Anal. Chem. **2001,** *73,* 4821−4829

Single-Element Solution Comparisons with a High-Performance Inductively Coupled Plasma Optical Emission Spectrometric Method

Marc L. Salit,* Gregory C. Turk, Abigail P. Lindstrom, Therese A. Butler, Charles M. Beck II, and Bruce Norman

Chemical Science and Technology Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899-8391

A solution-based inductively coupled plasma optical emission spectrometric (ICP-OES) method is described for elemental analysis with relative expanded uncertainties on the order of 0.1% relative. The single-element determinations of 64 different elements are presented, with aggregate performance results for the method and parameters for the determination of each element. The performance observed is superior to that previously reported for ICP-OES, resulting from a suite of technical strategies that exploit the strengths of contemporary spectrometers, address measurement and sample handling noise sources, and permit rugged operation with small uncertainty. Taken together, these strategies constitute *high-performance* ICP-OES.

Since early 1997, inductively coupled plasma optical emission spectroscopy (ICP-OES) has been used to perform comparisons of candidate elemental solution Standard Reference Materials (SRMs) against well-characterized primary materials. These SRMs—*the 3100 series*— provide a basis for the accuracy of inorganic elemental analysis. They are prepared in bulk and batch certified for the mass fraction of the constituent element, typically at 10 g/kg levels. The results of these comparisons are now an integral part of the SRM certification process, establishing traceability of the SRM to the primary materials.

ICP-OES is being employed here as an element-specific "two-pan balance." To obtain performance comparable to isotope dilution and classical methods (titration and gravimetric analysis), we have developed a suite of tools which, used together, constitute *high-performance* ICP-OES (HP-ICP-OES). A key enabler is a drift correction procedure invented to address what was the major source of uncertainty observed in our ICP-OES results.[2] The other essential components of HP-ICP-OES are described and developed in a paper describing the characterization of a $LiAlO_2$ ceramic material.[3]

Using HP-ICP-OES, we typically observe relative expanded uncertainties on the order of 0.1%. This level of uncertainty is quantitatively different from that previously reported for ICP-OES results. Different chemical information becomes available with this ability to discriminate between solutions of very similar composition—an improvement in *concentration resolution*. Additionally, at this level of uncertainty, uncertainty is dominated by effects other than spectroscopic measurement (e.g., sample handling and preparation).

Measurements are performed using unmodified commercially available equipment and are significantly less costly than classical analysis. The opportunity to achieve results of the quality expected of classical analysis with instrumental efficiency enables new analytical applications. In contrast to classical analysis, instrumental automation permits the analysis of multiple samples with little incremental cost per sample. Similar to classical analysis, this method is suitable for determination of "major" and "minor" constituents, with analytes typically introduced to the instrument at 10 mg/kg, with no concomitant elements present at levels high enough to cause interferences and, therefore, no expectation of bias.

HP-ICP-OES has been used in the certification analyses for 64 different single element SRMs in the 3100 series (some elements have been certified more than once with HP-ICP-OES). Additional analyses include a Key Comparison (K8) of the *Comité Consultatif pour la Quantité de Matière* of the *Comité International des Poids et Mesures* (the CCQM—*Consultative Committee for Amount of Substance* − of the CIPM—*International Committee for Weights and Measures*)[4] and two multielement analyses: the certification of the major constituents of a high-temperature alloy SRM[5] and the characterization of $LiAlO_2$.[3]

This paper will serve to describe how HP-ICP-OES can be used to determine major inorganic constituents in solution with uncertainty on the order of 0.1% relative. A performance overview and a detailed procedural guide for the single-element determination of 64 elements are presented.

EXPERIMENTAL SECTION

HP-ICP-OES is composed of several technical strategies, as outlined in refs 2 and 3. It is a ratio method, where correlated

* To whom correspondence should be addressed. E-mail: salit@nist.gov.

(1) Salit, M. L.; Turk, G. C. *Anal. Chem.* **1998**, *70*, 3184−3190.
(2) Salit, M. L.; Vocke, R. D., Jr.; Kelly, W. R. *Anal. Chem.* **2000**, *72*, 3504−3511.
(3) *Guide to the Expression of Uncertainty in Measurement*, 1st ed.; ISO: Switzerland, 1993.
(4) http://kcdb.bipm.fr/BIPM-KCDB/AppendixB/specific_comparison3_4.asp.Aaccessed 16 April 2001.
(5) Ceritificate of Analysis, Standard Reference Material® 2175, Refractory Alloy MP-35-N. National Institute of Standards and Technology, Gaithersburg, MD, 10 October 2000.

10.1021/ac0155097
Published on Web 09/19/2001

noise sources cancel through the simultaneous measurement of an internal standard element reference signal with the analyte element signal.[6,7] It is often the case that the dominant short-term noise in the measured ICP emission signal is correlated for different elements. This correlation occurs in the noise regime where signal-carried noise is dominant—where the signal-to-noise ratios of the emission signals are sufficiently greater than shot or detector read noise. This signal-carried noise typically arises from the common-mode sample input noise carried by all the emission signals.[6,8,9] Correlated noise does not appear in the signal ratio.

Accurate and precise ratios are best measured with solid-state array detector-based ICP-OES spectrometers. Such instruments typically allow flexible selection and simultaneous measurement of multiple emission lines and the spectral background adjacent to each. Background correction is essential for calculation of accurate element signal ratios, and simultaneous measurement of signal and background permits background correction with no flicker-noise penalty.

Various approaches are taken to address remaining noise sources, notably drift correction to mitigate longer term, sample-to-sample noise that cannot be addressed with internal standardization. Other important sources of uncertainty that cannot be mitigated with the measurement scheme—e.g., those arising from chemical form or from sample preparation and handling—are quantified using a suitable experiment design.

The signal measurement strategies associated with HP-ICP-OES are predicated on moderately high signal levels—this is not a method that measures at or near the analyte detection limit. HP-ICP-OES was designed to make traceable measurements of elemental composition with small uncertainty. In such an application, it is typical that nominal analyte levels are known, and method development can be optimized for small uncertainties.

Sample Handling. We have developed a robust and practical scheme of sample handling that minimizes sample-handling errors and their impact. Gravimetric solution handling is employed, exploiting the accuracy and ease of use of computer-integrated electronic force balances. Amount fraction is typically determined as mass fraction, eliminating uncertainty associated with density and its temperature dependence. This sample-handling scheme, adopted from isotope dilution mass spectrometry, is of general utility, whether using primary materials for calibration (as we do at NIST) or where any suitable reference material is employed as a calibrant.

Sample-handling contributions to analysis uncertainty include the uncertainty in the element amount ratios (amount of analyte to amount of internal standard) in calibration solutions and uncertainty in the sample mass-to-internal standard mass ratios in unknown samples. These "amount ratios" can be expressed in any set of consistent units—the measured signal ratio is proportional to the ratio of the number density of emitters in the observed volume of the plasma, and any proportionality to this number density (e.g., atomic weight) ends up as a multiplicative factor in the calibration relationship.

Aliquots of sample and internal standard are weighed into the same vessel to minimize these uncertainties. Once the solutions are added and mixed, the amount ratio is fixed. No quantitative transfers are required before (because the same vessel is used for all weighings) or after "spiking" with internal standard (because the amount ratio is fixed upon mixing sample and spike), eliminating several sources of variability. All further handling can be performed without regard to quantitation, so long as the amount ratio is not perturbed (e.g., dilution, but *not* separations). The usually straightforward constraint is that all constituents remain in solution upon mixing.

It is impractical and unnecessary for every solution to contain the same amount of internal standard, as is typical when volumetry is used for sample preparation. Though a target analyte-to-internal standard ratio is established to abet precision photometry, the target is a range, usually spanning a factor of 2.

Method Development. For single-element analysis, analyte-to-internal standard amount ratio and solution mass fractions are selected to optimize signal quantification. Measurements reported in this work were performed on PerkinElmer Instruments Optima 3000XL and 3300DV ICP-OES instruments.[10] The spectrometers in these instruments match the $\sim 10^9$ dynamic range of the plasma to the dynamic range of the spectrometer through a combination of on- and off-detector signal integration.[11,12] These instruments are capable of on-detector integration on the order of 10^5 photoelectrons, after which signal must be accumulated off-detector. This arrangement permits both weak and strong emissions to be integrated with high precision. Long integration (on the order of 5−10 s for this work), is accomplished through multiple short integrations (typically on the order of 100 ms). Long integration enhances signal-ratio quantification, even for strong emission lines, because the noise-power spectrum of emission is dominated by frequencies higher than a few hertz.[13]

Optimal internal standard noise cancellation is achieved when analyte and internal standard emission signals accumulate at similar rates, such that it is possible to simultaneously integrate both signals at high signal-to-noise ratio. The analyte-to-internal standard amount ratio is thus selected to balance photoelectron accumulation rates.

Solution mass fraction is typically established such that an on-detector integration time between 50 and 1000 ms can be employed. Such signal accumulation rates are typical (for the instruments used in this work) when measurements are in the signal-carried noise domain. Shorter on-detector integration times can be used (to a minimum of 1 ms), but with a consequent increase in readout overhead and reduction in measurement duty cycle. Longer on-detector integration times are unusual, but are occasionally required due to poor emission behavior (and poor signal-to-noise ratio) of an element in the ICP. Sample-to-sample cross-contamination, or *carryover*; signal linearity; and signal-to-

(6) Myers, S. A.; Tracy, D. H. *Spectrochim. Acta* **1983**, *38B*, 1227−1253.
(7) Ivaldi, J. C.; Tyson, J. F. *Spectrochim. Acta* **1996**, *51B*, 1443−1450.
(8) Cicerone, M. T.; Farnsworth, P. B. *Spectrochim. Acta* **1989**, *44B*, 897−907.
(9) Olesik, J. W.; Fister, J. C., III. *Spectrochim. Acta* **1991**, *46B*, 851−868.

(10) To adequately describe experimental procedures, 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.
(11) Barnard, T.; Crockett, M.; Ivaldi, J.; Lundberg, P.; Yates, D.; Levine, P.; Sauer, D. *Anal. Chem.* **1993**, *65*, 1231−1239.
(12) Barnard, T.; Crockett, M.; Ivaldi, J.; Lundberg, P. *Anal. Chem.* **1993**, *60*, 1225−1230.
(13) Goudzwaard, M. P.; de Loos-Vollebregt, M. T. C. *Spectrochim. Acta* **1990**, *45B*, 887−901.

blank ratio also play a role in determining appropriate nominal mass fractions for analysis.

Method development typically begins with measurement of a 10 μg/g solution of analyte, permitting the instrument controller to determine the appropriate on-detector integration time for this mass fraction level. The mass fraction of analyte in the solution to be analyzed is then adjusted to permit on-detector integration time on the order of 100 ms (e.g., if the instrument selects a 20-ms integration time for the 10 μg/g solution, the analyst might select 2 μg/g as the nominal mass fraction for the analysis). A similar process is followed for the internal standard selected, targeting the same integration time as selected for the analyte. These nominal mass fractions are then used to establish the sample spiking and dilution scheme. Mass fractions above 20 μg/g are typically avoided to minimize cross contamination and carryover—as noted above, on-detector integration can be increased to several seconds as needed to achieve reasonable total signal counts.

If too long an integration time is selected by the analyst, the signal will saturate and an error will be detected. If too short an integration time is selected, no error will be detected, but the signals will likely be noisy, and poor correlation between analyte and internal standard may be observed. The integration times vary from instrument to instrument, or for a given instrument, as conditions vary.

We have developed a simple, practical set of criteria for internal standard selection. Selection is based upon the following: the mutual absence of the internal standard from the sample and the analyte from the internal standard solution, chemical compatibility to ensure that the elements remain in solution, the absence of spectral interferences at the wavelengths of interest, low likelihood of contamination of the sample with the internal standard by the laboratory environment, periodic similarity, excitation energy matching, and wavelength matching. The most often used internal standard element is scandium. Scandium has numerous emission lines to select from; is scarce in samples and laboratory environments; and is a strong emitter, permitting it to be used at low mass fraction. In practice, a small number of Sc lines suffice as internal standards for most of the elements.

Line selection for the analyte is similarly unconstrained. Strong "analytical" lines are generally used, affording high signal-to-noise photometry at low mass fraction. Here again, care is taken to avoid spectral interference from nonanalyte sources.

Spectra of single-element solutions of the analyte and internal standard are measured in the region of the analyte and internal standard lines, to determine that no cross-contamination or spectral overlaps occur. Also at this point, the background correction parameters are established to ensure accurate estimation of the background under both lines. The instruments we use permit the selection of different entrance slit widths, permitting a balance between spectral resolution and light acceptance. Where the nature of the spectra permit (no nearby interferences), the lowest resolution slit (greatest slit width) is selected to achieve maximum signal.

Manufacturer-suggested default plasma conditions—*compromise* conditions—are typically used for analysis (Table 1). Throughout the work presented here on single-element solutions, the analyst selected the analyte mass fraction for suitably high signal-to-noise ratio under default conditions. Exceptions were made in the case of several of the alkali elements, where emission lines of the atomic spectra were observed for quantitation, and a lower power and higher nebulizer flow than the default was used in an attempt to suppress ionization.

Table 1. ICP Operating Conditions

ICP Source Operating Parameters	
plasma flow	15 L min^{-1}
auxiliary flow	0.5 L min^{-1}
nebulizer flow	0.8 L min^{-1}
power	1300 W
sample uptake	1 mL min^{-1}
autosampler probe rinse	15 s in 2% volume fraction HNO_3
Spectrometer Operating Parameters	
signal measurement mode	peak integration, low-resolution readout
background correction	manually selected, 2-point interpolation
measurement time	10 s
replicate measurements	7

Axial viewing of the plasma was used for most of the analyses, again an instrument default condition for the equipment in our laboratory. Several of our instruments permit radial viewing, which offers the option to avoid viewing through the cool plasma tail plume and the option to integrate over a shorter path length. Radial viewing was employed where a resonance line (or a line from a low-lying lower energy level) of the atomic spectrum was observed for quantitation, to avoid self-absorption from cool atoms (e.g., Na) or where a very strong line emits so much light that the decreased path length makes it easier to use manageable mass fractions in sample preparation (e.g., Ba).

Different configurations of sample input system have been employed for these measurements: a glass concentric nebulizer with a cyclonic spray chamber; a "cone-spray"-type high-solids nebulizer, also with a cyclonic spray chamber; and a sapphire orifice cross-flow nebulizer with Scott-type spray chamber. Used appropriately, any of these arrangements is satisfactory.

The analyte and internal standard wavelengths, nominal analyte and internal standard mass fractions for the solutions introduced to the instrument (the samples being analyzed typically have 100–1000 times higher mass fractions before preparation), and experimental notes are listed for the 64 elements discussed in this study, in Table 2.

Calibration. HP-ICP-OES is a relative method that compares the analyte-to-internal standard signal ratio measured in an unknown sample to those ratios measured in mixtures whose amount ratio is well known. A calibration relationship is established to infer composition of unknown samples from their measured signal ratios. Equation 1 is the relationship that permits

$$\text{mass fraction}\left(\frac{\text{mg}}{\text{g}}\right) = \left(\frac{\left(\frac{I_{\text{Analyte}}}{I_{\text{IntStd}}}\right)_{\text{Unknown}}}{\left(\frac{I_{\text{Analyte}}}{I_{\text{IntStd}}}\right)_{\text{Calibrant}}}\right)\left(\frac{\left(\frac{\text{mg}_{\text{Analyte}}}{\text{g}_{\text{IntStd}}}\right)_{\text{Calibrant}}}{\left(\frac{\text{g}_{\text{Sample}}}{\text{g}_{\text{IntStd}}}\right)_{\text{Unknown}}}\right) \quad (1)$$

the calculation of analyte mass fraction in an unknown sample from the measured signal and mass ratios of the calibrants and the sample.

Table 2. Method Parameters and Performance Results for 64 Elements

analyte			internal standard				performance		
	wavelength (nm)	nominal mass fraction (μg/g)		wavelength (nm)	nominal mass fraction (μg/g)	notes	rel std uncertainty of signal ratio (%)	rel std uncertainty of replicate preps (%)	difference from gravimetry[a]
Ag	328.068	5	Sc	361.383	0.5		0.046	0.026	0.0390
Al	386.153	2	Mn	403.075	2		0.028	0.022	0.0066, 0.0005
As	193.696	20	Se	196.026	5		0.145	0.148	
Au	208.209	10	In	230.606	10		0.036	0.047	0.0084
B	249.773	5	Sc	361.383	0.2	matrix was 3% mass fraction mannitol, in 2% volume fraction of nitric acid, to reduce memory effects	0.092	0.043	0.0052
Ba	493.408	5	Sr	421.552	2	radial viewing	0.022	0.037	
Be	265.045	5	Sc	357.253	0.5		0.066	0.134	
Bi	223.061	10	Sc	361.383	0.5		0.023	0.024	0.0150
Ca	396.847	1	Sc	361.383	1		0.036	0.080	
Cd	226.502	10	Sc	361.383	0.5		0.016	0.014	
Ce	413.765	1	Mn	403.076	10		0.177	0.013	
Co	238.892	10	Sc	361.383	0.2		0.014	0.013	0.0210
Cr	205.560	50	Mn	257.610	1		0.025	0.079	
Cs	455.531	250	Sc	424.683	0.2	1200 W, 1.1 L min^{-1} nebulizer flow	0.180	0.145	
Cu	327.396	10	Mn	257.610	10		0.013	0.019	−0.0001
Dy	394.468	10	Sc	424.683	0.5		0.032	0.027	
Er	349.910	1	Sc	361.383	1		0.017	0.026	
Eu	412.970	1	Sc	424.683	0.5		0.078	0.055	
Fe	259.940	10	Sc	361.383	0.5		0.017	0.041	0.0004
Ga	417.206	10	Sc	424.683	0.5		0.029	0.036	
Gd	342.247	10	Y	371.029	1		0.005	0.018	
Ge	209.426	10	In	230.606	10		0.036	0.083	0.0070
Hf	264.141	5	Sc	361.383	0.5		0.023	0.090	−0.0070
Hg	253.652	50	In	325.609	50	$Cr_2O_7^{2-}$ ion was used to stabilize Hg: 10% $K_2Cr_2O_7$ in water added to concentrated solutions for spiking; after dilution, $K_2Cr_2O_7$ was 0.05% mass fraction	0.036	0.057	0.0023
Ho	339.898	10	Sc	361.383	0.5		0.079	0.015	
In	230.606	10	Sc	361.383	0.2		0.017	0.033	0.0200
K	766.490	5	Sc	424.683	0.2		0.021	0.047	
La	379.478	1	Sc	361.383	0.2		0.040	0.026	
Li	610.364	10	Mn	403.076	50	NB: it must be assured that any difference in atomic weight between samples and calibrants is accounted for	0.050	0.018	
Lu	261.542	2	Sc	361.383	0.5		0.026	0.010	
Mg	285.213	2	Mn	257.610	1		0.025	0.023	−0.0047
Mn	403.076	20	Sc	424.683	0.2		0.052	0.048	
Mo	281.615	10	Sc	361.383	0.2		0.050	0.030	
Na	589.592	20	Sr	407.771	0.1	radial viewing	0.023	0.029	−0.0077
Nb	269.706	10	Mn	260.568	1		0.021	0.058	0.0220
Nd	401.225	1	Sc	424.683	0.5		0.013	0.051	
Ni	232.003	10	Sc	361.383	0.2		0.021	0.033	
P	213.618	10	Se	196.026	5		0.075	0.068	
Pb	220.353	10	Co	228.616	2		0.022	0.019	0.0073
Pd	340.458	10	Sc	361.383	0.2		0.030	0.012	−0.0087
Pr	414.311	10	Sc	424.683	0.5		0.010	0.029	
Pt	214.423	10	In	230.606	5		0.020	0.022	−0.0290
Rb	780.020	10	Sc	424.683	0.2		0.087	0.018	
Re	197.248	2	Sc	361.383	0.04	sample-to-sample memory effects	0.117	0.378	
Rh	233.477	10	In	230.606	10		0.032	0.029	
Sb	217.582	20	Sc	361.383	0.2		0.147	0.069	0.0064
Sc	361.383	0.2	Co	239.892	10		0.036	0.030	
Se	203.985	50	Sc	361.383	0.2		0.050	0.100	−0.0028
Si	251.611	25	Mn	257.610	1	uncertainty dominated by variability of calibration standards	0.131	0.205	
Sm	359.260	1	In	325.609	10		0.027	0.023	
Sn	283.998	20	In	325.609	10		0.042	0.022	0.0203
Ta	240.063	10	Zr	339.198	0.1	diluted Ta solution before addition of IS to prevent precipitation.	0.037	0.034	−0.0100

Table 2 (Continued)

analyte			internal standard				performance		
	wavelength (nm)	nominal mass fraction (μg/g)		wavelength (nm)	nominal mass fraction (μg/g)	notes	rel std uncertainty of signal ratio (%)	rel std uncertainty of replicate preps (%)	difference from gravimetry[a]
Tb	350.917	10	Mn	260.569	5		0.085	0.024	
Te	214.281	50	Sc	361.383	0.2		0.022	0.049	
Ti	334.940	5	Mn	257.610	1	uncertainty dominated by variability of calibration standards	0.040	0.014	−0.0034
Tl	351.924	10	Sc	361.383	0.2		0.019	0.027	−0.0030
Tm	313.126	2	Sc	361.383	0.2		0.018	0.050	
U	385.958	20	Sc	361.383	0.2		0.019	0.022	
V	292.402	5	Sc	361.383	0.5		0.036	0.023	0.0103
W	239.708	10	Mo	202.031	5	uncertainty dominated by variability of calibration standards	0.045	0.022	−0.0020
Y	327.228	1	Sc	361.383	0.2		0.008	0.025	
Yb	369.419	1	Sc	361.383	0.2		0.028	0.037	
Zn	202.548	10	Sc	361.383	0.2		0.047	0.018	0.0100
Zr	339.197	1	Y	371.029	1	diluted Zr solution before addition of IS to prevent precipitation	0.066	0.100	−0.0180

[a] HP-ICP-OES, gravimetry.

The calibration produces an indirect inference—the calibration estimates the analyte-to-internal standard amount ratio in an unknown sample. The amount of analyte in the unknown sample is calculated from knowledge of the amount of internal standard (spike) added. The amount fraction (typically mass fraction) of analyte in the sample is calculated from knowledge of the amount of sample that was spiked.

The experiment is simplified by using a single, thoroughly mixed solution of internal standard solution to spike all samples and calibrants in an analysis. This permits the mass of spike solution to be used in lieu of internal standard element amount in all amount ratios. Another source of uncertainty is eliminated because there is no need to accurately know the spike solution mass fraction. Analyte-to-internal standard amount ratio is expressed in somewhat peculiar units: mass of analyte element to mass of *spike solution*, instead of mass of analyte element to mass of internal standard element.

The calibration between signal ratio and amount ratio is a simple, straight-line relationship that passes through zero, so long as the signal ratios are calculated from background-corrected intensities and the blank level is either small relative to the signal level or is measured and corrected for. HP-ICP-OES analyte and internal standard levels are selected to be significantly greater than blank levels; and the multiplex detectors in commercially available ICP-OES spectrometers permit background correction with no flicker-noise penalty, so every line intensity measurement is made with an interpolated estimate of the plasma background under the line center.[14]

Calibration Materials. HP-ICP-OES lends itself to the use of calibration materials that can be prepared, stored, and used accurately. We calibrate using weighed aliquots of accurate solutions gravimetrically prepared from well-characterized primary materials. The mass of analyte element in each aliquot is well known. It is expected that the mass of analyte contained in such aliquots, packaged in single-use plastic bottles (typically LDPE), is stable over long periods of time. The analyte mass in solution is not affected by transpiration (of solvent only) from the container. It is anticipated that no significant loss of analyte through interaction with the container materials or formation of volatile compounds occurs. Excellent stability over several months has been established (variance indistinguishable from other noise sources). Long-term (>3 y) stability of analyte mass in the aliquots is being evaluated for a number of different analytes.

For use in HP-ICP-OES (or other ratio techniques), internal standard spikes are weighed directly into the calibration aliquot containers, typically at the time of analysis. The solutions are well mixed, fixing the amount ratios, and diluted to the proper level for analysis. Alternatively, the spike can be weighed and mixed into the calibrant aliquots at any time, and aliquots of this same spike solution can be weighed out, storing this set of solutions as a "kit". Regardless of whether the spike is added to samples and calibrants at the time of analysis or whether calibrants are prespiked and samples are added to preweighed spikes, no quantitative transfers are required.

Our calibration hierarchy is based on high-purity solid materials designated as NIST Primary (NP) materials; solutions made from these NP materials, NIST Primary Solutions (NPS); and weighed aliquots of NPS solutions, NPS Aliquots. NPS materials are prepared in replicate, typically two solutions from each of two analysts. Directly after preparation, NPS aliquots are weighed out and the weights recorded in a database.

NPS materials generally contain 1 g of analyte/kg of solution, a mass fraction that is stable for most elements in solution. The usual matrix is dilute HNO_3. Aliquots are typically ~30 g in a 60-mL bottle, containing ~30 mg of analyte. This leaves adequate volume for spike addition.

(14) Ivaldi, J. C.; Barnard, T. W. *Spectrochim. Acta* **1993**, *48B*, 1265−1273.

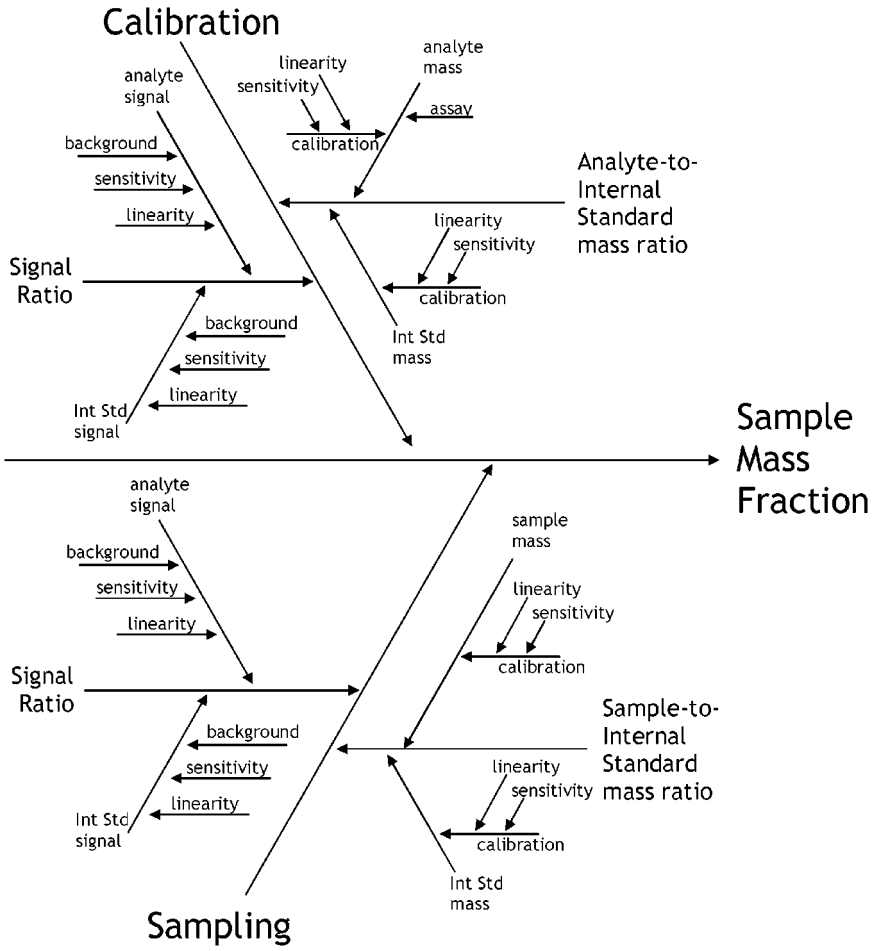

Figure 1. Cause and effect analysis for uncertainty contributions.

Buoyancy Correction. The varying densities of materials being weighed may introduce bias from air buoyancy effects on apparent mass, unless accounted for by correction to true mass (mass in vacuo). A relative bias on the order of 1 part-per-thousand is introduced when solutions of density 1 g cm^{-3} in standard air are weighed. Where a ratio of two masses of matter of similar density (e.g., an unknown and a spike solution) is being calculated, buoyancy correction is typically ignored. However, because the analyte and the solution into which it is dissolved typically have different densities, both the mass of analyte in the NPS aliquots we use and the mass fraction of the 3100 series SRMs are always corrected to true mass. When these materials are used, the mass of spike solution added to the calibration materials must be buoyancy-corrected so the ratios are on a consistent scale. In practice, true mass is used for all calculations.

RESULTS AND DISCUSSION

Essential to the HP-ICP-OES method is an experiment design that permits robust and accurate quantitative evaluation of the uncertainty of the determined amount fraction. As demonstrated in the $LiAlO_2$ work,[3] uncertainty sources other than measurement dispersion contribute significantly to the uncertainty of the comparison, and care must be taken to quantify them.

Uncertainty Budget. Equation 1 describes the calculation of the mass fraction of an unknown solution from the measured quantities. The result is the product of two ratios—an intensity ratio (actually, a ratio of ratios) and a mass ratio (again, a ratio of ratios). Both dispersion and the potential for bias contribute to uncertainty in the measured quantities and, ultimately, the mass fraction. Figure 1 depicts these quantities and their influences.

While this "cause-and-effect" diagram[15,16] appears complex, it is highly symmetric, with most factors appearing in both numerator and denominator of the ratios that appear in eq 1. HP-ICP-OES owes much of its robustness to this − correlated dispersion and biases that cancel. The sole violation of symmetry is the "assay" component, which is a bias correction for the purity of the primary material used for calibration.

Intensities. Potential biases in the intensity measurements include spectral background offset and deviation from a linear relation between signal and solution mass fraction. These are mitigated with simultaneous spectral background correction and measurement in a linear region of mass fraction for both analyte and internal standard. While variation might be observed for these biases, the dispersion from variation in the "sensitivity" as a function of time—the *noise*—dominates intensity variability. Noise in the intensity ratio is quantified through replicate ratio measurements.

Masses. Biases in each mass measurement include a "sensitivity" error in balance calibration and deviation from linearity in

(15) Ellison, S. L. R.; Barwick, V. J. *Analyst* **1998**, *123*, 1387−1392.
(16) *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement*, 2nd ed.; Laboratory of the Government Chemist, London, 2001.

balance response. Several considerations mitigate the effects of these biases on the method. First, all weighings for a given solution are typically performed on a single balance within a short time period and are of similar magnitudes (typically on the order of 3 g on a top-loading balance with 1-mg readability). Used in this manner, the biases related to the calibration state of the balance cancel. Second, the magnitudes of these biases can be determined from balance specifications, and experiments performed such that uncertainty associated with the presence of these biases is small relative to the (also specified) dispersion. It is interesting to note that only *relative* spike weights are required—the units (and hence, the balance sensitivity) are immaterial but must be linear. This is another robust element of this sample handling routine.

Experiment Design. The experiment design permits quantitative evaluation of the uncertainty from sample and calibrant preparation and handling. In most ICP-OES experiments, variation of the measured signal intensities dominates the uncertainty, and quantifying the signal variability as a standard deviation suffices. Because the variation due to handling includes the variation of the measured signal ratios, the ratio measurement standard deviation is used solely for diagnostic purposes and does not appear directly in the uncertainty budget.

All steps in the preparation of solutions for measurement must be considered as sources of variability. Because the calibration material must be dissolved before analysis, multiple solutions are prepared and analyzed to assess dispersion from variability in this process. Similarly, to address the possibility of solution heterogeneity, replicate samples of the calibrants and unknowns are prepared and analyzed.

We typically calibrate with duplicate aliquots of each of four different solutions, two each prepared by two different analysts. These eight solutions are measured to determine the slope and population distribution of the calibration curve, permitting proper evaluation of the uncertainty of the slope. Before calculating the uncertainty, care is also taken to determine the number of independent data contributing to the mean, so the standard uncertainty can be calculated as the standard deviation of the mean. For instance, where no significant differences are observed among the calibrants, there are eight data; if the four different solutions can be distinguished, there are only four; and if the solutions from each analyst can be distinguished, there may only be two. The importance of duplicate spiking for analysis is clear when one is trying to determine the population of calibrants.

When the certification measurements for the 3100 series SRMs are performed, the batch is packaged and three randomly selected containers (either high-density polyethylene bottles or glass ampules) are sampled in duplicate. This helps to ensure that the comparison is made using a representative sample of the population of the solutions being delivered and that the uncertainty estimate includes any sample-to-sample heterogeneity (potentially due to inadequate mixing). Here again, spiking of replicate samples from each container is critical. Container-to-container variability can be distinguished from preparation variability, which permits detection of and distinction between heterogeneity and blunders.

Data Evaluation. We employ a graphical tool for simple evaluation of the results on an HP-ICP-OES analysis. This chart compares the calibration slopes—the ratio of the signal ratio-to-mass ratio—observed for each solution. The data are normalized such that the mean of the calibrant slopes is 100, so uncertainties and deviations can be read directly in relative percent. These data are the relative residuals from the fitted calibration curve forced through zero—consistent with the calibration strategy used. Examining the residuals is a sensitive way to observe the population of results for both calibrants and samples at different levels of mass fraction—examining the calibration curve directly only shows large discrepancies, and the typical population scatter we observe would be dominated by the change in mass ratio.

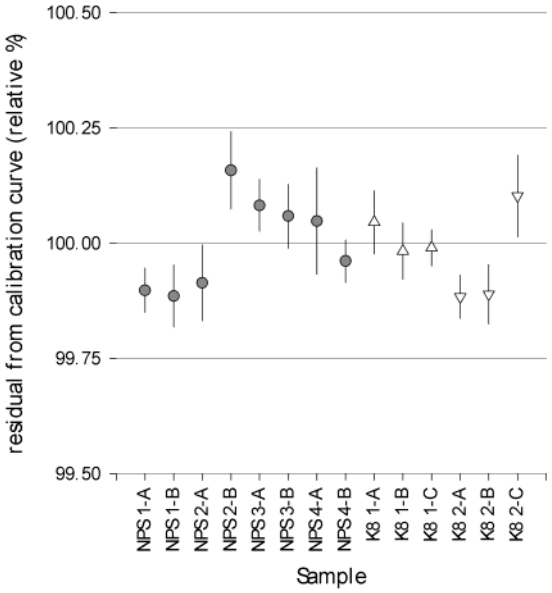

Figure 2. HP-ICP-OES analysis performance presented as relative residuals, for Fe in a CCQM key comparison.

Such a graph is in Figure 2, for the determination of Fe in two single-element solutions in an international comparison. The eight solutions used to calibrate are labeled "NPS" and the samples (triplicate preparations of a single sample of each of the two different solutions) are labeled "K8". The error bars are the standard deviation of the drift-corrected signals. Preparation-to-preparation effects may be present in two cases—NPS 2-A and -B disagree as does K8 2-C disagree with -A and -B. The conservative approach treats these results as part of the population and retains them in the data analysis. The overall scatter is small, and the NPS solutions appear to arise from a single population. The observed range of calibrant slopes is 0.27%, and the standard uncertainty of the slope is 0.04% relative. The standard uncertainties for the two different K8 samples are 0.02% and 0.07%, and the relative uncertainty in the calibration material purity is 0.0028%. Estimates of the degrees of freedom using the Welch–Satterthwaite formula[17] were 9 and 3, suggesting expansion factors of 2.26 and 3.18. The combined expanded uncertainty of the first K8 sample is 0.09% $((0.04\%^2 + 0.02\%^2 + 0.0028\%^2)^{1/2} \times 2.26)$ and for the second K8 sample is 0.26% $((0.04\%^2 + 0.07\%^2 + 0.0028\%^2)^{1/2} \times 3.18)$. The results reported for this analysis agreed with the gravimetric reference value for the first sample and with the

(17) Taylor, B. N.; Kuyatt, C. E. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, 2nd ed.; NIST Technical Note 1297; NIST: Gaithersburg, MD, 1994.

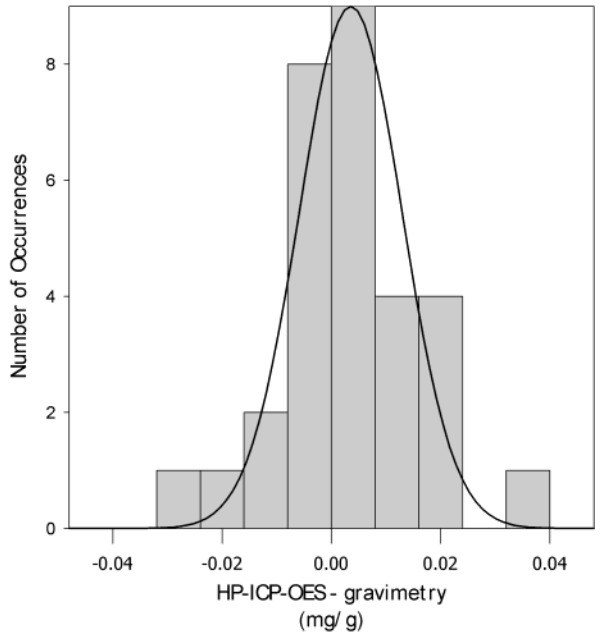

Figure 3. Population distribution of differences between HP-ICP-OES and gravimetry ($N = 30$). Solution mass fractions were nominally 10 g/kg for all solutions except B (5 g/kg), the second Al listed, and Cu, Fe, and Mg (all 1 g/kg).

consensus value (the only reference value available) for the second.

Bias. Differences between HP-ICP-OES and gravimetric results were tabulated for 30 single-element comparisons. These differences were calculated wherever reliable gravimetric results were available and are included in Table 2. Though not completely independent—the gravimetric preparation results were often based upon the same material as that used to prepare the HP-ICP-OES calibrants—these gravimetric results represent our best approximation to an unbiased estimate. Equivalence of HP-ICP-OES and gravimetric results demonstrates that we are, to the best of our ability, establishing HP-ICP-OES as an element-specific "two-pan" balance.

The frequency distribution of these differences is charted in Figure 3. These data pass a Kolmogorov–Smirnov test for normality[18] at the 0.05 probability level. A fitted Gaussian is overlaid on the frequency histogram. The mean difference between the HP-ICP-OES and gravimetric results was 0.003 52 ± 0.004 84 mg g^{-1} (95% confidence interval). There is no evidence of bias from these data.

Dispersion. Figure 4 charts the frequency distribution of the dispersion of the measured signal ratios for the 64 elements in our study. These dispersions are the average of, for between 12 and 24 solutions, the relative standard deviations of the means of between 5 and 10 replicate measurements. This tailed distribution has a median of 0.032%, with a maximum of 0.18%. As would be expected, the poorer ICP emitting elements are at the high tail of the distribution (As, Sb, Ce, Cs). These data are included in Table 2 as the relative standard uncertainty of signal ratio.

ANOVA was used to test the measured ratios of replicate preparations of homogeneous solutions (the three candidate SRM

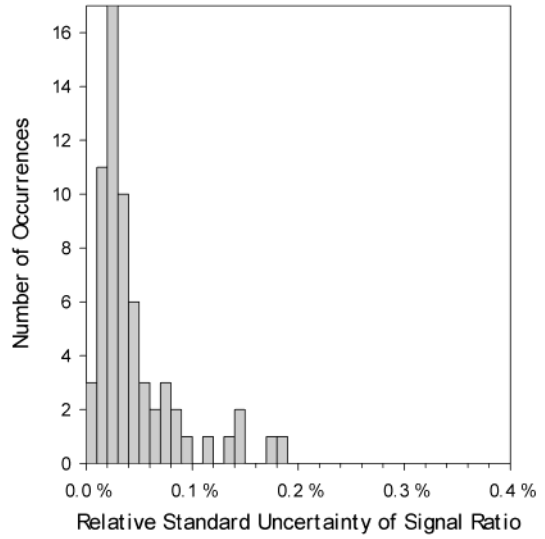

Figure 4. Population distribution of mean signal ratio uncertainty for 64 elements.

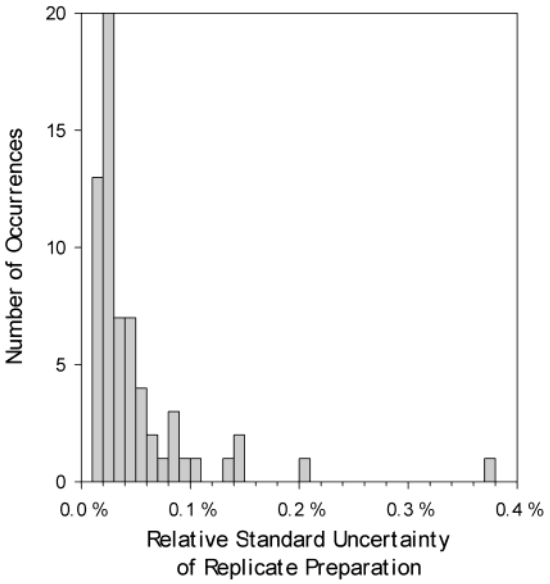

Figure 5. Population distribution of replication standard uncertainty for 64 elements.

samples, from which duplicate spikes were prepared) for statistically significant "preparation" effects. This ANOVA tests whether the difference between preparations was greater than would be expected by chance, given the dispersions of the measured ratios for a given preparation. Of 21 experiments (21 different elements) examined with ANOVA, 15 showed statistically significant preparation effects among the 6 solutions (with at least 99% confidence), and 6 showed that the differences among preparations could be due to the dispersion of the measured signal ratios. This analysis justifies our inclusion of preparation as a component of uncertainty in our experiment and uncertainty budget.

In addition to the ANOVA, the distribution of the standard uncertainty of replicate preparation (standard deviation of the mean of the different preparations) was tabulated. This tailed distribution is charted in Figure 5 and has a median of 0.029%. This dispersion is of the same magnitude as the dispersion of the signal ratios, and the two distributions are quite similar—suggesting that neither source dominates the uncertainty. These

(18) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1992; pp 620–628

data are included in Table 2 as the relative standard uncertainty of replicate preparations.

CONCLUSIONS

Evidence is presented demonstrating that the HP-ICP-OES method is generally useful for 64 elements and is an unbiased method of comparison with small uncertainty for solutions containing predominantly a single element. This comparison technique is relevant in many inorganic applications, including traceable reference material dissemination, demonstration of international comparability of measurement systems, material assay, bulk compositional analysis of samples, and determination of element ratios.

The underlying concepts of HP-ICP-OES are being extended to alternate spectroscopies and trace element analysis,[19] with great promise.

ACKNOWLEDGMENT

The authors thank Dennis Yates for useful discussions during the preparation of the manuscript.

Received for review April 17, 2001. Accepted July 29, 2001.

AC0155097

(19) Turk, G. C.; Yu, L. L.; Salit, M. L.; Guthrie, W. F.; *Fresenius J. Anal. Chem.*, in press.