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Sediment certified reference materials
by V. Cheam

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**Bioassessment of
Aquatic Sediment
Quality**

Edited by
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SEDIMENT CERTIFIED REFERENCE MATERIALS

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ABSTRACT

A review was made of the world's certified sediment reference materials, which are available for use as calibration standards or quality control samples in chemical analysis of toxic metals and organics. The review traces the development of these important standards back to around the turn of the 20th century. The complete developmental process from the initial plan to certification process and delivery to end-users was given. Recommendations on developing new ones were also given. (EC business line = clean environment).

MANAGEMENT PERSPECTIVE

Title: Sediment Certified Reference Materials

Authors: V. Cheam

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EC Priority/Issue: This is part of Environment Canada's Action Plan (Conserving Canada's Ecosystems) addressing the sediment certified reference materials, its development, its availability and its uses.

Current Status: There are several organizations around the world, which develop sediment reference materials. Still more are needed to satisfy the innumerable matrices and contaminant concentrations worldwide.

Next Steps: Find cost-effective ways to develop new certified reference materials.

Matières de référence certifiées pour les sédiments

RÉSUMÉ

On a examiné les matières de référence certifiées pour des sédiments offertes dans le monde pour l'étalonnage ou comme échantillons de contrôle de la qualité, pour l'analyse chimique de métaux et de composés organiques toxiques. Cette étude fait l'historique du développement, depuis le début de XX^e siècle environ, de ces étalons qui jouent un rôle important. Elle présente le processus de développement complet, du plan initial au processus de certification et à la prestation de services aux utilisateurs finals, ainsi que des recommandations pour le développement de nouvelles matières de référence (secteur d'activité « Un environnement sain » d'EC).

SOMMAIRE À L'INTENTION DE LA DIRECTION

Cette étude fait partie du Plan d'action d'Environnement Canada (Conservation des écosystèmes au Canada), qui porte sur les matières de référence certifiées utilisées pour les sédiments, leur développement, leur disponibilité et leurs utilisations.

Plusieurs organisations du monde entier développent des matières de référence pour les sédiments, et beaucoup d'autres sont requises pour répondre aux besoins dus aux innombrables matrices et concentrations de contaminants dans le monde entier.

On recherche des méthodes économiques pour le développement de nouvelles matières de référence certifiées.

chapter five

Sediment certified reference materials

Venghuot F. Cheam

5.1 Introduction

It is often said that bad data are worse than no data at all. After all, bad data lead to bad conclusions and decision making. "Even under very conservative estimates, costs resulting from unreliable measurements run into billions of dollars per year" (Cali, 1976). On the other hand, it can also be said that data are as good as the quality assurance associated with the data generation process. It is not sufficient to merely generate data. The data must be ensured as reliable and interpreted with wisdom and understanding.

Although the funds allocated for environmental studies have steadily increased over the past two to three decades, more dramatic is the increase in the fraction of those funds dedicated to quality assurance/quality control (QA/QC) programs, which have been designed to pursue data reliability. For instance, funds for the development of clean rooms, certified reference materials (CRMs), more sensitive instruments, and more reliable analytical methods are just a few examples of resources allocated for QA/QC.

An effective QA program, whose primary aim is to ensure that the generated analytical data are a true, authentic representation of the sample content just before the sampling takes place, comprises several domains. Some key ones are the following (Uriano and Gravatt, 1977; Hunter, 1980; Lawrence et al., 1982; Chau, 1983; Taylor, 1985):

1. Sample integrity
2. Analytical methods
3. Well-trained and experienced analysts
4. Intralaboratory QC program
5. Interlaboratory QC program

Sample integrity is the first and foremost domain that must be assured, for if it falters, the rest of QA is immaterial or, at best, relative. Sample integrity is achieved by using proven procedures/protocols for labware cleaning, type of containers, sampling procedure, procedure and field blanks, preservation, clean room practice, and properly trained personnel. Each procedure is specific to a class of analytes of interest. For example, containers for samples collected for the determination of trace metals require a specific, lengthy acid-cleaning procedure (Tramontano et al., 1987), which is different from the cleaning procedure for containers for samples collected for the determination of organic contaminants. Similarly, containers for samples collected for the determination of trace metals should generally be plastic, whereas those for samples for the determination of organic contaminants should be made of glass. If a certain procedure becomes dubious with time, an improved or new one must be developed and ascertained.

Analytical methods must be properly developed and validated against pertinent CRMs and reference methods. The proper methods and equipment in sound working condition are the right tools for an effective QA program.

Well-trained and experienced analysts are another prerequisite, as they have acquired the expertise and the maturity to effectively apply the various facets of interweaving procedures. It has often been observed via interlaboratory QC studies that laboratories which consistently perform well with experienced analysts would perform less well with freshly trained analysts.

Intralaboratory QC is a fundamental routine that a laboratory must establish and follow to assure in-house operations are in control. Key QC activities incorporate proper/acceptable blank, duplicate run, spike recovery, control charts, uniformly spaced standard recalibration, confirmation by another validated method, and use of relevant CRMs. An intralaboratory QC program without pertinent CRMs, no matter how rigorous it may be, may provide in-house (i.e., within-laboratory) precision but not necessarily accuracy and thus not necessarily data reliability. Therefore, the QC program should also include development of pertinent in-house/secondary reference materials (even certified ones), if such CRMs are not available commercially.

Interlaboratory QC must also be an integral part of an effective QA program, for even if the above aforementioned four domains are in check, the data are generated from only one laboratory, one method, and possibly one analyst. No laboratory can exist in isolation without outside interaction. It must know its performance with respect to its counterparts. This involves participating regularly in one or more multilaboratory intercomparison studies to assess the effectiveness of its in-house QC and to obtain a measure of performance among peers (Cheam et al., 1988; Quevauviller et al., 1994a,b; others discussed in more detail below). Again, an interlaboratory study may

provide interlaboratory (between-laboratory) comparability but not necessarily accuracy and thus not necessarily data reliability if pertinent CRMs are not incorporated in the study or used somewhere in the process. Intercomparison studies are usually run by a qualified "QA group," which has several important activities, one of which is the development of pertinent CRMs (Lawrence et al., 1982; Community Bureau of Reference, 1994; Analytical Quality Control Services, 1995).

From the above, it is obvious that CRMs are a key requirement in most of the above domains. Many authors have dealt with the subject of reference materials, for example, Cali et al. (1975), Taylor (1985), Roelandts (1989), Cantillo (1992), Govindaraju (1994), and Willie and Berman (1994). This chapter deals specifically with sediment CRMs in more detail. Sediment CRMs are relatively young compared to other types of CRMs. The first sediment reference material was issued only some 70 years after the first, mostly industry related, CRMs were on the market at the turn of the century, when environmental issues were not as important as they are at present. The preparation, certification, literature review, and availability of most, if not all, sediment CRMs listed in the scientific literature are presented in this chapter. Readily useful information on each CRM is given to assist analysts in identifying the appropriate ones for their applications.

5.2 Certified reference materials: literature review

The National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards) issued the first four NIST Standard Reference Materials (SRMs) for cast iron in chip form in 1906, one of which (SRM 4M) has been reissued numerous times and is still in use to provide accuracy for the determination of gray cast irons (Cali, 1976; Uriano, 1980). NIST has been the largest producer of CRMs in the world. (Note that the term SRM refers to a CRM produced and issued by NIST). By 1911, approximately 140 SRMs had been produced for purity or compositional determination of steels, ores, brasses, and sugars or for combustion applications. By 1951, NIST had about 500 different CRMs available. In 1979, some 38,000 SRMs were distributed. In England, a number of metal and ore reference materials had been issued as "British Chemical Standards" by 1920 (Uriano, 1980).

Globally, there has been a rapid increase in the development of CRMs in recent years, particularly in developed countries. Different types of CRMs exist for physical properties such as surface area, color, wavelength, etc.; for compositional properties, such as organic and inorganic substances in various media; and for engineering properties, such as sieve sizing, color standards, etc. CRMs also exist in all three states: gaseous (e.g., N₂, Ar, etc.), liquid (e.g., sea water, fresh water, etc.), and solid (e.g., tissues, rocks, soils, sediments, etc.) (Uriano and Gravatt, 1977, 1980; Taylor, 1985; Cantillo, 1992;

Willie and Berman, 1994). The first sediment CRM may have been NIST-SRM 4350, a river sediment certified for 12 radionuclides which was issued around the mid-1970s (Cali, 1976). The development of sediment CRMs intensified with an increase in research studies on aquatic sediments, whether of a geochemical nature, interactions at the sediment-water interface or interstitial waters, or sediment dredging/disposal regulatory tests. Diversified sediment studies require diversified sediment matrices, analytes, and concentration levels. The more diversified CRMs are, the more one of them is closer to the ideal state of matrix and concentration matching with samples. This should maximize the accuracy of measured analytical data.

Manheim et al. (1976) of the U.S. Geological Survey (USGS) reported a marine sediment standard, MAG-1, a gray-brown very fine-grained clayey mud collected from the Wilkinson Basin of the Gulf of Maine. It was the first sediment standard of its kind among the many rock standards reported since 1951 (Fairbairn et al., 1951). Note that the hot spring deposit sample, GXR-3 of the USGS, reported by Alcott and Lakin (1975) could be considered and included as a sediment reference material. However, there appears to be some significant variation between bottles, and much caution should be exercised when using it (Govindaraju, 1994).

NIST issued another certified river sediment reference material, SRM 1645, dated November 1978 (National Bureau of Standards [NBS], 1978). The SRM was prepared from dredged bottom sediment of the Indiana Harbor Canal, Chicago, Illinois. Other sediment CRMs are SRM 1646 and SRM 2704 for inorganic constituents; SRM 1941 and SRM 1939 for polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs); and SRM 4350, SRM 4350B, and SRM 4354 for radionuclides.

For over 30 years, the International Atomic Energy Agency (IAEA) in Austria, through Analytical Quality Control Services (AQCS), has initiated and supported improvements in the accuracy of analytical chemistry and radiometric measurements and their traceability to basic standards. They carried out an intercomparison run in 1977 on a candidate CRM sediment sample, SL-1. The sediment was collected at the Sardis Reservoir, Panola County, Mississippi (IAEA, 1977; Dybczynski and Suschny, 1979). SL-1 was certified and distributed in 1981 (IAEA, 1980; AQCS, 1992). Other sediment CRMs include SL-3, IAEA-356, and SD-M-2/TM for inorganic constituents; IAEA-356 for methyl mercury and IAEA-357 for PAHs, PCBs, and other organics; and SL-2, SD-N-2, IAEA-135, IAEA-300, IAEA-313, IAEA-314, IAEA-315, IAEA-367, and IAEA-368 for various radionuclides.

The Canadian Certified Reference Materials Project (CCRMP), administered by the Canada Centre for Mineral and Energy Technology (CANMET), Ottawa, Ontario, had its beginning in 1955; by 1962, it had released for sale three phosphor bronze discs (Steger, 1984). Several rocks, soils, and slag reference materials had also been issued (Steger, 1980). In about 1983, eight sediment samples were proposed in collaboration with the Geological Survey of Canada (Abbey, 1983): four of lake origin (LKSD-1 to LKSD-4) and

four of stream origin (STSD-1 to STSD-4). Lynch (1990) and Bowman (1990) published provisional values for both total and extractable metal constituents for all eight sediment samples.

The National Water Research Institute (NWRI), Burlington, Ontario, initiated its development of reference standards for waters and sediments in about 1975, and by 1979 the first paper of a series on the preparation and purification of photomirex was published (Chau and Thompson, 1979). Preparation of the first sediment reference materials, WQB-1 and WQB-2, was initiated in 1974 (NWRI, 1988), and its certification was finished in 1983 (Cheam and Chau, 1984; NWRI, 1990a). Other sediment CRMs for both organic and inorganic parameters followed (NWRI, 1990b,c, 1992a,b,c, 1995b): EC-1, EC-2, and EC-3 for PAHs, PCBs, and chlorobenzenes; DX-1 and DX-2 for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); WQB-3 for trace metals; and several other uncertified sediment reference materials.

Since 1981, the National Research Council of Canada (NRCC), Ottawa, Ontario, has issued more than 30 matrix standards and CRMs for shellfish toxins, PCBs, PAHs, PCDDs, PCDFs, organometallics, and trace metals (Berman et al., 1994). The first sediment CRMs released were MESS-1 and BCSS-1, which were announced in the *Geostandards Newsletter* in 1981 by Berman. Preparation of these two materials began in 1978 (Guevremont and Jamieson, 1982). Other sediment CRMs are MESS-2, BEST-1, and PACS-1 for inorganic parameters (PACS-1 is also for organotin); CS-1, HS-1, and HS-2 for PCBs and PCB congeners; and several uncertified sediment reference materials.

The Community Bureau of Reference (BCR, presently Measurements and Testing Programme) of the European Commission has produced various CRMs over the last 15 years (Quevauviller, 1994). These materials are of environmental matrix, food and agriculture, biomedical, physical properties, and industrial raw materials (BCR, 1994 and 1995 addendum). The coastal sediment CRM 462 was successfully certified via a recent interlaboratory study for di- and tributyltins (Quevauviller et al., 1994a). Other sediment materials include CRM 277 (estuarine sediment), CRM 280 (lake sediment), and CRM 320 (river sediment).

The National Institute for Environmental Studies (NIES) of the Japan Environmental Agency has produced a number of CRMs for the past several years, such as chlorella, vehicle exhaust particulates, rice flour and fish tissue, and a pond sediment called NIES No. 2 (NIES, 1981; Iwata et al., 1983a,b; Okamoto and Fuwa, 1985). The sediment was collected from the surface of the bottom of Sanshiro pond within the grounds of Tokyo University in 1977 and was certified in July 1981.

The South African Committee for CRMs (SACCRM) was appointed in 1974 to direct the production of reference materials and has produced several rock standards (SACCRM, 1992; Ring, 1993; Frick, 1981). In addition to these, three stream sediment CRMs (i.e., SARM-46, SARM-51, and SARM-

52) were prepared in 1978 and were apparently certified in 1992 (Ring, 1993).

The Institute of Geophysical and Geochemical Exploration (IGGE) and the Institute of Rocks and Mineral Analysis (IRMA) of the People's Republic of China prepare and certify reference materials. The first eight stream sediment samples, GSD 1 to 8, were prepared in 1980 (Mingcai et al., 1980) and certified in 1983 using interlaboratory data (Xie et al., 1985a). Another suite of four stream sediments, GSD 9 to 12, as well as eight soil samples and six rock samples were collected and processed between 1980 and 1983 (Xie et al., 1985b) and certified in 1989 (Xie et al., 1989).

The Geological Survey of Japan issued 17 rock reference samples, igneous rock series, in 1986 and 1989 (Ando et al., 1987, 1989). Another suite of rock reference samples, sedimentary rocks series, started in 1986 and was issued in 1989. The latter series included four sediment samples: a lake sediment (Jlk-1) and three stream sediments (Jsd-1, Jsd-2, Jsd-3) (Terashima et al., 1990).

In 1975, the Research Institute of Applied Physics (RIAP), Irkutsk, Russia, and the Institute of Oceanography of the Russian Academy of Sciences jointly began investigation of three marine sediment reference samples, SDO-1, SDO-2, and SDO-3. Berkovits and Lukashin (1984) reported the certification of the three samples, certified for major, minor, and trace elements. Berkovits et al. (1991) reported a series of 19 certified reference samples for clay, nodule, crust, etc. and four sediments, coded OOKO201-04, using the data from a collaborative study involving more than 100 laboratories. Preparation of the latter sediment samples, which are called anomalous and background sediments, was started in 1983 jointly by RIAP and the Institute of Geochemistry (Siberian Branch).

5.3 Developmental procedures for certified reference materials

5.3.1 Criteria for selecting a certified reference material

In selecting a CRM for use in a QA domain, a set of practical criteria should be met (Uriano and Gravatt, 1977; International Organization for Standardization, 1981; Chau, 1983; Taylor, 1985). It is scientifically sound for a CRM to:

1. Have the certified values of analytes (properties) reliably derived
2. Be homogeneous and stable with respect to analytes of interest
3. Have a comparable matrix to that of the samples
4. Have certified analyte concentrations comparable to those in the samples
5. Specify minimum usable weight and handling instructions
6. Have authentic traceability

A certified value (or best estimate of the true value, or a recommended value) of a property should be obtained using a dependable certification procedure and provided with a statistically derived uncertainty or confidence level. Ideally, both the matrix and analyte concentrations of the CRM should be identical to those of the sample to maximize the accuracy of the measurement. In reality, however, it seems inconceivable or even unreasonable to consider that such an ideal situation ever exists; therefore, in practice, one would often be forced to aim for a close match of the CRM and sample properties. For example, in analyzing lake sediment samples, it makes sense to choose one or more lake sediment CRMs rather than marine sediments or, even worse, plant/fish CRMs. Also, if the sediment samples are contaminated, CRMs collected at contaminated sites should be used to satisfy the criteria of similar matrix and analyte concentration. Instructions such as minimum weight to be used (e.g., 0.1 or 0.5 g), storage conditions (e.g., -20 or 4°C), drying before use (e.g., 110°C for 2 hr in a desiccator over P_2O_5), or how mixing should be carried out prior to the use of the CRM are necessary to preserve the integrity of CRMs. Should new findings generate uncertainty, a CRM's authentic certificate of analysis or other publications become important documents and should be used to trace the certification process to its source. The above criteria are also useful in the planning and preparation of CRMs intended for certain specific applications (see below).

A reference material (RM) is defined here as a material that has been prepared by exactly the same procedure as a CRM (see below) and sufficiently characterized to provide a certain degree of confidence in the value(s) of one or more properties. However, none of its properties have been certified.

5.3.2 Procedures for preparing a sediment reference material.

5.3.2.1 Selection of suitable sampling site

Background information on potential sites for collecting sediment should be obtained from the literature. The properties of interest, such as matrix, presence, and levels of certain analytes, should be considered and carefully evaluated. Preliminary in-house analyses should be made, if called for, to clarify the presence and concentrations of different analytes before the actual sampling takes place, to ensure beforehand that the key requirements specified in the above selection criteria are satisfactorily met.

5.3.2.2 Sample collection

This topic has been adequately dealt with by Mudroch and Azcue (1995).

5.3.2.3 Drying

Preliminary drying is essential because it removes about 50% of the water from the sediment. The wet sediment is first frozen at -20°C for a minimum of 4 days in galvanized garbage containers. The containers are then brought out of the cold room and pierced uniformly to make 50 to 100 holes about

5 mm in diameter. The sediment is allowed to thaw at room temperature for at least 3 days, during which time the water drains out, leaving the sediment in a semi-dried state. The partially dried sediment is then subdivided into lots of 20 to 25 kg, which are then freeze-dried at reduced pressure and an elevated temperature in a freeze-drying oven (Chau and Lee, 1980; Cheam and Chau, 1984).

Air-drying on filter paper for about 2 weeks has also been practiced following preliminary drying by suction to remove the sediment pore water (NIES, 1981). Quevauviller et al. (1994a) first air-dried their candidate sediment for 7 days at room temperature on a cotton sheet, followed by air-drying at 55°C for 100 hr.

5.3.2.4 *Homogenization and homogeneity test on bulk sediment*

The aggregated dried sediment is then ground and sieved through a series of vibrating screens of ascending mesh size, such as a 50-mesh or 300- μm sieve, followed by a 100-mesh or 150- μm sieve, a 200-mesh or 71- μm sieve, and a 325-mesh or 45- μm sieve. The sieved sediment is then combined and blended, for example, in a 600-L conical steel blender for several hours (usually 8 hr) or until the sample homogeneity is adequately proven (Epstein et al., 1989; Ring, 1993). Some examples of the final screen size used are 100 mesh for the river sediment SRM 2704 (Epstein et al., 1989); 200 mesh for the pond sediment NIES No. 2 (NIES, 1981), for a Great Lake sediment WQB-1 (Cheam and Chau, 1984), and for stream sediments GSD 1 to 8 (Xie et al., 1985a); 325 mesh for a lake sediment for PCBs analysis (Chau and Lee, 1980); and 75- μm sieve (Ring, 1993; Quevauviller et al., 1994a).

Before bottling (i.e., subsampling) can take place, homogenization of the bulk sediment must be demonstrated. The homogeneity test is usually performed by using an analysis of variance (ANOVA) for most, if not all, of the analytes of interest. Even though their analysis showed sample homogeneity with respect to sodium and silicon, Epstein et al. (1989) had to reblend their sediment because of the observed bottle-to-bottle inhomogeneity for Cr and Fe. An established homogeneity test for ore reference materials (Sutarno and Faye, 1975) was successfully used for demonstrating the homogeneity of a bulk sediment to be certified for As, Se, and Hg (Cheam and Chau, 1984). Six samples were taken from the bulk sediment in the blender: two from the top, two from the middle, and two from the bottom. Five replicate analyses were made on each sample and for each of the three elements. The two-way ANOVA technique (Snedecor and Cochran, 1967), which tests for compatibility of all between-bottle and within-bottle means, was performed on each of the three 6×5 matrices of analytical results (one matrix of results per element). The calculated variance ratios (F) for both between-bottle and within-bottle effects were found to be smaller than the critical values at a 95% confidence level, which indicates bulk sample homogeneity. Had the test shown sample inhomogeneity, the bulk sample would be reblended until satisfactory homogeneity was achieved. It is noteworthy

that if the test showed inhomogeneity with respect to, for example, Hg, the certification process could still continue, but only for As and Se.

5.3.2.5 *Subsampling and homogeneity test on subsamples*

Subsampling of a predetermined amount of sediment, usually within the range of 10 to 100 g, is then done in precleaned glass or plastic bottles. Because bottling can take several days for a few hundred kilograms of material, frequent mixing of the bulk sediment should be carried out during bottling to ensure identical sample representation in each and every bottle. The bottled subsamples are then radiation sterilized with 2 to 2.8 Mrad of ^{60}Co to minimize biodegradation which may occur by microbiological activities (NIES, 1981; Epstein et al., 1989). Instead of radiation sterilization, Quevauviller et al. (1994a), in their certification of butyltins, recommended heat sterilization at 120°C for 2 hr following drying at 60°C for 48 hr, followed by grinding and sieving of a sediment CRM candidate. These authors and Epstein et al. (1989) subsampled the sediment after the sterilization process. Xie et al. (1989) also used heat sterilization at 120°C for 24 hr for their stream sediments certified for 72 inorganic constituents.

During bottling, a finite fraction of bottles (e.g., 1 out of every 50 bottles) is systematically put aside for testing the homogeneity of subsamples to ensure that all subsamples are the same. These samples are then analyzed for each or most of the analytes of interest. If the coefficient of variation for the analytical results of an analyte is within a set limit (e.g., $\pm 5\%$) the subsamples are considered homogeneous with respect to that specific analyte. The stability study and the certification process can follow simultaneously.

5.3.2.6 *Storage and stability*

Sediment materials intended for the determination of organic compounds are usually stored at -20°C. For the determination of butyltins, the sediments are stored at 4°C in the dark (Quevauviller et al., 1994a). For trace metals, it is usually sufficient to store the materials in a cool room in the dark. Long-term stability of the properties of interest must be monitored and confirmed. For example, the long-term stability of PCBs, chlorobenzenes, and PAHs for two sediment CRMs stored at 4°C in the dark has been recently reported to be holding for more than 10 years (Stokker and Kaminski, 1995).

5.3.3 *Procedures for certifying a sediment reference material*

There are several certification procedures used by the various CRM-producing agencies.

5.3.3.1 *Definitive method within a laboratory*

A definitive method is defined as "the most accurate method available to measure a given chemical property" (Uriano and Gravatt, 1977). This procedure is preferred by NIST for certifying its reference materials (SRMs, which are CRMs specific to NIST). However, other producers call such

materials CRMs. The method used at NIST is two or more analysts working independently to obtain the true concentration of analytes, where the uncertainty is basically the precision of the method. An example of a definitive method is isotope dilution mass spectrometry, used to determine calcium in serum (Moore and Machlan, 1972). This method was also used to certify thallium, thorium, and uranium in the river sediment reference material SRM 1645. The CCRMP also uses this approach to certify the uranium content in three ores (Steger, 1984). A variation of this procedure is the use of a definitive method by two or more laboratories.

5.3.3.2 Two or more independent, reliable methods within a laboratory

This procedure is presently more popular than the definitive method procedure, judging from the various certificates of analysis which show that two or more methods have been used to certify the concentrations of most analytes. The procedure has been used extensively by NIST and the NRCC. The methods are usually used within the CRM-producing laboratory, but sometimes a few selected outside laboratories contribute some data. The certified concentrations are usually the means or weighted means of the pooled results, and the uncertainties are expressed as 95% prediction interval plus an allowance for systematic error among the methods used (NIST, 1990a) or 95% tolerance limit for an individual subsample (NBS, 1978). This limit means that 95% of the subsamples from any bottle would give concentrations within the specified range 95% of the time. The NWRI also uses this procedure, in addition to using interlaboratory results, for confirmation, as discussed further in Section 5.3.3.5.

5.3.3.3 Interlaboratory comparison studies

This approach is used by several agencies such as the IAEA (Austria), BCR (Belgium), CANMET (Canada), IGGE in collaboration with the IRMA (China), NIES (Japan), RIAP (Russia), and Council for Mineral Technology (South Africa). Each agency uses its own statistical analysis to treat the data leading to certification of the tested material.

The originating agency, such as the IAEA, organizes and distributes the candidate material to the participating laboratories, which report the analytical results from replicate analyses back to the agency within a specified time (e.g., 3 to 6 months). Materials "which have one or more properties sufficiently well established from statistical evaluation of previous interlaboratory comparison studies..." become reference materials with specified reference values and confidence intervals (AQCS, 1994). The BCR also organizes and runs interlaboratory (i.e., round-robin) studies involving expert laboratories of the member states using different methods to acquire data which are then statistically treated to obtain best estimate values (mean of all acceptable data) and uncertainties which are the half-width of the 95% confidence intervals (BCR, 1994; Quevauviller et al., 1994a,b).

CANMET also utilizes the interlaboratory procedure, where a consensus approach is used for certification. Each of the "at least ten" participating laboratories uses its method of choice. Before the consensus values (i.e., usually the mean values) can be calculated, the interlaboratory data must meet a set of certification criteria. A set of results with very high imprecision and the outliers (i.e., results which differ by more than twice the standard deviation of the overall mean) are rejected. A one-way ANOVA is then used to compute the consensus value and its variance (Steger, 1980, 1984).

The IGGE initiated the preparation of eight stream sediment reference materials (GSD 1 to 8) in 1978. The collaborative study started in 1980–81 with 41 participating laboratories in China using different methods. The sediments were certified in 1983, and the recommended values for 50 minor and trace elements were derived by a method of repetitive elimination of outliers and calculation of a central "tendency" from several central values (Xie et al., 1985a). Three other stream sediments were prepared and certified in 1989 by the IGGE in collaboration with the IRMA (Xie et al., 1989). Forty-five laboratories participated in the last certification exercise, which resulted in 72 certified values for major, minor, and trace elements. The IRMA also certified a marine sediment, GSMS-1 (Wang, 1994).

The NIES issued a certified pond sediment reference material in 1981. Each certified value was based on interlaboratory results from at least three independent methods used by 20 to 30 qualified participating laboratories (NIES, 1981; Iwata et al., 1983a,b; Okamoto, 1994; Okamoto and Fuwa, 1985). The uncertainty was estimated based on two standard deviations of the mean of acceptable values and the 95% confidence intervals for the mean of individual methods.

The Council for Mineral Technology (MINTEK) of the South Africa Bureau of Standards had 19 laboratories in five countries participating in the analytical program. Each laboratory uses its own method. A certified value is assigned to a constituent using the Gastwirth median of a data set which has met four predetermined criteria and which has a slightly skewed distribution (Ring, 1993).

RIAP had 32 Soviet, 1 Czechoslovakian, and 1 Bulgarian laboratories participating in the interlaboratory study to certify three marine sediments, SDO-1, SDO-2, and SDO-3 (Berkovits and Lukashin, 1984; Berkovits et al., 1984, 1991). Each certified value was determined as a weighted average, with the 95% confidence level estimated on the basis of Chebyshev's inequality. For certification of other sediments (the OO series), 113 laboratories participated (Berkovits et al., 1991).

The interlaboratory approach is a multilaboratory, multimethodology approach, where the certified values are obtained based solely or mainly on intercomparison results. A variation would be the use of a multilaboratory, single definitive method approach.

5.3.3.4 *Select laboratories method*

Several authors recognize that subjective judgment is on occasion chosen over rigorous statistical considerations and that the interlaboratory approach has its pitfalls, namely, interlaboratory factors, which cause discrepancies in analytical data (De la Roche and Govindaraju, 1969; Ingamells, 1978; Steele et al., 1978; Morrison, 1980). The select laboratories method, introduced by Abbey (1970) and continually refined by Abbey (1983), addresses these factors in a constructive manner. The method is based on three principles, which are, according to Abbey (1983):

1. All results for a given constituent in a given sample are classified as "good," "fair," or "poor" on the basis of their position.
2. Each contributing laboratory is given a rating, based on its relative numbers of good, fair, and poor results.
3. Only the results reported by laboratories with ratings above a specified level are used in arriving at the desired value.

This procedure reduces the original data to a relatively small group of selected results, presumably from good laboratories, thus minimizing the systematic errors which are often prominent in interlaboratory studies. Xie et al. (1989) used this method to confirm their best estimated values calculated from several central values.

5.3.3.5 *"Quasi-interlaboratory" procedure*

At the NWRI, the interlaboratory studies form part of the certification process, but their results are used for confirmation only, to provide laboratory performance, or as an additional data set to the pooled data, the bulk of which comes from in-house analyses and selected, contracted laboratories of known performance. A minimum of two independent, reliable methodologies must be used, and the compatibility of the methodology must be no less than 10% most of the time (Cheam and Chau, 1984; Lee et al., 1986, 1987; Lee and Chau, 1987; Cheam et al., 1989; Stokker and Kaminski, 1995). In certain cases, such as Se determination, the compatibility of three independent methodologies was high (i.e., 25%, resulting from three independent groups of results of 1.02, 1.11, and 1.31 $\mu\text{g/g}$ of Se). However, it was considered acceptable due to both the low level of Se and the recognized difficulty of Se analysis (Cheam et al., 1989). In the certification of metals in sediments, a methodology refers to a group of methods that use one type of instrument/spectrometer; for example, atomic absorption spectrometric methodology can include several different methods using an atomic absorption spectrometer as the base instrument of detection, whereas GC-FID and GC-MS are taken as two different methods in the determination of organic compounds (Lee et al., 1987), and GC-ECD/ultrasonic extraction and GC-ECD/Soxhlet extraction under various conditions are considered to be different methods (Lee and Chau, 1987).

5.3.3.6 Single method, single laboratory

Terashima et al. (1990, 1992) of the Geological Survey of Japan used one method, presumably in-house, to certify a series of sedimentary rocks, including four aquatic sediments.

5.4 Discussion, recommendations, and conclusions

5.4.1 Role of certified reference materials

The role of CRMs has been previously discussed at length by several authors (Cali et al., 1975; Uriano and Gravatt, 1977; Taylor, 1985). CRMs are essentially used for:

1. Intralaboratory QC to ensure accuracy of analyses
2. Calibration of an instrument or a measurement process
3. The primary standard for determination of a chemical
4. Interlaboratory QC to determine method accuracy and method compatibility and to help establish certified values for CRM candidates
5. Method development/evaluation to ascertain method accuracy
6. Development of new CRMs or secondary reference materials
7. Direct primary calibration in the field (Uriano and Gravatt, 1977)

5.4.2 Sediment certified reference materials

Table 5-1 lists the sediment reference materials which have recommended trace metal values reported in a recent extensive compilation of 383 geostandards by Govindaraju (1994), as well as other sediment CRMs not listed in the compilation. For each CRM, the sediment type, name, producer, origin, and a key reference are given. Table 5-2 summarizes the recommended values for the 13 U.S. Environmental Protection Agency priority elements for each of the CRMs listed in Table 5-1. The major, minor, and other trace elements are too numerous to be included here.

Table 5-3, following the same format as Table 5-1, shows sediment CRMs for organic compounds which have recommended values reported in a large compilation report by Cantillo (1992), as well as in the latest information sheets and journal publications. Table 5-4 gives the recommended values for each of the certified analytes and for each CRM listed in Table 5-3. Organometallics are also incorporated in these two tables.

Table 5-5 lists the sediment CRMs for radionuclides, again using the format of Table 5-1. Table 5-6 gives the recommended values for each of the certified analytes and for each CRM listed in Table 5-5.

5.4.3 Sediment certified reference materials in preparation

During the preparation of this chapter, several sediment samples were, or will be, prepared for future CRMs. The following is a list of some of them:

Table 5-1 Sediment Certified Reference Materials for Inorganic Parameters

CRM type	Name	Producer ^a	CRM origin	Reference
Anomalous sediment	OOKO201	RIAP	Yakut SSR (N-E part): Composite of two portions of loose sediments, subsoil horizon (Yakutia)	Petrov et al., 1988
	OOKO204	RIAP	Yakut SSR (N-E part): Composite of three portions of loose sediments, subsoil horizon (Yakutia)	Petrov et al., 1988
Background sediment	OOKO202	RIAP	Yakut (N-E part): Subsoil horizon of Aldan Region, Yakutia (fine sand-clay)	Petrov et al., 1988
	OOKO203	RIAP	Yakut (N-E part): Subsoil horizon of Oymyakon region, Yakutia (fine sand-clay)	Petrov et al., 1988
Coastal sediment Estuarine sediment	IAEA-356	IAEA	"Hot spot," polluted marine sediment	AQCS, 1994, 1995
	CRM 277	BCR	Lyophilized sediment from the Scheldt Estuary	BCR, 1994
	BEST-1	NRCC	Sediment from the Beaufort Sea (Hg only)	NRCC, 1990
	MESS-1	NRCC	Sediment from the Miramichi Estuary, Gulf of St. Lawrence	NRCC, 1981
	NBS1646	NIST	Dredged sediment from Chesapeake Bay	NBS, 1982
Lake sediment	CRM 280	BCR	Lyophilized sediment from Lake Maggiore	BCR, 1992
	Jlk-1	GSJ	Lake Biwa, freshwater lake sediment (sedimentary rock series), Shiga Prefecture, Japan	Terashima et al., 1990
	LKSD-1	CCRMP	Joe Lake and Brady Lake, Ontario (Canadian Shield: National Topographic System 31F and 31M)	Lynch, 1990
	LKSD-2	CCRMP	Composite sample: Calabogie Lake, Ontario, and two locations from Northwest Territories, Canada	Lynch, 1990
	LKSD-3	CCRMP	Composite sample: Calabogie Lake, two locations from Manitoba and six locations from Ontario	Lynch, 1990
	LKSD-4	CCRMP	Big Gull Lake, Ontario, Key and Sea Horse Lake, Saskatchewan, Canada	Lynch, 1990
	SL-1 SL-3	IAEA IAEA	Sardis Reservoir Panola County, Mississippi Sardis Reservoir Panola County, Mississippi	AQCS, 1994, 1995 AQCS, 1994, 1995

	WQB-1	NWRI	Lake Ontario sediment, Canada	Cheam et al., 1984
	WQB-3	NWRI	Sediment mixture from Hamilton Harbor (53 kg) and Lake Ontario (160 kg), Canada	Cheam et al., 1989
Marine mud	MAG-1	USGS	Very fine grey-brown bottom sediment from the Wilkinson Basin of the Gulf of Maine	Manheim et al., 1976
	GBW 07313	NRCCRM	Central part of Pacific, collected during the HY4-871 cruise of R/V Haiyang of the MGMR, China	IMG, 1990
	SD-M-2/TM	IAEA	Lyophilized, produced in cooperation with the regional seas program of UNEP	AQCS, 1994, 1995
	MESS-2	NRCC	Estuarine sediment from the Beaufort Sea	NRCC, 1994
	BCSS-1	NRCC	Estuarine sediment from the Bay des Chaleurs, Gulf of St. Lawrence	NRCC, 1994
	PACS-1	NRCC	Harbor sediment from Esquimalt Harbor in British Columbia, Canada	NRCC, 1994
	GSMS-1	IRMA	Central part of Pacific, cruise HY3-871, conducted by Haiyang IV, People's Republic of China	Wang, 1994
	SDO-1	RIAP	Eastern Pacific, 2962 m deep, dark grey and reduced viewed as terrigenous clay	Berkovits and Lukashin, 1984; Berkovits et al., 1991
	SDO-2	RIAP	Central Pacific near Hawaiian Islands, 4680 m deep, oxidized deep-sea clay	Berkovits and Lukashin, 1984; Berkovits et al., 1991
	SDO-3	RIAP	Red Sea, 1350 m deep, oxidized white-colored, calcareous ooze	Berkovits and Lukashin, 1984; Berkovits et al., 1991
Pond sediment	NIES 2	NIES	Surface sediment of Sanshiro Pond within university grounds, University of Tokyo, Japan	NIES, 1981
River sediment	CRM 320	BCR	Lyophilized sediment from the River Toce	BCR, 1994
	GBW 08301	NRCCRM	No information given	NRCCRM, 1992
	GSD-9	IGGE	River sediment in Yangtze River upstream from Wulham, Hubei Province, China	IGGE, 1986

Table 5-1 Sediment Certified Reference Materials for Inorganic Parameters (continued)

CRM type	Name	Producer ^a	CRM origin	Reference
River sediment (continued)	NBS1645	NIST	Dredged material from bottom of Indiana Harbor Canal near Gary, Indiana	NBS, 1978
	NBS2704	NIST	Collected from the bottom of the Buffalo River, by Ohio Street Bridge, Buffalo, New York	NIST, 1990a
Stream sediment	GBW 07309	NRCCRM	No information given	NRCCRM, 1992
	GBW 07310	NRCCRM	No information given	NRCCRM, 1992
	GBW 07311	NRCCRM	No information given	NRCCRM, 1992
	GBW 07312	NRCCRM	No information given	NRCCRM, 1992
	GSD-1	IGGE-IRMA	Tributary flowing through the biotite granite in Shanxi Province, China	IGGE, 1986
	GSD-2	IGGE-IRMA	Tributary flowing through the biotite granite in Jiangxi Province, China	IGGE, 1986
	GSD-3	IGGE-IRMA	Mixture of two sources from Jiangxi, China: porphyry deposit and phyllite rocks	IGGE, 1986
	GSD-4	IGGE-IRMA	From area of carbonate rocks in Anhui Province, China	IGGE, 1986
	GSD-5	IGGE-IRMA	Pond sediment from area of diorite, carbonate rocks in Anhui Province, China	IGGE, 1986
	GSD-6	IGGE-IRMA	From high and cold mountainous terrain of diverse rocks in Qinghai Province, China	IGGE, 1986
GSD-7	IGGE-IRMA	From lead-zinc area; drainage basin: mica schist, in Liaoning Province, China	IGGE, 1986	
GSD-8	IGGE-IRMA	From a region with acidic to intermediate volcanic rocks in Quangxi, China	IGGE, 1986	
GSD-9	IGGE-IRMA	River sediment in Yangtze River upstream from Wulham, Hubei Province, China	IGGE, 1986	
GSD-10	IGGE-IRMA	From a tributary draining carbonate rocks in Yishan, Guangxi Province, China	IGGE, 1986	

GSD-11	IGGE-IRMA	Various rocks from the Shizhuyuan ore field in Binzhou, Hunan Province, China	IGGE, 1986
GSD-12	IGGE-IRMA	From a tributary draining various rocks in Yangchun ore field Guangdong, China	IGGE, 1986
SARM46	MINTEK	Prepared by National Institute of Metallurgy and South African Geological Survey	Ring, 1993
SARM51	MINTEK	Prepared by National Institute of Metallurgy and South African Geological Survey	Ring, 1993
SARM52	MINTEK	Prepared by National Institute of Metallurgy and South African Geological Survey	Ring, 1993
JSd-1	GSJ	Composite sample of northern region, Ibaraki Prefecture, Japan	Terashima et al., 1990
JSd-2	GSJ	Composite sample of eastern region, Ibaraki Prefecture, Japan	Terashima et al., 1990
JSd-3	GSJ	Composite sample of central region, Ibaraki Prefecture, Japan	Terashima et al., 1990
STSD-1	CCRMP	Lavant Creek, Ontario, Canada (31F in National Topographic System)	Lynch, 1990
STSD-2	CCRMP	Hirok Stream Composite Sample 4, British Columbia, Canada (104F, 93A, 93B in NTS)	Lynch, 1990
STSD-3	CCRMP	Hirok Stream and Lavant Creek Composite Sample 4, Canada (104P, 31F, 93A, 93B in NTS)	Lynch, 1990
STSD-4	CCRMP	Composite Sample 5 and 4, Canada (31F, 93A, 93B in NTS)	Lynch, 1990

^a BCR = Community Bureau of Reference (now Measurements and Testing Program), Commission of the European Community, Belgium; CCRMP = Canada Centre for Mineral and Energy Technology, Certified Reference Material Project, Ottawa, Canada; GSJ = Geological Survey of Japan, Yatabe, Tsukuba, Ibaraki, 305 Japan; IAEA = International Atomic Energy Agency, Analytical Quality Control Services, Vienna, Austria; IGGE = Institute of Geophysical and Geochemical Exploration, Ministry of Geology, Beijing, China; IRMA = Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, People's Republic of China; MINTEK = Council for Mineral Technology, SABS, Pretoria, South Africa; NIES = National Institute for Environmental Studies, Yatabe-machi, Japan; NIST = National Institute of Standards and Technology, Gaithersburg, Maryland; NRCC = National Research Council of Canada; NRCCRM = National Research Center for CRMs, Beijing, China; NWRI = National Water Research Institute, Burlington, Ontario, Canada; RIAP = Research Institute of Applied Physics, Irkutsk State University, Russia; USGS = U.S. Geological Survey, Denver, Colorado.

Table 5-2 Certified Values for U.S. EPA Priority Elements
in Sediment Certified Reference Materials

CRM type	CRM name	Producer ^b	Recommended values for EPA priority elements ($\mu\text{g/g}$) ^a			
			Ag	As	Be	Cd
Anomalous sediment	OOKO201	RIAP	35	8000	4	9
	OOKO204	RIAP	2.3	60	-3	3
Background sediment	OOKO202	RIAP	0.06	—	2	—
	OOKO203	RIAP	0.1	40	2.1	—
Coastal sediment	IAEA-356	IAEA	8.4	26.9	—	4.47
Estuarine sediment	CRM 277	BCR	—	47.3	—	11.9
	BEST-1	NRCC	—	—	—	—
	MESS-1	NRCC	—	10.6	1.9	0.59
	NBS1646	NIST	—	11.6	1.5	0.36
Lake sediment	CRM 280	BCR	-1.2	51	-3.0	1.6
	JLk-1	GSJ	-0.205	27.7	2.9	1.5
	LKSD-1 ^c	CCRMP	0.6	40	1.1	—
	LKSD-2 ^c	CCRMP	0.8	11	2.5	—
	LKSD-3 ^c	CCRMP	2.7	27	1.9	—
	LKSD-4 ^c	CCRMP	—	16	1	—
	SL-1	IAEA	—	27.5	—	0.26
	SL-3	IAEA	—	3.2	—	—
	WQB-1	NWRI	—	23	—	-2.1
	WQB-3	NWRI	—	18.8	—	-3.85
Marine mud	MAG-1	USGS	-0.08	-9.2	3.2	0.202
Marine sediment	GBW 07313	NRCCRM	—	5.8	—	—
	SD-M-2/TM	IAEA	—	18.3	—	113
	MESS-2	NRCC	0.18	20.7	2.32	0.24
	BCSS-1	NRCC	—	11.1	1.3	0.25
	PACS-1	NRCC	—	211	—	2.38
	GSMS-1	IRMA	—	5.8	—	—
	SDO-1	RIAP	—	—	1.4	—
	SDO-2	RIAP	—	—	1.8	—
	SDO-3	RIAP	—	—	0.1	—
Pond sediment	NIES 2	NIES	—	12	—	0.82
River sediment	CRM 320	BCR	—	76.7	-2.5	0.533
	GBW 08301	NRCCRM	—	56	-3.5	2.45
	GSD-9	IGGE	0.089	8.4	1.8	0.26
	NBS1645	NIST	-1.76	66	-0.75	10.2
	NBS2704	NIST	—	23.4	—	3.45
Stream sediment	GBW 07309	NRCCRM	0.089	8.4	1.8	0.26
	GBW 07310	NRCCRM	0.27	25	0.9	1.12
	GBW 07311	NRCCRM	3.2	188	26	2.3
	GBW 07312	NRCCRM	1.15	115	8.2	4
	GSD-1	IGGE-IRMA	0.048	1.96	3	0.088
	GSD-2	IGGE-IRMA	0.066	6.2	17.1	0.065
	GSD-3	IGGE-IRMA	0.59	17.6	1.5	0.1
	GSD-4	IGGE-IRMA	0.084	19.7	2.4	0.19
	GSD-5	IGGE-IRMA	0.36	75	2.3	0.82

Table 5-2 Certified Values for U.S. EPA Priority Elements in Sediment Certified Reference Materials (continued)

Recommended values for EPA priority elements ($\mu\text{g/g}$) ^a								
Cr	Cu	Hg	Ni	Pb	Sb	Se	Tl	Zn
75	250	—	24	100	150	-2	1	390
29	240	—	18	150	-30	-0.2	-2	140
65	44	—	31	14	-0.4	-0.2	-0.6	54
120	50	—	55	15	-5	-0.2	-0.4	86
69.8	365	7.62	36.9	3.47	8.33	—	—	977
192	101.7	1.77	43.4	146	-4	2.04	—	547
—	—	0.092	—	—	—	—	—	—
71	25.1	—	29.5	34	0.73	0.34	—	191
76	18	0.063	32	28.2	0.4	0.6	0.5	138
114	70.5	0.67	73.6	80.2	-1.4	0.68	-0.7	291
69	59.8	—	36.9	45	—	—	1.11	1.51
31	44	—	16	82	1.2	—	—	331
57	37	—	26	44	1.1	—	—	209
87	35	—	47	29	1.3	—	—	152
33	31	—	31	91	1.7	—	—	194
104	30	—	44.9	37.7	1.31	—	—	223
—	—	—	—	—	0.56	—	—	—
—	-80	1.09	-59.3	-85.7	—	1.02	—	-279
—	-83.4	2.75	52	-243	—	1.15	—	1396
97	30	-0.017	53	24	0.96	1.16	-0.59	130
58.4	424	—	150	29.3	1.85	—	—	160
77.2	32.7	54	56.1	22.8	0.99	—	—	74.8
106	39.3	0.092	49.3	21.9	1.09	0.72	-0.98	172
123	18.5	—	55.3	22.7	0.59	0.43	-0.6	119
113	452	4.57	44.1	404	171	1.09	—	824
58.4	424	—	150	29.3	1.83	—	—	160
62	160	—	190	—	—	—	—	260
240	180	—	150	—	—	—	—	130
31	33	—	35	—	—	—	—	110
75	210	-1.3	40	105	-2	—	—	343
138	44.1	1.03	75.2	42.3	-0.6	0.214	-0.5	142
90	53	0.22	-32	79	—	0.39	—	-251
85	32.1	0.083	32.3	23	0.81	0.16	0.49	78
3	109	1.1	45.8	714	51	1.5	1.44	1720
135	98.6	1.47	44.1	161	3.79	1.12	1.06	438
85	32.1	0.083	32.3	23	0.81	0.16	0.49	78
136	22.6	0.28	30.2	27	6.3	0.28	0.21	46
40	78.6	0.072	14.3	636	14.9	0.2	2.9	373
35	1230	0.056	12.8	285	24.3	0.25	1.76	498
194	21.8	0.018	76	24.4	0.22	-0.11	0.61	79
12.2	4.9	0.04	5.5	32	0.46	-0.21	1.9	44
87	177	0.05	25.6	40	5.4	1.06	0.58	52
81	37.3	0.044	40	30.4	1.84	-0.28	1.2	101
70	137	0.1	34	112	3.9	-0.26	1.16	243

Table 5-2 Certified Values for U.S. EPA Priority Elements
in Sediment Certified Reference Materials (continued)

CRM type	CRM name	Producer ^b	Recommended values for EPA priority elements (µg/g) ^a			
			Ag	As	Be	Cd
Stream sediment (continued)	GSD-6	IGGE-IRMA	0.36	13.6	1.7	0.43
	GSD-7	IGGE-IRMA	1.05	0.84	2.7	1.05
	GSD-8	IGGE-IRMA	0.062	2.4	2	0.081
	GSD-9	IGGE-IRMA	0.089	8.4	1.8	0.26
	GSD-10	IGGE-IRMA	0.27	25	0.9	1.12
	GSD-11	IGGE-IRMA	3.2	188	26	2.3
	GSD-12	IGGE-IRMA	1.15	118	8.2	4
	SARM46	MINTEK	—	—	—	—
	SARM51	MINTEK	—	—	—	—
	SARM52	MINTEK	—	—	—	—
	JSd-1	GSJ	~0.036	2.36	1.3	1148
	JSd-2	GSJ	~1.04	39.4	0.8	3580
JSd-3	GSJ	~3.01	261	10	6175	
STSD-1c	CCRMP	—	23	1.6	—	
STSD-2 ^c	CCRMP	0.5	42	5.2	—	
STSD-3 ^c	CCRMP	—	28	2.6	—	
STSD-4 ^c	CCRMP	—	15	1.7	—	

^a ~ = proposed or for information only value; — = value not given.

^b BCR = Community Bureau of Reference (now Measurements and Testing Program), Commission of the European Community, Belgium; CCRMP = Canada Center for Mineral and Energy Technology, Certified Reference Material Project, Ottawa, Canada; GSJ = Geological Survey of Japan, Yatabe, Tsukuba, Ibaraki, 305 Japan; IAEA = International Atomic Energy Agency, Analytical Quality Control Services, Vienna, Austria; IGGE = Institute of Geophysical and Geochemical Exploration, Ministry of Geology, Beijing, China; IRMA = Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, People's Republic of China; MINTEK = Council for Mineral Technology, SABS, Pretoria, South Africa; NIES = National

- NIES No. 12: Marine sediment for organotin compounds, information sheet 1995 (Okamoto, 1994)
- NIES No. 16: River sediment (1995 National Institute for Environmental Studies information sheet/J. Yoshinga)
- GSMS-2 and GSMS-3: Marine sediments, by IRMA (Govindaraju, 1994)
- IAEA-383: Coastal sediment for sterols, fecal (AQCS, 1994)
- IAEA-315: Marine sediment, Arabian Sea, for transuranics, γ and β emitters (AQCS, 1994)

5.4.4 Availability

The following producers of sediment CRMs can be contacted for information or to purchase or obtain CRMs free of charge:

Table 5-2 Certified Values for U.S. EPA Priority Elements in Sediment Certified Reference Materials (continued)

Recommended values for EPA priority elements ($\mu\text{g/g}$) ^a								
Cr	Cu	Hg	Ni	Pb	Sb	Se	Tl	Zn
190	383	0.045	78	27	1.25	-0.3	1.08	144
122	38	0.053	53	350	2.6	-0.31	0.93	238
7.6	4.1	0.042	2.7	21	0.24	-0.15	0.78	43
85	32.1	0.083	32.3	23	0.81	0.16	0.49	78
136	22.6	0.28	30.2	27	6.3	0.28	0.21	46
40	78.6	0.072	14.4	636	14.9	0.2	2.9	373
35	1230	0.056	12.8	285	24.3	0.25	1.8	498
559	566	—	-125	-1300	—	—	—	5900
509	268	—	178	5200	—	—	—	2200
1300	219	—	182	1200	—	—	—	264
22	22.2	—	6.9	14	—	—	0.404	99
104	1114	—	94	151	—	—	—	2070
35	4.26	—	19.6	82	—	—	—	139
67	36	—	24	35	3.3	—	—	178
116	47	—	53	66	4.8	—	—	246
80	39	—	30	40	4	—	—	204
93	65	—	30	18	7.3	—	—	107

Institute for Environmental Studies, Yatabe-machi, Japan; NIST = National Institute of Standards and Technology, Gaithersburg, Maryland; NRCC = National Research Council of Canada, Ottawa, Canada; NRCCRM = National Research Center for CRMs, Beijing, China; NWRI = National Water Research Institute, Burlington, Ontario, Canada; RIAP = Research Institute of Applied Physics, Irkutsk State University, Russia; USGS = U.S. Geological Survey, Denver, Colorado.

^a Recommended values are those from Govindaraju (1994). However, those given by Lynch (1990) and Bowman (1990) are provisional.

Canada Centre for Mineral and Energy Technology (CANMET) Certified Reference Materials Project (CCRM)

555 Booth Street, Ottawa, Ontario K1A 0G1, Canada

Community Bureau of Reference (BCR, now Measurements and Testing Programme)
Commission of the European Community, Rue de la Loi 200, B-1049 Brussels, Belgium

Council for Mineral Technology (MINTEK)

South Africa Bureau of Standards, Private Bag X191, Pretoria, Transvaal 0001, Republic of South Africa

Geological Survey of Japan (GSJ)

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Table 5-3 Sediment Certified Reference Materials for Organic Parameters

CRM type	Name	Producer ^a	Origin	Reference
Coastal sediment	CRM 462	BCR	Arcachon Bay, France	BCR, 1994
	IAEA-356	IAEA	"Hot spot," polluted marine sediment for MeHg	AQCS, 1995
	IAEA-357	IAEA	"Hot spot," polluted marine sediment collected from Lagoon of Venice, Italy	AQCS, 1994, 1995
Lake sediment	DX-1	NWRI	Great Lakes sediment	NWRI, 1995a
	DX-2	NWRI	Great Lakes sediment	NWRI, 1995a
	EC-1	NWRI	Hamilton Harbor, Ontario, Canada	Lee et al., 1987
	EC-2	NWRI	Lake Ontario, near Niagara River, Ontario, Canada	Lee et al., 1986
	EC-3	NWRI	Niagara River plume in Lake Ontario, Canada	NWRI, 1992e,f,g
Marine sediment	CS-1	NRCC	Laurential Channel midway between Nova Scotia and Newfoundland, Canada	NRCC, 1982
	HS-1	NRCC	Organic- and sulfur-rich sediment from Nova Scotia Harbor, Canada	NRCC, 1982
	HS-2	NRCC	Organic- and sulfur-rich sediment from Nova Scotia Harbor, Canada	NRCC, 1982
	PACS-1	NRCC	Harbor sediment from Esquimalt Harbor in British Columbia, Canada	NRCC, 1990
	SRM 1941	NIST	Chesapeake Bay at the mouth of Baltimore (Maryland) Harbor	NIST, 1989
River sediment	SRM 1939	NIST	Hudson River, New York	NIST, 1990b

^a BCR = Community Bureau of Reference, Commission of the European Community, Belgium; IAEA = International Atomic Energy Agency, Analytical Quality Control Services, Vienna, Austria; NIST = National Institute of Standards and Technology, Office of Standard Reference Materials, Gaithersburg, Maryland; NRCC = National Research Council of Canada, Ottawa, Canada; NWRI = National Water Research Institute, Burlington, Ontario, Canada.

Table 5-4 Certified Values for Organics in Sediment Certified Reference Materials

CRM type	Name	Producer ^a	Certified compounds (and values)
Coastal sediment	CRM 462	BCR	Di- and tributyltin (as dibutyltin = $128 \pm 16 \mu\text{g/g}$, as tributyltin = $70 \pm 14 \mu\text{g/kg}$)
	IAEA-356	IAEA	Methyl mercury (as Hg = $5.46 \mu\text{g/g}$)
	IAEA-357	IAEA	PAHs, PCBs, and other organics — see certified compounds and values below
Lake sediment	DX-1	NWRI	Chlorinated dioxins and furans — see certified compounds and values below
	DX-2	NWRI	Chlorinated dioxins and furans — see certified compounds and values below
	EC-1	NWRI	PAHs and PCBs — see certified compounds and values below
	EC-2	NWRI	Chlorobenzenes, hexachlorobenzenes, PAHs — see certified compounds and values below
	EC-3	NWRI	PAHs and chlorobenzenes — see certified compounds and values below
Marine sediment	CS-1	NRCC	PCBs (as Aroclor 1254 = $1.15 \pm 0.60 \mu\text{g/kg}$)
	HS-1	NRCC	PCBs (as Aroclor 1254 = $21.8 \pm 1.1 \mu\text{g/kg}$) — see certified compounds and values below
	HS-2	NRCC	PCBs (as Aroclor 1254 = $111.8 \pm 2.5 \mu\text{g/kg}$) — see certified compounds and values below
	PACS-1	NRCC	Tributyltin (1.27 ± 0.22), dibutyltin (1.16 ± 0.18), and monobutyltin (0.28 ± 0.17) (all in $\mu\text{g/g}$ of Sn)
	SRM 1941	NIST	PAHs: phenanthrene, anthracene, pyrene, fluoranthene — see certified compounds and values below
	River sediment	SRM 1939	NIST

Table 5-4 Certified Values for Organics in Sediment Certified Reference Materials (continued)

Compound	IAEA-357 (ng/g)	Congener	DX-1 (pg/g)	DX-2 (pg/g)
Anthracene	2100 ± 120	2378-TCDD	263 ± 53	262 ± 51
Aroclor 1254	940 ± 202	Total TCDD	416 ± 121	418 ± 125
Benz[<i>a</i>]anthracene	74 ± 1200	12378-PeCDD	22 ± 8	28 ± 14
Benzo[<i>a</i>]pyrene	6900 ± 1000	Total PeCDD	226 ± 143	253 ± 150
Benzo[<i>e</i>]pyrene	6100 ± 3300	123478-HxCDD	23 ± 7	25 ± 8
Benzo[<i>ghi</i>]perylene	5200 ± 1000	123678-HxCDD	77 ± 27	85 ± 33
Chrysene	8900 ± 1500	123789-HxCDD	53 ± 24	58 ± 19
HCB	2.4 ± 0.7	Total HxCDD	669 ± 185	739 ± 218
Heptachlor	1.5 ± 0.6	1234678-HpCDD	634 ± 182	757 ± 320
Indeno[1,2,3- <i>cd</i>]pyrene	4900 ± 600	Total HpCDD	1251 ± 361	1486 ± 476
<i>p,p'</i> -DDD	30 ± 6	OCDD	3932 ± 933	4402 ± 1257
<i>p,p'</i> -DDE	25 ± 7	Total PCDD	6490 ± 1309	7294 ± 1733
<i>p,p'</i> -DDT	35 ± 12			
PCB 52	47 ± 4	2378-TCDF ^b	89 ± 44	134 ± 61
PCB 101	73 ± 6	Total TCDF	659 ± 259	975 ± 588
PCB 138	74 ± 16	12378-PeCDF	39 ± 14	46 ± 10
PCB 170	15 ± 5.2	23478-PeCDF	62 ± 32	88 ± 28
Phenanthrene	10400 ± 750	Total PeCDF	790 ± 489	916 ± 351
Phytane	720 ± 280	123478-HxCDF	714 ± 276	825 ± 348
Pyrene	15100 ± 2700	123678-HxCDF	116 ± 37	153 ± 61
Resolved aromatics (µg/g)	130 ± 27	123789-HxCDF ^b	28 ± 42	36 ± 45
Sigma alkanes C14-34	14200 ± 5100	234678-HxCDF ^b	57 ± 36	70 ± 47
		Total HxCDF	1800 ± 809	2111 ± 662
		1234678-HpCDF	2397 ± 796	3064 ± 745
		1234789-HpCDF	137 ± 62	152 ± 84
		Total HpCDF	3567 ± 1165	4068 ± 1306
		OCDF	7122 ± 2406	7830 ± 3087
		Total PCDF	13676 ± 3777	15981 ± 4177

Compound	EC-1 ($\mu\text{g/g}$)	Compound	EC-2
Anthracene	1.2 \pm 0.6	1,2,3,4-Tetrachlorobenzene (ng/g)	36.5 \pm 4.8
Benz[a]anthracene	8.7 \pm 1.6	1,2,3,5-Tetrachlorobenzene (ng/g)	5.2 \pm 0.7
Benzo[b]fluoranthene	7.9 \pm 1.8	1,2,4,5-Tetrachlorobenzene (ng/g)	84 \pm 9.8
Benzo[k]fluoranthene	4.4 \pm 1.0	1,2,3-Trichlorobenzene (ng/g)	6.1 \pm 1.3
Benzo[a]pyrene	5.3 \pm 1.3	1,2,4-Trichlorobenzene (ng/g)	80.7 \pm 10.8
Benzo[e]pyrene	5.3 \pm 1.3	1,3,5-Trichlorobenzene (ng/g)	34.3 \pm 5.2
Benzo[ghi]perylene	4.9 \pm 1.3	1,2-Dichlorobenzene (ng/g)	18.1 \pm 2.5
Fluoranthene	23.2 \pm 4.1	1,3-Dichlorobenzene (ng/g)	74.7 \pm 10.1
Indeno[1,2,3-cd]pyrene	5.7 \pm 1.2	1,4-Dichlorobenzene (ng/g)	84.4 \pm 17.6
Phenanthrene	15.8 \pm 2.5	Hexachlorobenzene (ng/g)	200.6 \pm 26.4
Pyrene	16.7 \pm 3.9	Hexachlorobutadiene (ng/g)	21.3 \pm 3.2
Total PCBs	2.00 \pm 0.15	Pentachlorobenzene (ng/g)	48.6 \pm 4.8
		Benzo[a]anthracene ($\mu\text{g/g}$)	1.42 \pm 0.51
		Benzo[b]fluoranthene ($\mu\text{g/g}$)	2.48 \pm 0.86
		Benzo[k]fluoranthene ($\mu\text{g/g}$)	1.93 \pm 0.72
		Benzo[ghi]perylene ($\mu\text{g/g}$)	1.47 \pm 0.65
		Benzo[a]pyrene ($\mu\text{g/g}$)	1.21 \pm 0.56
		Benzo[e]pyrene ($\mu\text{g/g}$)	1.91 \pm 0.72
		Dibenz[a,h]anthracene ($\mu\text{g/g}$)	0.49 \pm 0.21
		Fluoranthene ($\mu\text{g/g}$)	3.55 \pm 0.83
		Indeno[1,2,3-cd]pyrene ($\mu\text{g/g}$)	1.55 \pm 0.53
		Pyrene ($\mu\text{g/g}$)	2.92 \pm 0.63
Compound	EC-3 (ng/g)		
Benzo[a]pyrene	386 \pm 100		
Benzo[e]pyrene	450 \pm 98		
Benzo[a]anthracene	312 \pm 56		
Fluoranthene	558 \pm 92		
Phenanthrene	293 \pm 66		
Pyrene	436 \pm 94		
1,3,5-Trichlorobenzene	113.6 \pm 19.0		
1,2,3-Trichlorobenzene	8.9 \pm 2.4		
1,2-Dichlorobenzene	20.7 \pm 6.2		
1,3-Dichlorobenzene	105.4 \pm 35.0		
Hexachlorobenzene	279.0 \pm 66.2		
Hexachlorobutadiene	61.3 \pm 13.8		
Pentachlorobenzene	65.4 \pm 16.4		

Table 5-4 Certified Values for Organics in Sediment Certified Reference Materials (continued)

Congener	HS-1 ($\mu\text{g}/\text{kg}$)	HS-2 ($\mu\text{g}/\text{kg}$)	Compound	SRM 1941 ($\mu\text{g}/\text{g}$)
101	1.62 \pm 0.21	5.42 \pm 0.34	Phenanthrene	0.577 \pm 0.059
138	1.98 \pm 0.28	6.92 \pm 0.52	Anthracene	0.202 \pm 0.042
151	0.48 \pm 0.08	1.37 \pm 0.07	Pyrene	1.080 \pm 0.020
153	2.27 \pm 0.28	6.15 \pm 0.67	Fluoranthene	1.220 \pm 0.240
170	0.27 \pm 0.05	1.07 \pm 0.15	Benzo[<i>a</i>]anthracene	0.550 \pm 0.079
180	1.17 \pm 0.15	3.70 \pm 0.33	Benzo[<i>b</i>]fluoranthene	0.780 \pm 0.190
194	0.23 \pm 0.04	0.61 \pm 0.07	Benzo[<i>k</i>]fluoranthene	0.444 \pm 0.049
196	0.45 \pm 0.04	1.13 \pm 0.12	Benzo[<i>a</i>]pyrene	0.670 \pm 0.130
199	0.57 \pm 0.07	1.39 \pm 0.09	Perylene	0.422 \pm 0.033
209	0.33 \pm 0.10	0.90 \pm 0.14	Benzo[<i>ghi</i>]perylene	0.516 \pm 0.083
			Indeno[1,2,3- <i>cd</i>]pyrene	0.569 \pm 0.040

^a BCR = Community Bureau of Reference, Commission of the European Community, Belgium; IAEA = International Atomic Energy Agency, Analytical Quality Control Services, Vienna, Austria; NIST = National Institute of Standards and Technology, Office of Standard Reference Materials, Gaithersburg, Maryland; NRCC = National Research Council of Canada, Ottawa, Canada; NWRI = National Water Research Institute, Burlington, Ontario, Canada.

^b Provisional values only.

Table 5-5 Sediment Certified Reference Materials for Radionuclides

CRM type	Name	Producer ^a	Origin	Reference
Lake sediment	SL-2	IAEA	Origin not given	AQCS, 1994, 1995
Marine sediment	IAEA-135	IAEA	Collected in June 1991 near Sellafield, Irish Sea, for radionuclides	AQCS, 1994, 1995
	IAEA-300	IAEA	Baltic Sea sediment	AQCS, 1994, 1995
	IAEA-367	IAEA	Collected at nuclear test sites at the Enewetak, Marshall Islands, Pacific Ocean	AQCS, 1994, 1995
	IAEA-368	IAEA	Marine surface sediment from the Lagoon of Mururoa Atoll, Pacific Ocean	AQCS, 1994, 1995
	SD-N-2	IAEA	Origin not given	AQCS, 1994, 1995
Stream sediment	IAEA-313	IAEA	Collected from Sibolga area, west coast of North Sumatra, Indonesia	AQCS, 1994, 1995
	IAEA-314	IAEA	Collected from Kalan area, west Kalimantan (Borneo), Indonesia	AQCS, 1994, 1995
River sediment	SRM 4350	NIST	River sediment	Gladney et al., 1987
	SRM 4350B	NIST	River sediment (1981 certificate of analysis)	NBS, 1981
Lake sediment	SRM 4354	NIST	Gyttja freshwater lake sediment (1986 certificate of analysis)	NBS, 1986

^a IAEA = International Atomic Energy Agency, Analytical Quality Control Services, Vienna, Austria; NIST = National Institute of Standards and Technology, Gaithersburg, Maryland.

Table 5-6 Certified Radionuclides in Sediment Certified Reference Materials

CRM type	Name	Producer ^a	Certified radionuclides (Bq/kg) for sediment CRMs
Lake sediment	SL-2	IAEA	K-40 = 240, Cs-137 = 2.4
Marine sediment	IAEA-135	IAEA	K-40 = 560, Co-60 = 4.8, Cs-134 = 5.2, Cs-137 = 1108, Eu-154 = 6.8, Eu-155 = 5.5, Ra-226 = 23.9, Ra-228 = 36.7, Th-232(t) = 36.9, Pu-238 = 43, Pu-239+240 = 213
	IAEA-300	IAEA	K-40 = 1059, Co-60 = 1.5, Sb-125 = 11, Cs-134 = 66.6, Cs-137 = 1056.6, Eu-155 = 4.95, Pb-210 = 360, Po-210 = 340.5, Ra-228 = 61.6, U-234 = 69, U-238 = 64.7, Pu-239+240 = 3.55, Am-241 = 1.38
	IAEA-367	IAEA	Co-60 = 1.0, Sr-90 = 102, Cs-137 = 195, Pu-239+240 = 38
	IAEA-368	IAEA	Co-60 = 0.6, Eu-155 = 3.8, Pb-210 = 23.2, Ra-226 = 21.4, Pu-238 = 8.5, U-238 = 31, Pu-239+240 = 31
Stream sediment	SD-N-2	IAEA	K-40 = 220, Cs-137 = 0.8, Th-232 = 4.9, Pu-239+240 = 8.8 mBq/kg
	IAEA-313	IAEA	Ra-226 = 342, Th = 77.1 mg/kg, U = 18.2 mg/kg
	IAEA-314	IAEA	Ra-226 = 732, Th = 17.8 mg/kg, U = 56.8 mg/kg
River sediment	SRM 4350	NIST	Co-60 = 148, Ac-228 = 34, Cs-137 = 100, Eu-154 = 52, K-40 = 540, Mn-54 = 2.1, Pu-239 = 1.4, Sr-90 = 10.3, Zn-65 = 13 (activities as of January 1, 1975)
	SRM 4350B	NIST	Co-60 = 4.64, Cs-137 = 29, Eu-152 = 30.5, Eu-154 = 3.78, Ra-226 = 35.8, Pu-238 = 13 mBq/kg, Pu-239+240 = 0.51, Am-241 = 0.15
Lake sediment	SRM 4354	NIST	Co-60 = 320, Sr-90 = 1090, Cs-137 = 59.2, Th-228 = 28.6, Th-232 = 26.8, U-235 = 0.75, U-238 = 17.4, Pu-238 = 0.26, Pu-239+240 = 4.0, Am-241 = 1.1

^a IAEA = International Atomic Energy Agency, Analytical Quality Control Services, Vienna, Austria; NIST = National Institute of Standards and Technology, Office of Standard Reference Materials, Gaithersburg, Maryland.

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Institute of Rocks and Mineral Analysis (IRMA)
Ministry of Geology and Mineral Resources, 26 Baiwanzhuang Road, Beijing 100037, China

International Atomic Energy Agency (IAEA)
Analytical Quality Control Services, Laboratory Seibersdorf, P.O. Box 100, A-1400 Vienna, Austria

National Institute for Environmental Studies (NIES)
Environment Agency of Japan, Yatabe-machi, Tsukuba, Ibaraki, 305, Japan ("reasonable" amounts of NIES CRMs may be obtained on request at no charge from Dr. J. Yoshinaga, Environmental Chemistry Division, National Institute for Environmental Studies, 16-2 Onogawa, Ibaraki 305, Japan)

National Institute of Standards and Technology (NIST)
Office of Standard Reference Materials, Gaithersburg, MD 20899

National Research Center for CRMs (NRCCRM)
Office of CRMs, No. 7 District 11, Hepingjie, Chaoyangqu, Beijing, 100013, China

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Research Institute of Applied Physics (RIAP)
Irkutsk State University, Russia (can be purchased from ASSO USSR Association of Reference Materials Producers, 4 Krasnoarmeyskaya Street, Sverdlovsk, 620219, USSR, fax (3452) 55 21 78 or from Breitlander, P.O. Box 8046, D-59035 Hamm, Germany, fax (02381) 40 31 89)

U.S. Geological Survey (USGS)
Branch of Geochemistry (Attention: Steve Wilson), Denver Federal Center, Box 25046, MS 473, Denver, CO 80225.

5.4.5 Recommendations

1. It is a prerequisite to stock a good selection of pertinent sediment CRMs in any laboratory that analyzes sediments to generate usable analytical data.

2. While it is highly desirable to satisfy the ideal state of matching the matrices and analyte levels (Cheam et al., 1989), it is inconceivable in the near future that such a state can ever be attained. To effectively diversify the matrices and concentrations of analytes, it is recommended that mixing existing CRMs be investigated. This may achieve or approach the ideal state.

5.4.6 Conclusions

1. The development and use of CRMs are paramount in an effective QA program.
2. A measurement process that does not use one or more CRMs for QC generates questionable data and thus questionable conclusions and decision making. Unreliable data are more expensive than no data at all.
3. The development of sediment CRMs consumes time and resources and is inefficient. An easy, cost-effective approach for any laboratory would be to mix existing CRMs to produce secondary ones that are tailored to have the desirable matrix and analyte levels.

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