#### **REVIEW**

# Standard Reference Materials<sup>®</sup> (SRMs) for measurement of inorganic environmental contaminants

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Abstract NIST has developed an extensive collection of environmental SRMs, starting with fuel and biologically related materials in the late 1960s and now encompassing all sectors of environmental research. Advances in analytical methodology, including multi-element isotope-dilution mass spectrometry (IDMS) and expanded instrumental neutron-activation analysis (INAA) capabilities, enable value assignment based on fewer but better-characterized independent analytical techniques. The special advantages of IDMS for determination of S and Hg and for multielement characterization of small-sample air particulate matter (SRM 2783) by IDMS and INAA are emphasized.

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Hollings Marine Laboratory, National Institute of Standards and Technology (NIST), 331 Fort Johnson Road, Charleston, SC 29412, USA e-mail: Clay.Davis@noaa.gov Developments in materials production include the issuance of fresh-frozen biological materials and of jet-milled natural-matrix materials with improved homogeneity, including highly homogeneous air particulate matter and sediment SRMs for small-sample analytical techniques.

Keywords Cryogenic processing · Homogeneity · Instrumental neutron-activation analysis · Isotope-dilution mass spectrometry · Mercury · Optical-emission spectrometry · Sulfur · Trace elements · X-ray fluorescence spectrometry

### Introduction

It has been almost a century since the National Bureau of Standards (NBS) issued its first reference material (Standard Sample No. 1, Argillaceous Limestone, dated July 1, 1910). At that time few people gave much thought to environmental measurements. The first truly environmental Standard Reference Materials<sup>®</sup> (SRMs) were two "Sulfur in Residual Fuel Oil" SRMs issued in 1967 (SRMs 1621 and 1622), which were certified for their sulfur content. Since then NBS and its successor, the National Institute of Standards and Technology (NIST), has produced more than 200 new SRMs for environmental analysis of inorganic constituents, not including SRM gases.

NIST began substantial development of environmental SRMs in the early 1970s, starting with the production and certification of the first ever natural matrix, multi-element botanical SRM 1571, Orchard Leaves. This SRM was a radical departure from the reference materials of the previous 50 years, which were mostly industrial and commercial materials, produced mainly in cooperation with the American Society for Testing and Materials. The need

for such a natural matrix reference material certified for major, minor, and trace elements was established through a survey of scientists working in trace-element analysis. The selection of a botanical material for this first SRM of its type was the result of strong support from the American Society of Agronomy. The Orchard Leaves SRM was designed to fulfill needs for environmental trace-element analysis and for agriculture, medical, and other fields of chemical analysis.

For NIST, the development of this new type of SRM required the development of new methods and techniques in environmental trace-element analysis. These development efforts included an extensive search of the literature on the subject of trace element sample preparation and analysis, discussions with a number of scientists already working in the field, and laboratory studies on dried and powdered materials of many kinds. Element homogeneity, effectiveness of different drying techniques, long-term stability, and analytical accuracy and precision were evaluated in our laboratories [1].

Because the cost of preparation, evaluation, and certification of such a material was substantial, the decision was made to prepare sufficient material to fulfill an estimated 10year demand for the reference material, to amortize these costs over sufficient time to keep the cost per unit reasonable. For the Orchard Leaves, this meant obtaining over 500 kg (dry mass) of handpicked leaves (apple, cherry, and peach leaves), then drying, homogenization, packaging, and sterilization. Only then could chemical analysis begin. The technical aspects of obtaining, handling, and processing such large amounts of material while minimizing contamination and inhomogeneity also required research.

The preparation for this project was started in 1966; material was obtained in 1968 and SRM 1571 issued in 1971 [2]. A total of 25 elements, including Pb, Cd, As, Hg, Se, Cr, Ni, Be, Th, and U, were certified in the Orchard Leaves SRM. In addition, non-certified information data were included for 12 more elements. Fourteen different analytical methods were used to obtain the certification data, with neutron-activation analysis used for more than twice as many element certifications as any other method [3]. The supply of Orchard Leaves was exhausted by 1988, and replacement materials SRM 1515 Apple Leaves and SRM 1547 Peach Leaves were issued in 1991. Another biological material issued early in the program was SRM 1577 Bovine Liver (1972) with 16 key biological and contaminant elements certified, including Ca, Mg, Fe, Cu, Zn, Se, Cr, Cd, As, Pb, and Hg, using a similar array of analytical methods.

NIST expanded its SRM program quickly to other significant environmental materials during the 1970s. In addition to the two mentioned above, that decade saw the development of two more sulfur in fuel oil SRMs (1623 and 1624, both in 1971), Trace Mercury in Coal (SRM 1630, also

in 1971), Sulfur in Coal (SRM 1631, in 1973), two mercury in water SRMs (trace and concentrate in 1974), and then several multi-element materials. Three energy-related environmental SRMs, Trace Elements in Coal (SRM 1632), Trace Elements in Coal Fly Ash (SRM 1633), and Trace Elements in Fuel Oil (SRM 1634) were issued in 1975, followed by a river sediment (SRM 1645) in 1978. These multi-element SRMs had a significant affect on the analytical community. The coal, fly ash, and fuel oil SRMs were part of a large interlaboratory comparison study before their release, in cooperation with the United States Environmental Protection Agency (US EPA). The purpose of this study was to assess the analytical capabilities of the participating environmental analytical laboratories at that time. Coal and fly ash were particularly popular with laboratories that were keen to demonstrate their capabilities because of the large number of trace elements reported in the certificates. This was shown in the compilation of published element concentrations for these materials [4]. One material from this decade that warrants special mention is Urban Particulate Matter, SRM 1648. This material was collected in a specially designed bag house in the St Louis, MO area for a period of more than 12 months, combined in a single lot, sieved (<125 µm), blended, and issued as a bottled air particulate sample material in 1978. Together with its sister material, SRM 1649 (collected in Washington, DC, for organic components), it provided a benchmark for aerosol measurements. A renewal certification of this material is currently in progress using the same stock material.

The current range of NIST SRMs for measurement of inorganic contaminants in environmental materials encompasses several principal categories: calibration materials, biological tissues, and fluids; soils, sediments, geological materials, and mineral and fossil fuel related material; crosscutting samples from the aforementioned types and water samples for measurements in the aquatic environment; and particulate matter and gases for atmospheric research. The discussion below will focus on a selection of solid and liquid SRMs that cover key environmental measurement concerns for both polluting and naturally occurring trace elements, reflecting new trends and capabilities in analytical chemistry and recent core requirements for environmental monitoring and health effect studies. Some important aspects of the production of NIST SRMs and the analytical approach to the certification are summarized in this paper.

### Advanced methods for certification of elements

The task of certification, namely the assignment of mass fraction values and limits of uncertainty, is a most demanding challenge in standards development and poses varying degrees of difficulty depending on the matrix and elements certified. It is generally accepted that a property can be certified when the value is confirmed by several analysts/laboratories working independently using either one primary method, or preferably, two or more fully evaluated methods with known and independent sources of uncertainty. The selected approach depends on the required (fit for purpose) traceability, limits of uncertainty, capability of the analytical techniques, and compliance with the NIST certification criteria [5]. Consolidation of inorganic analytical techniques to principally four, mass spectrometry, optical-emission spectrometry, neutron-activation analysis, and X-ray fluorescence analysis, has occurred in recent years.

#### Isotope-dilution mass spectrometry (IDMS)

NIST has used IDMS to certify the concentration of inorganic elements in SRMs since 1969 [6]. Early application of IDMS at NIST involved the use of thermal ionization mass spectrometry (TIMS), but after the introduction of inductively-coupled plasma mass spectrometry (ICP-MS) in the mid 1980s, use of ICP-MS at NIST eclipsed use of TIMS for all but a handful of elements. IDMS relies on the use of an enriched isotope of the analyte of interest as an internal standard. If this "spike" is equilibrated with the sample during the dissolution process, total analyte recovery is not required for accurate quantification. Partial precipitation, which often occurs in solutions of complex matrices, will not affect the accuracy of the result. Sample manipulation to isolate the analyte and eliminate matrix-induced biases need not be quantitative. A variety of separation schemes have been developed by the mass spectrometrists at NIST and used for accurate certification of inorganic analytes in environmental reference materials. These include use of anion, cation, and chelating chromatography [7–9], elementspecific resins [9, 10], precipitation [11, 12], and cold vapor generation [13]. Recent analytical advances enable the development of procedures to mitigate spectral interference instrumentally. These include use of cold plasma ICP-MS [14, 15], high-resolution (HR) ICP-MS [16], and collision cell ICP-MS [17].

Quantification and evaluation of uncertainties in isotope dilution analysis involves, principally, three types of sample: spiked calibration samples, procedure blanks, and analytical samples. On addition and equilibration of a known amount of the enriched isotope, these sample types are characterized, by use of the isotope-dilution equation, by measurement of the altered isotope intensity ratios. Measurement of intensity ratios is inherently more precise than measuring absolute signal intensities. The relative standard deviation (RSD) of ICP–MS ratio measurement is typically 0.1 to 0.5%, compared with 0.05 to 0.1% RSD for TIMS ratio measure

ment. A fourth type of sample, composition samples, are measured for elements such as Pb and S whose isotopic composition varies in nature, and as a means of assessing spectral interference. By reducing sources of bias, by careful experimental design, ratio-measurement precision becomes the dominant source of uncertainty in IDMS analysis of a perfectly homogeneous material.

As with all solution-based methods, bias can occur during IDMS sample preparation, because of incomplete dissolution and contamination during preparation. Contamination is controlled by use of high-purity reagents and clean-room technology. Complete dissolution is achieved by wet-ashing with nitric and perchloric acids or by use of closed-vessel systems capable of withstanding high temperature and pressure. Bias in isotope ratio measurement can occur because of isobaric interference, mass bias in the spectrometer, and, for pulse-counting systems, detector dead time. Isobaric interference is evaluated and minimized by use of matrix-separation schemes or instrumentally, for example by use of high-resolution ICP-MS. Calibrating the enriched isotope concentration by reverse IDMS and carefully matching and controlling the altered ratios of the spike calibration and analytical samples reduce the effects of mass bias and detector dead time. Details of an IDMS uncertainty budget as applied to the analysis of SRM 2783 Air Particulate on Filter Media are shown in Table 1. Type A components include the standard uncertainty of filter sample measurements, which provides a measure of sample heterogeneity, the standard uncertainty of the spike calibration samples, which provides a measure of preparation and ratio measurement uncertainty, and, finally, the standard uncertainty of the blank, which provides a measure of contamination. Type B components include an estimate of bias because of uncertainty in the calibrant assay; uncertainty in instrument factors affecting ratio measurement, which includes background drift, unresolved spectral interference, and mass bias resulting from the slightly imperfect match between the sample and spike ratios; uncertainty in the isotopic composition of the sample; and, finally, uncertainty in the isotopic composition of the spike solution containing the mixture of enriched isotopes, an important factor of multi-element IDMS analyses.

Inductively-coupled plasma optical-emission spectrometry (ICP–OES)

The enabling technology for high-performance ICP–OES has been the arrival of well-engineered commercial spectrometers based on solid-state array detectors. These instruments, thousands of which are installed in commercial laboratories in the US, can be used unmodified for measurements. Multiplexed, precision photometry makes flexible, time-correlated internal standardization possible, enabling

Element	Sb	Cu	Ni	Pb	Ba	Cd	U
Mass on filter samples (n	g)						
Average	70.5	409	79.8	330.4	333	$(2.91)^{a}$	1.234
Standard deviation	2.4	26	8.4	6.4	13	$(0.83)^{\rm a}$	0.029
Ν	8	8	8	8	8	7	8
RSD	3.5%	6.3%	10.4%	1.9%	3.9%	28%	2.3%
Spike calibration samples	$(nmol g^{-1})$						
Average	1.0902	10.611	1.1915	2.2380	2.7098	0.02680	0.010989
Standard deviation	0.0042	0.057	0.0050	0.0047	0.0054		0.000015
Ν	4	4	4	4	3	3	4
RSD	0.39%	0.54%	0.42%	0.21%	0.20%	0.19%	0.14%
Procedure blanks (ng)							
Average	0.26	0.59	0.24	0.41	0.25	0.022	0.0011
Standard deviation	0.49	0.52	0.08	0.44	0.17	0.017	0.0012
Ν	7	4	7	7	6	7	6
Method validation: SRM	1648 Urban Air	r Particulate (µg	$g^{-1}$ )				
Measured	$46.0 \pm 1$	590±16	$83.2 \pm 0.9$	6521±41	756±15	$73.9 {\pm} 0.6$	$5.39 {\pm} 0.01$
Certified	45	$609 \pm 27$	82±3	$6550 \pm 80$	737	75±7	$5.5 \pm 0.1$
Uncertainty budget (% re	lative)						
Type A							
Sample	1.2	2.2	3.6	0.68	1.4		0.82
Calibration	0.20	0.27	0.21	0.10	0.11	0.11	0.069
Blank	0.27	0.064	0.038	0.051	0.021	0.21	0.036
Туре В							
Primary Standard	0.16	0.15	0.15	0.057	0.15	0.27	0.15
Ratio measurement	0.14	1.3	0.25	0.087	0.03	1.8	0.029
Composition	0.028	0.029	0.025	0.030	0.03	0.029	0.029
Coverage factor	2.4	2.2	2.4	2.4	2.4		2.4
Expanded uncertainty	2.9	5.7	9.0	1.6	3.3	а	2.0

Table 1 ID ICP-MS determination of Sb, Cu, Ni, Pb, Ba, Cd, and U in SRM 2783 Air Particulate on Filter Media: filter samples, spike calibration samples, procedure blanks, and uncertainty budget

<sup>a</sup>Not certified because of gross heterogeneity

precision spectrometry using ICP, whose signal-carried noise is largely mitigated by this ratio measurement. The ratiobased measurement is analogous to isotope-dilution mass spectrometry, and high-performance (HP)-ICP–OES gravimetric sample and spike handling are identical with those of that well-established primary method [18].

Early experiments demonstrated that low-frequency noise, i.e. drift, was the limiting uncertainty in some measurements, which use long measurement times to achieve low, well-characterized uncertainty. A novel strategy was devised for post-measurement drift correction, modeling the low-frequency noise function and removing the noise [19]. This modeling is intimately coupled with an experiment design, which was needed to enable evaluation of uncertainty which might very well be dominated by sample handling and even solution heterogeneity. Experience with this method includes its application to more than 50 elements, both in single and simultaneous multi-element analysis [20]. Total measurement time for a multi-element analysis of ~20 samples has been as much as 24 h. Analysis of data subsets has revealed an opportunity to improve efficiency with shorter experiment times, and recent optimization work has reduced measurement time to 2 h.

#### Neutron-activation analysis (NAA)

NAA at NIST is based on the Center for Neutron Research's outstanding source of neutrons [21]. Applications to environmental SRMs are predominantly instrumental NAA (INAA) procedures, supplemented by radiochemical (RNAA) procedures for lowest detection limits and neutron capture prompt-gamma activation analysis (PGAA), chiefly for elements whose activation products do not emit gamma rays in their decay [22]. INAA does not require chemical sample preparation and separation, enabling direct analysis independent of "chemical yields" and generally free from analytical blanks. In common practice INAA requires an external calibration using comparator standards of known composition, i.e. high-purity metals or compounds and their dilute solutions, which are activated and measured in the same way as the samples. INAA is, typically, a multi-step procedure with



Fig. 1 Multi-element INAA procedure used in homogeneity and certification analysis of SRM 2783

several irradiations and measurements performed sequentially on each individual sample [23], as depicted in Fig. 1 for SRM 2783, to obtain optimum information.

The basic activation analysis equations for the comparator technique have several independent variables that can substantially affect the combined uncertainty of the result. Some of these uncertainties are predetermined by the design of the procedure, and limits well below 1% relative (1s) can be achieved for many components of uncertainty [24]. Several evaluated INAA-specific uncertainties are listed in Table 2. Recording of a statistically sufficient number of signal pulses is chiefly determined by limits on the handling of radioactive samples, the throughput of the counting system, and the element concentrations in the sample. Uncertainties because of different decay and counting times can be significant for nuclides with relatively large uncertainties in their decay constants. To minimize these uncertainties differences in decay and counting should be minimized and/or decay constants can be re-determined experimentally. The neutron flux ratio among samples and standards may be subject to differences in matrices and is strongly affected by variations in the flux density during irradiation. Correction factors needed for highly neutron-absorbing materials can usually be calculated with less than 0.2% uncertainty; flux variations in the NIST irradiation channels are below 0.2%. Counting efficiency, which is affected by sample matrix, geometry, and compensation of counting losses, is usually made a negligible component of uncertainty.

### X-ray fluorescence spectrometry (XRF)

XRF is used in many industrial settings including geological/ mineralogical applications. The technique is used to test intermediate and finished products, for example cement, metals, ceramics, glass, and many by-products of mining, ore processing, and quarrying, including ash, slag, tailings, and sludge. These materials are extremely relevant in their potential impact on the environment. All are available for testing as solid or powdered SRMs. Like industry, NIST makes use of XRF to analyze these types of material; some are tested directly with minimal sample preparation whereas others must be prepared by grinding and fusing with borate flux.

XRF has become a principal technique for homogeneity testing at NIST, in addition to quantitative analysis. The primary reason for this is the inherent stability of XRF spectrometers, with secondary factors being minimal sample preparation and unattended spectrometer operation. XRF has unmatched repeatability among common elemen-

**Table 2** Relative INAA stan-<br/>dard uncertainties (%) for SRM2783 with n=29 degrees of<br/>freedom for most type A<br/>uncertainties

Source of uncertainty	Type A	Type B
Preparation of samples and standards		
Aerosol loading on filters $(n=29)$	0.51	
Concentration of comparators (standards)		< 0.1
Amount of standard solution deposited $(n \ge 3)$	< 0.15	< 0.1
Blank (chromium) $(n=29)$	1.5	
Irradiation		
Neutron flux stability $(n=29)$	0.055-0.1	
Irradiation geometry differences $(n=29)$		0.3
Neutron self-shielding/scattering differences; interferences		< 0.01
Timing $(n=29)$	0.12	
Gamma-ray spectrometry		
Counting statistics	0.1-1.86	
Counting geometry differences		0.01
Pulse pile-up and dead-time corrections $(n=29)$	0.001-0.3	
Decay time (half-life related)		0.0007-0.01
Gamma-ray self-shielding		< 0.005
Gamma-ray interferences		< 0.01
Peak integration method (n=29)		0.03-0.2

tal analysis techniques. For SRMs, this level of precision is used to advantage for homogeneity testing of packaged SRMs with typical performance enabling decisions on within-unit and between-unit heterogeneity to better than 1% relative standard deviation.

XRF is, in contrast, at a disadvantage among common instrumental techniques when there is a need for quantitative determinations. It is well-known that XRF does not have the sensitivity for ultra-trace determinations without substantial sample preparation. In addition, XRF is prone to several matrix effects, which complicate calibration and increase overall uncertainty. To make XRF more independent of its matrix effects, NIST scientists apply the technique of borate fusion to prepare samples along with calibrants that very nearly match the composition of the fused samples [25, 26]. This approach has the advantage of controlling matrix effects, because there are no significant differences between the composition of calibrants and specimens. It has the further advantage of creating a direct link of traceability to the mole, because the calibrants are prepared from high-purity metals, compounds of known stoichiometry, and NIST spectrometric solution SRMs, which are prepared from pure substances. Borate fusion is highly repeatable and capable of retaining several elements that may be lost during such procedures as wet-ashing and dry-ashing.

NIST has used the combination of XRF and borate fusion for bulk quantitative analysis of a variety of soils, minerals, and mineral by-products, including SRM 1d Argillaceous Limestone, soil SRMs 2709, 2710, 2711, 2586, and 2587, SRM 2780 Hard Rock Mine Waste, cement SRMs in the 1880a series [26], SRM 2696 Silica Fume, the proposed SRM 57b Silicon Metal, and steel and titanium alloys [27]. Cement, limestone, and silica fume are not typically listed as being of environmental concern. Cement, however, is being increasingly used as a repository for ash, slag, and other solid waste. All silica fume was once sent to landfills, but is now an important additive of stronger concrete formulations that are less susceptible to acid rain. The proposed SRM 57b and steel and titanium alloys reveal the performance achievable for materials made entirely of reduced metals and containing key elements such as arsenic, cobalt, zinc, and copper. As analysts gain experience with the borate-fusion XRF method, it is being successfully applied to lower concentrations of analytes in a wider range of materials. Recently analyzed materials contained analytes in the range 10 to 100 mg kg<sup>-1</sup> with relative total expanded uncertainty estimates in the range of 1 to 10%. Most notable of these is proposed SRM 695, a common fertilizer formulation.

The techniques described above are typically applied because of their multi-element capabilities, their complementary nature in element coverage, and the fundamental differences and independent characteristics of chemically destructive and non-destructive analysis. Table 3 provides an overview of the uses of these techniques with an indication of their operating range given by the lowest element mass fraction determined in the specified environmental SRMs. Limits of detection are typically one to two orders of magnitude lower than the values listed. Selected uses of these techniques are described below to exemplify their state-of-the-art implementation and their effect in the certification process.

# Certification of sulfur in SRMs by isotope-dilution mass spectrometry

The transport fuels distillate fuel oil and gasoline are the two most important categories with regard to sulfur regulations and, therefore, sulfur content. Before 1992 the sulfur content of diesel fuel was not regulated and was approximately 3000  $\mu$ g g<sup>-1</sup> or higher. From October 1 1993 the US EPA regulations required on-road diesel fuel to contain less than 500  $\mu g \ g^{-1}$  sulfur. To assist the petroleum industry in meeting this low level, NIST issued SRM 2724 with a certified value for sulfur of  $425\pm4 \ \mu g \ g^{-1}$ . The economic impact of this single SRM was enormous, as has been documented in an Economic Assessment Report issued in February 2000 [28]. The United States (US) and the European Union (EU) have recently mandated ultra-low sulfur diesel (ULSD) fuel for on-road use to enable more efficient exhaust emission after-treatment technology, which will result in substantially reduced particulate emissions from diesel engines. The EU mandated a 10 µg  $g^{-1}$  (ppm) sulfur limit in diesel starting in 2005, and the US will phase in a 15  $\mu$ g g<sup>-1</sup> limit starting June 2006. The accurate determination of sulfur in ULSD at these levels is a major measurement challenge with enormous economic consequences, mostly in avoided costs, for petroleum refineries and in every link in the distribution system. On the positive side, it is estimated by the EPA that the health and welfare benefits to the American public will be approximately \$150 billion annually. Per capita benefits in the EU should be similar, because their consumption of diesel is slightly greater than in the US and their population is larger. Although the regulated levels are different for the EU and the US, the demands on refineries are essentially identical because in both cases the refineries will need to produce diesel fuel with a sulfur concentration near 7 µg  $g^{-1}$  to ensure that the level at the retail outlets meets the mandated specifications. Diesel fuel in the US is moved long distances by pipelines, which make it more susceptible to contamination. The new US limit is 30 times lower (15  $\mu$ g g<sup>-1</sup> compared with 500  $\mu$ g g<sup>-1</sup>) than the current regulatory limit. To meet this challenge cost-effectively and with the least disruption in product availability, the industry must have highly accurate real-matrix sulfur standards. Currently available distillate fuel oils and gasoline SRMs

**Table 3** Principal NIST methods used for certification of elements in environmental SRMs including lowest values measured in the specified SRMs as an indication of lowest operational levels for value assignment. Limits of detection are commonly one or two orders of magnitude lower

# Element Lowest values (mg kg<sup>-1</sup>), SRM number, and specific method variants

	ICP-OES	ID ICP-MS	NAA	XRF
Li		3.83 (956a)	N/A	N/A
Be	0.05 (2677)	N/A	N/A	N/A
В		0.3 (1640) T	2.5 (1548) P	N/A
F		N/A	64 (2695)	N/A
Na	20.23 (1643e)	N/A	6.1 (1567)	109 (1d)
Mg	7.84 (1643e)	10.62 (956a)	400 (1567)	
Al	15.89 (2718)	N/A	0.0037 (1598) C	
Si			2.1 (1577b) R	
Р	88.34 (1682c)	N/A	1000 (1575a) R	220 (1886a)
S		4.7 (2298)	258 (1548)	
Cl		1139 (1632c) T	580 (1515)	19 (1889a)
Κ	1.984 (1643e)	77.21 (956a)	186 (1400)	
Ca	31.5 (1643e)	83.15 (956a)	1967 (1548a)	
Sc		N/A	8E-4 (1548a)	
Ti	276.4 (1085b)	100.4 (1084a)	200 (1635)	186 (695)
V	6.52 (3280)	0.007 (1568a)	1.0E-4 (1598) C	67 (695)
Cr	1.18 (1849)	98.3 (1084a)	1.0E-4 (1598) R	24 (1886a)
Mn	3.85 (2385)	N/A	0.0038 (1598) C	129 (695)
Fe	0.0957 (1643e)	0.034 (1640) T	1.78 (1549) R	550 (2696)
Со		0.0079 µg (2783)	0.0041 (1549)	48 (695)
Ni	10.8 (1632c)	9.2E-4 (1598a)	N/A	108 (695)
Cu	1.0 (2385)	0.085 (1640)	0.7 (1549) R	980 (695)
Zn	8.61 (2385)	0.053 (1640)	11.6 (1567a)	22 (1d)
As		N/A	0.0019 (1549) R	48.8 (2780)
Se			0.008 (2670)	
Br			1.8 (1515)	
Rb		0.002 (1640) T	0.68 (1567)	
Sr	0.31 (1643e)	0.12 (1640)	25 (1515)	84 (695)
Zr			N/A	18 (57b)
Мо	1.60 (1849)	0.047 (1640)	0.0115 (1598) R	13 (695)
Ag		0.0076 (1640)	0.039 (1577b)	
Cd	313.8 (1085b)	4.6E-5 (1598a)	5E-4 (1549) R	
In			1.0 (1648)	
Sn		97.2 (1084a)	0.0019 (1549) R	
Sb		0.07 µg (2783)	2.7E-4 (1549) R	
Ι		0.088 (2670a)	0.76 (1548a) R	
Cs		N/A	0.0098 (1548a)	
Ba	0.53 (1643e)	0.33 µg (2783)	49 (1515)	33 (1d)
La			0.2 (1575)	
Ce			0.4 (1575)	
Sm			0.09 (1566a)	
Eu			3.0E-4 (1548)	
Hf			0.04 (1566a)	
Та			0.003 (1566a)	
W			8E-4 (1567a)	
Pt		697.4 (2556)	8E-6 (2670) R	
Au			8E-6 (2670) RHg	
Hg		4.2E-5 (2721)	(3.0E-4) (1549) R	
T1		1.62E-5 (2670a)	N/A	
Pb	286.2 (695)	4.9E-4 (2670a)	N/A	242 (695)
Th		5.3E-6 (2670a)	0.0367 (1566b)	
U		1.13E-4 (2670)	0.006 (1515)	
		T=TIMS; N/A=not applicable;	C=chelating column preconcentration INAA,	As oxides: Na, P, Cr, Zn, Ba 57b and 695
		µg: mass loading on filter	P=PGAA, R=RNAA, (in quartz vial)	not yet certified, values subject to change

are listed in Table 4. Of particular interest to the industry is the "zero-level" sulfur diesel fuel, RM 8771.

Paulsen et al. [29, 30] developed a spark source mass spectrometric method based on isotope dilution using isotopically enriched sulfur of mass 34 as the internal standard and using a Carius tube for a closed system for dissolution. Using this very sensitive and intrinsically accurate technique they obtained a sulfur concentration in SRM 342 (nodular cast iron) of 23  $\mu$ g g<sup>-1</sup>, which was almost a factor of 3 lower than the certified value of 60 µg  $g^{-1}$ . It was clear that standards and all measurements below 100  $\mu g g^{-1}$  sulfur could be highly biased. The procedure was significantly improved (primarily the precision of ratio measurement) by employing thermal ionization mass spectrometry. This procedure was based on the discovery that arsenic sulfide mixed with silica gel on a Re ribbon would yield thermal molecular ions of AsS<sup>+</sup> with high ionization efficiency [31]. Paulsen and Kelly [32] and Kelly and Paulsen [33] extended the technique to the measurement of sulfur in Cu-based and Fe-based materials. The first application of this new technique to an organic matrix was the determination of sulfur in bovine liver, SRM 1577a, in early 1982 (S concentration  $0.7845 \pm 0.0008\%$  (1s), n=6). The high precision of this determination demonstrated that the technique was capable of a relative accuracy and precision approaching 0.1%, which made it ideal for certification of sulfur in coal and fuel oils. Certification of the well-known SRM 2680s series of coals was completed in late 1982 and demonstrated and established this technique as the method of choice for the determination and certification of sulfur in organic matrices. Table 5 lists the sulfur content of all currently available coal SRMs, with recently determined mercury values from the work described below [34]. The relatively large uncertainties for the coals are a result of the intrinsic heterogeneity of these

 Table 4
 Sulfur content of SRM transportation fuels

samples. This is illustrated by comparing the uncertainties of SRM 2685b, a coal, and SRM 2717, a coke; they have the same sulfur content but the uncertainty for the latter is almost a factor of 10 smaller (1.4% compared with 0.17%).

#### Certification of mercury in SRMs

Since the Minamata disaster in Japan in the mid 1950s there has been an increasing focus on the management of mercury releases into the environment. Although many industrial and commercial anthropogenic sources of mercury have been dramatically reduced, coal-fired power plants remain the single largest anthropogenic contributor to atmospheric mercury. Re-deposition of atmospheric mercury results in bioaccumulation in the aquatic food chain and, subsequently, potentially excessive exposure risk to susceptible human population groups.

NIST has provided traceability and calibration support to environmental measurements of mercury for several decades by provision of suitable SRMs, primarily relying on the use of cold-vapor atomic absorption spectrometry (CVAAS) [35] and RNAA [36] for the certification process. Although both of these techniques work relatively well for biological and environmental materials with a fairly simple matrix, overall uncertainties tend to increase as the matrix becomes more complex. For example, CVAAS is prone to positive interferences in the presence of concomitant organic species which absorb at the resonance wavelength of 254 nm. Similarly NAA is subject to interferences with <sup>203</sup>Hg in the presence of selenium, which is commonly present in fossil fuels and, therefore, requires radiochemical separation [37]. CVAAS and NAA also suffer from somewhat insufficient detection limits, especially when considering today's low-level requirements in complex types of matrix. With these limitations, there was clearly a need for

SRM #	SRM name	S $\mu g g^{-1}$	Expanded uncertainty (U) $\mu g g^{-1}$
Distillate fuel oils			
1616b	Sulfur in Kerosene	8.41	0.12
1617a	Sulfur in Kerosene	1730.7	3.4
1624d	Sulfur in Diesel Fuel	3882	20
2723a	Sulfur in Diesel Fuel	11.0	1.1
2724b	Sulfur in Diesel Fuel	426.5	5.7
2770	Sulfur in Diesel Fuel	41.57	0.39
RM 8771	Sulfur in Diesel Fuel Blend Stock	0.071	0.014
Gasolines			
2294	Reformulated Gasoline (11% MTBE)	40.9	1.0
2295	Reformulated Gasoline (15% MTBE)	308	2
2296	Reformulated Gasoline (13% ETBE)	40.0	0.4
2297	Reformulated Gasoline (10% Ethanol)	303.7	1.5
2298	Sulfur in Gasoline (High Octane)	4.7	1.3
2299	Sulfur in Gasoline (Reformulated)	13.6	1.5

SRM #	SRM Name	S%	U	Hg (µg kg <sup>-1</sup> )	U
Oil					
2721	Crude Oil (Light-Sour)	1.5832	0.0044	0.0417	0.0057
2722	Crude Oil (Heavy-Sweet)	0.21037	0.00084	0.129	0.013
Coal					
2682b	Sulfur and Mercury in Coal (Subbituminous)	0.4917	0.0079	108.8	2.9
2683b	Sulfur and Mercury in Coal (Bituminous)	1.955	0.041	90.0	3.6
2684b	Sulfur and Mercury in Coal (Bituminous)	3.076	0.031	97.4	4.7
2685b	Sulfur and Mercury in Coal (Bituminous)	4.730	0.068	146.2	10.6
1632c	Trace Elements in Coal (Bituminous)	1.462	0.051	93.8	3.7
1635	Sulfur and Mercury in Coal (Subbituminous)	0.3616	0.0017	10.9	1.0
2692b	Sulfur and Mercury in Coal (Bituminous)	1.170	0.020	133.3	4.1
2693	Sulfur and Mercury in Coal (Bituminous)	0.4571	0.0067	37.3	7.7
Coke					
2718	Green Petroleum Coke	4.7032	0.0079		
2719	Calcined Petroleum Coke	0.8877	0.0010		
2775	Sulfur in Foundry Coke	0.5816	0.0051		
2776	Sulfur in Furnace Coke	0.825	0.016		
Fly ash					
1633b	Trace Elements in Coal Fly Ash	0.2075	0.0011	143.1	1.8

a new high-performance definitive method for the determination and certification of mercury, having the capabilities of high specificity, very low detection limits, rapid sample throughput, and high accuracy.

Such a method was developed in 2001 [13] and is based on ICP-MS. Traditionally, this approach involves liquid sample introduction by using a pneumatic nebulizer system, but this results in very poor detection limits and excessive sample washout times as a result of mercury becoming attached to the surfaces of the sample-introduction system. In the new method, mercury vapor is generated by reduction with tin(II) chloride, using a gas-matrix separator cell, and introduced into the ICP-MS system as Hg<sup>0</sup> vapor by use of a carrier stream of argon. This results in extremely high sensitivity, with instrument detection limits below 0.1 pg  $g^{-1}$  and immunity from spectral interferences. The introduction of Hg<sup>0</sup> also results in short sample washout times, which enables rapid sample throughput and complete removal of the residual sample matrix. The use of ICP-MS also enables use of an isotope-dilution certification scheme, providing a definitive measurement capability and traceability to the SI. The new method has revolutionized certification of mercury in SRMs at NIST. There is now the capability to accurately certify total mercury in almost any matrix, and the method has been used to certify a wide range of environmental SRMs, including fish tissue, marine organisms, sediments, waste, urine, and blood. The method has been further refined by Long and Kelly to enable measurement of mercury in fossil fuels by using Carius tube combustion as a sampleprocessing step [36]. This approach, which uses a completely closed high-pressure system, is capable of destroying all of the organic material in the sample and converting it to CO<sub>2</sub>. Loss of mercury during the combustion and isotopic spike equilibration process is eliminated by use of a closed-system. Accurate certification of mercury in coal with low uncertainty was not possible before the development of this method, and no SRMs were available. The new method has now been used to certify mercury in eight coal SRMs, in crude oils at very low concentrations [38], and in a coal fly-ash (Table 5).

The provision of high-quality SRMs certified for mercury has coincided very well with recent US EPA regulations resulting in the need for more stringent monitoring and measurement of mercury. Further support is being provided by development of the method to determine mercury in gas streams. This is intended to provide a NIST traceability basis for continuous emissions-monitoring systems (CEM) for coal-fired power plant stack emissions. This will be critical to the success of the recent US EPA Clean Air Mercury Rule (CAMR), based on a market-based cap and trade program which was promulgated in 2005.

# Use of INAA and ID ICP–MS in the certification of SRM 2783 Air Particulate on Filter Media

Atmospheric air particles are associated with numerous adverse health effects, including asthma, heart attacks, premature death, and cancer. The US EPA has promulgated new national ambient air-quality standards for particulate matter in the 2.5  $\mu$ m range (PM2.5) and has established quality-assurance requirements for state and local air monitoring stations. Standard methods for determination of elements in aerosol particles involve collection of

 Table 6
 Certified and reference mass loadings for SRM 2783
 Air

 Particulate Matter on Filter Media
 Filter M

Elements	Mass loading on filter (ng)	Element	Mass loading on filter (ng)
Certified valı	ies		
Al <sup>a,b,d,e</sup>	23210±530	Mg <sup>a,e</sup>	$8620 \pm 520$
As <sup>a,e</sup>	$11.8 \pm 1.2$	Mn <sup>a,b,e</sup>	320±12
Ba <sup>a,b,c,e</sup>	$335 \pm 50$	Na <sup>a,d,e</sup>	$1860 \pm 100$
Ca <sup>a,b,e</sup>	$13200 \pm 1700$	Ni <sup>b,c,e</sup>	68±12
Co <sup>a,d</sup>	7.7±1.2	Pb <sup>b,c,e</sup>	317±54
Cr <sup>a,b,e</sup>	135±25	Sb <sup>a,b,c</sup>	71.8±2.8
Cu <sup>a,b,c,e</sup>	404±42	Ti <sup>a,b,e</sup>	$1490 \pm 240$
Fe <sup>a,b,e</sup>	26500±1600	V <sup>a,d,e</sup>	$48.5 \pm 6.0$
K <sup>a,b,e</sup>	$5280 \pm 520$	Zn <sup>a,b,e</sup>	$1790 \pm 130$
Reference val	lues		
Ce <sup>a</sup>	23.4±3.5	Sm <sup>a</sup>	$2.04 \pm 0.15$
Rb <sup>a,b</sup>	24.0±5.5	Th <sup>a</sup>	$3.23 \pm 0.59$
S <sup>b,e</sup>	$1050 \pm 260$	U <sup>c</sup>	$1.234 {\pm} 0.024$
$Sc^{a}$	$3.54 {\pm} 0.28$	W <sup>a</sup>	$5.0 \pm 1.8$
Si <sup>a,b,e</sup>	$58600 \pm 1600$		

<sup>a</sup> Instrumental neutron-activation analysis (INAA)

<sup>b</sup> Energy-dispersive X-ray fluorescence (EDXRF), including micro-EDXRF

<sup>d</sup> Inductively coupled plasma mass spectrometry (ICP-MS)

<sup>e</sup> Proton induced X-ray emission analysis (PIXE), including micro-PIXE

particles on filters then analysis by XRF, atomic-absorption spectrometry (AAS), and, more recently, ICP–MS [39]. In response to the new air-quality standards and the analytical monitoring requirements, NIST embarked on the preparation of a standard composed of air particulate reduced in size to simulate PM2.5.

SRM 2783 provides 0.5 mg fine air particulate matter on a polycarbonate filter membrane. The air particulate matter selected for preparation of the SRM had been prepared and characterized by INAA and other techniques ensuring micro homogeneity at the International Atomic Energy Agency's Laboratories Seibersdorf [40]. The SRM samples were prepared by filtering 5 mL aliquots containing 0.5 mg air particulate matter in aqueous suspension through each individual filter and drying under Class 10 air flow. Fifteen batches of approximately 150 filters each were prepared for the SRM. Homogeneity of the mass loading was determined gravimetrically and element homogeneity was assayed during the certification analyses. The procedures of the two principal techniques, INAA and ID ICP–MS, used at NIST for value assignment were, briefly, as follows.

For INAA, filters were used whole in each determination. To protect the deposits they were covered with a blank filter and these sandwiches were subsequently sealed in clean linear polyethylene envelopes. Multielement standards were pipetted and dried on similar size Whatman 41<sup>1</sup> filters, which were then matched with the samples for irradiation. For assay of short-lived nuclides one filter and standard each were fitted into the irradiation capsule, irradiated, and measured; for longer-lived nuclides eight samples, standards, and blanks were irradiated together and measured after appropriate decay. The filter sandwiches were measured without the polyethylene packaging to minimize the blank to the content of the filters. Analyzing both blank and deposited filter together doubled the blank contribution for one critical element, chromium. The elements depicted in Fig. 1 were characterized in SRM 2783. Some other elements included in the standards, for example Ag, Cl, Cs, Mo, and U, were not detected in the filter samples by INAA. The small standard uncertainties in the INAA of the filter-based SRM 2783 demonstrate the technique's capabilities very well. These uncertainties are summarized on an elementby-element basis in Table 7, which includes results from analysis of SRM 2703. In both instances Kurfürst elemental homogeneity factors,  $H_{\rm E}$  [41], were calculated as discussed below, to obtain information about the homogeneity of the SRMs.

Seven elements, Sb, Cu, Ni, Pb, Ba, Cd, and U, were quantified by IDMS in a single set of eight filters of SRM 2783, taking advantage of the extremely high sensitivity of HR-ICP-MS instruments. Matrix-related inference with determination of Ni was eliminated by using the mediumresolution mode (nominal 3000) of the instrument. For the IDMS procedure filters were folded in half and carefully transferred to clean TFM-polytetrafluoroethylene Teflon microwave vessels. Aliquots of a single spike mix solution containing enriched <sup>61</sup>Ni, <sup>65</sup>Cu, <sup>111</sup>Cd, <sup>123</sup>Sb, <sup>137</sup>Ba, <sup>206</sup>Pb, and <sup>238</sup>U were added by mass difference to the vessels. In addition, two method-validation samples of SRM 1648 Urban Particulate Matter weighing 0.1 g and 0.025 g were processed in the same manner. Procedure blanks were measured by adding a smaller amount of the same spike mix solution to clean microwave vessels. All samples were digested in a microwave oven using high-purity nitric, perchloric, and hydrofluoric acids. After digestion the acids were evaporated by placing the vessels on a hot plate in a fume hood with Class 10 air quality. Samples were diluted to 5 mL with 2% HNO<sub>3</sub> and stored in Nalgene low-density polyethylene (LDPE) bottles. Further dilution was performed to furnish the optimum concentration for analysis of each element. Concurrent with sample preparation, calibration samples were prepared for quantification of the

<sup>&</sup>lt;sup>c</sup> Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP–MS)

<sup>&</sup>lt;sup>1</sup> Certain commercial equipment, instrumentation, or materials are identified in this article to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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Table 7	INAA uncertaint	y and results from	determination of	f element homogeneit	y in	SRM 2783 a	and SRM 2703
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Element	SRM 2783 Relative Standard Uncertainty (%)				SRM 27	SRM 2703 Relative Standard Uncertainty (%)				
	s <sub>o</sub>	SC	Sa	s <sub>h</sub>	$H_{\rm E}$	So	SC	Sa	s <sub>h</sub>	$H_{\rm E}$
Al	0.36	0.10	0.40	_a	_a	0.92	0.37	0.5	0.68	0.61
As	1.35	0.60	0.48	1.1	0.78	2.22	0.84	0.7	1.93	1.62
Ca	1.11	0.47	0.40	0.9	0.64	Not dete	rmined by IN	AA		
Ce	4.17	0.44	0.91	4.0	2.83	1.17	0.91	0.5	0.54	0.45
Со	2.02	0.30	0.59	1.9	1.34	1.26	0.89	0.5	0.74	0.62
Cr	2.30	0.37	0.65	2.2	1.56	Heteroge	eneity detected			
Fe	0.68	0.30	0.40	0.5	0.35	1.09	0.72	0.5	0.65	0.54
Hf	1.30	0.79	0.49	0.9	0.64	Not dete	rmined by IN	AA		
La	2.47	0.47	0.62	2.3	1.63	1.30	0.79	0.7	0.76	0.63
Mg	1.06	0.89	0.40	0.4	0.28	Not dete	rmined by IN	AA		
Mn	0.53	0.20	0.42	0.3	0.21	1.08	0.50	0.7	0.65	0.58
Na	0.73	0.47	0.40	0.4	0.28	0.80	0.79	0.7	a	_a
Rb	2.14	1.86	0.62	1.4	0.99	Not deter	rmined by IN	AA		
Sb	0.61	0.23	0.44	0.4	0.28	Not dete	rmined by IN	AA		
Sc	0.71	0.20	0.44	0.5	0.35	1.16	0.99	0.5	0.34	0.28
Sm	1.04	0.34	0.46	0.9	0.64	Not deter	rmined by IN	AA		
Th	0.89	0.53	0.46	0.6	0.42	1.51	1.03	0.5	0.98	0.82
Ti	4.72	0.88	0.40	4.6	3.25	Not dete	rmined by IN	AA		
V	0.65	0.45	0.43	0.2	0.14	1.49	0.90	0.5	1.08	0.96
W	3.14	1.74	0.72	2.5	1.77	Not dete	rmined by IN	AA		
Zn	2.12	0.11	1.01	1.9	1.34	1.31	1.10	0.5	0.51	0.42

<sup>a</sup> Calculated "zero" heterogeneity component, therefore  $H_{\rm E}$  cannot be determined

concentrations of the enriched isotopes by reverse IDMS. Aliquots from each of two gravimetrically prepared primary standard solutions were added to weighed aliquots of the spike mix solution, resulting in three to four calibration samples for each element. Spike calibration samples were prepared with ratios similar to those of the analytical samples and were measured concurrent with the analytical samples. Mass ratios were measured on a double-focusing magnetic sector field ICP–MS.

Results from the complete analysis including filter samples, spike calibration samples, procedure blanks, and method validation samples are summarized in Table 1 for each element. Also listed in Table 1 are the individual components of uncertainty for the ID HR ICP-MS determination and the expanded uncertainty based on a 95% confidence level. Variation among spike calibration samples provides a good measure of the uncertainty attributable to the analytical procedure, because both sample preparation and ICP-MS ratio measurement are involved. The relative standard deviation of spike calibration samples ranged from 0.14% relative (1s, n=4) for U to 0.54% relative for Cu (1s, n=4). The variability observed among filter samples was always greater than the variability of the analytical procedure; this is indicative of sample heterogeneity. Results obtained for well-characterized standards enable true validation of the analytical procedure and assessment of uncertainty. ID HR ICP-MS results for two SRM 1648 Urban Air Particulate samples, listed as mean±standard deviation, are in excellent agreement with certified and information values. These results for SRM 2783 and SRM 1648 demonstrate the multi-element capability, and high precision, accuracy, and sensitivity achievable for complex matrices with ID HR ICP–MS. Uranium, which could not be detected in SRM 2783 by other methods, was measured at the ng level with an expanded uncertainty of 2% relative.

The NIST analytical values determined by INAA and ID HR ICP–MS were used with values from collaborating laboratories to assign certified values and uncertainties to the SRM, as shown in Table 6. Certified values are weighted means of results from two or more analytical methods [42]. The uncertainty listed with each value is an expanded uncertainty, with coverage factor 2 (approximately 95% confidence), calculated by combining a betweensource variance incorporating inter-method bias with a pooled within-source variance, and a component of variance for material heterogeneity. The reporting follows the ISO/NIST Guide to the Expression of Uncertainty in Measurements [43].

## Advanced natural matrix reference materials

In addition to the accurate information on the certified mass fraction of an element in a material, it must be ensured that the elemental mass fraction in the SRM is stable with time and is the same in each test portion taken from the entire lot of the SRM. These two properties, stability and homogeneity, have proven to be a significant challenge with the development of more advanced materials, e.g. fresh frozen materials and materials for element speciation, and with development of analytical methods that generate analytical results from ever-decreasing quantities of sample, e.g. solid sampling techniques.

# Stability of fresh-frozen SRMs for element species (methylmercury)

Since the 1960s, natural-matrix SRMs have been issued in the form of dried, sterilized powders with excellent longterm compositional stability when properly stored and handled [44]. At that time they had the closest possible resemblance to the natural samples that were analyzed daily in laboratories. These materials are clearly unlike most analyzed environmental and biological samples, however. They have different physical characteristics, the element fractions are higher, because of the drying, and they normally require a modified treatment for destruction, which makes them less comparable with natural samples. In addition, variable uptake of moisture during storage and possible associated changes in composition must be considered for the dried materials. Fresh-frozen SRMs were introduced in the early 1990s [45, 46]; frozen SRMs certified for trace elements are listed in Table 8. They are produced from the natural materials by cryogenic milling and homogenization. They truly mimic samples that are actually analyzed in the laboratory and, therefore, eliminate commutability concerns.

Fresh-frozen SRMs prepared from natural materials seem to be particularly suitable for characterization of organic and inorganic compounds that are subject to degradation in nature and whose stability can be maintained at low temperatures. The stability of one typical compound, methylmercury, has been studied in these materials with improved analytical methods and use of sensitive, hyphenated instrumental techniques, i.e. gas and liquid chromatography coupled to ICP–MS.

NIST has used solid-phase micro-extraction (SPME) then gas chromatography with atomic-emission detection (GC-AED) [47] or gas chromatography-mass spectrometry (GC-MS), depending on the concentrations in the material, as in-house methods for certification of methylmercury in environmental SRMs. Recently, species-specific isotope dilution (SID) [48, 49] has been developed and used at NIST for Hg-species certification. The use of speciesspecific isotopically labeled spikes enables quantification of individual species and measurement of their degradation and/or transformation during the analytical process. Quantification of monomethyl and inorganic mercury by "double spike" SID-GC-ICP-MS has been developed for the certification of mercury species in NIST SRMs. The procedure utilizes isotopically enriched spikes of CH<sub>3</sub><sup>202</sup>Hg<sup>+</sup> and <sup>201</sup>Hg<sup>+2</sup> and microwave-assisted extraction, then volatilization of the mercury species by derivatization with sodium tetraethylborate, then back extraction into hexane. SID-MS maintains the advantages of IDMS (primary method) while enabling correction for the degradation encountered in the analytical process.

This new methodology has been used for retrospective analysis of species previously certified by GC–AED. For example, the certified values for methylmercury in the fresh-frozen SRM 1946 Lake Superior Fish Tissue are based on the combined results from analyses by NIST (SPME–GC–AED) and two collaborating laboratories—the Institute of Applied Physical Chemistry, Research Centre Jülich (Jülich, Germany) (LC–CVAAS) and the Joef Stefan Institute (Ljubljana, Slovenia) (GC–ECD) [47]. Figure 2 shows results from individual measurements of methylmercury in SRM 1946 by SID-GC–ICP–MS and the total mercury determinations from the sum of the individual species. The results of the SID measurements during the 2005 calendar year are in good agreement with the certified values, demonstrating the stability of the mercury species

 Table 8
 Fresh-frozen biological tissues and fluids (listing for inorganic constituents only)

SRM	Description	Certified constituents	Reference constituents	Year issued
1974b	Organics in Mussel Tissue (Mytilus edulis)	Mercury, methylmercury	Ag, As, Cd, Cr, Cu, Fe, Ni, Pb, Se, Sn, Zn	2003
1946	Lake Superior Fish Tissue	Mercury, methylmercury, arsenic, iron	Cd, Ca, Cu, K, Mg, Na, P, Se, Zn	2002
1947	Lake Michigan Fish Tissue	Mercury, methylmercury	Trace elements	In preparation
955b	Lead in Bovine Blood	Lead		1998
956b	Electrolytes in Frozen Human Serum (3 levels)	Ca, K, Li, Mg, Na		2004
966	Toxic Metals in Bovine Blood (2 levels)	Pb, Cd, Hg, methylmercury		2000
1598a	Animal Serum	Trace elements	Trace elements	In preparation

Fig. 2 Individual measurements during the year 2005 of MeHg and Total Hg (sum of individual mercury species) for SRM 1946 Lake Superior Fish Tissue (solid lines reflect certified values and expanded uncertainties). Expanded uncertainties of single measurements are based on repeat measurements of similar matrix SRMs



since the material was made available in 2003. This new methodology has also been used for certification of the methylmercury content of two new fresh frozen SRMs, Lake Michigan Fish Tissue (available in 2006) and SRM 1974b Organics in Mussel Tissue (now available). Additional retrospective studies on freeze-dried SRMs originally issued between 1998 and 2001 (1566b Oyster Tissue, 2976 Mussel Tissue (Trace Elements and Methylmercury), and 2977 Mussel Tissue (Organic Contaminants and Trace Elements) have shown that the SID measured values for methylmercury and total mercury fall within the expanded uncertainty listed on the respective Certificates of Analysis.

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#### Highly homogeneous materials

Table 9

Natural materials are usually heterogeneous and thus creation of an SRM lot requires extensive preparation to achieve adequate between-sample reproducibility. Milling, grinding, and sieving are routinely used to achieve a more homogeneous particle size distribution; this is followed by mixing and blending in SRM production. A very effective way of reducing particle sizes is by air jet milling. This usually contamination-free process has resulted in much better homogeneity for several environmental SRMs (Table 9).

The increasing use of small-sample analytical techniques with air particulate matter and geological samples led to the recent development of highly homogeneous SRMs-SRM 2783 Air Particulate on Filter Media and SRM 2703 Sediment for Solid Sampling (Small Sample) Analytical Techniques. In both productions, air jet milling was used to reduce the natural particle sizes of already rather homogeneous fine particulate material, vielding a more uniform distribution of 2.5 to 3.5 µm (Fig. 3). The units of SRM

jet-milling	SRM	Description	Certified constituents	Reference constituents	Year issued
	1515	Apple Leaves	22 elements	(21 elements) <sup>a</sup>	1993
	1547	Peach Leaves	22 elements	(16 elements) <sup>a</sup>	1993
	1573a	Tomato Leaves	21 elements	(20 elements) <sup>a</sup>	1993
	1575a	Pine Needles	12 elements	11 elements	2002
	1566b	Oyster Tissue	22 elements and methylmercury	8 elements	2001
	1577c	Bovine Liver	Trace elements	Trace elements	In preparation
	2783	Air Particulate on Filter Media	18 elements	9 elements	2001
	2703	Sediment for Solid Sampling (Small Sample) Analytical Techniques	22 elements	7 elements	2005
	695	Trace Elements in Multi-nutrient	16 elements	6 elements	In preparation
<sup>a</sup> Information only, no assigned uncertainties		Fertilizer			- •

Fig. 3 Particle-size distribution in jet-milled urban dust used for SRM 2783, compared with ambient urban dust SRM 1648a, and in jet-milled sediment used for SRM 2703, compared with native sediment SRM 2702



2783 are 0.5 mg particulate matter deposited on a polycarbonate filter whereas the 5-g units of SRM 2703 are in powder form. The homogeneity of both materials was principally tested by an INAA procedure developed for small-sample analysis [50].

In homogeneity testing, the crucial problem is differentiation of measurement uncertainty from uncertainty arising as a result of sample heterogeneity. The special suitability of INAA for homogeneity testing is because of its non-destructive character, simultaneous multi-element capability, high sensitivity for many elements, and the well-understood and experimentally assessed sources of uncertainty. Unlike non-radiometric methods of analysis, uncertainty modeling in INAA is facilitated by the existence of counting statistics. Although in principle an additional source of uncertainty, this parameter is instantly available from each measurement. If the method is under statistical control and the uncertainty of the counting statistics is small, the major source of variability in addition to analytical uncertainty can be attributed to sample heterogeneity. The relationship  $s_h = \sqrt{(s_a^2) - (s_a^2)}$ , where  $s_{\rm h}$  is the heterogeneity expressed as the standard deviation due to heterogeneity, can be easily resolved from the overall observed variance  $s_o^2$  and the total analytical variance  $s_a^2$ , the latter being accurately assessed in the INAA procedure. For this purpose, high-accuracy, highprecision INAA procedures are used at NIST, including high-rate counting techniques to minimize the statistical counting uncertainties. These techniques provide the analytical data to quantify the uncertainty components due to heterogeneity in the investigated materials for a significant number of elements, covering amounts of element ranging over 7 to 8 orders of magnitude. To express the sample heterogeneity in numerical terms, Ingamells and Pitard [51]

introduced the term "sampling constant"  $K_s = R_s^2 \times m$ , where  $R_s^2$  is the sampling variance (determined as discussed above) and *m* the mass of the sample. The square root of this expression leads to the Kurfürst elemental homogeneity factor  $H_E = R_s \times \sqrt{m}$  [41], which is numerically equal to the relative standard deviation (with 68% confidence) due to heterogeneity (sampling uncertainty) for the unit of mass (1 mg) used in the determination. The  $H_E$  values determined by INAA for SRM 2783 and SRM 2703 are given in Table 7.

In the process of homogeneity determination at NIST, INAA is normally complemented by XRF analysis, and, for small samples, by laser-ablation mass spectrometry, with collaborating laboratories providing micro-beam XRF, micro-PIXE, and solid-sampling GFAAS measurements. Two SRMs currently in the certification process, SRM 1648a Urban Particulate and SRM 1577c Bovine Liver, will be fully characterized for their sampling properties by a combination of these methods.

### Conclusions

NIST continues to update its large range of more than 200 different materials with applications in the assay of environmentally relevant inorganic constituents. These updates are in response to regulatory requirements, industrial needs, and emerging environmental research, and to progress in analytical methodology. The requirements for improved analytical results are served by smaller uncertainties of the certified values and a continuing effort to characterize lower levels of the elements with high environmental impact, for example sulfur and mercury. Two particular developments have affected the recent production of environmental SRMs: First, the need to better mimic fresh field samples and considerations of the stability of sensitive compounds has led to an increase in the production of fresh-frozen materials, which is currently extending to other application fields, for example clinical and nutritional related SRMs. Second, development and increased use of solid (small) samples in trace-element analytical techniques require more homogeneous SRMs certified at the actual sample intake levels. Highly homogeneous materials can be produced and characterized; the objective of current efforts with the renewal of SRM 1648a Urban Dust and SRM 1577c Bovine Liver is to achieve this new requirement for SRMs. Advances in analytical measurements and in the selection and preparation of SRMs are made to improve utility to the users. User communities have provided essential input to the current SRMs, and their input is indispensable for future developments in this program.

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