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Real and composite emission lines as internal standards in the determination of As, Se and Sb by inductively coupled plasma optical emission spectrometry

Fumin Pan and Julian F. Tyson

A method that enlarges the pool of potential internal standards for axially viewed inductively coupled plasma optical emission spectrometry has been developed and evaluated. This method is based upon the visualization of the similarity of matrix-induced behavior among emission lines by principal component analysis according to the procedure suggested by Grotti *et al.* (*J. Anal. At. Spectrom.*, 2003, **18**, 274). For a certain analytical line, more choices of internal standards are provided from composite spectral lines created by combining real spectral lines in such a way as to integrate their characteristic behaviors. The method was applied in the determination of As, Sb and Se in solutions that modelled plant and food sample digests, to compensate for the matrix effect due to the presence of nitric or hydrochloric acids as well as a variety of matrix elements including aluminium, calcium, iron, magnesium, manganese, phosphorus, potassium, sodium, sulfur, and zinc. Under robust plasma conditions, the matrix-induced errors, which averaged between 8 and 23%, were decreased to an average of between 2 and 5% by the composite internal standards procedure. The methodology was validated by the accurate analysis of two certificated reference materials (DORM-2 and DOLT-3).

Introduction

Changes in matrix composition strongly affect the analytical results in ICP-OES due to the changes of aerosol production,[1–3] transportation processes,[4–6] and the shifts in the locations in the plasma where vaporization, atomization and ionization occur.[7] The extent of the effects on individual emission lines are different and depend on properties such as the excitation and/or the ionization potential,[8] the sum of ionization and excitation potential,[9] whether the lines are atomic or ionic,[10] and possibly other factors as yet unknown.

Internal standardization, to compensate for matrix effects, is a well established procedure. The major difficulty in applying this method is to find suitable reference lines whose intensity responses to a complex matrix and random instrumental fluctuations are similar to those of the analyte lines. Considerable effort has been put into finding appropriate operating conditions to facilitate internal standardization. Myers and Tracy[11] developed a signal compensation method with a single internal standard that could compensate for matrix effects and improve precision[12] by appropriate choice of ICP-OES operating conditions. Romero *et al.*[13] discussed the efficiency of internal standardization in relation to the robustness of the ICP conditions using high power and long residence times. They showed that robust conditions[14] led to the efficient use of a single internal standard, while the use of non-robust conditions made the use of internal standardization complex. Dubuisson *et al.*[15] investigated internal standardization as a

function of the observation mode in ICP-OES to compensate for sodium matrix effects on accuracy. They concluded that axial viewing did not provide the same quality of results in terms of efficiency of internal standardization compared with that of radial viewing.

Harmse and McCrindle[16] suggested that an analytical spectral line and an internal standard spectral line should have similar wavelengths and first ionization potentials, according to which, cadmium at 228.802 nm (excitation potential, E_{ep} 5.419 eV, and first ionization potential, E_{ip}, 8.641 eV) was selected as the internal standard for antimony at 206.833 nm (E_{ep} 5.994 eV, E_{ip} 8.641 eV). With more complicated matrix effects and multiple analytes, with emission lines of various characteristics, more than one internal standard becomes necessary to compensate for the various signal suppression effects.[17–19] Sun and co-workers[20] pointed out that a single internal standard was inadequate for compensating for the different responses of the analyte spectral lines to various matrix elements. They added Sc and Ni to 0.6 g L^{-1} of Mn and Ca solutions as internal standards. Significant improvement in the accuracy was achieved for all the spectral lines considered. Boer and Velterop[21] used Sc and Y as the internal standards for correction of single (Ca or Na) and combined (Ca + Na) matrix effects by a modified internal standardization they called the proportional correction method. Their results showed good performance for samples with very high matrix concentrations, for which errors of 18% were decreased to 4%. Al-Ammar and Barnes[22] also used two spectral lines to compensate for matrix effects. Unlike the traditional internal standard methods, their technique was based on the simultaneous measurement of two different spectral lines of the same

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analyte. The linear regression of the ratio of the intensities as a function of the sample composition was used to estimate a matrix correction factor.

Grotti et al.[23] developed a systematic procedure for the selection of optimal internal standards in ICP-OES. In this method, the empirical behaviors of the emission lines of analytes and potential internal standards with respect to single and combined matrices were visualized by principal component analysis: the closer the analyte and the reference lines in the score plot, the more similar is their behavior. They applied the method[24] to correct for the effects of major elements, hydrochloric, nitric, sulfuric acids, both singly and in mixtures, and showed that errors could be reduced from 10–40% to less than 5% for As, Cd, Cr, Cu, Mn, Mo, Ni, P, Pb, Sb, Se, Sr, V, Zn, with Sc (424 nm) and Co (238 nm) as internal standards. They also showed a significant improvement in accuracy with Lu (291 nm) or Be (313 nm) for several emission lines. In contrast, they found that for a few spectral lines, such as As (188 nm), As (193 nm), Cu (324 nm), P (213 nm), Pb (220 nm), Sb (206 nm), and Se (196 nm), the proposed method could not successfully compensate for the acid effects. This may due to the fact that the behavior of atomic lines is more complex, even under robust conditions.[15] There are also some other factors limiting the full effective use of this method, for instance, the restricted number of potential reference lines due to the presence of the appropriate elements in complex matrices.

Ivaldi and Tyson[25] obtained precision improvement factors of 3–4 by a real-time internal standardization procedure for an axially-viewed inductively coupled plasma using the yttrium ion line at 371.030 nm as the internal standard. However, they found the procedure was less effective for atomic lines where the improvement factors were between only 1.5 and 3. They concluded that the amplitude of the noise on the atomic line signals prevented the full benefit of internal standardization from being obtained.

In this paper, we propose a method for the selection of internal standards in ICP-OES based on principal component analysis of empirical data,[23] which allows the visualization of a matrix-induced relationship between the behavior of analyte and reference spectral lines. Based on these relationships, a number of artificial lines can be produced that are more effective as internal standards, which are either a composition of two spectral lines or a single line modified by a factor. The proposed method was evaluated by correcting the errors for some atomic lines produced by matrix effects arising from the presence of other elements and of mineral acids for an axially viewed ICP with a segmented-array charged-coupled device (SCD) detector operated under robust conditions.

Experimental

Instrumentation

A PerkinElmer Optima 4300DV (Shelton, CT, USA) ICP optical emission spectrometer was operated in the axial viewing mode. This instrument is equipped with a 40 MHz free-running generator and an SCD detector, allowing the simultaneous measurement of several line intensities as well as the

Table 1 Operating conditions

Instrument	PE Optima 4300DV
Nebulizer	Concentric
Spray chamber	Cyclonic
Detector	SCD
RF/W	1400
Argon flow rate/L min^{-1}	
Plasma	16
Auxiliary	0.2
Nebulizer	0.65
Solution uptake rate/ml min^{-1}	1.5
Plasma viewing mode	Axial
Integration and read time/s	Auto/5
Resolution	Normal
Replicates	5

background signals. The sample introduction system consisted of a concentric nebulizer with a cyclonic spray chamber. The ICP operating parameters, optimized for simultaneous determination of As, Se and Sb under robust plasma conditions, are given in Table 1. Samples were digested in a CEM Model MDS-2100 (Matthews, NC) microwave digestion system.

Reagents

Stock solutions (10 g l^{-1}) of matrix elements Na, K, Ca, and Mg were prepared from NaCl (Mallinckrodt, Phillipsburg, NJ, USA), KNO$_3$, CaNO$_3$ and MgNO$_3$ (Fisher, Fairlawn, NJ, USA), respectively. Standard solutions (10 mg ml^{-1}) of S and P were from Merck (Darmstadt, Germany) and Spectrum (Gardena, CA, USA), respectively. Stock standard solution (1000 µg l^{-1}) of As, Se and Sb were PE Pure Atomic Spectroscopy Standards. Standard solutions (1000 mg l^{-1}) of the selected reference elements and the matrix elements of Fe, Mn, Al and Zn were purchased from Alfa Aesar Specpure (Ward Hill, MA, USA). Analytical grade nitric acid (Mallinckrodt Chemicals, USA) and hydrochloric acid (Fisher Scientific) were used as matrix components. High-purity water for preparing reagents and synthetic samples was produced by an E-pure Deionized Water System (Barnstead, Dubuque, Iowa, USA). The certified reference materials were digested in concentrated nitric acid and 30% hydrogen peroxide (EMScience, affiliate of Merck, KGaA, Darmstadt, Germany). Certified reference materials, DORM-2 (Dogfish Muscle tissue) and DOLT-3 (Dogfish Liver tissue), were obtained from the National Research Council (NRCC, Ottawa, Ontario, Canada).

Sample preparation

Three samples (0.5 g) of each CRM were accurately weighed and transferred to PTFE vessels to which were added 2.0 ml of concentrated nitric acid and 1.0 ml of 30% hydrogen peroxide. The vessels were sealed, put aside for 30 min and then heated in a microwave oven. The microwave heating program is shown in Table 2. After cooling, the solution was transferred to a glass beaker and evaporated to near dryness. Then, 2.5 ml of concentrated nitric acid was added and the solution transferred into a 25-ml calibrated flask; 25 µl of 1000 µg l^{-1} Tb, Be, and Ge standard solutions were added and the solution diluted to volume.

Table 2 Microwave digestion program

	Stage			
	1	2	3	4
Power (% of 800 W)	25	80	80	80
Pressure/psi	20	50	90	120
Time/min	3	5	10	10
Time at pressure/min	2	3	5	5
Temperature/°C	120	160	200	200

Wavelength selection for potential internal standards

In order to correct the matrix effects in the determination of As, Se and Sb in plant and food samples, a number of elements and their spectral lines were chosen to serve as internal standards according to the following principles: (1) they did not occur in the plant and food samples; (2) there were no significant spectral interferences from analyte elements; (3) there were no spectral interferences from matrices of Na, K, Ca, Mg plus HNO_3 or HCl; (4) they covered a wide range of energies (from 4.04 eV for Bi I at 306.767 nm to 13.87 eV for Sn II at 189.927 nm); (5) they included both atomic and ionic lines. The intensity ratio Mg II 280.270 nm/Mg I 285.213 nm was used as a quick, simple gauge of the robustness of the plasma.[14] The selected reference lines as well as analyte and diagnostic lines are listed in Table 3.

Optimization of plasma conditions

In order to achieve high efficiency of internal standardization and low detection limits for simultaneous determination of As, Se and Sb, the optimal operating conditions should create a robust plasma, which can be obtained by a combination of high power and a long residence time, and should give a high signal to background ratio (SBR) and low relative standard deviation of the background (RSDB). It is known that higher rf power favours plasma robustness and lower rf power favors higher SBR.[26] The figure of merit chosen was sensitivity while maintaining robust conditions. Although it might seem logical to optimize for minimum matrix interference, this was not considered practical for a large number of analytes and matrix components.

Performance parameters

The LOD were calculated for single element standards in the absence of any significant matrix, according to the treatment by Boumans.[27,28] Eqn (1) gives the relationship between detection limit, c_L, SBR-RSDB, and the concentration of a low standard c_0:

$$c_L = k \times 0.01 \times \text{RSDB} \times \frac{c_0}{\text{SBR}} \qquad (1)$$

Procedure

Solutions of plant and food samples contain relatively high concentrations of Na, K, Ca and Mg in the range of 0–500 mg l^{-1} after appropriate treatment with the nitric or hydrochloric acids that are usually used for digestion. As it is known that the extent of analyte signal depression is a function of the concentrations of the matrix elements, the effects of concentrations of Na, K, Ca and Mg of 0, 100 mg l^{-1}, 200 mg l^{-1}, 300 mg l^{-1} and 500 mg l^{-1} were investigated. The acid concentration was 10% (w/w) and the concentration of both analytes and internal standards was 1.0 mg l^{-1}. According to Grotti et al.,[23] the experiments for data processing by PCA must be performed according to a suitable experimental design and so the single and combined effects of matrix elements and inorganic acids were studied by preparing a group of solutions according to a 2^4 full factorial design. The experimental plan for the matrix concentrations up to 100 mg l^{-1} is shown in Table 4. The same plan was applied for the higher concentrations. However, this is not the only approach: an alternative could be the application of a single experimental design at

Table 3 Selected spectral lines and characteristics

Element (label)	Atom/ion	λ/nm	Potential/eV[a]	Element	Atom/ion	λ/nm	Potential/eV[a]
Analytical lines				Bi (Bi4)	I	222.281	5.58
As (As1)	I	188.979	6.57	Ge (Ge1)	I	209.426	5.92
As (As2)	I	193.696	6.40	Ge (Ge2)	I	303.906	4.08
As (As3)	I	197.197	6.29	Ge (Ge3)	I	265.118	4.68
Se (Se1)	I	196.026	6.32	Ge (Ge4)	I	206.866	5.99
Se (Se2)	I	203.985	6.08	Mo (Mo1)	II	202.031	13.24
Sb (Sb1)	I	206.836	6.00	Mo (Mo2)	II	203.845	13.18
Sb (Sb2)	I	217.582	5.70	Mo (Mo3)	II	204.597	13.16
Sb (Sb3)	I	231.144	5.36	Mo (Mo4)	II	281.616	11.50
Reference lines				Sn (Sn1)	I	235.485	5.27
Au (Au1)	I	267.597	4.63	Sn (Sn2)	I	283.998	4.37
Au (Au2)	I	242.795	5.11	Sn (Sn3)	I	242.170	5.12
Au (Au3)	II	208.208	15.18	Tb (Tb1)	II	350.917	9.39
Be (Be1)	II	313.107	13.28	Tb (Tb2)	II	384.873	9.08
Be (Be2)	II	313.042	13.28	Te (Te1)	I	214.281	5.79
Be (Be3)	I	234.861	5.28	Te (Te2)	I	238.578	5.20
Be (Be4)	I	265.045	4.68	Tl (Tl1)	II	190.801	12.61
Bi (Bi1)	I	223.061	5.56	*Diagnostic lines*			
Bi (Bi2)	II	190.171	13.81	Mg	I	285.213	4.35
Bi (Bi3)	I	306.767	4.04	Mg	II	280.270	12.07

[a] Excitation potential (E_{exc}) for atomic lines and energy sum ($E_{ion} + E_{exc}$) for ionic lines.

Table 4 Experimental plan

| Solution | Coded values (2^4 full factorial design) | | | | Real values/mg l^{-1} | | | | |
	Na	K	Ca	Mg	Na	K	Ca	Mg	HNO$_3$ or HCl (% w/w)
1	−1	−1	−1	−1	0	0	0	0	10
2	+1	−1	−1	−1	100	0	0	0	10
3	−1	+1	−1	−1	0	100	0	0	10
4	+1	+1	−1	−1	100	100	0	0	10
5	−1	−1	+1	−1	0	0	100	0	10
6	+1	−1	+1	−1	100	0	100	0	10
7	−1	+1	+1	−1	0	100	100	0	10
8	+1	+1	+1	−1	100	100	100	0	10
9	−1	−1	−1	+1	0	0	0	100	10
10	+1	−1	−1	+1	100	0	0	100	10
11	−1	+1	−1	+1	0	100	0	100	10
12	+1	+1	−1	+1	100	100	0	100	10
13	−1	−1	+1	+1	0	0	100	100	10
14	+1	−1	+1	+1	100	0	100	100	10
15	−1	+1	+1	+1	0	100	100	100	10
16	+1	+1	+1	+1	100	100	100	100	10

more than one level, such as the central composite design. In this case, the result is a single plot that displays the behaviour of the emission lines at various matrix concentrations.

The data collection and processing procedures described by Grotti et al. were followed.[23] In our experiments, solutions 2–16 of Table 4 were analyzed and the percentage relative matrix-induced analytical errors were calculated according to eqn (2):

$$E_n = 100 \times (C_1 - C_n)/C_1 \qquad (2)$$

where C_1 and C_n are the analyte concentrations in solutions 1 and n, respectively, calculated from an external standard calibration curve for each analytical and reference spectral line. Finally, all the data were arranged so that the spectral lines were objects (rows) and the matrix-induced errors were variables (columns) and then processed by principal component analysis (PCA), with XLSTAT Pro 7.5 (Addinsoft, USA).[29] The procedure was repeated for each concentration range of matrix elements. The resulting plots were examined for objects that tracked the analyte lines over the entire range of matrix concentrations.

Validation of the results

In order to validate the effectiveness of the internal standards selected on the basis of the results shown in Figs. 1 and 2, 40 synthetic samples were prepared containing As, Se and Sb at one of two concentrations (0.1 or 0.5 mg l^{-1}), together with up to 10 major elements in either 10% HNO$_3$ or 10% HCl. The matrix mixtures were prepared to approximate the matrix composition resulting from the complete digestion of 0.5 g of 10 food and plant certified reference materials in a volume of 25 ml. Elements, the concentrations of which were larger than 5 mg l^{-1}, were considered to be matrix components. The matrix compositions are listed in Table 5. The number associated with each solution refers to the number of a NIST CRM material as follows: Apple Leaves (1515), Peach Leaves (1547), Spinach Leaves (1570a), Tomato Leaves (1573a), Pine Needles (1575a), Non-fat Milk Powder (1549), Oyster Tissue (1566b), Wheat Flour (1567a), Rice Flour (1568a), and Bovine Liver

(1577b). As further confirmation of the efficiency of the single and composite internal standardization method, two certified reference materials, DORM-2 (Dogfish Muscle) and DOLT-3 (Dogfish Liver), whose matrix components fall into the ranges considered, were analyzed following nitric acid digestion.

Results and discussion

Operating conditions and detection limits

The optimum conditions selected were 1400 W rf power, 0.65 l min^{-1} as nebulizer flow rate and 1.5 ml min^{-1} as sample uptake rate, for which the high Mg II/Mg I intensity ratio of >9 indicated the robustness of the plasma. The other operating conditions are listed in Table 1. The detection limits, under these conditions were: As 3 µg l^{-1}, Sb 2.5 µg l^{-1}, and Se 4.5 µg l^{-1}.

Optimum internal standards

The PCA object score plots for HNO$_3$ and HCl are shown in Figs. 1 and 2, respectively. It should be noted that the plots have been zoomed out for a clearer view. As can be seen from the axis of each plot the first two principal components account for more than 96% of the variation in the data in all cases for nitric acid and for more than 94% of the variation in the case of hydrochloric acid.

In contrast to the experimental design of Grotti et al.,[23,24] several matrix concentration ranges (from 0–100 mg l^{-1} to 0–500 mg l^{-1}) were considered instead of just a single matrix concentration range. If only one concentration range is considered the matrix-induced depression rate cannot be followed. It is possible that two spectral lines may exhibit similar behaviors for low concentrations of matrix elements, while at high concentrations the behaviors are different. By comparing the score plots for different matrix concentration ranges, those reference objects that always stay close to the analyte objects can be considered as internal standards. The closer two objects are the higher is their "similarity" with respect to the matrix effect.[23] According to the data displayed in Figs. 1 and
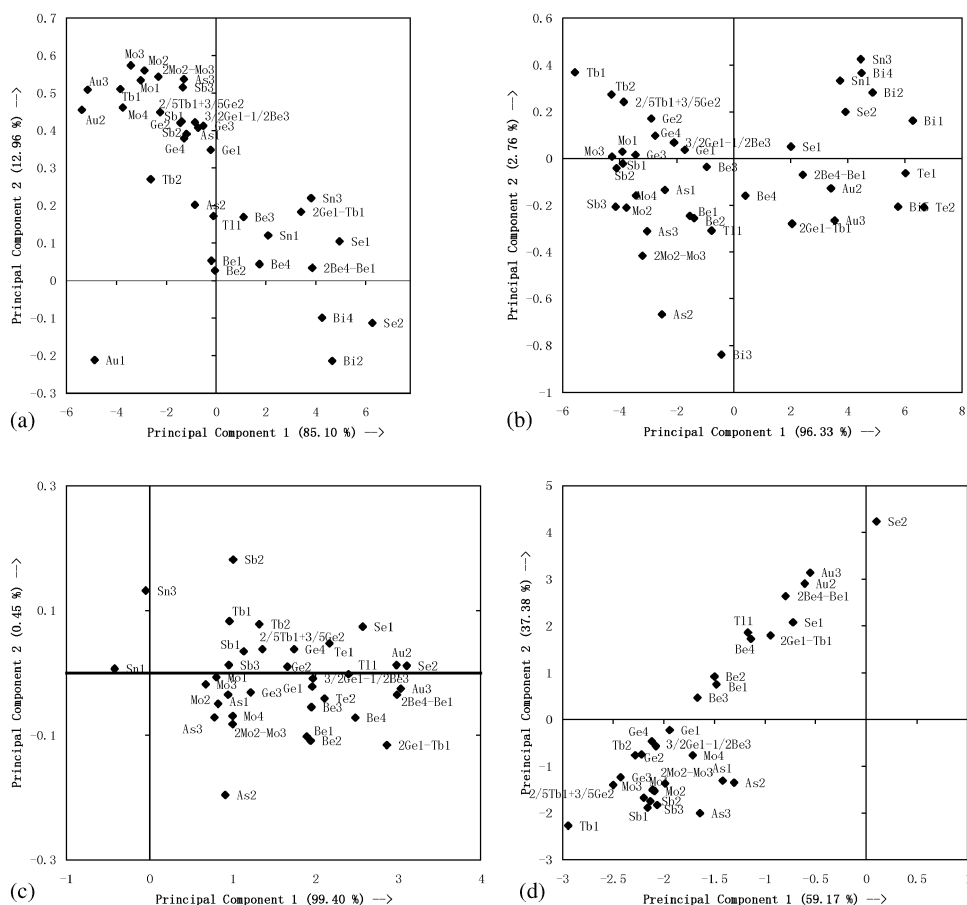
Fig. 1 Score plots (zoom) for matrix with HNO_3. Matrix concentration ranges of Na, K, Ca, and Mg: (a) 0–100 mg l^{-1}; (b) 0–200 mg l^{-1}; (c) 0–300 mg l^{-1}; (d) 0–500 mg l^{-1}. (For object labels see Table 2.)

2, the distribution of objects changes with the change of matrix concentration range, which makes the choice of appropriate internal standards for a wide range of samples difficult. This would be especially difficult for some atomic lines, which have complicated matrix effect patterns.

The concept of composite internal standards is also based on analyzing these score plots, especially when none of the objects constantly stays close to the analytes, which means that a single internal standard cannot serve to correct for matrix effects across the entire concentration range. One typical example is the selection of optimal internal standards for Se1 (196.026 nm).

From Fig. 1, it can be seen that no object persistently stayed close enough to Se1, while two groups of three objects exhibited constant relationships: Be1, Be4, and Se1; and Tb1, Ge1, and Se1. Taking the latter group as an example, Ge1 was half way between Tb1 and Se1 regardless of the distance between Tb1 (or Ge1) and Se1. The point A, which has a linear relationship with Tb1 and Ge1, such that the three points exhibit the same characteristics as Tb1, Ge1 and Se1, namely that Ge1 = (Tb1 + A)/2, would therefore be described by A = (2Ge1−Tb1).

In this principal component analysis, if we add the composite line as an object and the linear combination of matrix-induced errors of Ge1 and Tb1 as variables, we would get a score plot with Ge1 always in the middle of Tb1 and the created point that stays close to Se1. According to the theory that the closer two objects are the higher is their "similarity" with respect to the matrix effect,[23] a suitable combination of reference lines whose individual behaviour differs from that of the analyte may be able to account for the matrix effects when used in a linear combination as a composite internal standard.

In the same way, the composite internal standard (3/2Ge1−1/2Be3) is suitable to compensate for the effects of the matrix on As1 (188.979 nm). In Fig. 2, As1 constantly appears close to the middle point of Tb1 and Mo1 (or Mo2, Mo3), which leads to (1/2Tb1 + 1/2Mo1) or (1/2Tb1 + 1/2Mo1) as one choice of internal standards for As1. With regard to Se1 in HCl matrices, a single emission line of Be3 or Be4 can serve as internal standard according to Fig. 2. However, the use of the composite internal standards (1/2Mo1 + 1/2Tl1) and (3/Mo2 + 1/4Tl1) tends to give more accurate results due to their closer relationship to Se1 on the score plots. From the raw data, the overall matrix-induced error after the use of (1/2Mo1 + 1/2Tl1) as internal standard is only 55% of that error resulting from the use of Be3 as internal standard.
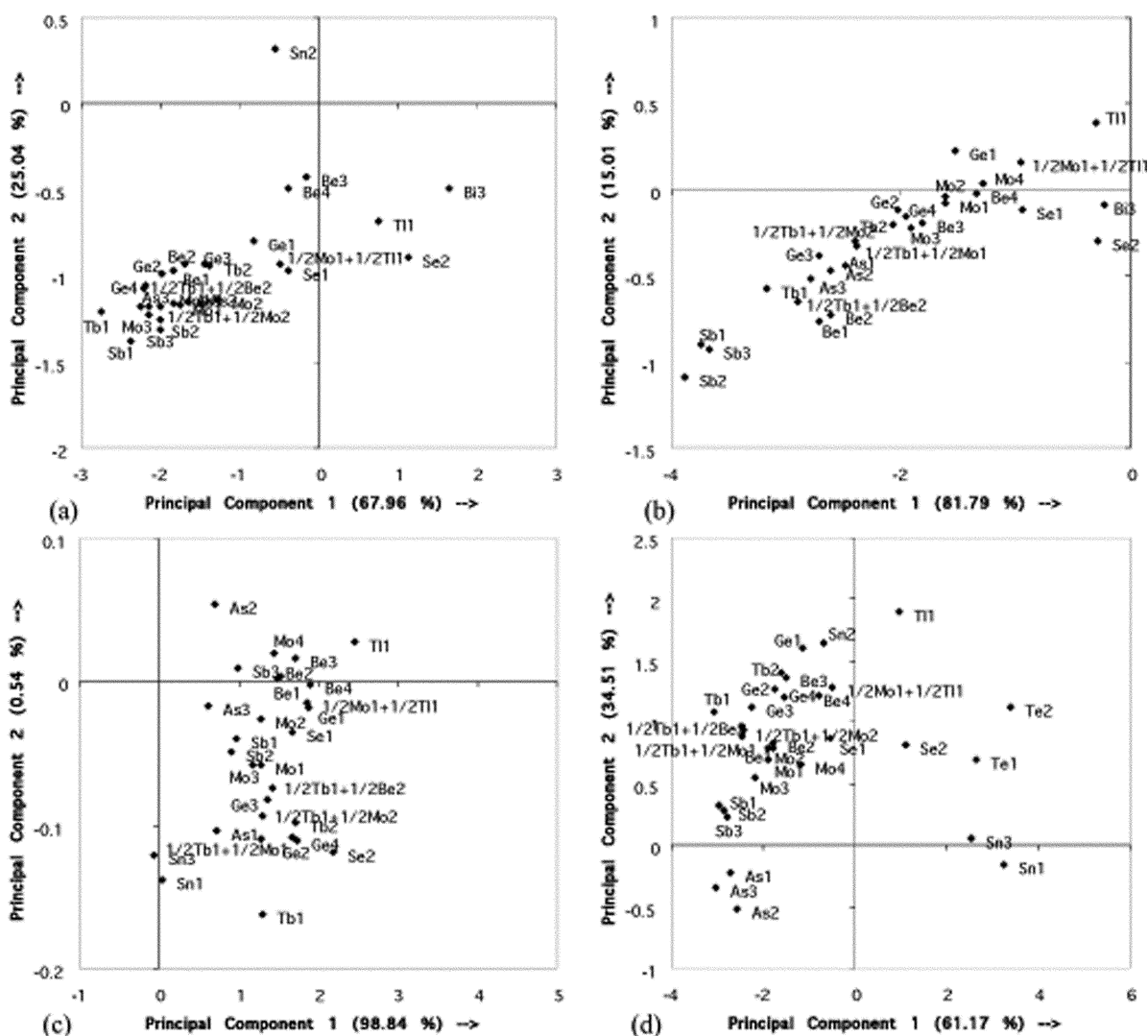
Fig. 2 Score plots (zoom) for matrix with HCl. Matrix concentration ranges of Na, K, Ca, and Mg: (a) 0–100 mg l^{-1}; (b) 0–200 mg l^{-1}; (c) 0–300 mg l^{-1}; (d) 0–500 mg l^{-1}. (For object labels see Table 2.)

Table 5 Major element compositions in synthetic sample solutions

Element	Plants/mg l^{-1}						Foods/mg l^{-1}			
	1515	1547	1570a	1573a	1575a	1549	1566b	1567a	1568a	1577b
Na			364			99	66			48
K	322	486	581	540	83	338	130	26	26	199
Ca	305	312	305	1010	50	260	17			
Mg	54	85	178	240		24	22	8	11	12
S	36	40	92	192		70	138	33	24	157
P	32	27	104	43	21	212		27	31	220
Al	6	5	6	12	12					
Fe				7						
Mn				5	10					
Zn							28			

Validation of the results

Some representative results for the analysis of the synthetic digests are shown in Tables 6 and 7, for nitric and hydrochloric acid matrices, respectively. By comparing the analytical errors before and after internal standard compensation, it can be seen that the matrix effects are considerably decreased at each concentration, and that the averages of the analytical errors are reduced to about 2–5%.

Table 6 Percentage errors for the determination of As, Sb, and Se in simulated SRM digests (10% nitric acid)

Matrix	Conc./mg l^{-1}	Analytical line	Analytical error (%) Internal standard			Analytical line	Analytical error (%) Internal standard		
		As1 188	None	Ge3	3/2Ge1−1/2Be3	Se1 196	None	2Be4−Be1	2Ge1−Tb1
1515	0.5		14.7	2.9	−1.6		23.5	4.1	0.8
1547	0.5		15.9	−2.8	−2.2		24.4	2.8	−0.4
1570a	0.5		16.1	−5.1	−5.5		25.6	3.1	−2.1
1573a	0.5		18.1	−4.6	−2.3		27.9	3.2	−0.3
1575a	0.5		12.5	−1.6	−1.2		21.2	−12.3	−1.6
1549	0.5		15.7	−1.1	−1.0		24.2	4.2	0.5
1566b	0.5		10.3	−4.4	−3.6		22.2	2.0	0.9
1567a	0.5		10.6	−2.2	−3.2		23.8	5.7	1.3
1568a	0.5		10.4	−2.6	−3.8		22.4	4.7	−1.2
1577b	0.5		11.5	−4.6	−6.9		22.3	2.6	−5.1
1515	0.1		23.8	9.5	9.6		21.8	0.5	2.3
1547	0.1		25.2	9.3	9.8		24.4	1.4	3.2
1570a	0.1		26.8	8.7	8.6		23.2	−1.3	−1.6
1573a	0.1		32.0	13.8	14.3		33.2	4.3	7.9
1575a	0.1		15.7	3.9	3.7		16.4	21.9	−2.6
1549	0.1		28.5	15.2	15.7		24.0	5.8	5.4
1566b	0.1		10.7	−3.4	−2.8		20.4	0.6	1.9
1567a	0.1		10.5	−1.2	−2.2		23.2	4.0	4.5
1568a	0.1		10.7	−0.9	−1.7		22.8	4.8	3.6
1577b	0.1		13.4	−2.0	−3.2		21.5	0.9	−0.1
		Average[a]	16.7	5.0	5.1	Average[a]	23.42	4.5	2.4
		As3 197	None	Mo1	2Mo2-Mo3	Sb3 231	None	2/5Tb1+3/5Ge2	
1515	0.5		10.2	2.4	−2.1		13.1	−1.2	
1547	0.5		11.6	2.0	−2.8		14.5	−0.9	
1570a	0.5		12.3	0.2	−4.3		15.2	−2.4	
1573a	0.5		13.2	−1.5	−4.0		19.4	1.3	
1575a	0.5		9.4	5.9	2.9		10.3	−0.1	
1549	0.5		10.8	2.8	−0.7		12.6	−0.9	
1566b	0.5		10.9	6.0	3.2		10.4	−0.7	
1567a	0.5		10.2	7.4	7.6		8.0	−1.1	
1568a	0.5		9.4	6.8	6.8		8.5	−0.8	
1577b	0.5		9.4	5.2	5.2		10.3	−1.8	
1515	0.1		6.2	−1.5	−4.7		13.5	−0.4	
1547	0.1		8.3	−0.7	−4.6		18.9	4.3	
1570a	0.1		8.5	3.0	−7.9		20.8	4.0	
1573a	0.1		11.6	−1.8	−7.5		34.8	19.9	
1575a	0.1		4.5	1.3	−1.4		9.7	−0.3	
1549	0.1		9.8	2.2	−1.6		15.2	1.9	
1566b	0.1		13.9	10.8	10.6		21.4	11.5	
1567a	0.1		8.8	6.7	7.1		9.1	0.3	
1568a	0.1		8.3	6.7	7.3		11.1	2.7	
1577b	0.1		5.9	0.6	1.1		5.7	−8.2	
		Average[a]	9.7	3.8	4.7	Average[a]	14.1	3.2	

[a] Average of absolute analytical errors (%).

Analysis of real samples

The results of the analysis of the two certified reference materials DORM-2 (Dogfish Muscle) and DOLT-3 (Dogfish Liver) are shown in Table 8. It can be seen that the matrix depressions for both As at 188 nm and Se at 196 nm are corrected by either single or composite internal standards, in agreement with the findings from the score plots (Fig. 1) and the analysis of the synthetic samples (Tables 6 and 7). For both DORM-2 and DOLT-3, similar improvements in accuracy were achieved with Ge3 and (3/2Ge1−1/2Be3) for As at 188 nm, while for the correction of Se at 196 nm, the composite internal standard (2Ge1−Tb1) performed better than (2Be4−Be1), as indicated by the average analytical errors, shown in Table 6, of 4.5% for (2Be4−Be1) and 2.4% for (2Ge1−Tb1).

Conclusion

A flexible internal standardization procedure for ICP-OES has been developed that extends the choices of possible internal standards (in the determination of As, Sb and Se, at least) and has the potential for greater accuracy than traditional internal standardization based on one standard. A procedure can be described for the general application of the method to other sample matrices as follows.

(1) Samples are grouped on the basis of similar matrix compositions and concentration ranges.

(2) Candidate internal standard elements, not present in the samples, are selected and preliminary experiments performed to select wavelengths that avoid spectral interferences.

(3) Principal components analysis is performed to visualize the behavior of all spectral lines. The experimental design

Table 7 Percentage errors for the determination of As, Sb, and Se in simulated SRM digests (10% hydrochloric acid)

Matrix	Conc./mg l⁻¹	Analytical line	Analytical error (%) Internal standard			Analytical line	Analytical error (%) Internal standard		
		As1 188	None	1/2Tb1 + 1/2Mo1	1/2Tb1 + 1/2Mo2	Sb1 206	None	Be1	1/2Tb1 + 1/2Be2
1515	0.5		9.8	−1.8	1.8		11.2	0.1	0.1
1547	0.5		11.0	−1.8	1.7		12.3	−0.5	0.1
1570a	0.5		12.7	0.1	0.1		11.7	−3.6	−1.6
1573a	0.5		16.9	1.0	0.9		15.2	−5.3	−2.1
1575a	0.5		6.4	−1.2	−1.1		7.6	1.9	0.8
1549	0.5		10.7	−0.2	−0.2		10.1	0	−0.6
1566b	0.5		4.9	2.4	−2.4		6.2	1.5	−0.1
1567a	0.5		4.6	−0.7	−0.6		3.0	2.1	−0.4
1568a	0.5		4.3	−1.2	−1.2		3.1	2.1	−0.4
1577b	0.5		5.9	−1.4	−1.3		7.0	2.6	0.6
1515	0.1		15.6	3.7	3.8		8.0	−4.8	4.4
1547	0.1		17.7	5.1	5.1		9.6	−3.2	−3.3
1570a	0.1		17.9	5.3	5.3		9.7	−5.1	−4.4
1573a	0.1		25.7	11.0	11.1		13.6	−6.5	−4.4
1575a	0.1		7.0	−1.5	−1.4		6.9	0.5	−0.5
1549	0.1		16.3	6.7	6.7		7.5	−3.0	−2.7
1566b	0.1		1.6	−6.8	−6.7		3.7	−2.0	−3.4
1567a	0.1		−2.2	−8.2	−8.1		0.6	−0.7	−2.8
1568a	0.1		1.2	−4.2	−4.1		1.7	−0.4	−1.5
1577b	0.1		4.3	−4.0	−3.9		4.3	1.5	−3.0
		Average[a]	9.6	3.4	3.4	Average[a]	7.7	2.4	1.9
		Se1 196	None	Be3	1/2Mo1 + 1/2Tl1	Sb2 217	None	Be1	1/2Tb1 + 1/2Be2
1515	0.5		16.0	3.1	−0.1		14.0	3.3	3.3
1547	0.5		17.2	2.8	−0.4		15.2	2.9	3.4
1570a	0.5		20.2	4.6	0.8		15.0	0.2	2.2
1573a	0.5		25.2	4.8	2.8		27.8	10.3	13.1
1575a	0.5		8.8	−0.6	−2.2		10.4	4.9	3.8
1549	0.5		16.4	4.2	1.3		12.3	2.5	1.9
1566b	0.5		11.6	3.0	1.2		6.8	2.1	0.5
1567a	0.5		6.8	3.0	0.1		2.6	2.1	−0.8
1568a	0.5		7.2	2.9	−0.1		3.3	2.3	−0.2
1577b	0.5		11.8	3.1	1.7		8.2	3.9	1.9
1515	0.1		18.9	5.2	1.8		17.3	5.8	6.1
1547	0.1		19.0	5.0	0.6		22.1	11.1	11.0
1570a	0.1		19.5	4.6	0.3		22.5	9.8	10.4
1573a	0.1		33.9	16.3	13.1		23.5	5.7	7.6
1575a	0.1		4.3	−6.2	−8.3		17.8	12.2	11.2
1549	0.1		15.6	3.1	0.4		17.5	8.1	8.4
1566b	0.1		11.8	2.3	0.4		6.7	1.2	−0.2
1567a	0.1		6.9	2.5	−0.4		1.6	0.3	1.8
1568a	0.1		6.7	1.6	−0.9		1.3	−0.8	2.0
1577b	0.1		11.3	1.4	0.1		2.3	−3.6	−5.1
		Average[a]	14.5	4.0	1.9	Average[a]	12.4	4.6	4.8

[a] Average of absolute analytical errors (%).

Table 8 Analysis of the certified reference material DORM-2 and DOLT-3[a]

Analytical line	CRM	Certified/mg kg⁻¹	Found/mg kg⁻¹		
			Without IS	Ge3	3/2Ge1−1/2Be3
As 188 nm	DORM-2	18.0 ± 1.1	16.2 ± 0.4	18.4 ± 0.7	18.3 ± 1.0
	DOLT-3	10.2 ± 0.5	9.0 ± 0.3	9.8 ± 0.5	9.8 ± 0.7
			Without IS	2Be4−Be1	2Ge1−Tb1
Se 196 nm	DORM-2	1.40 ± 0.09	1.18 ± 0.09	1.44 ± 0.10	1.52 ± 0.12
	DOLT-3	7.06 ± 0.48	5.28 ± 0.11	6.23 ± 0.12	7.02 ± 0.16

[a] Mean values and 95% confidence limits for the analysis of three samples.

should be as broad as possible, taking into consideration various matrix effects and analyte concentrations.

(4) In all the score plots, constant close relationships between analytical and reference lines indicate that the reference lines are suitable as internal standards. The reference lines can be single spectral lines or a linear combination of different spectral lines.

We suggest that the concept of composite internal standards could possibly be applied to measurements with other

techniques for which internal standardization is commonly employed, such as plasma-source mass spectrometry.

Acknowledgements

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