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Determination of As, Cd, Cr, and Hg in SRM 2584 (Trace Elements in Indoor Dust) by high-resolution inductively coupled plasma mass spectrometry

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Abstract Standard reference material (SRM) 2584 (Trace Elements in Indoor Dust) was developed as a reference standard for evaluating field methods and for validating laboratory and reference methods for the assessment of lead contamination and exposure. In addition to lead, the toxic trace elements As, Cd, Cr, and Hg, at approximately 17, 10, 140, and 5 $\mu\text{g g}^{-1}$, respectively, have been certified in the SRM. These four analytes were successfully determined by use of high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Isobaric interferences at masses of As and Cr were resolved by using the high resolution mode (nominal 8000) and the medium resolution mode (nominal 3000), respectively, of the instrument.

The effects of a significant drift in analyte sensitivity in the course of measurement were rectified by use of internal standardization, single spike standard addition, and an optimized analysis sequence. The results were compared with those obtained by instrumental neutron activation analysis (INAA) and isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). The results for the quality control, SRM 2704 (Buffalo River Sediment), were in good agreement with the certified values, indicated by the uncertainty intervals of the measured values overlapping the certified intervals at 95% confidence level.

Introduction

Lead poisoning is a major environmental health hazard for children. A child exposed to high levels of lead can

suffer from a variety of health effects, including hyperactivity, lethargy, hearing or memory loss, or learning disabilities [1]. A primary source of the lead contamination in the indoor environment is the lead-based paint that was widely used in residential areas before the 1970s. As a result, the United States Environmental Protection Agency (EPA) included prevention of lead-based paint poisoning as part of the Toxic Substances Control Act, which is codified in the Federal Regulations [2]. Standard Reference Material® (SRM) 2584 (Trace Elements in Indoor Dust) was developed at the request of EPA. The SRM contains a nominal mass fraction of 1% lead, and is designed to be a reference material for indoor dust contaminated by lead-based paint. It serves as a tool in assisting field method development, in evaluating sampling methods, and in validating laboratory methods for the assessment of lead contamination and exposure [3, 4].

As part of the certification program the mass fractions of the toxic metals As, Cr, Cd, and Hg in SRM 2584 were determined by plasma source mass spectrometry [5]. Because complete digestion of the dust sample requires perchloric acid, determination of As and Cr by quadrupole ICP-MS is susceptible to interferences by $^{40}\text{Ar}^{35}\text{Cl}^+$, $^{35}\text{Cl}^{16}\text{O}^+\text{H}^+$, and $^{37}\text{Cl}^{16}\text{O}^+$ at $^{75}\text{As}^+$, $^{52}\text{Cr}^+$, and $^{53}\text{Cr}^+$, respectively. As an alternative to quadrupole ICP-MS, which cannot resolve isobaric interferences at the masses of As and Cr, As is routinely measured by atomic absorption spectrometry (AAS) [6], and Cr is measured by inductively coupled plasma optical-emission spectrometry (ICP-OES) [7] or X-ray fluorescence (XRF) [8].

High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is capable of resolving many plasma-, water-, and matrix-based polyatomic interferences, and the technique has been used for the successful determination of elements subject to spectral interference in samples with complex matrices [9]. The argide, chlorine hydroxide, and chlorine oxide ion interferences with ^{75}As , ^{52}Cr , and ^{53}Cr can be resolved at resolutions greater than 7800, 1700, and 2600, respectively. The trade-off for using a higher resolution mode in the determinations of As and Cr is reduced analyte sensitivity. Here we report

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an evaluation of our recently acquired HR-ICP-MS as a tool for certification analysis in low, medium, and high-resolution modes. The mass fractions of As, Cd, Cr, and Hg in SRM 2584 were determined in the process.

Experimental

Instrumentation.¹ A Finnigan-MAT (Bremen, Germany) Element double-focusing sector field high-resolution mass spectrometer equipped with a Scott-type spray chamber and a Fassel torch was used. The instrument has three fixed resolution settings: high, medium, and low for nominal $m/\Delta m$ of 8000, 3000, and 300, respectively. The resolution settings for ^{75}As , ^{52}Cr , ^{53}Cr , ^{111}Cd , and ^{202}Hg were high, medium, medium, low, and low, respectively. Aerosols of the solutions were generated by use of a model MCN-100 micro-concentric nebulizer from Cetac Technology (Omaha, NE, USA) pumped with a Spetec model Perimax 12 peristaltic pump (Erding Germany). A model ASX-100 autosampler from Cetac Technology was used for sample introduction. A model MLS 1200 Mega microwave system equipped with a model HPR 1000/6 rotor from Milestone Laboratory Systems (Monroe, CT, USA) was used for sample digestion.

Procedure. Six bottles of SRM 2584 (Trace Elements in Indoor Dust) and two bottles of SRM 2704 (Buffalo River Sediment) as quality controls were used for this analysis. A sample from each bottle (ca. 0.1 g) was weighed into a microwave cell and HNO_3 (4 mL), HClO_4 (2 mL), and HF (0.5 mL) were added to the cell for sample digestion. Separately, a sample (0.5 g) from each bottle was dried in an oven at 110 °C for 2 h. The difference between the weights of the sample before and after drying was used to calculate the moisture-content of the sample; all values reported here were calculated on a dry mass basis. The six samples of SRM 2584, two samples of SRM 2704, and four procedural blanks were digested in a microwave oven set to 250 W for 5 min, and then at 500 W for 30 min. The resulting solutions were clear with no precipitates or residues. Each digest was diluted to approximately 125 g with deionized water. An aliquot (20 g) of each digest was mixed with $\text{K}_2\text{Cr}_2\text{O}_7$ solution (1% by mass fraction, 1 mL) as a stabilizer for the determination of Hg. Rh (ca. 0.2 μg) was added to each solution as an internal standard. The method of standard addition was used for quantification of all analytes.

All calibration standards were prepared from SRMs 3106a, 3108, 3112a, and 3133 spectrometric solutions of As, Cd, Cr, and Hg, respectively. The 1% solution of $\text{K}_2\text{Cr}_2\text{O}_7$ was prepared from SRM 136e potassium dichromate oxidimetric standard. All acids were purified at NIST by sub-boiling distillation. The measurement uncertainties reported in this work are at 95% confidence intervals unless otherwise stated.

Results and discussion

Spectral interferences

A potential isobaric interference at mass 111, $^{95}\text{Mo}^{16}\text{O}^+$ cannot be resolved from the $^{111}\text{Cd}^+$ signal at the highest resolution (nominal 8000) of the HR-ICP-MS. To determine the presence or absence of this interference the digests of SRMs 2584 and 2704 and four single-element standards of 16 ng g^{-1} Cd were measured at low resolution

¹Certain commercial instruments are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment identified is necessarily the best for the purpose.

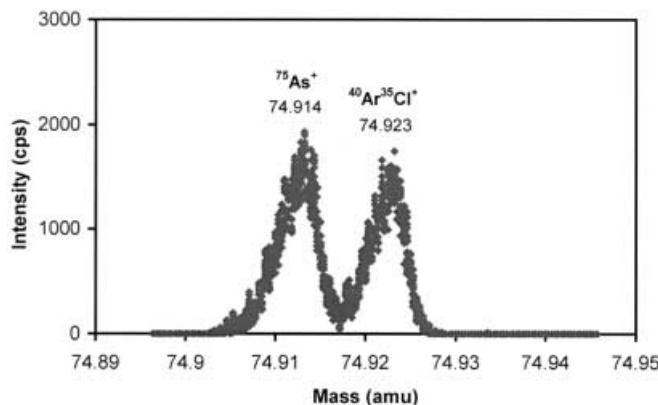


Fig. 1 Mass spectrum obtained from an SRM 2584 solution containing approximately 13 ng g^{-1} ^{75}As

for intensities at masses 111, 112, 114, and 118. The $^{111}\text{Cd}/^{112}\text{Cd}$ and $^{111}\text{Cd}/^{114}\text{Cd}$ values were calculated after subtraction of the Sn intensities at masses 112 and 114 by using the intensity at mass 118 [10]. The $^{95}\text{Mo}^{16}\text{O}^+$ interference in the digests of the two SRMs was negligible because the $^{111}\text{Cd}/^{112}\text{Cd}$ and $^{111}\text{Cd}/^{114}\text{Cd}$ values of the SRMs were statistically indistinguishable from those for the standards. No spectral interference was observed at ^{202}Hg either; Cd and Hg were therefore determined in the low-resolution mode at masses 111 and 202, respectively.

The spectrum of $^{75}\text{As}^+$ in SRM 2584 is shown in Fig. 1. The intensity of the $^{75}\text{As}^+$ peak on the left is approximately the same as that of the $^{40}\text{Ar}^{35}\text{Cl}^+$ peak on the right. The actual resolution determined at the experimental setting was approximately 9000 ($m/\Delta m$, 10% valley). A centered mass window of 50% of the full $^{75}\text{As}^+$ peak width was used for the analysis. A 2-fold larger mass window could have been used without interference from the $^{40}\text{Ar}^{35}\text{Cl}^+$ peak, but could run the risk that drift in the mass calibration might result in the $^{40}\text{Ar}^{35}\text{Cl}^+$ peak drifting into the integration window.

Chromium has four isotopes at masses 50, 52, 53, and 54 with nominal abundances of 4.35%, 83.79%, 9.5%, and 2.37%, respectively. Chromium at masses 50 and 54

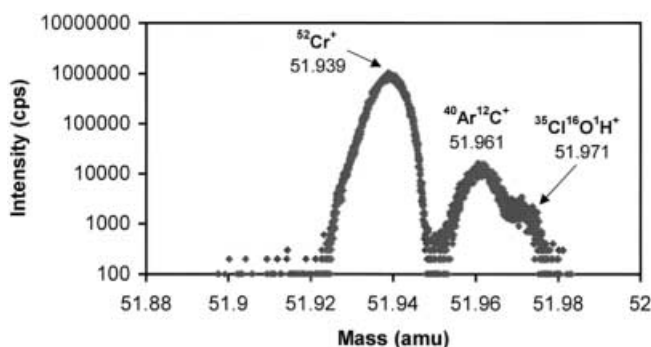


Fig. 2 Mass spectrum obtained from an SRM 2584 solution containing approximately 100 ng g^{-1} Cr, with the spectral intensities in log scale

was not measured for this analysis, because the isobaric interferences of ^{50}Ti and ^{50}V at ^{50}Cr , and that of ^{54}Fe at ^{54}Cr cannot be resolved by use of the high-resolution mode of HR-ICP-MS. The spectrum of $^{52}\text{Cr}^+$ in SRM 2584 is shown in Fig. 2 with intensities on a log scale. The $^{52}\text{Cr}^+$ peak is the first from the left at mass 51.939. On the basis of their positions relative to the $^{52}\text{Cr}^+$ peak, the peak at mass 51.961 was identified as $^{40}\text{Ar}^{12}\text{C}^+$ and the small peak on the right shoulder of the $^{40}\text{Ar}^{12}\text{C}^+$ peak as $^{35}\text{Cl}^{16}\text{O}^+\text{H}^+$. The intensities of $^{52}\text{Cr}^+$, $^{40}\text{Ar}^{12}\text{C}^+$, and $^{35}\text{Cl}^{16}\text{O}^+\text{H}^+$ are 1.0×10^6 counts per second (cps), 1.6×10^4 cps, and 3.4×10^3 cps, respectively. The $^{52}\text{Cr}^+$ peak is fully resolved from the $^{40}\text{Ar}^{12}\text{C}^+$ and $^{35}\text{Cl}^{16}\text{O}^+\text{H}^+$ peaks, and the overall intensity of the interferences is less than 2% of the $^{52}\text{Cr}^+$ intensity in SRM 2584. The signals for $^{53}\text{Cr}^+$ and $^{37}\text{Cl}^{16}\text{O}^+$ were also measured; the peak intensity of the latter was approximately 10% of the former in SRM 2584. The peak intensity of $^{52}\text{Cr}^+$ was used for the certification analysis because ^{52}Cr is the most abundant of the four Cr isotopes, and interference at ^{52}Cr was minimal. The intensity of $^{53}\text{Cr}^+$ was also measured for comparison.

Drift

A common problem affecting repeatability and the accuracy in mass spectrometric measurements is drift of the signal intensity. Rhodium and In are frequently used as internal standards for drift correction in mass spectrometric measurements [11]. For these analyses a known quantity of Rh was added to each sample as an internal standard to compensate for this drift. Figure 3 shows the normalized intensities of Rh as a function of time for low-, medium-, and high-resolution modes of the HR-ICP-MS. A 60% decrease of Rh sensitivity was observed in the high-resolution mode over the course of a measurement that lasted approximately 90 min. During a similar period, the sensitivity of Rh decreased by 50% in the medium-resolution mode. The sensitivity of Rh drifted down by 30% at low resolution over a period of 3 h, and the sensitivity was down by approximately 19% in the first 90 min. The SRM 2584 samples analyzed by HR-ICP-MS contained ap-

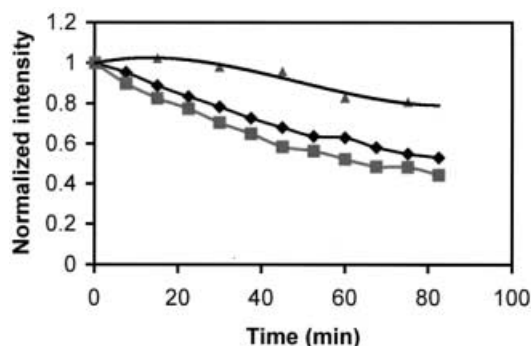


Fig. 3 Sensitivity of Rh in SRM 2584 as a function of time with the HR-ICP-MS set to (▲) normal resolution, (◆) medium resolution, and (■) high resolution

proximately 0.04% total dissolved salt (TDS), which was well within the working range of the MCN-100, which is capable of aspirating solutions containing more than 0.5% TDS. Consequently, the nebulizer seemed to have been aspirating normally throughout the measurements. The clogging of the sampler cone as the cause of the drift was eliminated because there was no noticeable build up around the orifice after the measurements. This amount of drift was not observed when neat solutions prepared in 0.2 mol L^{-1} nitric acid were aspirated, suggesting that the drift was induced by the sample matrix.

The drift of the analyte intensity was corrected to a large extent by normalizing the analyte intensity against the sensitivity of the internal standard. Because of the dissimilar chemical and physical properties of the analyte and the internal standard, a small residual drift component might remain [12]. A single spike standard addition method was used for each sample during this work. Any drift that occurs between the measurement of the unspiked and spiked samples will result in a bias. The unspiked and the spiked samples were measured as sequenced pairs, with the order for unspiked and the spiked solutions alternated so that the systematic effects of any residual unidirectional drift was accounted for as a random uncertainty of the measurement.

Results for SRM 2584

Certified values for an SRM are often established using at least two independent analytical methods [13]. For the certification of SRM 2584, the second independent technique for As, Cr, and Hg was instrumental neutron activation analysis (INAA); for Cd it was isotope dilution with quadrupole ICP-MS (ID-ICP-MS) determination.

Table 1 compares the mass fraction and expanded uncertainty of As, Cd, Cr, and Hg in SRM 2584 determined by HR-ICP-MS with those determined by the second method in this study [14]. The As mass fraction of $16.8 \pm 0.9 \text{ mg kg}^{-1}$ determined by HR-ICP-MS is in good agreement with the INAA result of $17.6 \pm 1.8 \text{ mg kg}^{-1}$. Despite the 60% drift of the analyte intensity during the measurement, the relative uncertainty of the measurement for As, defined as the expanded uncertainty divided by the mean, is only 5.6%, an evidence that the effect of the drift of the analyte intensity was successfully corrected. The Cd and Hg mass fractions in SRM 2584 measured by HR-ICP-MS are $10.2 \pm 0.6 \text{ mg kg}^{-1}$ and $5.28 \pm 0.32 \text{ mg kg}^{-1}$, respec-

Table 1 The mass fraction (mg kg^{-1}) of As, Cd, Cr, and Hg in SRM 2584 (Trace Elements in Indoor Dust)

	As	Cd	Cr	Hg
HR-ICP-MS	16.8 ± 0.9	10.2 ± 0.6	129.8 ± 7.7	5.28 ± 0.32
Second method	17.6 ± 1.8	9.99 ± 0.40	140.2 ± 2.05	5.14 ± 0.36

The uncertainties expressed in the table are expanded uncertainties at 95% confidence level [14]

Table 2 The mass fraction (mg kg⁻¹) of As, Cd, Cr, and Hg in the quality control, SRM 2704 (Buffalo River Sediment)

	As	Cd	Cr	Hg
Sample 1	21.7 ± 1.1	3.52 ± 0.24	135 ± 5	1.39 ± 0.06
Sample 2	22.7 ± 1.5	3.54 ± 0.09	130 ± 1	1.44 ± 0.07
Certified value	23.4 ± 0.8	3.45 ± 0.22	135 ± 5	1.47 ± 0.07

The uncertainties expressed in the table are expanded uncertainties at 95% confidence level [14]

tively. These values are in excellent agreement with the Cd and Hg mass fractions of 9.99 ± 0.40 mg kg⁻¹ and 5.14 ± 0.36 mg kg⁻¹ obtained by ID-ICP-MS and INAA, respectively.

The Cr result from HR-ICP-MS, 129.8 ± 7.7 mg kg⁻¹, does not fall within the uncertainty of 140.2 ± 2.05 mg kg⁻¹ obtained by INAA. The cause of the discrepancy between Cr results obtained by HR-ICP-MS and INAA is not yet clear, because visual inspection suggested the samples were completely digested. Cr is, however, known to be a difficult element to digest, except by lithium metaborate fusion [15]. In this study, both ⁵²Cr and ⁵³Cr were used to quantify the total mass fraction of Cr. The values were 129.8 ± 7.7 mg kg⁻¹ and 128.3 ± 6.3 mg kg⁻¹ obtained at the masses ⁵²Cr and ⁵³Cr, respectively. The good agreement between the two numbers suggests that the Cr peaks are resolved at medium resolution and that the aforementioned discrepancy could not arise from the spectral interferences at Cr masses. The lower value obtained relative to INAA might be an indication of incomplete digestion or loss of Cr [15].

Table 2 lists the measured mass fractions and the expanded uncertainties of the analytes for the two samples of SRM 2704 (Buffalo River Sediment) that were used as quality controls for the analysis. The certified values of the SRM are also included in the table. The type-A uncertainty of As, Cd, and Cr was obtained from ten replicate measurements of each SRM 2704 sample [14]. Mercury was determined in subsamples of the digests containing K₂Cr₂O₇ stabilizer, and a longer wash-out time was used between samples for the element compared with the other analytes. Type-A uncertainty for Hg was obtained from eight replicate measurements of each SRM 2704 sample. Except for As, measured values for each analyte are within the 95% confidence interval of the certified value of the analyte. The measured As values barely overlap with the certified values. Measurements performed at NIST over several years have indicated that the As mass fraction in the SRM, which was developed in 1985 and is now discontinued, has been slowly decreasing over time. This would account for the measured values being on the lower end of the certified range.

Conclusion

As, Cd, Cr, and Hg were successfully determined in digests of soil samples containing a large mass fraction of chlorine by use of a single analytical technique – HR-ICP-MS. It was demonstrated that HR-ICP-MS is not only a powerful diagnostic tool for determining and resolving spectroscopic interferences, but also a versatile technique for quantitative determination of analytes at low, medium, and high resolution. Significant drift of analyte sensitivity was observed; the effects of the drift on the repeatability and accuracy of the results were minimized by use of internal standardization, single spike standard addition, and by using an optimized order of the analysis sequence.

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