affected or are only slightly affected by this format mismatch. So far only the US National Institute of Standards and Technology (NIST) has offered, for some time, cryo-ground, frozen materials for biota (SRM 1974a, Organics in Mussel Tissue) [29] and a freeze-dried version of the same starting material (SRM 2974); SRM 2974 is out of stock and will be replaced by a freeze-dried material. The comparatively high costs and complicated logistics of distributing frozen materials using dry-ice transportation severely limit the widespread use of this alternative technology.

Table 2 CRMs for inorganic analytes in soil

Certifying body	Certified reference material	Matrix	Certified properties
CMI	CMI7001	Light sandy soil	Total content: Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn; Aqua regia extractable: As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn; Boiling 2 mol L^{-1} nitric acid extractable: As, Be, Co, Cr, Cu, Mn, Ni, Pb, V, Zn; Cold 2 mol L^{-1} nitric acid extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn
	CMI7002	Light sandy soil	Total content: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn; Aqua regia extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn; Boiling 2 mol L^{-1} nitric acid extractable: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn; Cold 2 mol L^{-1} nitric acid extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn
	CMI7003	Silty clay loam	Total content: Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn; Aqua regia extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn; Boiling 2 mol L^{-1} nitric acid extractable: Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn; Cold 2 mol L^{-1} nitric acid extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn
	CMI7004	Loam	Total content: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn; Aqua regia extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn; Boiling 2 mol L^{-1} nitric acid extractable: As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn; Cold 2 mol L^{-1} nitric acid extractable: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn
IRMM	BCR-141R	Calcareous soil	Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn; Aqua regia soluble content: Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
	BCR-142R	Light sandy soil	Cd, Co, Cu, Hg, Mn, Ni, Pb; Aqua regia soluble content: Cd, Ni, Pb, Zn
	BCR-143R	Sewage sludge-amended soil	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn; Aqua regia soluble content: Cd, Cr, Hg, Mn, Ni, Pb, Zn
	BCR-483	Sewage sludge-amended soil	EDTA extractable: Cd, Cr, Cu, Ni, Pb, Zn; Acetic acid extractable: Cd, Cr, Cu, Ni, Pb, Zn
	BCR-484	Sewage sludge-amended (terra rossa) soil	EDTA extractable: Cd, Cu, Ni, Pb, Zn; Acetic acid extractable: Cd, Cu, Ni, Pb, Zn
	BCR-700	Organic-rich soil	EDTA extractable: Cd, Cr, Cu, Ni, Pb, Zn; Acetic acid extractable: Cd, Cr, Cu, Ni, Pb, Zn
	ERM-CC690	Calcareous soil	Ce, Dy, Gd, La, Nd, Sc, Sm, Tb, Tm, Yb, Th, U
LGC	LGC6141	Soil contaminated with clinker/ash	Aqua regia extractable: As, Cr, Cu, Ni, Pb, Zn
	LGC6144	Gas works-contaminated soil	As, Cr, Cu, Hg, Ni, Pb, Se, V, Zn, chloride, sulfate
	ERM-CC135	Brick works soil	Total content: As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, V, Zn; Aqua regia extractable: Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Se, V, Zn,
NIST	SRM-2709	San Joaquin soil	Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Se, Si, Sr, Ti, Tl, V, Zn
	SRM-2710	Montana I soil	Ag, Al, As, Ba, Ca, Cd, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Si, Ti, V, Zn
	SRM-2711	Montana II soil	Ag, Al, As, Ba, Ca, Cd, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Se, Si, Sr, Ti, Tl, V, Zn
	SRM-2586	Soil containing lead from paint	As, Cd, Cr, Pb
	SRM-2587	Soil containing lead from paint	As, Cd, Cr, Pb

Table 2 (continued)

Certifying body	Certified reference material	Matrix	Certified properties
National Analysis Center for Iron and Steel in China	ZC73001	Soil	Ag, Al_2O_3, As, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K_2O, La, Li, Lu, MgO, Mn, Mo, N, Na_2O, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sc, Se, SiO_2, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, organic carbon

Use of certified reference materials

Calibration of a measurement system by using properly prepared calibration materials is the essential means of establishing traceability for chemical measurements. To determine an unknown quantity the signal produced by the measurement system is referenced to the calibration materials used. In most practical situations, testing laboratories prepare their calibration materials by dissolving a pure substance (the analytes of interest) in a suitable

Table 3 CRMs for inorganic analytes in sediment

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-462	Coastal sediment	Tributyltin, dibutyltin
	BCR-646	Freshwater sediment	Tributyltin, dibutyltin, monobutyltin, triphenyltin, diphenyltin, monophenyltin
	BCR-667	Estuarine sediment	Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Yb, Th, U
	BCR-684	River sediment	Extractable phosphorus in sediment following a five-step extraction procedure (NaOH-extractable P, HCl-extractable P, inorganic P, organic P, conc. HCl-extractable P
	BCR-701	Lake sediment	Extractable trace elements in sediment following a sequential extraction procedure. Step 1: Cd, Cr, Cu, Ni, Pb, Zn; Step 2: Cd, Cr, Cu, Ni, ,Pb, Zn; Step 3: Cd, Cr, Cu, Ni, Pb, Zn
	ERM-CC580	Estuarine sediment	Total Hg, Methyl-Hg
LGC	LGC6137	Estuarine sediment	Aqua regia extractable: Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, V, Zn
	LGC6156	Harbour sediment	Aqua regia extractable: Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sn, V, Zn
	LGC6187	River sediment	Aqua regia extractable: As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, V, Zn
NIST	SRM-1646a	Estuarine sediment	Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, S, Se, Si, Ti, V, Zn
	SRM-2702	Marine sediment	Al, As, Ba, Cd, Ce, Co, Cr, Fe, Hg, K, La, Mn, Na, Ni, P, Pb, Rb, Sb, Sc, Sr, Th, Ti, Tl, V, Zn
	SRM-2703	Sediment for solid sampling (small sample) analytical techniques	Al, As, Ba, Cd, Ce, Co, Fe, Hg, K, La, Mn, Na, Pb, Rb, Sb, Sc, Sr, Th, Ti, U, V, Zn
	SRM-4350b	River sediment-radioactivity	^{241}Am, ^{60}Co, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{238}Pu, $^{23}9Pu$ + ^{240}Pu, ^{226}Ra
	SRM-4354	Freshwater lake sediment-radioactivity	^{241}Am, ^{60}Co, ^{137}Cs, ^{238}Pu, ^{239}Pu + ^{240}Pu, ^{90}Sr, ^{228}Th, ^{232}Th, ^{235}U, ^{238}U
	SRM-4357	Ocean sediment-radioactivity	^{241}Am, ^{60}Co, ^{137}Cs, ^{238}Pu, ^{239}Pu + ^{240}Pu, ^{90}Sr, ^{228}Th, ^{232}Th, ^{235}U, ^{238}U
NIES	NIES-12	Marine sediment	Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Rb, Si, Sn, Sr, Ti, V, Zn tributyltin, triphenyltin

Table 3 (continued)

Certifying body	Certified reference material	Matrix	Certified properties
NRC	HISS-1	Sandy sediment	Ag, Al, As, Be, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Ti, V, Zn
	HIPA-1	Marine sediment	Tributyltin (as Sn)
	MESS-3	Estuarine sediment	Ag, Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn
	PACS-2	Harbour sediment	Ag, Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, Ti, V, Zn, monobutyltin, dibutyltin, tributyltin
	SOPH-1	Marine sediment	Dibutyltin, tributyltin
National Analysis Center for Iron and Steel in China	NCS DC73311	Chinese stream sediment	Ag, Al_2O_3, As, B, Ba, Be, Bi, CaO, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, F, FeO, Ga, Gd, Ge, Hf, Hg, Ho, In, K_2O, La, Li, Lu, MgO, Mn, Mo, Na_2O, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, SiO_2, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr
	NCS DC78301	River sediment	As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb, Se

solvent using calibrated equipment (balance, volumetric glassware, thermometer). Performing such operations is regarded as rather trivial by many analysts. Calibration is, therefore, not usually regarded as a substantial source of bias affecting the trueness of measurement results. Consolidated experience from the European Commission's CRM programme-previously known as the BCR programme-and other interlaboratory comparisons organised by the JRC-IRMM has proven that agreement of results improved when the same calibration material was made available to the participants. Certified calibration solutions, a special form of CRMs, free the end-user from the burden of manipulating small amounts of (hazardous) substances and provide an easy means of building a traceability chain. The uncertainty associated with the certified concentration or mass fraction value contributes directly to the overall uncertainty of the measurement results. A very comprehensive guideline on calibration and the use of CRMs in setting up calibration functions can be found elsewhere [6].

The other main field of application of CRMs is in assessment of trueness as part of the validation of an analytical method, and related processes (verification of the correct use of a standardised method, qualification of operators, etc). Matrix CRMs, preferably matching as closely as possible the samples investigated (matrix type, analyte level, matrix format, etc.) are needed for this crucial step. Although most certificates of analysis that accompany CRMs describe in detail the properties of the materials (certified values, uncertainties, traceability, recommended minimum sample intake, storage conditions, expiry dates, etc.) information about how to make best use of the CRM for, for example, estimating trueness is often not directly available; the difficulty users encounter when evaluating and reporting results from estimation of trueness using CRMs have been emphasized by Jorhem [30, 31], who has

Table 4 CRMs for inorganic analytes in sewage sludge

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-144R	Sewage sludge (domestic origin)	Total content: Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn; Aqua Regia extractable: Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
	BCR-145R	Sewage sludge (mixed origin)	Total content : Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn ; Aqua Regia extractable : Cr, Cu, Ni, Pb, Zn
	BCR-146R	Sewage sludge (industrial origin)	Total content: Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn; Aqua Regia extractable: Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
LGC	LGC6181	Sewage sludge	Aqua Regia extractable: Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, Zn
	ERM-CC136	Sewage sludge	Aqua Regia extractable: Al, Ba, Co, Cr, Cu, Fe, K, Mg, Mn Na, Ni, Pb, Zn
NIST	SRM-2781	Domestic sludge	As, Cd, Cu, Hg, Mo, N, Ni, Pb, Se, Zn
	SRM-2782	Industrial sludge	As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn

also made several proposals about how to use CRMs correctly for this purpose [32]. ISO published a guideline for the use of CRMs (ISO Guide 33) [33]; it is currently under revision.

A straightforward means of assessing whether the average analytical results obtained for a CRM are biased has been published by van der Veen [34]. In essence, the measurement is regarded as unbiased if the difference

Table 5 CRMs for inorganic analytes in water

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-403	Sea water	Cd, Cu, Mo, Ni, Pb, Zn
	BCR-408	Simulated rainwater	Ca, Mg, Na, hydronium, chloride, nitrate, sulfate
	BCR-409	Simulated rainwater	Ca, K, Mg, Na, ammonium, chloride, hydronium, nitrate, sulfate
	BCR-479 and BCR-480	Fresh water	Nitrate (low and high level)
	BCR-505	Estuarine water	Cd, Cu, Ni, Zn
	BCR-579	Coastal sea water	Hg
	BCR-609 and BCR-610	Ground water	Al, As, Cd, Cu, Pb (low and high levels)
	BCR-611 and BCR-612	Ground water	Bromide (low and high level)
	BCR-616	Artificial ground water-low carbonate content	Ca, K, Mg, Mn, Na, chloride, nitrate, phosphate, sulfate
	BCR-617	Artificial ground water-high carbonate content	Ca, K, Mg, Mn, Na, chloride, nitrate, sulfate
	BCR-713	Wastewater effluent	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn
	BCR-714	Wastewater influent	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn
	BCR-715	Wastewater industrial effluent	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn
LGC	LGC6016	Estuarine water	Cd, Cu, Mn, Ni, Pb
	LGC6017	Rainwater (roof run-off)	Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn
	LGC6019	River water	Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Pb, Zn
	LGC6020	River water	Chloride, nitrate, phosphate, sulfate
	LGC6175	Landfill leachate	B, Ca, Fe, K, Mg, Mn, Na, Ni, Zn
	LGC6176	Landfill leachate	Chloride, ammonium, sulfate, COD, TOC
	LGC6177	Landfill leachate	B, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, Zn
	ERM-CA010a	Hard drinking water	Ag, Al, As, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Zn
	ERM-CA021a	Soft drinking water	Ag, Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Zn
NIST	SRM-1640	Natural water	Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Fe, Mn, Mo, Pb, Sb, Se, Sr, V
	SRM-1641d	Natural water	Hg
	SRM-1643e	Simulated fresh water	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Ru, Sb, Se, Sr, Te, Tl, V, Zn
NMIJ		River water (natural level)	Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Zn
		River water (elevated level)	Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Zn
NRC	CASS-4	Coastal seawater	As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn
	MOOS-1	Sea water	Nitrite, nitrite plus nitrate, orthophosphate, silicate
	NASS-5	Sea water	As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn
	ORMS-3	River water	Hg
	SLEW-3	Estuarine water	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn
	SLRS-4	River water	Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sr, U, V, Zn

Table 6 CRMs for inorganic analytes in fly ash and particulate materials

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-038	Fly ash from pulverised coal	As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Na, Pb, Zn, chloride, fluoride
	BCR-128	Fly ash on artificial filters	As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Na, Pb, Zn
	BCR-545	Welding dust (on filter)	Cr (VI), total leachable Cr
	BCR-605	Urban dust	Trimethyllead
	BCR-723	Road dust	Pd, Pt, Rh
LGC	LGC6180	Pulverised fuel ash	Aqua regia extractable content: Al, As, Ba, Ca, Co, Cr, Cu, K, Mg, Mn, Na, Ni, Pb, V, Zn
NIST	SRM-1633b	Coal fly ash	Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Nd, Ni, Pb, S, Se, Si, Sr, Th, Ti, U, V
	SRM-1648	Urban particulate matter	Al, As, Cd, Cr, Cu, Fe (total), K, Na, Ni, Pb, Se, U, V, Zn
	SRM-2583	Indoor dust	As, Cd, Cr, Hg, Pb
	SRM-2584	Indoor dust	As, Cd, Cr, Hg, Pb
	SRM-2689	Coal fly ash	Al, Ca, Fe (total), K, Mg, Na, P, Si, Ti
	SRM-2690	Coal fly ash	Al, Ca, Fe (total), K, Mg, Na, P, S, Si, Ti
	SRM-2691	Coal fly ash	Al, Ca, Fe (total), K, Mg, Na, P, S, Si, Ti
	SRM-2783	Air particulate on filter media	Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Ti, V, Zn
NIES	NIES-8	Vehicle exhaust particulates	Ag, Al, As, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, K, La, Lu, Mg, Mo, Na, Ni, P, Pb, Rb, Sb, Sc, Se, Sm, Sr, Th, V, Zn
National Analysis Center for Iron and Steel in China	NCS ZC78001	Coal fly ash	As, Be, Cd, Co, Cr, Cu, Fe, Mn, Pb, Se, V, Zn

between the result obtained and the certified property value is less than the expanded uncertainty of this difference:

$$|x_{obs} - x_{CRM}| < k \times \sqrt{u_{obs}^2 + u_{CRM}^2}$$

where x_{obs} is the average result obtained from analysis of the CRM, x_{CRM} the certified value of the property for the CRM, u_{obs} the uncertainty of the result, u_{CRM} the uncertainty of the certified property value, and k

Table 7 CRMs for inorganic analytes in biota

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-060	Aquatic plant (*Lagarosiphon major*)	Al, Cd, Cu, Hg, Mn, Pb, Zn
	BCR-062	Olive leaves (*Olea europea*)	Al, Cd, Cu, Hg, Mn, Pb, Zn
	BCR-100	Beech leaves	Al, Ca, Cr, K, Mg, N, P, S, chloride
	BCR-101	Spruce needles	Al, Ca, Mg, Mn, N, P, S, Zn, chloride
	BCR-279	Sea lettuce (*Ulva lactuca*)	As, Cd, Cu, Pb, Se, Zn
	BCR-482	Lichen	Al, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn
	BCR-596	Aquatic plant (*Trapa natans*)	Cr
	BCR-670	Aquatic plant (*Lemna minor*)	Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, U, Y, Yb
	BCR-414	Plankton	As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, Zn
	BCR-688	Mussel tissue	Ce, Dy, Er, Eu, Gd, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Th, U
	BCR-627	Tuna fish	Arsenobetain, dimethylarsinic acid, total As
	BCR-463	Tuna fish	Total Hg, methylmercury
	ERM-CE464	Tuna fish	Total Hg, ethylmercury
	ERM-CE278	Mussel tissue	As, Cd, Cr, Cu, Hg, Mn, Pb, Se, Zn
	ERM-CE477	Mussel tissue	Tributyltin, dibutyltin, monobutyltin
LGC	LGC7162	Strawberry leaves	As, Ba, Ca, Cd, Co, Cr, Fe, Hg, K, Mg, Mn, Mo, N, Ni, P, Pb, S, S, Zn

Table 7 (continued)

Certifying body	Certified reference material	Matrix	Certified properties
NIES	NIES-1	Pepperbush leaves	As, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Rb, Sr, Tl, Zn
	NIES-9	Sargasso sea weed	Ag, Al, As, Br, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, Hg, I, K, Mg, Mn, Na, P, Pb, Rb, S, Sb, Sc, Se, Sr, Ti, U, V, Zn
	NIES-11	Fish	Sn, tributyltin, triphenyltin
NIST	SRM-1515	Apple leaves	Al, As, B, Ba, Ca, Cd, Cu, Fe, Hg, K, Mg, Mn, Mo, N, Na, Ni, P, Pb, Rb, Se, Sr, V, Zn, chloride
	SRM-1547	Peach leaves	Al, As, B, Ba, Ca, Cd, Cu, Fe, Hg, K, Mg, Mn, Mo, N, Na, Ni, P, Pb, Rb, Se, Sr, V, Zn, chloride
	SRM-1566b	Oyster tissue	Ag, Al, As, Ca, Cd, Cl, Co, Cu, Fe, Hg (total), K, Mg, Mn, Na, Ni, Pb, Rb, S, Se, Th, V, Zn, methylmercury
	SRM-1570a	Spinach leaves	Al, As, B, Ca, Cd, Co, Cu, Hg, K, Mn, N, Na, Ni, P, Se, Sr, Th, V, Zn
	SRM-1573a	Tomato leaves	Al, As, B, Ca, Cd, Co, Cr, Cu, Hg, K, Mn, N, Na, Ni, P, Se, Sr, Th, V, Zn
	SRM-1575a	Pine needles	Al, Ba, Ca, Cd, Cu, Fe, Hg, K, P, Rb, Zn, chloride
	SRM-2635	Vegetation (Timothy grass)	Fluoride
	SRM-2976	Mussel tissue	As, Cd, Cu, Fe, Pb, Se, Zn, methylmercury
	SRM-2977	Mussel tissue	Cd, Cu, Mn, Ni, Pb, Sr, methylmercury
NRC	DOLT-3	Dogfish liver	Ag, As, Cd, Cu, Fe, Hg, Ni, Pb, Se, Zn
	DORM-2	Dogfish muscle	Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn, methylmercury, arsenobetaine, tetramethylarsonium
	LUTS-1	Non-defatted lobster hepatopancreas	Ag, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, Pb, Se, Sr, Zn, methylmercury
	TORT-2	Lobster hepatopancreas	As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sr, Va, Zn, methylmercury

the coverage factor (usually 2, which corresponds to approximately 95% confidence).

A similar approach to trueness estimation is recommended by the European Reference Materials (ERM) initiative [35].

Another important aspect of every quality-assurance programme is demonstration that the temporal performance of validated methods remains under statistical control. Various charting techniques have been proposed for this purpose [36]. All of these techniques rely on the availability of a homogenous and stable test material. CRMs are ideally suited to this, because of their demonstrated stability and homogeneity. Use of CRMs for charting not only enables checking of whether the process is under control over time but also concomitant assessment of the trueness of the method.

Certified reference materials for environmental studies

The number of analyte/matrix combinations potentially needed by the environmental chemist is gargantuan, even though, at first glance, the number of "classical" environmental matrices seems to be rather limited: soil, sediment, water, air. From each compartment, however, an enormously wide range of samples differing in composition and physicochemical properties, e.g. clay, sandy, calcareous, humic-rich soils, etc, may be presented to the chemist for analysis.

CRM producers therefore try to address these challenges by offering "typical" matrices for analytes of global interest or concern. Examples of currently available matrix CRMs are given in Tables 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12; they are complemented by a sufficiently wide range of pure element/compound and pure element/compound in solution CRMs, which are primarily used for instrument calibration (data not shown)

For the analysis of elements a rather wide array of analyte/matrix combinations and analyte levels, covering all relevant compartments, is currently available as exemplified by the entries given in Tables 2, 3, 4, 5, 6 and 7. CRMs certified for content of different elements were among the first to be produced by certifying bodies. These started with the pioneering work of H.J.M. Bowen (Bowen's Kale) in the 1960s and this was followed by activity of the US National Bureau of Standards who produced NBS Orchard Leaves. As a result of these longstanding efforts the analyst can choose a CRM which best suits his needs, in terms of analyte levels and matrix properties, from a substantial variety of soil, sediment, sewage sludge, water, particulate matter, and biota CRMs certified for a wide range of elements.

Because the eco-toxicology and mobility of metals in the environment are very dependent on their chemical forms (species) and their binding to particulate matter, several soil and sediment CRMs are offered for which, in addition to the total content of various elements, the extractable (leachable) part is also certified. One example is BCR-483, a sewage sludge-amended soil certified for acetic acid and EDTA-extractable metal content. Because these are method-dependent properties, the user is required to follow the same procedure as used for certification analysis. Reporting total concentrations of trace elements is no longer sufficient when elucidating the toxicity of environmental samples, because the toxicity of some elements depends on whether they are present as inorganic or organic species [38]. Metal speciation, therefore, has recently become increasingly important. To support quality-assurance programmes for speciation analysis CRMs are available for which not only the total amounts of elements such as As, Cr, Pb, and Sn are certified, but also individual organometallic species of eco-toxicological concern [39]. Several materials are available which are certified for their content of organotin (BCR-462, BCR-646, ERM-CE477, NIES-11, NIES-12, HIPA-1, PACS-2, SOPH-1), organomercury (BCR-463, ERM-CC580, ERM-CE464, DORM-2, LUTS-1, TORT-2, SRM-1566b, SRM-1974b, SRM-2976, SRM-2977), organolead (BCR-605), and organoarsenic (BCR-627, DORM-2) compounds.

The range of environmental CRMs for organic trace analysis is more limited and, usually, restricted to compounds regarded as persistent organic pollutants (POPs), for example PCBs, PAHs, PCDD/Fs, and organochlorine pesticides (OCPs), e.g. hexachlorobenzene, α-HCH, γ-HCH, heptachlor epoxide, oxychlordane, mirex,

Table 8 CRMs for organic analytes in soil

Certifying body	Certified reference material	Matrix	Certified properties
BAM	ERM-CC007	Soil	α-HCH, β -HCH, *p*,*p*′-DDE, *o*,*p*′-DDT, *p*,*p*′-DDT
	ERM-CC08, ERM-CC09	Soil	Pentachlorophenol
	ERM-CC010, ERM-CC-011, ERM-CC012	Soil	AOX
	ERM-CC013, ERM-CC014	Soil	Phenanthrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, fluorene, acenaphthylene, naphthalene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, dibenzo[*ah*]anthracene, benzo[*a*]pyrene, benzo[*k*]fluoranthene, chrysene, pyrene, anthracene, fluoranthracene
IRMM	BCR-481	Industrial soil	PCB congeners 101, 118, 128, 149, 153, 156, 170, 180
	BCR-524	Contaminated industrial soil	Pyrene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*b*]naphtho[2,1-*d*]thiophene, indeno[1,2,3-*cd*]pyrene, pentachlorophenol
	BCR-529	Industrial sandy soil	1,2,3-Trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene, 3,4-dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF
	BCR-530	Industrial clay soil	1,2,3-Trichlorobenzene, 3-chlorophenol, 3,4-dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol, 1,2,3,6,7,8-HeCDD, 1,2,3,7,8,9-HeCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HeCDF, 1,2,3,6,7,8-HeCDF, 2,3,4,6,7,8-HeCDF
LGC	LGC6113	Soil	PCB congeners 28, 52, 118, 101,138, 153, 180
	LGC6140	Soil	Acenaphthylene, fluoranthene, anthracene, fluorine, benzo[*a*]anthracene, indeno[1,2,3-cd]pyrene, benzo[*b*]fluoranthene, naphthalene, benzo[*k*]fluoranthene, phenanthrene, benzo[*ghi*]perylene, pyrene, benzo[*a*]pyrene, total PAH
	LGC6144	Gas works-contaminated soil	Acenaphthylene, anthracene, benzo[*ghi*]perylene, benzo[*a*]anthracene benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, dibenzo[*ah*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene, pyrene, acenaphthene, total PAH

Table 9 CRMs for organic analytes in sediment

Certifying body	Certified reference material	Matrix	Certified properties
BAM	ERM-CC015	Sediment	Total petrol hydrocarbons
IRMM	BCR-535	Freshwater harbour sediment	Pyrene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene
	BCR-536	Freshwater harbour sediment	PCB congeners 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 163, 170, 180
LGC	LGC6188	River sediment	Acenaphthene, dibenzo[*ah*]anthracene, anthracene, fluoranthene, chrysene, fluorine, benzo[*a*]anthracene, indeno[1,2,3-*cd*]pyrene, benzo[*b*]fluoranthene, naphthalene, benzo[*k*]fluoranthene, phenanthrene, benzo[*a*]pyrene, pyrene, benzo[*ghi*]perylene
NIST	SRM-1939a	River sediment	PCB congeners 44, 49, 52, 66, 99, 105, 110, 118, 128, 138, 149, 151, 153, 156, 170, 180, 183, 187, 194, 206, *cis*-chlordane, 4,4-DDD, 4,4-DDT
	SRM-1941b		Naphthalene, fluorene, phenanthrene, anthracene, 3-methylphenanthrene, 2-methylphenathrene, 1-methylphenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*aj*]anthracene, dibenz[*ac*]anthracene, dibenz[*ah*]anthracene, benzo[*b*]chrysene, picene, PCB congeners 8, 18, 28, 31, 44, 49, 52, 66, 87, 95, 99, 101, 105, 110, 118, 128, 138, 149, 153, 156, 170, 180, 183, 187, 194, 195, 201, 206, 209, hexachlorobenzene, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, 4,4-DDE, 4,4-DDD
	SRM-1944	New York/New Jersey waterway sediment	Naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*c*]phenanthrene, benzo[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*aj*]anthracene, dibenzo[*ac*]anthracene, dibenzo[*ah*]anthracene, pentaphene, benzo[*b*]chrysene, picene, PCB congeners 8, 18, 28, 31, 44, 49, 52, 66, 87, 95, 99, 101, 105, 110, 118, 128, 138, 149, 151, 153, 156, 170, 180, 183, 187, 194, 195, 206, 209, hexachlorobenzene, *cis*-chlordane, *trans*-nonachlor, 4,4-DDT
NMIJ		Marine sediment (low pollutant concentration)	PCB congeners 3, 15, 28, 31, 70, 101, 105, 138, 153, 170, 180, 194, 206, 209; 4,4′-DDT, 4,4′-DDE, 4,4′-DDD, y-HCH
		Marine sediment (high pollutant concentration)	PCB congeners 3, 15, 28, 31, 70, 101, 105, 138, 153, 180, 194, 206, 209; 4,4′-DDT, 4,4′-DDE, 4,4′-DDD, y-HCH

Table 10 CRMs for organic analytes in sewage sludge

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-088	Sewage sludge	Pyrene, benzo[*b*]fluoranthene, benzo[*a*]anthracene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[b]naphtho[2,1-*d*]-thiopene, benzo[*e*]pyrene, indeno[1,2,3-*cd*]pyrene
	BCR-677	Sewage Sludge	2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HpCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF
LGC	LGC6182	Sewage sludge	Acenaphthene, chrysene, anthracene, fluoranthene, benzo[*a*]anthracene, fluorene, benzo[*b*]fluoranthene, indeno[1,2,3-*cd*]pyrene, benzo[*k*]fluoranthene, naphthalene, benzo[*ghi*]perylene, phenanthrene, benzo[*a*]pyrene, pyrene
	LGC6184	Sewage sludge	PCB congeners 101, 118, 153

Table 11 CRMs for organic analytes in fly ash, particulate materials, and transformer oil

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-420	Waste mineral oil	PCB congeners 28, 101, 118, 153, 180
	BCR-449	Waste mineral oil	PCB congeners 28, 52, 101, 105, 118, 128, 153, 156, 170, 180
	BCR-490	Fly ash	2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF
	BCR-615	Fly ash (low level)	2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HeCDF, OCDF,
LGC	LGC6147	Waste oil	PCB congeners 28, 52, 101, 105, 118, 128, 138, 153, 156, 170, 180
NIST	SRM-1649a	Urban dust	Phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, anthanthrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*aj*]anthracene, dibenzo[*ac*]anthracene, dibenzo[*ah*]anthracene, pentaphene, benzo[*b*]chrysene, picene, PCB congeners 8, 18, 28, 31, 44, 49, 52, 66, 87, 95, 99, 101, 105, 110, 118, 128, 138+163+164, 151, 153, 156, 170+190, 180, 183, 187+159+182, 194, 195, 206, 209, hexachlorobenzene, *trans*-chlordane (gamma-chlordane), *cis*-chlordane (alpha-chlordane), *trans*-nonachlor, 2,4-DDE, 4,4-DDE, 4,4-DDD, 4,4-DDT
	SRM-1975	Diesel particulate extract	Phenanthrene, fluoranthene, benzo[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene
	SRM-2585	House dust	Naphthalene, dibenzothiophene, phenanthrene, anthracene, 4*H*-cyclopenta[*def*] phenanthrene, 3-methylphenanthrene, 2-methylphenathrene, 9-methylphenanthrene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[*ghi*]fluoranthene, benzo[c]phenanthrene, benz[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, benzo[*ghi*] perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*aj*]anthracene, dibenz[*ac*]anthracene, dibenz[*ah*]anthracene, benzo[*b*]chrysene, picene, coronene, dibenzo[*bk*] fluoranthene, dibenzo[*ae*]pyrene, PCB congeners 18, 28 , 31, 44, 52, 56, 70,74, 87, 92, 95, 99, 101, 105, 107, 110, 118, 138, 146, 149, 151, 153+132, 158, 163, 170, 174, 180, 183, 187, 206, 4,4-DDE, 4,4-DDD, 2,4-DDT, 4,4-DDT, PBDE congeners 17, 28+33, 47, 49, 85, 99, 100, 138, 153, 154, 155, 183, 203, 206, 209
	SRM-2975	Diesel particulate matter	Phenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, triphenylene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, benzo[*ghi*]perylene
	SRM-3075	Transformer oil	Aroclor 1016
	SRM-3076	Transformer oil	Aroclor 1232
	SRM-3077	Transformer oil	Aroclor 1242
	SRM-3078	Transformer oil	Aroclor 1248
	SRM-3079	Transformer oil	Aroclor 1254
	SRM-3080	Transformer oil	Aroclor 1260

Table 12 CRMs for organic analytes in biota

Certifying body	Certified reference material	Matrix	Certified properties
IRMM	BCR-349	Cod liver oil	PCB congeners 28, 52, 101, 118, 153, 180
	BCR-350	Mackerel oil	PCB congeners 28, 52, 101, 118, 153, 180
	BCR-682	Mussel tissue (canned)	PCB congeners 28, 52, 118, 138, 149, 153, 170, 180
	BCR-683	Beech wood	Pentachlorophenol, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene
	BCR-718	Herring (canned)	PCB congeners 28, 52, 101, 105, 118, 128, 13 8, 149, 153, 156, 170, 180
	BCR-719	Chub (canned)	PCB congeners 77, 81, 126, 169
NIST	SRM-1588b	Cod liver oil	PCB congeners 18, 28, 31, 44, 49, 52, 66, 87, 95, 99, 101, 105, 110, 118, 128, 138, 149, 151, 153, 156, 170, 180, 183, 187, 194, 206, 209; 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, 4,4′-DDT, hexachlorobenzene, γ-HCH, α-HCH, heptachlor epoxide, *cis*-chlordane, *cis*-nonachlor, *trans*-nonachlor, dieldrin, oxychlordane, mirex
	SRM-1945	Whale blubber	PCB congeners 18, 44, 49, 52, 66, 87, 95, 99, 101+90, 105, 110, 118, 128, 138+163+164, 149, 151, 153, 156, 170+190, 180,183, 187, 194, 195, 201, 206, 209, hexachlorobenzene, α-HCH, γ-HCH, heptachlor epoxide, oxychlordane, mirex, *cis*-chlordane, *cis*-nonachlor, *trans*-nonachlor, 2,4′-DDE, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, 4,4′-DDT
	SRM-1946	Fish tissue (frozen)	PCB congeners 44, 49, 52, 66, 70, 74, 77, 87, 95, 99, 101, 105, 118, 126, 128, 138, 146, 149, 153, 156, 169, 170, 180, 183, 187, 194, 195, 206, 209, hexachlorobenzene, α-HCH, γ-HCH, heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, dieldrin, mirex, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 4,4′-DDT
	SRM-1974b	Mussel tissue (frozen)	Naphthalene, fluorene, phenanthrene, anthracene, 1-methylphenanthrene, 2-methylphenathrene, 3-methylphenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*ah*] anthracene, PCB congeners 18, 28, 31, 44, 49, 52, 66, 70, 74, 82, 87, 95, 99, 101, 105, 107, 110, 118, 128, 132, 138, 146, 149, 151, 153, 156, 158, 170, 180, 183, 187, *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, 2,4-DDE, 4,4-DDE, 2,4-DDD, 4,4-DDD, methylmercury
	SRM-2977	Mussel tissue	Fluorene, phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*ah*] anthracene, benzo[*b*]chrysene, picene, PCB congeners 8, 18, 28, 31, 44, 52, 66, 87, 95, 99, 101+90, 105, 110, 118, 128, 138+163+164, 149, 151, 153, 156, 170, 180, 183, 187+159+182, 194, *cis*-chlordane, *trans*-nonachlor, dieldrin, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 4,4′-DDT

cis-chlordane, *cis*-nonachlor, *trans*-nonachlor, 2,4′-DDE, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, and 4,4′-DDT, which are of global concern and for which worldwide, supra-national monitoring programmes exist (e.g. UN Environment Programme, Arctic Monitoring and Assessment Programme, OSPAR Commission, etc). Several suppliers offer CRMs for POPs in different matrices (soil, sediment, sewage sludge, particulate matter, biota), but also for method defined properties such as AOX in soil (ERM-CC010, ERM CC-011, ERM-CC012) and total petrol hydrocarbons in sediment (ERM-CC015) (Tables 8, 9, 10, 11 and 12).

CRMs for organic compounds in water do not exist, mainly because of stability problems and the large sample volumes (mostly 1–2 L) necessary, which complicates CRM distribution. Alternative concepts for production of water-based CRMs for organic trace analysis, based on "freeze-dried water", stabilization of pesticides in a starch-rich matrix (pills which must be reconstituted), and spiking and matrix surrogate solutions, have been developed and are discussed elsewhere [40–43], although none of these alternatives has been commercialised.

CRMs for the vast group of so-called "emerging pollutants" are currently scarce, although the objective of several development programmes is to remedy this. For many of these emerging contaminants there are no national or international limits, because of incomplete or insufficient information about occurrence, risk assessment, or eco-toxicology. These man-made substances are not necessarily new-some have often been in use for a long time-but their presence and impact on the environment are only now being recognised. NIST has recently quantified some polybrominated diphenyl ether congeners (PBDEs) and toxaphenes, which are stable in the environment and readily bioaccumulate in wildlife and human tissue, in three marine SRMs (SRM 1588b Organics in Cod Liver Oil, SRM 1945 Organics in Whale Blubber, SRM 1946 Lake Superior Fish Tissue). Although certified values have not yet been assigned, the materials are certainly fit-for-purpose as quality-control materials. A European Commission-funded research project explored the feasibility of preparing CRMs for PBDEs in flounder and sediment and technology for providing sufficiently homogenous and stable materials containing these analytes has been developed (BROC project, J. de Boer, personal communication). The objective of another EU-funded project currently in progress (NORMAN, www.emerging-pollutants.net) is to establish a network of reference laboratories for monitoring emerging environmental pollutants; QA/QC tools are expected from the project.

The EU Water Framework Directive [44] requires monitoring of some of the emerging pollutants which have been grouped together on the list of Priority Substances [45]. Table 13 gives a non-exhaustive overview of relevant classes of emerging pollutants in the environment [46–48]. Because wastewater-treatment plants are major point sources for discharge of these substances, sewage sludge or sludge-amended soil might be a suitable matrix for CRM production.

Conclusions

Chemical measurements play an ever increasing role in many economic, political, environmental, medical, and legal decisions; reliable and comparable data form an integral part of the decision-making process. CRMs are undoubtedly a key element in analytical data-quality assurance, because these tools enable building of a traceability chain to established and acknowledged reference systems and enable comprehensive assessment of the performance of a measurement method. The variety of matrices and substances encountered in environmental chemistry necessitates provision of a wide range of matrix (C)RMs by specialised RM producers. A perfect match (matrix composition and format, analyte level, etc.) between a particular CRM and a natural sample is difficult to achieve, however, and a compromise is usually necessary. A sufficiently large supply of CRMs is available for environmental studies, at least for most elements and "classical" organic pollutants, for example PCBs, PAHs, etc. Regular use of matrix CRMs by laboratories is seen as a key aspect of setting up internal quality-control and assurance programmes, because they enable the perfor-

Table 13 Emerging pollutants in the environment (modified after [46, 47])

Alkylphenols (*n*-octylphenols, *n*-nonylphenols)	Polychlorinated naphthalenes
Polybrominated flame retardants (tetrabromobisphenol-A, hexabromocyclododecane, polybrominated diphenyl ethers)	Polar pesticides and their degradation products (alachlor, atrazine, chlorfenvinphos, chlorpyrifos, dicofol, diuron, isoproturon, simazine, trifluralin)
C_{10}-C_{13} Chloroalkanes,	Fragrances (nitro, polycyclic, and macrocyclic musks)
Endocrine-disrupting substances (natural and synthetic hormones, phthalates, ethoxylates, parabenes)	Polyfluoralkylated substances
Pharmaceutical products (antibiotics, analgesics and anti-inflammatory drugs, psychiatric drugs, lipid metabolism regulators, β-blockers, contraceptives, X-ray contrast media)	Detergents (aromatic and alkylated sulfonates)
Personal care products (sun-screen agents, e.g. benzophenone, ethylhexyl methoxycinnamate, 4-methylbenzylidene camphor)	Drinking water disinfection by-products (chloroacetic, bromoacetic, and iodoacetic acids, bromoaldehydes, iodotrihalomethanes)

mance of methods applied by a particular operator or laboratory to be checked, irrespective of time constraints or the availability of collaborative study efforts. Consequently, regular use of CRMs has been made mandatory for laboratories accredited in accordance with ISO/IEC 17025, to ensure the comparability and reliability of chemical measurements.

References

1. ISO/IEC 17025 (2005) General requirements for the competence of testing and calibration laboratories, 2nd edn. International Organisation for Standardisation (ISO), Geneva, Switzerland
2. Fajgelj A, Parkany M (eds) (1999) Use of matrix reference materials in environmental analytical processes. Royal Society of Chemistry, London
3. Quevauviller Ph, Maier EA (1999) Interlaboratory studies and certified reference materials for environmental analysis-the BCR approach. Elsevier, Amsterdam
4. Zschunke A (2000) Reference materials in analytical chemistry. A Guide for selection and use. Springer, Berlin Heidelberg New York
5. Stoeppler M, Wolf WR, Jenks PJ (eds) (2000) Reference materials for chemical analysis. Wiley-VCH, Weinheim
6. Barwick V, Burke S, Lawn R, Roper P, Walker R (2001) Applications of reference materials in analytical chemistry. Royal Society of Chemistry, London
7. Maier EA (1991) Trends Anal Chem 10:340–347
8. Emons H, Ostapczuk P, Rossbach M, Schladot JD (1998) Fresenius J Anal Chem 360:398–401
9. De Boer J, McGovern E (2001) Trends Anal Chem 20:140–159
10. De Guillebon G, Pannier F, Seby F, Bennink D, Quevauviller Ph (2001) Trends Anal Chem 20:160–166
11. Rasberry SD (2001) Accred Qual Assur 6:95–99
12. Quevauviller Ph, Bennink D, Bøwadt S (2001) Fresenius J Anal Chem 370:11–15
13. Hafkenscheid Th, Baldana A, Quincey P, Cortez L, Dias F, Brown RH, Wright M, Gerboles M, Saunders (2005) Atmos Environ 39:3947–3965
14. Emons H, Linsinger TPJ, Gawlik BM (2004) Trends Anal Chem 23:442–449
15. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1993) International vocabulary of basic and general terms in metrology, 2nd edn. ISO, Geneva
16. Emons H, Fajgelj A, van der Veen AMH, Watters R (2006) Accred Qual Assur 10:576–578
17. De Bièvre P (2006) Accred Qual Assur 10:459–460
18. ISO Guide 34 (2000) General requirements for the competence of reference material producers. International Organisation for Standardisation (ISO), Geneva, Switzerland
19. ISO Guide 35 (2006) Reference materials-General and statistical principles for certification. International Organisation for Standardisation (ISO), Geneva, Switzerland
20. Pauwels J, Lamberty A, Schimmel H (1998) Accred Qual Assur 3:51–55
21. Linsinger TPJ, Pauwels J, van der Veen AMH, Schimmel H, Lamberty A (2001) Accred Qual Assur 6:20–25
22. van der Veen AMH, Linsinger TPJ, Lamberty A, Pauwels J (2001) Accred Qual Assur 6:26–30
23. van der Veen AMH, Linsinger TPJ, Lamberty A, Pauwels J (2001) Accred Qual Assur 6:257–263
24. Milton MJT, Quinn TJ (2001) Metrologia 38:289–296
25. King B (2003) Accred Qual Assur 8:429–433
26. Hässelbarth W, Bremser W, Pradel R (1998) Fresenius J Anal Chem 360:317–321
27. Levenson MS, Banks DL, Eberhardt KR, Gill LM, Guthrie WF, Liu HK, Vangel MG, Yen JH, Zhang NF (2000) J Res Nat Inst Stand Technol 105:571–579
28. van der Veen AMH, Linsinger TPJ, Schimmel H, Lamberty A, Pauwels J (2001) Accred Qual Assur 6:290–294
29. Wise SA, Benner Jr BA, Christensen RG, Koster BJ, Kurz J, Schantz MM, Zeisler R (1991) Environ Sci Technol 25:1695–1704
30. Jorhem L (1998) Fresenius J Anal Chem 360:370–373
31. Jorhem L (2004) Accred Qual Assur 9:305–310
32. Jorhem L, Engman J, Schröder T (2001) Fresenius J Anal Chem 370:178–182
33. ISO Guide 33 (2000) Uses of certified reference materials. International Organisation for Standardisation (ISO). Geneva, Switzerland
34. van der Veen AMH (2003) Accred Qual Assur 8:555–558
35. Linsinger TPJ (http://www.erm-crm.org/ermcrm/jsp/documents/ERM_application_note_1.pdf)
36. Neidhart B, Wegscheider W (eds) (2001) Quality in chemical measurements-Training concepts and teaching materials. Springer, Berlin Heidelberg New York
37. Katz SA (2002) J Radioanal Nuclear Chem 251:3–5
38. Ebdon L, Pitts L, Cornelis R, Crews H, Donard OFX, Quevauviller Ph (2001) Trace element speciation for environment, food and health. Royal Society of Chemistry, London
39. Emons H (2001) Fresenius J Anal Chem 370:115–119
40. Wells DE (1998) Analyst 123:983–989
41. Gawlik B, Linsinger T, Kramer G, Lamberty A, Schimmel H (2001) Fresenius J Anal Chem 371:565–569
42. Eljarrat E, Barceló D (2003) Trends Anal Chem 22:655–665
43. Bercaru O, Gawlik BM, Ulberth F, Vandecasteele C (2003) J Environ Monit 5:697–705
44. Directive 2000/60/EC of the European Parliament and of the Council. OJ L 327:1–72
45. Decision 2455/2001/EC of the European Parliament and of the Council. OJ L331:1–5
46. Lopez de Alda MJ, Díaz-Cruz S, Petrovic M, Barceló D (2003) J Chromatogr A 1000:503–526
47. Roose P, Brinkman UATh (2005) Trends Anal Chem 24:897–926
48. Barceló D (ed) (2004) Emerging organic pollutants in waste waters and sludge. Springer, Berlin Heidelberg New York