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Using inductively coupled plasma–mass spectrometry for calibration transfer between environmental CRMs

Abstract Multielement analyses of environmental reference materials have been performed using existing certified reference materials (CRMs) as calibration standards for inductively coupled plasma–mass spectrometry. The analyses have been performed using a high-performance methodology that results in comparison measurement uncertainties that are significantly less than the uncertainties of the certified values of the calibration CRM. Consequently, the determined values have uncertainties that are very nearly equivalent to the uncertainties of the calibration CRM. Several uses of this calibration transfer are proposed, including, re-certification measurements of replacement CRMs, establishing traceability of one CRM to another, and demonstrating the equivalence of two CRMs. RM 8704, a river sediment, was analyzed using SRM 2704, Buffalo River Sediment, as the calibration standard. SRM 1632c, Trace Elements in Bituminous Coal, which is a replacement for SRM 1632b, was analyzed using SRM 1632b as the standard. SRM 1635, Trace Elements in Subbituminous Coal, was also analyzed using SRM 1632b as the standard.

Introduction

We have developed a methodology for performing inductively coupled plasma–optical emission spectrometry (ICP–OES) which has reduced measurement uncertainty by more than an order of magnitude. This high-performance methodology was first developed as a means of comparing single-element calibration solutions, and for this application we have routinely achieved relative expanded uncertainties of 0.1%. The high-performance ICP–OES methodology has also been used for determination of the major elements in a lithium aluminate ceramic material [1] and Standard Reference Material 1775, a high-temperature alloy. In this work we extend the application to trace analysis using ICP–mass spectrometry (ICP–MS), making high-performance multielement comparisons of complex natural matrix environmental standard reference materials (SRMs). The goals of this work are severalfold. First, we wish to demonstrate a calibration transfer between CRMs of similar matrix, using a certified SRM as a calibration standard for the analysis of a candidate CRM. Second, we wish to propose that measurements similar to those presented here would be appropriate for establishing traceability of a secondary natural matrix reference material to a NIST SRM or any CRM. Third, we will describe a high-performance comparison between two SRMs as a means of demonstrating their equivalence. Two data sets will be presented. The first is the multielement high-performance comparison of SRM 2704, Buffalo River Sediment, with a candidate replacement material. The second data set compares SRM 1632b, Trace Elements in Bituminous Coal with its replacement, SRM 1632c, and with SRM 1635, Trace Elements in Subbituminous Coal.

The use of natural matrix reference materials such as SRM 2704 and SRM 1632b is recommended for the validation of analytical methods, but not for calibration, and thus the work presented here contradicts this intended usage. The major impediment to using such SRMs as calibration standards is the significant uncertainties in their certified values, which need to be combined with the measurement uncertainty of a comparison when computing the uncertainty of the material being analyzed, leading to increased uncertainty. Using high-performance spectrochemical methods, comparison measurements can be made with uncertainties significantly less than the uncertainty of most certified values, and therefore a calibration can be transferred from one reference material to another

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with no significant increase in uncertainty. This can be an efficient approach for re-certification projects, that is, the certification of CRMs of similar matrix meant to replace a CRM that is no longer available.

Traceability is defined as the "property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties" [2]. Using high-performance spectrochemical measurements to compare a secondary reference material to a CRM is a means of establishing traceability to that CRM with little increase in uncertainty of that of the CRM.

The high-performance methodology is based on three interacting procedural tools. The first is the use of an internal standard. With modern ICP optical emission and mass spectrometers there is a high degree of correlation in the noise of different elements, which enables an internal standard to be used in a manner in which both short-term and long-term noise can be largely cancelled. Second is an experimental design in which the sequence of samples and standards is repeated at least five times in a measurement session that lasts several hours. In the examples shown here, total measurement times exceeded 15 h. The long measurement time improves precision through increased signal averaging, but oddly enough the most useful aspect of the long measurement is that it enables a better view of instrument drift. This leads to the third tool of the high-performance methodology, drift correction using the method of Salit and Turk [3]. This method combines the data from all samples in a manner that enables drift to be separated from short-term noise. The drift is then empirically modeled, and stripped from the raw data. In many situations, drift is the most significant source of measurement noise, and the drift correction procedure often results in improvement in precision of an order-of-magnitude or more.

SRM 2704, Buffalo River Sediment, is an important environmental CRM that was certified in 1985 for 28 elements, but this SRM is now exhausted. When the material was collected, a portion was set aside for possible use as an SRM to be certified for organic constituents. Unlike SRM 2704, this material was not radiation sterilized. The organic constituent SRM was never developed, and in 1995 the material that had been set aside was radiation sterilized, blended, bottled, and labeled Reference Material (RM) 8704. We analyzed RM 8704 by use of a high-performance method, ICP–MS, with SRM 2704 as the calibration standard.

SRM 1632b, Trace Elements in Bituminous Coal, was certified in 1985 for 25 elements, and is being replaced by SRM 1632c. Both coals were collected from the same seam (Pittsburgh seam), but at different times and locations. We have analyzed SRM 1632c by high-performance ICP–MS using SRM 1632b as the calibration standard. For method validation, we concurrently analyzed SRM 1635, Trace Elements in Subbituminous Coal, also using SRM 1632b as the calibration standard.

Table 1 ICP–MS mass list

Element	m/z	
	River sediments	Coals
As	75	
Ba	137, 138	136
Cd	111, 114	111
Co	59	59
Cr	52, 53	
Cu		63, 65
Fe	57	
Mg	10, 11	
Mn	55	55
Ni	60	60
Pb	206, 208	206, 208
Se		82
Ti	47, 49	
U	238	
V	51	
Zn	66, 68	66, 68

Experimental

Buffalo river sediments. Samples from eight bottles of SRM 2704 and eight bottles of RM 8704 were dissolved using a lithium metaborate fusion procedure. Each sediment sample weighed approximately 0.5 g and was mixed with approximately 1.5 g of lithium metaborate in covered platinum crucibles. All masses were controlled to within 1% of the target mass. Six blanks were also prepared. The samples and blanks were fused overnight at 1000 °C, and quantitatively dissolved in dilute HNO_3 (4%, v/v; 200 mL). The solutions were diluted by a factor of five and spiked with indium to a concentration of approximately 20 ng g^{-1}. Separate 0.5-g samples were taken from each bottle for moisture determination; all values are calculated on a dry-mass basis.

ICP–MS spectra including 28 masses covering different isotopes of the 17 elements certified in SRM 2704 and the internal standard were collected for each solution on a quadrupole ICP mass spectrometer (Elan 5000, Perkin & Elmer, Norwalk, CT, USA)[1]. Each spectrum required 354 s for data collection and was preceded by a delay time of 120 s for solution transfer and stabilization and was followed by a 60 s wash time. The six blank solutions were run first, followed by the SRM 2704 and RM 8704 solutions in a random order. Except for the blanks, the sequence of sample solutions was repeated a total of six times, and the total measurement lasted 16 h. Data at several masses were discarded because of isobaric interference or poor signal/noise ratio, including the Cu data, which were obscured by high blank levels. The mass of each of the remaining 21 isotopes of 14 elements is listed in Table 1.

Coals. Two samples from each of six bottles of SRM 1632b, two samples from each of six bottles of SRM 1632c, and six samples from one bottle of SRM 1635 were taken for analysis. In addition, a single sample was drawn from each bottle for moisture determination. All samples weighed approximately 0.5 g and dry mass corrections were applied. The samples were digested, by use of a

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[1] To describe experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular products or equipment are necessarily the best available for that purpose.

microwave procedure, with HNO_3 (4 mL), $HClO_4$ (2 mL), and HF (0.5 mL). Six reagent blanks were also prepared. The digests were diluted to approximately 50 g and spiked with rhodium as an internal standard to a concentration of approximately 20 ng g^{-1}.

ICP–MS measurements were made with a quadrupole instrument for 13 isotopes of 10 analyte elements, plus the internal standard and an additional mass for an isobaric interference correction. The masses are listed in Table 1. Isobaric interference corrections were applied for the interferences of $^{42}Ca^{16}O^1H^+$ on $^{59}Co^+$, $^{130}Ba^{2+}$ on $^{65}Cu^+$, $^{132}Ba^{2+}$ on $^{66}Zn^+$, and $^{136}Ba^{2+}$ on $^{68}Zn^+$. The corrections were based on fractional relationships established with pure element solutions between signals at $^{43}Ca^+$ and $^{136}Ba^+$ and the interfering isobars. Each solution was measured six times in random order, and the entire measurement sequence lasted 15.5 h.

Results and discussion

Net analyte-to-internal standard signal ratios were computed and each data set was drift-corrected using the Salit & Turk method [4]. A few examples of the drift observed in the Buffalo River Sediment data set are shown in Fig. 1. The figure shows mean-centered ratio data, where each point is the ratio of the analyte/internal standard ratio for a single measurement of a particular sample to the mean analyte/internal standard ratio from all of the measurements of that particular sample. The data are shown as a function of time and the drift is evident. Although the data from the three example analyte elements (V, Cd, U) were collected at the same time, the magnitude and direction of the drift differ substantially. The drift is least for Cd, which is close in mass to the indium internal standard. The patterning evident in the U data is an artifact resulting from the fact that the same run order was used in each of the six repeats of the solution set. For V and U the drift is much greater than the random short-term noise, and consequently the drift correction procedure yields a proportional improvement in measurement precision.

Fig. 1 Drift patterns for three elements during ICP–MS analysis of Buffalo River sediments
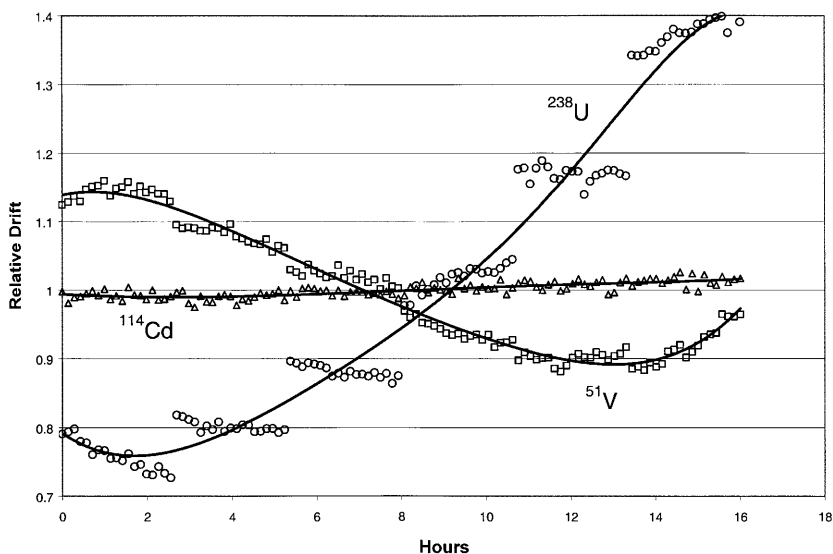

Fig. 2 Ratio of ICP–MS signals from RM 8704 and SRM 2704 for a variety of elements and isotopes. Error bars of ratios are 95% confidence intervals. The bold error bar to the left of each element represents the relative uncertainty of the certified value of that element in SRM 2704
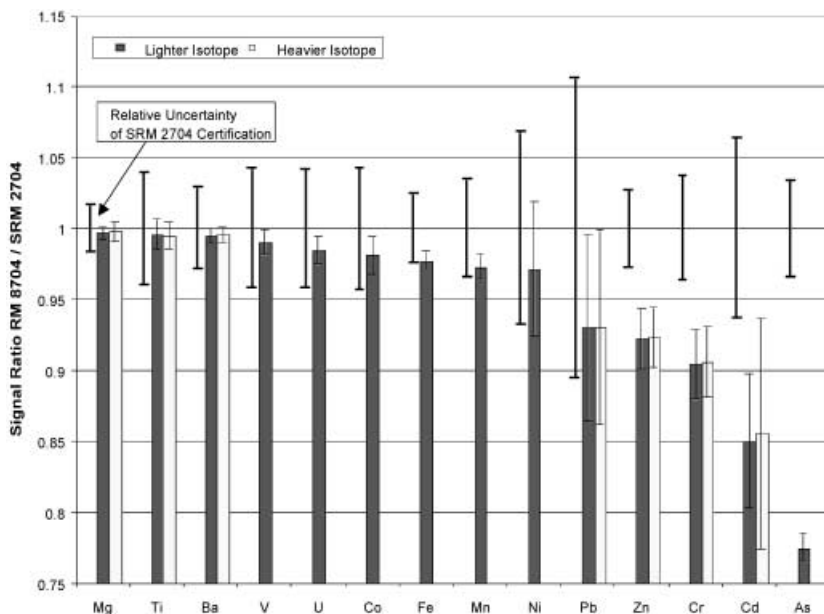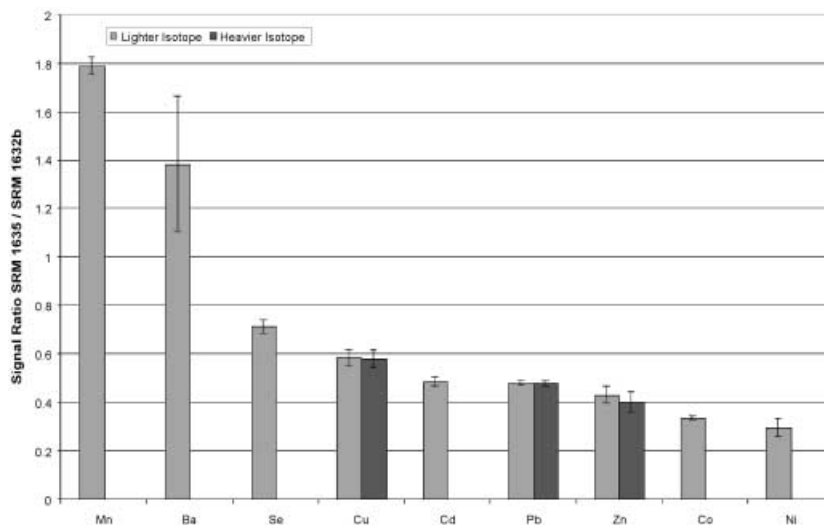
Fig. 3 Ratio of ICP–MS signals from SRM 1635 and SRM 1632b for a variety of elements and isotopes. Error bars of ratios are 95% confidence intervals

The Buffalo River Sediment data are summarized in Fig. 2, which displays for each isotope the ratio of the average signal found for RM 8704 to that of SRM 2704, which is being used as the calibration standard. Thus, the determined value for RM 8704 would be the measured ratio multiplied by the certified value of SRM 2704. The data show that the two materials are similar, but not identical, with several elements, notably As, significantly lower in RM 8704. The error bars shown for each measured ratio are 95% confidence intervals, computed from the standard deviations of the mean signals of the two materials. For comparison, Fig. 2 shows a bold error bar to the left of each element that represents the relative uncertainty of the certified values of SRM 2704. The point to note is that usually the measurement uncertainty of the comparison ratio measurements is substantially less than the certified uncertainty. The uncertainties of the determined values for RM 8704 must include both the uncertainties of the SRM 2704 certified values and the comparison ratio measurements (added in quadrature), but because the latter is small relative to the former, the relative uncertainties of determined values will be nearly identical to those of the certified values of SRM 2704.

The results for the SRM 1635, Subbituminous Coal, are summarized in Fig. 3, again shown as signal ratios, with the SRM 1632b signals in the denominator. The elemental composition of these two coals is not as similar as those of the river sediment examples. Table 2 lists the determined values and uncertainties for SRM 1635, using SRM 1632b as the calibrant. The uncertainties given are expanded uncertainties [4] at 95% confidence and were computed as twice the square root of the sum of the squares of the standard uncertainties of the SRM 1632b certified values and the comparison measurements. The uncertainties of the SRM 1632b certified values were treated as 95% confidence intervals, and the standard uncertainty of each certified value was taken to be one-half of the certified uncertainty. For comparison, Table 2 also gives the certified values of SRM 1635, which agree in all cases with the determined values. The agreement between

Table 2 Summary of results for SRM 1635, Trace Elements in Subbituminous Coal, and comparison with certified values

Element	m/z	Determined value (mg kg⁻¹)	Certified value (mg kg⁻¹)
Ba	136	93 ± 19	
Cd	111	0.028 ± 0.002	0.03 ± 0.01
Co	59	0.77 ± 0.06	
Cu	63	3.7 ± 0.3	3.6 ± 0.3
	65	3.6 ± 0.3	
Mn	55	22.2 ± 1.8	21.4 ± 1.5
Ni	60	1.81 ± 0.24	1.74 ± 0.10
Pb	206	1.76 ± 0.13	1.9 ± 0.2
	208	1.76 ± 0.13	
Rb	85	1.44 ± 0.13	
Se	82	0.92 ± 0.09	0.9 ± 0.3
Zn	66	5.1 ± 0.5	4.7 ± 0.5
	68	4.8 ± 0.6	

these two certified SRMs is a good example of a demonstration of their comparability. One can conclude from these results that either of these two SRMs behaves in a comparable manner for the elements determined using this method of analysis.

Figure 4 summarizes the comparison of SRM 1632c with SRM 1632b, shown in the same format as Fig. 1 with the SRM 1632b signal as the denominator. These two bituminous coals are quite similar in composition. Again, the relative uncertainties of the measured ratios are usually less than that of the relative uncertainties of the certified values of SRM 1632b. Table 3 lists the determined values and uncertainties for SRM 1632c. The uncertainties given are expanded uncertainties at 95% confidence and were calculated in the same manner as for SRM 1635. Certified values for SRM 1632c have not yet been issued, and will be based partially on these results. For comparison, Table 3 gives the results reported by independent analytical methods at NIST for SRM 1632c. With the ex-

Fig. 4 Ratio of ICP–MS signals from SRM 1632c and SRM 1632b for a variety of elements and isotopes. Error bars of ratios are 95% confidence intervals. The bold error bar to the left of each element represents the relative uncertainty of the certified value of that element in SRM 1632b
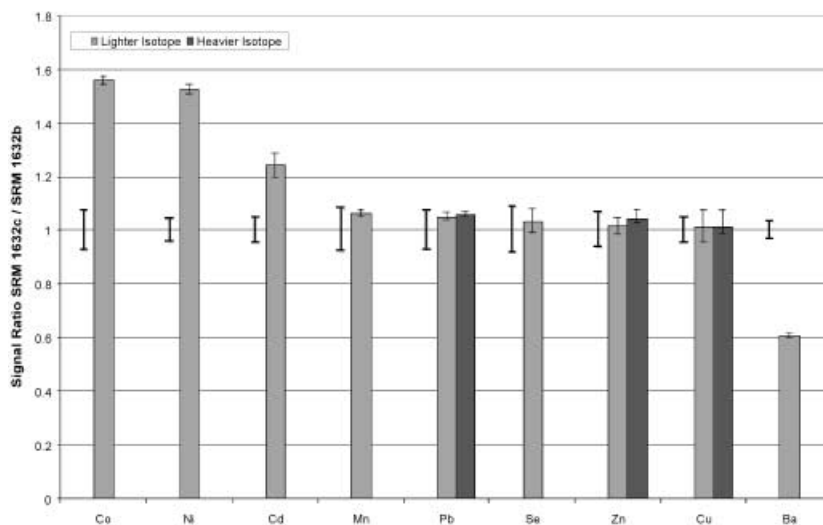

Table 3 Summary of results for SRM 1632c, Trace Elements in Bituminous Coal, and comparison with independent results by instrumental neutron activation analysis (INAA), isotope dilution ICP mass spectrometry (ID-ICP–MS), and standard additions ICP mass spectrometry (SA-ICP–MS)

Element	m/z	Determined value (mg kg^{-1})	INAA (mg kg^{-1})	ID-ICP–MS (mg kg^{-1})	SA-ICP–MS (mg kg^{-1})
Ba	136	41.1 ± 1.4	42 ± 1	40.2 ± 0.9	
Cd	111	0.071 ± 0.004			0.072 ± 0.007
Co	59	3.6 ± 0.3	3.385 ± 0.044		
Cu	63	6.4 ± 0.5			6.01 ± 0.25
	65	6.4 ± 0.5			
Mn	55	13.2 ± 1.1	12.9 ± 0.2		
Ni	60	9.3 ± 0.4			
Pb	206	3.86 ± 0.28			3.79 ± 0.07
	208	3.89 ± 0.28			
Rb	85	10.6 ± 1.0	7.64 ± 0.39	7.40 ± 0.23	
Se	82	1.34 ± 0.13	1.31 ± 0.04		
Zn	66	12.1 ± 0.9	12.2 ± 0.6		12 ± 2.4
	68	12.4 ± 0.9			

ception of one element, Rb, excellent agreement is achieved between the results reported here and the independent values. The high value obtained for Rb is not fully understood, but might be a result of an unexpected isobaric interference from $^{37}Cl^{16}O_3^+$.

Some notes of caution must be considered if calibration transfer between an existing CRM and a new CRM is contemplated. Obviously, the accuracy of any result will be tied to the accuracy of the calibration CRM, and the stability of the certified values of an old CRM might be an issue. Also, any new developments in measurement capabilities that might have occurred since the older CRM was certified will not be taken advantage of.

The results presented here demonstrate that detailed elemental comparisons between similar natural matrix CRMs can be made using a high-performance methodology for ICP–MS. Such comparisons can be used for CRM re-certifications, for establishing traceability of secondary CRMs to higher-level CRMs, or to demonstrate the equivalence of different CRMs.

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