On the use of line intensity ratios and power adjustments to control matrix effects in inductively coupled plasma optical emission spectrometry

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In inductively coupled plasma optical emission spectrometry, matrix effects can be substantially reduced by applying robust operating conditions, *i.e.* a high rf power level and a low nebulizer gas flow. However, dissimilar line intensity changes are still observed, in particular with varying salt matrices. Calcium and, to a lesser extent, Mg induce stronger effects than Na and K. In 0.1, 0.3 and 1.0% Ca matrices, signal changes for 29 atomic as well as ionic lines have been determined with respect to the Ca-free solution. The changes range from -5 to -30% for the 1.0% Ca matrix. Starting from robust conditions in radial viewing, the rf power has been adjusted until the Cr ion-to-atom line ratio measured for the calcium solutions equalled the ratio determined during the calibration (0% Ca). By this power adjustment, the changes are within $\pm 4\%$. No matrix effects originating from the sample introduction system are observed, probably due to the high acid concentrations used. The practical application of power adjustments is illustrated with results for certified sediment samples and with multiple line analysis for qualitative and semiquantitative analysis. The approach is an attractive alternative to matrix matching or standard additions. Internal standardization based on one atomic and one ionic line of the same element is indicated as another possibility.

When analysing series of samples in inductively coupled plasma optical emission spectrometry (ICP-OES), the sample matrices may vary in acid and/or salt composition. Variations in acid composition are not expected to be large, as fixed amounts are usually applied for digestion or storage of samples. The main components may vary appreciably, such as the transition elements in steel or the alkali and alkaline earth elements in sediment digestions. For proper calibration, one has to consider the sample matrix composition, and methods such as matrix matching, internal standardization, standard addition, optimization of ICP operating conditions and mathematical correction can be applied.[1] With matrix matching, the known amount of acid and the expected average amount of salt (if necessary) are added to all calibration solutions.

According to the insights obtained by Mermet's group,[2–9] matrix effects have their origin in different parts of the ICP instrument, *viz.* in the plasma itself and in the sample introduction system. It has been shown that the plasma can be made robust with respect to atomization, ionization and excitation by appropriate selection of the operating conditions.[2–4] The matrix effects can be substantially reduced by using operating conditions that lead to an efficient energy transfer between the plasma and the sample. With a high rf power level ($\geqslant 1200$ W), a low nebulizer gas flow ($\leqslant 0.6$ l min^{-1}) and a wide injector inner diameter ($\geqslant 2$ mm), all ionic lines having an energy sum between 8 and 16 eV are suppressed by more or less the same amount in the presence of a matrix as compared to the matrix-free situation. The suppression is quite insensitive to significant changes in the salt or acid matrix composition, and may originate from changes in the aerosol transport in the sample introduction system.[5–7] It can be compensated for by using matrix matched standards or internal standardization.[8] Robust plasma conditions are characterized by the high intensity ratio (>8) of the Mg II 280.270 nm line with respect to the Mg I 285.213 nm line.[9] Hence, the Mg II/I line ratio for standard and sample solutions can be measured to confirm the robustness of the analysis with respect to matrix effects.

The Mg II/I line ratio has also been used as a fast diagnostic tool in the control of ICP systems,[10] and in qualitative and semiquantitative analysis.[11–13] In this kind of analysis, the assessment of the presence of an element is based on the detection of the prominent emission lines and their relative line intensities compared with predetermined values of the pure element solution. To allow the comparison of relative line intensities, the plasma conditions on analysis should be close to the conditions at which the reference values were determined. In verification, the Mg II/I line ratio should be reproduced at its high value indicating robust and identical conditions. Otherwise, it was suggested[12] that the rf power level should be adjusted slightly in order to reproduce the Mg II/I line ratio.

Present-day ICP-OES instrumentation[14–17] includes an echelle grating in combination with a cross disperser to obtain a two-dimensional image of the emission spectrum. Charge transfer device detectors are then applied to generate the digital representation of the full spectrum. This instrumentation has allowed the development of semiquantitative survey analysis, where the full sample spectrum is compared with a set of pure element spectra.[18,19] Based on multicomponent analysis, all elements and all of their lines present in the spectrum are processed simultaneously. As about 70 elements can be detected by ICP-OES, the set of spectra should be determined in a once-only calibration using pure element solutions. The solutions contain 2% HNO_3 as the common matrix and the spectra include a large amount of atomic and ionic lines with widely different energy sums. This predetermined set of spectra is intended not only to calibrate sample signals over the lifetime of the instrument, but also to calibrate sample signals in divergent matrices. In order to reproduce the line patterns at a later time or in a different matrix (HCl, Na, K and Ca), rf power adjustments have successfully been applied[19] using a matrix matched monitor solution containing Ba, Cd, Cr, Cu and Ga and employing the line ratio of the

Cr II 267.716 nm and Cr I 357.869 nm lines as the sensitive criterion for appropriate adjustment.

Thompson *et al.*[20] found that matrix-induced changes in excitation conditions in the plasma and a change in the rf power supplied to the plasma produced a similar effect. This similarity was used to compensate for matrix effects as large as 30%. To all test solutions with Al, Ca, K, Mg, P and S as the matrix elements, the same Be amount was added and the rf power was automatically tuned proportional to the difference between the observed and the reference Be II intensity at 313 nm. Budič and Hudnik[21] also increased the power level by a small amount to correct for KCl and H_3PO_4 matrix effects which were found to correlate with the excitation energy of the ionic lines.

Mermet[7] reported that, when applying robust conditions, matrix effects can be minimized to almost the same extent, regardless of the elements, line characteristics and radial or axial viewing mode. However, close inspection of the available data[4,6,22] shows that the signal suppression still varies over the analytes or, even worse, over different ion lines of the same analyte. In the work of Brenner *et al.*,[23] matrix effects owing to $1 \, g \, l^{-1}$ Ca or Na were observed to be relatively small, but suppressions for most of the analytes were dissimilar. Such changes with matrix composition point at changes in plasma conditions. The main objective of this paper is to further investigate the dissimilar intensity changes of emission lines in ICP spectra. Starting from robust conditions, it will be shown to what extent line intensities can be reproduced, how rf power adjustments can help and how ion-to-atom line ratios can serve as the criterion. As solutions containing Ca exhibit a large matrix effect as compared to solutions containing Na, K or Mg, the Ca matrix is used as the worst case example. The approach of power adjustments is illustrated with several certified sediment samples. Herewith, a simple solution to an old and persistent problem of Zn analysis in sediments is presented. In addition, it is shown how semi-quantitative, multiple line analysis can benefit from power adjustments.

Experimental

ICP emission spectrometer and settings

This study was carried out with a Perkin-Elmer (Norwalk, CT, USA) Optima 3000 DV system. The sample introduction system consisted of a cross-flow nebulizer and a double-pass Scott-type spray chamber. According to the procedure described below, robust plasma conditions were realized by applying 1300 W rf power and $0.6 \, l \, min^{-1}$ nebulizer gas flow. The injector inner diameter was 2.0 mm. Most data were obtained in the radial viewing mode at 4 mm distance from the load coil.

The spectrometer consists of an echelle grating and separate cross-dispersers for the UV and visible channels. Both optical channels end up in separate segmented charge coupled device (SCD) detectors. The system measures simultaneously 6% of the continuous ICP spectrum from 167 to 782 nm on 201 subarrays. The subarrays cover one to four prominent analytical lines for each detectable element.

All pertinent operating conditions are summarized in Table 1.

Standards and samples

Test solutions of $1 \, mg \, l^{-1}$ Mg and $20 \, mg \, l^{-1}$ Cr were prepared in 5% HNO_3 and in $1000 \, mg \, l^{-1}$ Na, K, Mg or Ca using Merck (Darmstadt, Germany) single element standards. To study the Ca matrix effect, $10 \, mg \, l^{-1}$ dilutions of the Merck ICP multielement standard IV were made in solutions contain-

Table 1 Operating conditions of the Perkin-Elmer Optima 3000 DV spectrometer

Nominal rf power/W	1300
Plasma gas flow/l min^{-1}	15
Auxiliary gas flow/l min^{-1}	0.5
Nebulizer gas flow/l min^{-1}	0.6
Sample uptake rate/ml min^{-1}	1.0
Nebulizer	Cross-flow
Diameter of injector tube/mm	2.0
Viewing	Radial
View distance from coil/mm	4
Resolution	Normal
Read time	Auto
Minimum and maximum read time/s	2

ing 5% HNO_3 and 0, 0.1, 0.3 or 1.0% Ca. Suprapure $CaCl_2 \cdot 4H_2O$ was used.

The sediments BCR145, BCR277, BCR280, BCR320 and Maas were digested by dissolving about 2 g in 100 ml of 16% aqua regia. The Maas sediment is distributed by the Institute for Inland Water Management and Wastewater Treatment, Lelystad, The Netherlands. Calibration was performed using $10 \, mg \, l^{-1}$ Merck ICP multielement standard IV in 16% aqua regia.

Results and discussion

Robust conditions

Robust plasma conditions are applied as the reference conditions in the present study. As in the work of Mermet's group, the nebulizer flow was set as low as $0.6 \, l \, min^{-1}$ and the standard alumina injector tube was mounted. Among the available injectors, this tube has the largest inner diameter of 2.0 mm. The rf power was set to 1300 W. Although a more robust plasma can be obtained at the software controlled maximum power level of 1500 W, the lower setting was used to allow power adjustments when nebulizing heavy matrices.

The optimum distance from the rf coil was determined by nebulizing a test solution containing Mg and Cr. Intensities were measured for the Mg 280.270 nm and the Cr 267.716 nm ion lines and for the Mg 285.213 nm and the Cr 357.869 nm atom lines. The normalized line intensities as a function of distance are displayed in Fig. 1. The atom lines attain their maximum intensity around 4 mm, whereas the ion line intensities continue to increase at smaller distances. Fig. 2 shows the normalized ion-to-atom line ratios for Mg and Cr. In order not to measure too close to the coil, the 4 mm setting was selected as the proper distance. This optimum distance of a few millimetres from the coil was also selected in other work.[3,4]

As can be seen in Fig. 1, the Mg and Cr ion line intensities show the same behaviour as a function of distance from the coil. The Mg and Cr atom line intensities, however, behave differently: there is almost no change in the Cr I intensity. This is reflected in the ion-to-atom line ratios in Fig. 2: the Cr II/I ratio has the largest relative increase with decreasing distance. The same is true for the Cr II/I ratio with increasing rf power level, as displayed in Fig. 3 together with a large set of relative line ratios. This example was determined for a 0.1% Ca matrix relative to the matrix-free situation (at 1300 W). By using the multielement standard and subarrays available on the Perkin-Elmer Optima 3000 DV system, the change in the relative line ratios as a function of rf power was determined for the combinations: Cd 214/228, Cd 226/228, Cr 205/357, Cr 267/357, Cu 224/324, Cu 224/327, In 230/325, Mg 280/285, Ni 221/232, Ni 231/232, Pb 220/283, Tl 190/276, Zn 202/213 and Zn 206/213. From Fig. 3, the change is similarly large for the Cr 205/357, Cr 267/357 and Pb 220/283 combinations, smallest for the Mg 280/285, Ni 231/232 and Tl 190/276 combinations, and in between for the two Zn combinations.
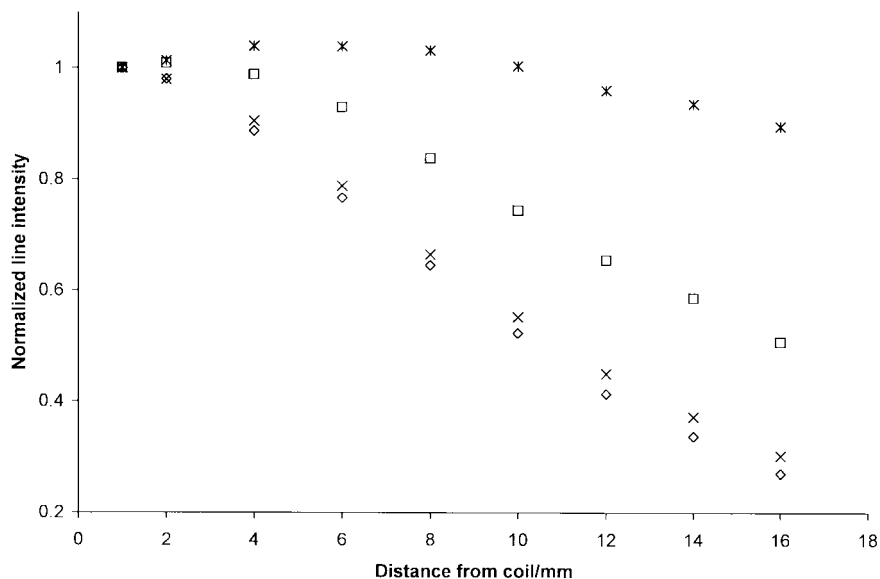
Fig. 1 Ionic and atomic line intensities for Mg and Cr as a function of the distance from the rf coil, normalized to the intensities at 1 mm distance. Rf power is 1300 W. ◇, Mg II 280.270 nm; □, Mg I 285.213 nm; ×, Cr II 267.716 nm; *, Cr I 357.869 nm.
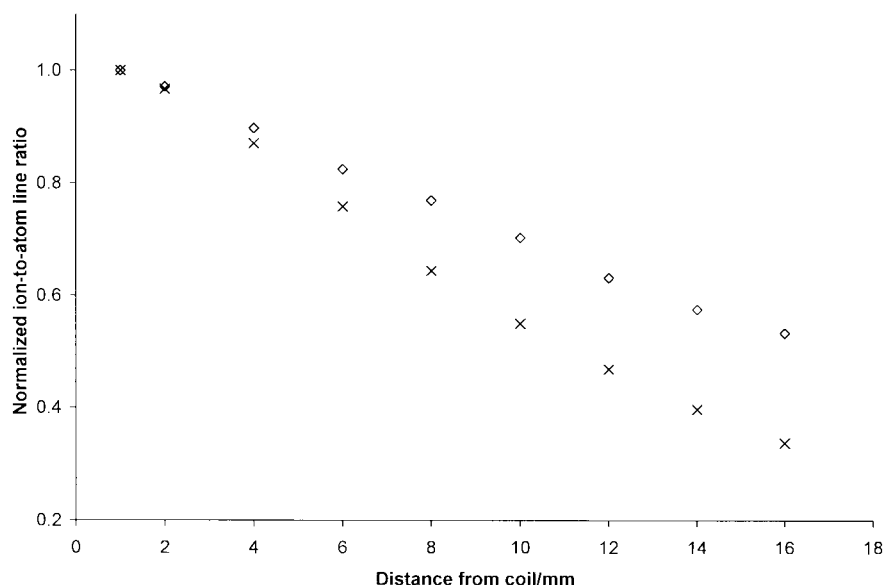
Fig. 2 Ion-to-atom line ratios for Mg and Cr as a function of the distance from the rf coil, normalized to the ratios at 1 mm distance. Rf power is 1300 W. ◇, Mg II/I; ×, Cr II/I.

In an earlier study,[19] the Cr 267/357 ratio was found to monitor, on average, the efficiency of atomization and ionization for the full set of elements detectable in ICP-OES. Owing to this fact and to its strong dependence on the rf power, the Cr 267/357 line ratio will be used in the present study when correcting matrix effects by power adjustments.

Robustness, nevertheless, has been characterized in general by the Mg II/I ratio, which should be larger than 8.[7] As in the Optima 3000 DV system the actual rf power applied to the ICP can differ from the nominal setting by ±50 W, the ratio was determined over several days for the operating conditions given in Table 1. The obtained average of 14.4 should be corrected for differences in the efficiencies of the echelle grating and the SCD detector. For one specific Optima 3000 DV instrument, a correction factor of 1.85 was reported.[24] Although the authors did not explain how they derived this value, the correction factor has been used by others for their instruments.[6,25–27] By measuring the background intensities in the Mg 280 nm and Mg 285 nm subarrays of our Optima 3000

DV instrument and by making the reasonable assumption that the ICP continuum background intensities are the same over a wavelength range of only 5 nm, our correction value equals 1.34. This results in an Mg II/I ratio of 10.7, confirming that the ICP operates under robust conditions.

It is clear that robustness can also be characterized using the Cr II/I ratio. However, efficiency corrections cannot easily be made in order to report values which can be compared from instrument to instrument, because of the large difference between the wavelengths of the two chromium lines.

Matrix effects from Na, K, Mg and Ca

Under robust conditions, changes in the plasma conditions are expected to be small when the matrix concentration is significantly modified. With an acidic matrix, changes in the amount of acid cause only minor changes in ionic line intensities.[2] Elements such as Na, K, Mg and Ca, however, are notorious for their matrix effects and, even under robust
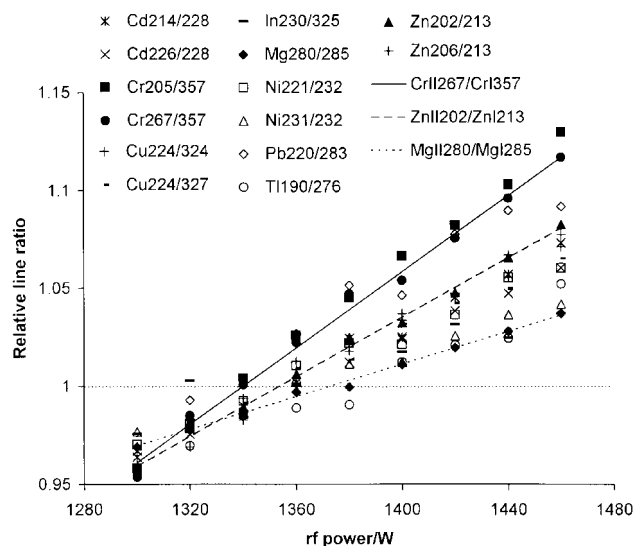
Fig. 3 Ion-to-atom line ratios with and without the presence of 0.1% Ca as a function of the rf power level. Distance from coil is 4 mm. The dotted line indicates a relative line ratio equal to 1.

conditions, dissimilar suppressive effects for various ionic lines up to tens of per cent have been observed.[4,6,22,23] As a consequence, the suppressive effect may not (only) be due to the sample introduction system,[5-7] but may be due to some further change in plasma conditions.

In order to clearly observe the remaining matrix effect under robust conditions, the alkali and alkaline earth elements were investigated to see which produced the strongest effect. Mg and Cr line intensities were measured in solutions containing 1000 mg l^{-1} of Na, K, Mg or Ca. Table 2 shows that the plasma is fully robust with respect to the Na and K matrices. For the Mg and Ca matrices, the Cr ion line is suppressed, whereas the atom line is not, and the Cr II/I ratio indicates a change in the plasma conditions. The Ca matrix shows the largest effect, as also observed by others,[19,23] and was selected to further investigate the dissimilar line intensity changes.

The Mg intensities varied over the respective matrices, owing to the small contamination in the suprapure salts and of course to the presence of Mg itself as the matrix. Therefore, for Mg, only the Mg II/I ratio is reported in Table 2. The Mg II/I ratio suggests that the plasma is still robust for the Ca matrix. Its low value of 8.8 in the Mg matrix reflects another problem with the use of the Mg II/I ratio, especially when analysing environmental samples. Owing to the high content and its strong emission, the intensity of the Mg II line is out of the linear dynamic range.

The effect of rf power adjustments

As the reference, intensities were measured from a 10 mg l^{-1} multielement standard in 5% HNO$_3$ under the robust conditions at an rf power level of 1300 W. Table 3 lists the 29 lines that were used. Then, the intensities were measured from the same multielement standard in 0.1, 0.3 and 1.0% Ca

Table 2 Chromium intensities (cps) and Cr and Mg ion-to-atom line ratios (not corrected for spectrometer efficiency) for different salt matrices of 1000 mg l^{-1}

Line	No salt	Na	K	Mg	Ca
Cr II 267	63200	62600	63800	60500	60200
Cr I 357	34500	34300	35000	34100	34600
Cr II/I	1.83	1.83	1.82	1.77	1.74
Mg II/I	12.0	12.0	12.0	8.8	11.7

Table 3 Lines (nm) used in the determination of line intensity ratios

|			
Al I 237	Cr II 205	Ga I 294	Pb II 220
Al I 396	Cr II 267	Ga I 417	Pb I 283
Ba II 455	Cr I 357	In II 230	Zn II 202
Cd II 214	Cu II 224	In I 325	Zn II 206
Cd II 226	Cu I 324	Mn II 257	Zn I 213
Cd I 228	Cu I 327	Ni II 221	
Co II 228	Fe II 238	Ni II 231	
Co II 230	Fe II 259	Ni I 232	

including 5% HNO$_3$ at 1300 W. Fig. 4 shows the line intensity ratios with and without the presence of 1% Ca as a function of the energy sum of the 29 lines. For the present Optima 3000 DV instrument, the observed change in the ratio is more or less linear with the energy sum and suggests that a change should be made to one of the plasma parameters. Here, we will adjust the rf power level to investigate to what extent the effects owing to different Ca matrices can be corrected for with the Cr II/I ratio as the criterion. Although the feedback electronics define the ultimate power level when switching on the plasma (± 50 W with respect to the nominal value), the power level is stable after the warming-up time and can be tuned to any desired level in a reproducible way.[18]

The ratios of the line intensities measured in the matrix and in 5% HNO$_3$ vs. the rf power are displayed in Fig. 5(a) for the 0.1% Ca matrix and in Fig. 5(b) for the 1.0% Ca matrix. In Fig. 5(a), it can be seen that, at 1300 W, some lines are suppressed by 10% while other lines are not suppressed at all. By increasing the power, the spread in suppression decreases, attains a minimum, the suppression changes into an enhancement and the spread in enhancement increases. The minimum spread occurs at the rf power level at which the line intensity ratios for the Cr II 267 nm and Cr I 357 nm lines are equal. Or, in other words, at the optimum power setting, the Cr II/I ratio in the matrix equals the reference value. The same behaviour is observed for the two other matrices, where, with increasing amount of Ca, the initial spread in the suppressions and the suppressions themselves increase and the optimum power level occurs at a higher setting, as is shown for the 1.0% Ca matrix in Fig. 5(b).

Table 4 lists the averaged suppression, i.e. the matrix effect, and the extreme values for the 29 lines measured in the different Ca matrices. The values are given at 1300 W and at the optimum rf power level for which the reference Cr II/I ratio is reproduced. At the optimum level, not only is the spread in the line intensity ratios at its minimum, but also the matrix effect has been removed.

The removal of the matrix effect by power adjustments shows that the signal suppression mainly has its origin in the plasma conditions and that the sample introduction system hardly generates a suppressive effect. The fact that all the solutions contained a similarly high acid level of 5% HNO$_3$ may assist in the similar aerosol transport of the test samples or in hiding the effect resulting from the sample introduction system. Even up to 1% of Ca, no matrix effect is present, but the spread in the line intensity ratios increases. Therefore, although one may adjust the power level to compensate for the Ca matrix effect, matrix matching may be preferred when the salt content of the sample differs widely from the salt content of the standards.

In the set of 29 lines, the smallest effects were observed for Cr I 357 nm, Al I 396 nm and Ga I 417 nm, whereas Zn II 202 nm, Zn II 206 nm and Cd II 214 nm showed the largest effects. Obviously, the magnitude of the effect corresponds with the atomic/ionic character of the line and its energy sum. The lines for Li, Na, Mg and K were used to determine the line intensity ratios for the 0.1% Ca solution with respect to the standard, but could not be used for the 0.3% and 1% Ca
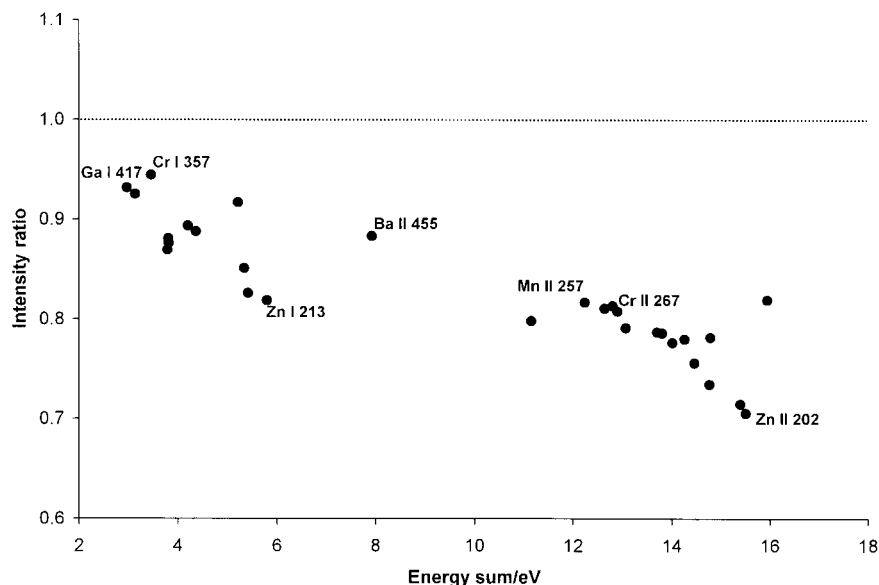
Fig. 4 Line intensity ratios with and without the presence of 1% Ca as a function of the energy sum of the 29 lines listed in Table 3. The dotted line indicates an intensity ratio equal to 1. Some lines discussed in the text have been specified.

solutions owing to the presence of these elements as contamination in the suprapure calcium salt. In all of our measurements, the Mg II/I ratio was reproduced at a 10–50 W higher power as compared to the optimum power level based on the Cr II/I ratio (see Fig. 3 for an illustration).

Analysis of certified sediment samples

In environmental analysis, samples such as soils and sediments are usually digested in 16% aqua regia and calibration standards are accordingly matrix matched. Samples may vary in
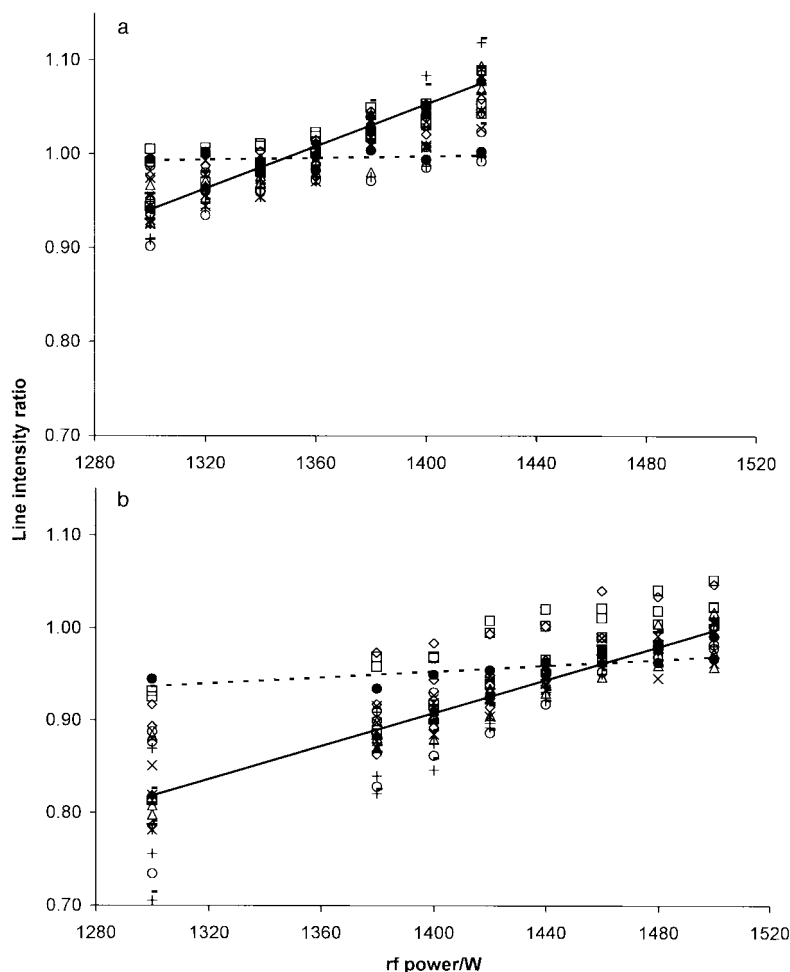
Fig. 5 Line intensity ratios for the 29 lines listed in Table 3. Intensities were measured from the 10 mg l^{-1} multielement standard in (a) 0.1% Ca and (b) 1.0% Ca in 5% HNO$_3$. The reference intensities were measured from the same multielement standard in 5% HNO$_3$ at 1300 W. Solid line: ratio for Cr II 267 nm; broken line: ratio for Cr I 357 nm.

Table 4 Averaged matrix effect (%) and its extreme values (%) for the 29 lines listed in Table 3, at 1300 W and at the optimum rf power level (W) for which the reference Cr II/I ratio is reproduced in different Ca matrices

	At 1300 W		At optimum power		
	Matrix effect	Extreme values	Optimum power	Matrix effect	Extreme values
0.1% Ca	−5	−10; 0	1350	−1	−3; 2
0.3% Ca	−7	−15; 0	1380	0	−3; 3
1.0% Ca	−17	−30; −5	1460	−2	−5; 4

salt content between several hundreds to several thousands of mg l^{-1} of Na, K, Mg and Ca. Typically, the ICP is supposed to be robust with respect to this range in matrix composition and no severe matrix effects are expected. However, based on the observations in the previous section, different changes in intensity for various lines could be expected.

In Table 5, the results are listed for the six elements of interest in the estuarine sediment BCR277, a reference material which is applied as a quality control sample in Dutch laboratories. External calibration matched for 16% aqua regia was used. For Cd and Pb, only one analyte line has been measured, as we do not intend to further complicate the present discussion by using prominent lines suffering from spectral interference by Fe. In particular, the results for the three Zn lines measured at 1300 W are remarkable: each line yields a different content, and no result equals the indicative reference value.

To investigate whether the salt content is responsible for these results, matrix matching was applied. Matrix matching is possible for BCR277 because of the known salt content. When about 1100 mg l^{-1} Ca and 200 mg l^{-1} Na, K and Mg were added to the calibration standard, the results shown in Table 5 were obtained. The results for the three Zn lines are the same and equal to the reference value. The results for Cr also improve. As outlined in the previous sections, robust conditions combined with acid matrix matching are not sufficient for this kind of analysis and the suppressions will be due mainly to the Ca and Mg content.

In the aqua regia matched calibration standard and in the BCR277 solution, the Cr II/I ratio was determined. The two values are different and the rf power requires an increase of 80 W for the BCR277 solution to reproduce the reference ratio. As can be seen from Table 5, this power adjustment

Table 5 The concentrations found (μg g^{-1}) for different elements and lines (nm) in the estuarine sediment BCR277. The indicative values per element are included

		Concentration found			
Power/W		1300	1300	1380	
External calibration at 1300 W matched for		Acids	Acids + salts	Acids	
Element line	Energy sum/eV				Indicative
Cd I 228	5.42	10.2	11.2	11.2	10.8
Cr II 205	12.8	130	140	142	145.6
Cr II 206	12.8	125	132	136	
Cr II 267	12.9	130	138	140	
Cr I 357	3.46	134	144	138	
Cu I 324	3.82	84	87	88	97.2
Cu I 327	3.79	89	94	92	
Ni II 231	14.0	33	41	37	34.9
Ni I 232	5.34	35	46	37	
Pb II 220	14.8	134	161	146	137.5
Zn II 202	15.5	476	558	548	557
Zn II 206	15.4	489	553	562	
Zn I 213	5.80	512	551	556	

results in the same three values for the Zn content which equal the reference value. The Cr results are also clearly improved. All line intensities increase on power adjustment, but the enhancement is stronger for the lines with a higher energy sum.

When using the Mg II/I ratio instead of the Cr II/I ratio, the rf power had to be increased even further. The Mg ratio is low at 1380 W owing to the 200 mg l^{-1} Mg present in the BCR277 solution. At this concentration level, the Mg II signal already suffers from non-linearity, whereas the reference signals were determined from the 10 mg l^{-1} calibration standard.

The effect of rf power adjustments was also measured in the axial viewing mode. The reference Cr II/I ratio in this mode differs from the value in the radial mode, and was determined to be 0.835 in the multielement standard. It is not possible to reproduce the Cr II/I ratio: in BCR277, values of 0.641 and 0.744 were measured at 1300 and 1500 W, respectively. On the contrary, the Zn 202/213 ratio was reproduced at 1500 W and the Zn 206/213 ratio at 1450 W. As the intensity of the Mg II line is beyond the range for BCR277, the Mg II/I ratio cannot be determined. It is concluded that the rf power adjustments cannot minimize the spread in line intensity ratios as well as in the radial viewing mode, although the robust conditions can minimize the suppressions to the same extent as for radial viewing.[7,22–24] In a very recent paper,[28] however, observations similar to ours have been reported when comparing ionic line-based internal standardization in axial and radial viewing modes to compensate for sodium effects on accuracy.

By measuring the Cr II/I ratios for different known salt contents in radial mode and by adjusting the rf power level for the reproduction of the reference ratio, the power adjustment as a function of the Cr II/I ratio can be determined to control the matrix effects. In a series of sediment samples with unknown salt content (in particular, the amount of Ca and Mg), all samples can be checked for their Cr II/I ratios. To deviate ratios, new rf power levels are estimated from the function and the corresponding samples must be rerun. This idea is illustrated with four reference samples in Table 6: the sewage sludge BCR145, the lake sediment BCR280 and the river sediments BCR320 and Maas. The intensities of Cr and Zn at their prominent lines were measured. Calibration was performed with the 10 mg l^{-1} multielement standard in 16% aqua regia at 1300 W. The samples which were digested in 16% aqua regia were run under the same conditions. Based on the measured Cr II/I ratios, the samples were rerun at the optimum power. As can be seen from Table 6, the applied power levels are closely correlated to the Ca (plus Mg) concentrations specified for the reference materials. The results for all samples clearly improve at all selected lines. In particular for the BCR145 and Maas samples, large power adjustments were made resulting in a much closer agreement for the Cr 205, Cr 206 and Cr 267 lines with respect to the Cr 357 line as well as much less variation over the Zn lines. The results averaged over the lines are closer to the indicative values. Intensities were also measured for the other lines listed in Table 5. The power adjustments induced a clear enhancement and improvement for Ni and Pb in BCR145 and Maas, but only minor changes for the other sediments and elements.

When analysing the series of sediment samples under robust conditions, several other actions may be taken.[1] Matrix matching, however, is not practical, as BCR280 and BCR320 require a different matrix composition of the standards than BCR145, BCR277 and Maas. Standard additions are not attractive in multielement analysis. In the present example, one has to spike six different elements in all the samples. When analysing unknown samples, an additional complication occurs, as, for matrix matching, one has to know in advance the salt content and, for standard additions, one should have at least an idea about the analyte concentrations in order to add the appropriate amounts of spikes.

Table 6 The concentrations (µg g^{-1}) found and indicative for several reference sediments. The external calibration was at 1300 W, matrix matched for 16% aqua regia. Samples were measured at 1300 W and at the optimum power level for which the Cr II/I ratio was reproduced. Salt matrix (mg l^{-1}) is given for the measured solution

| | Concentration found | | | |
	At 1300 W	At optimum power	Indicative	Salt matrix
BCR145		1420 W		Na, 40
Cr II 205	71	82	85.2 ± 16.3	K, 80
Cr II 206	72	78		Mg, 350
Cr II 267	75	85		Ca, 2100
Cr I 357	79	85		
Zn II 202	2470	2760	2772 ± 209	
Zn II 206	2570	2870		
Zn I 213	2650	2840		
BCR280		1310 W		Na, 350
Cr II 205	68	71	76 ± 5	K, 540
Cr II 206	68	71		Mg, 320
Cr II 267	70	73		Ca, 330
Cr I 357	71	73		
Zn II 202	263	275	290 ± 16	
Zn II 206	275	286		
Zn I 213	278	290		
BCR320		1330 W		Na, 400
Cr II 205	59	62	70.1 ± 7.7	K, 490
Cr II 206	60	62		Mg, 400
Cr II 267	58	62		Ca, 430
Cr I 357	60	63		
Zn II 202	107	123	124.4 ± 5.4	
Zn II 206	116	133		
Zn I 213	119	131		
Maas		1360 W		Na, 10
Cr II 205	153	164	169.2 ± 13.2	K, 40
Cr II 206	154	163		Mg, 190
Cr II 267	153	164		Ca, 1080
Cr I 357	160	160		
Zn II 202	2520	2810	2740 ± 135	
Zn II 206	2590	2840		
Zn I 213	2650	2820		

As the emission lines (also those of the same element) experience different suppressions, the use of one internal standard, such as the Sc II 361.384 nm line[23] or the Ar I 794.818 nm line,[29] cannot compensate for the different responses of the lines to various concentrations of Ca. Simulation of the change in energy transfer due to matrix mismatching reveals an almost continuous change in line intensities as a function of the energy sum.[8] A more or less linear change has indeed been observed by us, as illustrated in Fig. 4. This indicates that it should be possible to describe this change by means of two or three lines covering the actual energy sum range of the lines. It should even be possible to use one atomic and one ionic line of the same element, *e.g.* In, Pd or Rh, on the Optima 3000 DV instrument.

In view of the above discussion, rf power tuning based on the Cr II/I ratio is an attractive alternative to matrix matching, standard additions or internal standardization.

Multiple line analysis

In qualitative and semiquantitative analysis, the determination of whether an element is present is made from the observation of one or more of the most prominent lines of that element. If the lines exist in the sample spectrum, the relative line intensities may be checked to confirm the element presence[11,12,30,31] and to perform line selection.[32,33] Or, mathematical procedures based on multiple linear regression,[18,19] principal component regression,[34] target factor analysis[35–37] and matrix projection[38] can be applied. For multiple line analyses, a tailor-made version of a library is necessary, in

which the patterns of the lines are experimentally assessed for the actual ICP and spectrometer. When the library has been built, the samples must be measured under the same plasma conditions.

The daily variations in the plasma parameters and the sample matrix induce changes in the plasma conditions and, hence, in the line intensity ratios. As the strength of multiple line procedures is said to be the independence of a prior knowledge of the sample composition, matrix matching of standards is not feasible and large errors may occur if the plasma conditions are not fully under control.[39] As demonstrated in this work, the combination of robust ICP conditions and rf power adjustments based on the Cr ion-to-atom line ratio is an adequate alternative. If Cr happens to be absent in the unknown sample, other ion-to-atom ratios, such as those for Mg or Pb, will perform almost as well or the sample should be spiked with Cr.

Conclusions

The application of robust conditions is not sufficient to deal with matrix effects. Dissimilar line intensity changes are observed in various salt matrices. Starting from the robust conditions, at which a reference value for the Cr II 267.716 nm to Cr I 357.869 nm line ratio is determined, rf power adjustments are made for samples with matrices up to 1% Ca to reproduce the Cr II/I ratio. At the optimum rf power level, not only is the dissimilarity of the line intensities at a minimum, but also the matrix effect has been removed. For the 1% Ca matrix, no matrix effect is observed from the sample introduction system.

As compared to the Mg II/I ratio, the Cr II/I ratio varies more strongly with the coil distance and the rf power level, making this ratio a better criterion for rf power adjustments. The Mg II/I ratio is an appropriate indicator of the robustness of the plasma, and a procedure to correct the measured ratio for efficiency differences in the spectrometer is presented.

The Ca matrix is used as the worst case example, as this matrix shows larger and more dissimilar suppressions for the 29 atomic and ionic emission lines studied as compared to Mg and, in particular, to Na and K matrices.

The practical application of power adjustments is illustrated with several certified sediment samples. The rf power adjustments correspond to the Ca (and Mg) content of the sample solutions. Results for several analytes and for different lines of the same analyte improve. For instance, all three prominent Zn lines for BCR277 give identical results which equal the reference value. The power adjustment approach does not work properly in axial viewing, but is an attractive alternative in radial viewing to the application of matrix matching, standard additions or internal standards. It is argued that multiple line analysis in qualitative and semiquantitative analysis can benefit from power adjustments.

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