

Spectral Interference and Line Selection for Trace Element Analysis in a Multi-Component Matrix Using Inductively Coupled Plasma Atomic Emission Spectroscopy

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Summary: Environmental samples like waste waters are generally known to contain calcium, magnesium, sodium and potassium as major constituents. It is important to assess the amount of interference at analyte wavelengths arising from the matrix as well as other analytes to select suitable analysis lines. This paper reports the measurement of partial sensitivities of 49 prominent lines of 17 impurities of interest in waste water (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, Zn) using inductively coupled plasma atomic emission spectroscopy. Spectral scans for 300 pm wide windows centred (± 150 pm) around analyte wavelengths, were obtained under compromise operating conditions. Using the criterion of "true detection limit", Q -values for line interference [$Q_{ij}(\lambda_a)$] and Q -values for wing background interference [$Q_{Wj}(\Delta\lambda_a)$] due to Ca, K, Mg and Na have been worked out. The Q -values give a quantitative estimate of the extent of spectral interference and thus permit a rational selection of analysis lines. It is demonstrated that by varying the relative concentration of each matrix component independently, the true detection limit of an analyte line changes and line selection in a multi-component matrix is more complex than in a single element matrix. Therefore, prior quantitative knowledge of the matrix elements is inevitable for selection of a suitable line for trace element analysis. Trace element analysis in synthetically prepared samples indicates the presence of non-spectroscopic matrix effects.

Introduction

The knowledge of spectral interference is of prime importance for the effective use of inductively coupled plasma atomic emission spectroscopy (ICP-AES) in trace element analysis. Spectral interferences are observed in inductively coupled plasma (ICP) as in any other emission source. Selection of suitable lines for trace element analysis, therefore, is a prerequisite in ICP-AES. In case of a simple matrix, like deionized water, it is relatively easier to find lines that are free from spectral interference, and detection limits down to ppm or ppb level can be achieved. The problem worsens when the sample contains elements that emit line-rich spectra [1-3]. The result of a line-rich matrix is a substantial loss in detection power due to partial or complete overlap of analysis lines by lines of concomitants, a higher flicker noise contribution to the relative standard deviation (RSD) of the background intensity, and/or a decrease in signal to background ratio (SBR) owing to enhanced background.

Sodium, potassium, calcium and magnesium are known to be present in environmental samples, like waste-water, as major constituents. These

elements when present in high concentration produce considerable background enhancements in ICP emission spectra, thus causing deterioration of detection limits of trace impurities by influencing the SBR and RSD of the background. Consequently, the line selection for trace impurities in a multi-component matrix becomes more critical. Boumans and Vrakking [4,5] proposed the criterion of "true detection limit", which not only quantitatively expresses the effect of spectral interference but also provides a basis for rational line selection. An interfering line signal in the presence of a matrix is considered to be a contribution to the background and it can be measured only with much larger uncertainty than continuous background.

In case of a multi-component system, the true detection limit, $C_{L,true}$ [4] can be written as:

$$C_{L,true} = \frac{2}{5} \sum_j Q_{ij}(\lambda_a) C_{ij} + C_{L,conv} \quad (1)$$

Where, the conventional detection limit is

$$C_{L,conv} = 2\sqrt{2} \times 0.01 \times \text{RSDBL} \times \left[\text{BEC} + \sum_j Q_{ij}(\lambda_a) C_{ij} + \sum_j Q_{Wj}(\Delta\lambda_a) C_{ij} \right] \quad (2)$$

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RSDBL is the relative standard deviation of the total background and BEC is the background equivalent concentration of the analyte in solvent blank. Q -values for line interference and wing background interference are defined, respectively, as:

$$Q_{ij}(\lambda_a) = S_{ij}(\lambda_a) / S_A \quad (3)$$

$$Q_{wj}(\Delta\lambda_a) = S_{wj}(\Delta\lambda_a) / S_A \quad (4)$$

where $S_{ij}(\lambda_a)$, $S_{wj}(\Delta\lambda_a)$ and S_A are net sensitivities of interfering line, wing background and analyte line, respectively. C_{ij} is the interferent concentration of the interferent 'j'. Therefore, for a given ICP spectrometer, knowing the numerical values of $Q_{ij}(\lambda_a)$ and $Q_{wj}(\Delta\lambda_a)$ for a set of analyte lines and interferents, the best analysis lines for trace determination in samples of approximately known composition can be selected in a rational and rigorous manner by computing $C_{L,true}$ using Eqs. (1) and (2). The lines with the lowest values of $C_{L,true}$ should then be most suitable for analysis.

The main purpose of the present work is to demonstrate that even if analysis lines are free from line interference, the line selection for the determination of trace impurities in a multi-component matrix is more complex than in a single element matrix and the complexity lies in the fact that in real samples, the matrix components may occur in varying relative concentrations and enhance the background to different degrees. It will be shown that even if the selectivity term in Eq. (1) is zero, the wing background contribution can render the line unsuitable for analysis. Line selection for 17 impurities of interest in waste-water (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V and Zn), in the presence of a mixed matrix of calcium, potassium, magnesium and sodium, have been carried out using the criterion of "true detection limit". Using the best analysis lines, trace element analysis in two synthetically prepared samples was carried out. The results indicate the presence of non-spectroscopic effects due to high concentration of concomitants.

Results and Discussion

Spectral Interference

Two or three prominent lines for each of 17 analytes were selected from Boumans [6], Winge *et*

al. [7] and Kelly [8], which were free from inter-element interference with minimum interference from calcium, magnesium, sodium and potassium. Each analyte line was scanned in a 300 pm window, centred about the peak with a total of 107 steps, each step being 2.81 pm and having an integration time of 1 s per step. Each scan was performed for the analyte solution, interferent solution and solvent blank (doubly de-ionized water). As an example a scan for Pb II 405.783 nm line is shown in Fig. 1. Since the analyte concentrations as compared to those of the major concomitants are very small, the spectroscopic interferences are likely to arise from lines or background of the latter. Therefore, the spectral scans were studied for spectroscopic interferences in the presence of 2 mg/ml of Ca, K, Mg and Na each. The interfering lines were identified by measuring their position with respect to that of the relevant analysis line in a separate scan. Table-1 lists the wavelengths of the prominent analyte lines, the interfering lines, as well as the wavelength distance $\Delta\lambda$ of the interfering line from the analyte line. The interfering line given without reference means that it is not listed in the existing classical [9] or the ICP tables [10]. As can be seen in Table-1, only a few interfering lines of Ca and Mg have been observed in the scan windows of the analyte lines. An OH band starts at 306.36 nm and the scans of Al I 308.215, V II 311.838 and Be I 313.042 show interfering lines, which are most probably part of this band.

Table-1: Interfering lines affecting the analyte lines.

Analysis lines (nm)	Interfering matrix lines (nm)	($\Delta\lambda_a$) (pm)
Al I 308.215	OH 308.125	-90
	OH 308.156	-69
	OH 308.207	-8
	OH 308.325	+10
B I 182.640	Mg I 182.797 [8]	+157
Be I 313.042	OH 313.028	-14
	OH 313.056	+14
Cu I 327.396	Ca 327.478	+82
Mn II 293.930	Mg I 293.854 [10]	-76
Pb I 405.783	Mg 405.789	+3
	Ca I 405.893 [10]	+110
V II 311.838	OH 311.720	-118
	OH 211.779	-59
	OH 311.790	-48
	OH 311.973	+135
Zn II 202.548	Mg I 202.582 [6,7,10]	+34

Q -Values and True Detection Limits

The scans as shown in Fig. 1 were used to establish the type of spectral interferences in the way as discussed by Boumans *et al.* [11]. The total

Table-2: Sensitivity ratios $Q_{ij}(\lambda_a)$ for line interference and $Q_{Wj}(\Delta\lambda_a)$ for wing interference are shown for Ca, K, Mg and Na (each 2 mg/l) as interfering matrix. Q -values have been multiplied by 10^6 .

Interferent →	Ca		K		Mg		Na	
Analysis Line (nm)	$Q_I(\lambda_a)$	$Q_W(\Delta\lambda_a)$	$Q_I(\lambda_a)$	$Q_W(\Delta\lambda_a)$	$Q_I(\lambda_a)$	$Q_W(\Delta\lambda_a)$	$Q_I(\lambda_a)$	$Q_W(\Delta\lambda_a)$
Ag II 241.318	0	260.8	0	321.6	96.1	633.3	0	233.3
Ag I 328.068	0	6.3	3.0	5.1	0	3.3	2.6	3.0
Ag I 338.289	6.8	4.1	3.8	2.5	0	2.2	0	2.2
Al I 237.335	0	40.1	17.9	16.0	0	61.1	0	25.4
Al I 308.215	16.3	36.0	25.0	39.8	26.5	56.5	23.6	30.4
Al I 396.152	139.9	813.8	10.3	31.9	11.1	12.3	0	16.9
As I 193.759	0	92.2	0	0	0	40.5	0	0
As I 197.262	38.6	132.7	0	0	58.8	55.4	0	0
As I 228.812	23.8	51.7	0	0	5.9	105.3	0	21.4
B I 182.640	0	46.3	0	0	0	16.7	0	0
B I 208.959	0	17.1	7.7	0	8.4	14.7	11.4	0
B I 249.773	0	3.5	0	3.3	0	7.1	0	1.9
Ba II 230.424	5.1	3.0	0	1.4	0.9	5.4	0	1.8
Ba II 455.403	0	0.5	0.5	0.7	0.2	0.3	0.5	0.6
Ba II 493.409	0	0.6	0	1.9	0.4	0.5	0.2	0.8
Be I 234.861	0.2	0.3	0.1	0.1	0.1	0.5	0	0.2
Be I 249.473	0	12.2	0	12.4	0	26.8	4.6	8.8
Be II 313.042	0.4	0.2	0.4	0.1	0.4	0.2	0.1	0.3
Cd II 214.438	1.2	3.4	0	1.0	0.9	3.4	1.1	0
Cd II 226.502	0	3.1	0	0	0	5.7	1.1	0
Cd I 228.802	0	3.2	0	2.4	2.0	3.7	0.7	1.7
Co II 228.616	3.6	7.5	0	4.7	12.8	0	0	3.3
Co II 236.379	3.1	12.6	0	7.8	3.3	22.5	0	4.3
Co II 238.892	0	4.1	0	0	0	10.1	0	0
Cr II 206.149	0	14.3	3.9	3.7	0	10.7	0	0
Cr II 206.542	0	63.4	0	48.3	0	56.7	0	46.0
Cr II 267.716	0	5.1	0	5.4	2.6	20.5	0	3.4
Cu I 223.008	3.1	18.7	4.2	3.4	7.8	18.5	8.6	4.9
Cu I 324.754	2.9	5.6	2.0	4.6	1.2	3.5	0	4.3
Cu I 327.396	0	8.7	0	6.3	0	3.0	1.4	4.8
Fe II 238.204	0	4.5	0	3.1	0	10.7	2.0	1.7
Fe II 239.562	3.9	7.7	0	5.0	2.3	16.0	3.8	3.7
Fe II 259.940	0	4.1	0	3.4	0	12.7	0	2.6
Hg II 194.227	20.6	42.1	0	0	24.5	35.3	0	0
Hg I 253.652	0	53.2	15.7	50.1	0	143.3	14.9	40.1
Mn II 257.610	0	0.8	0	0.5	0	2.2	0	0.4
Mn II 260.569	0	0.6	0	0	0.4	5.8	0	0.3
Mn II 293.930	0	9.1	2.4	6.2	16.2	57.6	0	2.3
Ni II 217.467	0	44.4	0	13.6	0	46.6	0	18.7
Ni II 221.647	3.2	10.5	0	1.5	5.5	8.8	0	2.2
Ni II 231.604	0	11.0	2.9	6.5	0	16.0	0	4.4
Pb II 220.353	0	36.1	0	16.9	19.8	40.7	0	0
Pb I 405.783	60.9	2223.2	0	157.1	943.5	150.0	0	107.2
V II 290.882	0	6.5	4.7	0	18.3	332.9	0	4.1
V II 292.402	1.1	5.8	1.7	3.2	7.9	189.2	4.1	2.8
V II 311.838	0	8.6	0	6.4	0	10.6	2.4	4.4
Zn II 202.548	1.6	6.3	0	0	74.0	16.9	0.8	2.9
Zn II 206.200	6.7	11.5	4.9	0	0	11.1	0	4.4
Zn I 213.856	0	2.3	0	0	0	2.0	0	0.0

background signal x_{BL} was calculated using the following expression:

$$x_{BL} = x_B + \sum_j x_{Ij}(\lambda_a) + \sum_j x_{Wj}(\Delta\lambda_a) \quad (5)$$

where, x_B is the blank intensity due to source and

solvent, $x_{Ij}(\lambda_a)$ is the net interfering signal with respect to the wing background and $x_{Wj}(\Delta\lambda_a)$ is the wing background level with respect to x_B for interferent 'j' measured at a position with respect to λ_a .

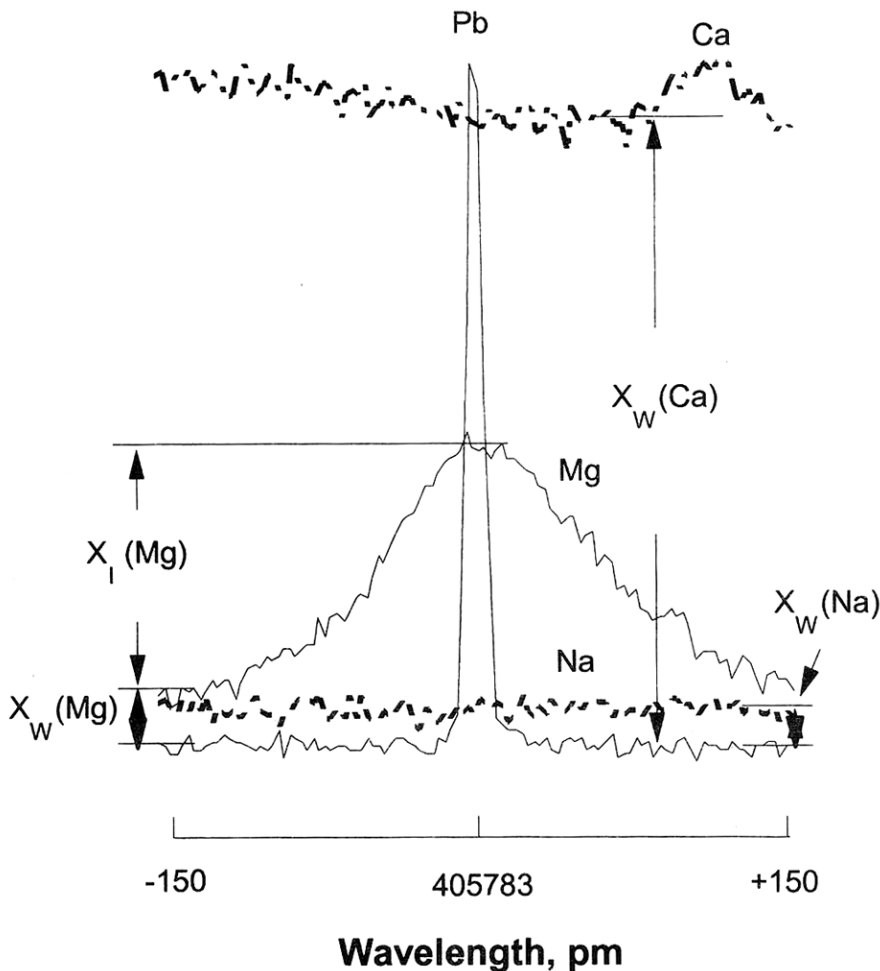


Fig. 1 Spectral scans of Pb (5 $\mu\text{g/ml}$), magnesium, calcium and sodium (2 mg/ml each) centred about Pb I 405783 pm .

Relative standard deviation of the total background signal (RSDBL) was calculated using the following empirical expression:

$$\text{RSDBL} = \sqrt{[\alpha^2 + \beta/x_{\text{BL}}]} \quad (6)$$

using the flicker noise coefficient $\alpha = 0.5\%$ and the shot noise coefficient $\beta = 10^4$, if RSDBL is expressed in %. The detector noise term was neglected in Eq. (6) to be insignificant for a photomultiplier tube detector.

Knowing the relevant parameters, a simple computer program was written to calculate $C_{\text{L,true}}$ and $C_{\text{L,conv}}$ according to Eqs. (1) and (2). Detection limit (C_{L}) for each analyte in solvent blank was determined experimentally. Table-2 lists the Q -values for individual interferent as determined for each analysis line. The detection limits $C_{\text{L,conv}}$, $C_{\text{L,true}}$ and C_{L} in ng/ml are given in the last three columns of Table-3. $Q_{\text{Wj}}(\Delta\lambda_a)$ values do not enter the selectivity term (first term) in Eq. (1) and affect the true detection limit only via conventional detection limit given in Eq. (2). Therefore, $C_{\text{L,true}}$ is mainly dictated by the magnitude of $Q_{\text{ij}}(\lambda_a)$. Comparatively smaller

Table-3: Conventional detection limits ($C_{L,conv}$), true detection limits ($C_{L,true}$) calculated using Q -values in Table-2, and experimentally determined detection limits (C_I) in pure solvent.

Analysis Line (nm)	$C_{L,conv}$ (ng/ml)	$C_{L,true}$ (ng/ml)	C_I (ng/ml)
Ag II	241.318	557	634
Ag I	328.068	7.3	12
Ag I	338.289	10.1	19
Al I	237.335	83	97
Al I	308.215	51	124
Al I	396.152	53	182
As I	193.759	166	166
As I	197.262	269	347
As I	228.812	129	148
B I	182.640	50	50
B I	208.959	29	55
B I	249.773	6.4	6.4
Ba II	230.424	7.8	13
Ba II	455.403	1.0	1.9
Ba II	493.409	1.7	2.2
Be I	234.861	0.6	0.9
Be I	249.473	20	23
Be II	313.042	0.5	1.5
Cd II	214.438	5.9	8.4
Cd II	226.502	6.4	7.3
Cd I	228.802	4.7	6.3
Co II	228.616	15	28
Co II	236.379	26	31
Co II	238.892	12	12
Cr II	206.149	21	24
Cr II	206.542	37	37
Cr II	267.716	9.2	11
Cu I	223.008	29	48
Cu I	324.754	8.2	13
Cu I	327.396	14	15
Fe II	238.204	10	12
Fe II	239.562	15	23
Fe II	259.940	8.5	8.5
Hg II	194.227	80	116
Hg I	253.652	88	113
Mn II	257.610	1.3	1.3
Mn II	260.569	2.3	2.6
Mn II	293.930	15	30
Ni II	217.467	66	66
Ni II	221.647	17	24
Ni II	231.604	20	24
Pb II	220.353	72	87
Pb I	405.783	327	1131
V II	290.882	27	45
V II	292.402	19	31
V II	311.838	13	15
Zn II	202.548	16	78
Zn II	206.200	17	27
Zn I	213.856	3.4	3.4

$Q_{ij}(\lambda_a)$ values in the presence of potassium and sodium in Table-2 suggest that the spectroscopic interference effect due to these concomitants is less than that of calcium and magnesium. Also high values of $Q_{wj}(\lambda_a)$ in the presence of calcium and magnesium show strong wing background effect on

analyte lines. The present Q -values in these two matrices are generally low as compared with those given in Ref. [12] where the values have been calculated from data obtained using a conventional ICP torch. This could also be due to a difference in operating conditions. The detection limits in pure solvent, experimentally determined in the present work, are considerably better than those given in Ref. [12].

The zero Q -values for line interference in Table-2 signify that $Q_{ij}(\lambda_a)$ are less than the minimum observable values. The minimum observable Q -value has been described by Boumans *et al.* [11] as:

$$Q_{ij}^L(\lambda_a) = \frac{C_L}{C_I}$$

where, C_L is the detection limit of the analyte in ng/ml and C_I is the interferent concentration. In the present case, the concentration of each interferent is 2 mg/ml, therefore,

$$Q_{ij}^L(\lambda_a) = \frac{C_L \times 10^{-6}}{2}$$

In Table-2, Q -values are listed as the actual values multiplied by 10^6 , and detection limits in Table-3 are expressed in ng/ml, therefore, the numerical value of the latter divided by 2 represent the minimum observable values $Q_{ij}^L(\lambda_a) \times 10^6$

Line Selection

The best analysis line for each analyte was chosen on the basis of the least value of true detection limit and is printed in bold face in Table-3. Because of line overlap of As I 228.812 nm with Cd II 228.802 nm, the second best lines were selected for these elements. Either of the lines Ni II 221.647 nm and Ni II 231.604 nm can be selected as the best line for analysis. It is not always safe to select the lines with $\sum Q_i = 0$ in a multi-component matrix since wing background interference can affect $C_{L,true}$ adversely. For example, $\sum Q_i$ -values for Cr II 206.542 nm line and Cr II 267.716 nm line are 0 and 2.6, respectively, and $\sum Q_w$ -values (wing background contribution) are 214.4 and 34.4, respectively. $C_{L,true}$ of the latter line is considerably lower than that of the former (Table-3), and hence its selection as the best

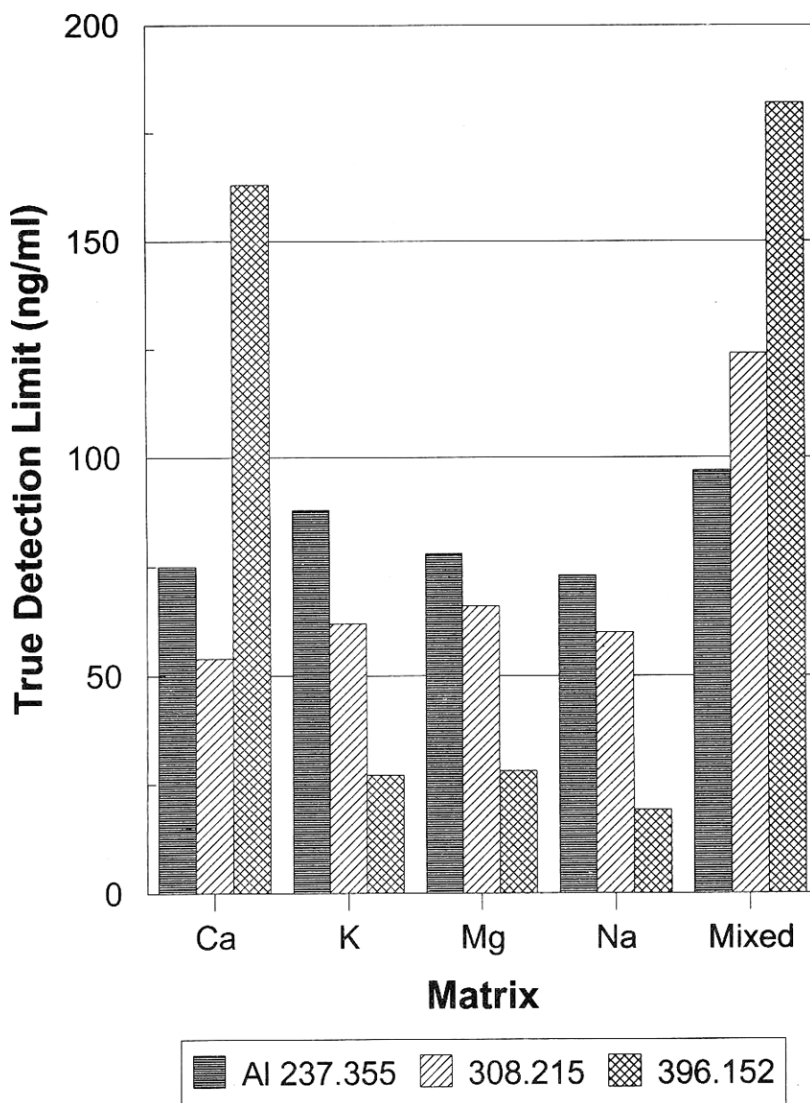


Fig. 2 True detection limits of Al prominent lines (nm) in single component matrices each of Ca, K, Mg and Na (2 mg/ml) and in a mixture of these containing 2 mg/ml of each concomitant.

line. The effect of the composition of the matrix on true detection limits of analyte lines, is illustrated in Fig. 2, where true detection limits of Al prominent lines in single component matrices of Ca, K, Mg and Na (2 mg/ml each) and in a mixture of these four elements containing 2 mg/ml of each, are plotted on a bar diagram. The best analysis line in Ca matrix is Al 308.215 nm, while in K, Mg and Na matrices the best

line is Al 396.152. In case of mixed matrix, Al 237.355 nm must be chosen for analysis. It should be pointed out that the true detection limit of a line for each concomitant can only be additive if a constant value of RSDBL is used. In practice this is not the case and the effects are not additive, which is evident from Fig. 2.

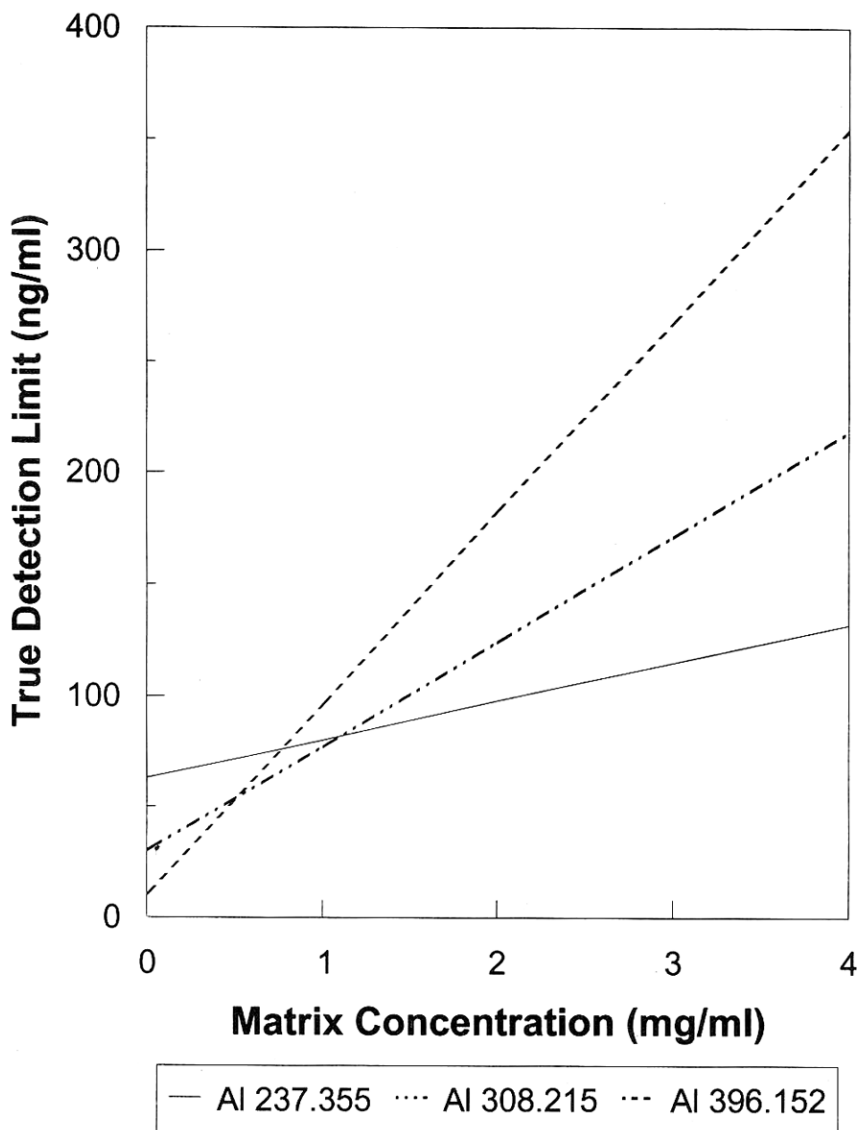


Fig. 3 Plots of true detection limits of three Al prominent lines (nm) as a function of mixed matrix concentration. Mixed matrix contains equal amounts of Ca, K, Mg and Na.

In case of a matrix comprising of a number of components with different concentrations, the analyte line selection may not be as simple as in the case of the single component matrix. First, a situation is considered where a matrix contains Ca, K, Mg and Na in equal concentrations. Fig. 3 shows true detection limits of three Al prominent lines, plotted

against varying concentration of the mixed matrix (matrix concentration shown is the concentration of each component). Below 0.5 mg/ml of matrix concentration, Al 396.152 nm line must be chosen as the best line. As the matrix concentration increases, the choice of best analysis line changes. Between about 0.5 mg/ml and 1 mg/ml of matrix concentra-

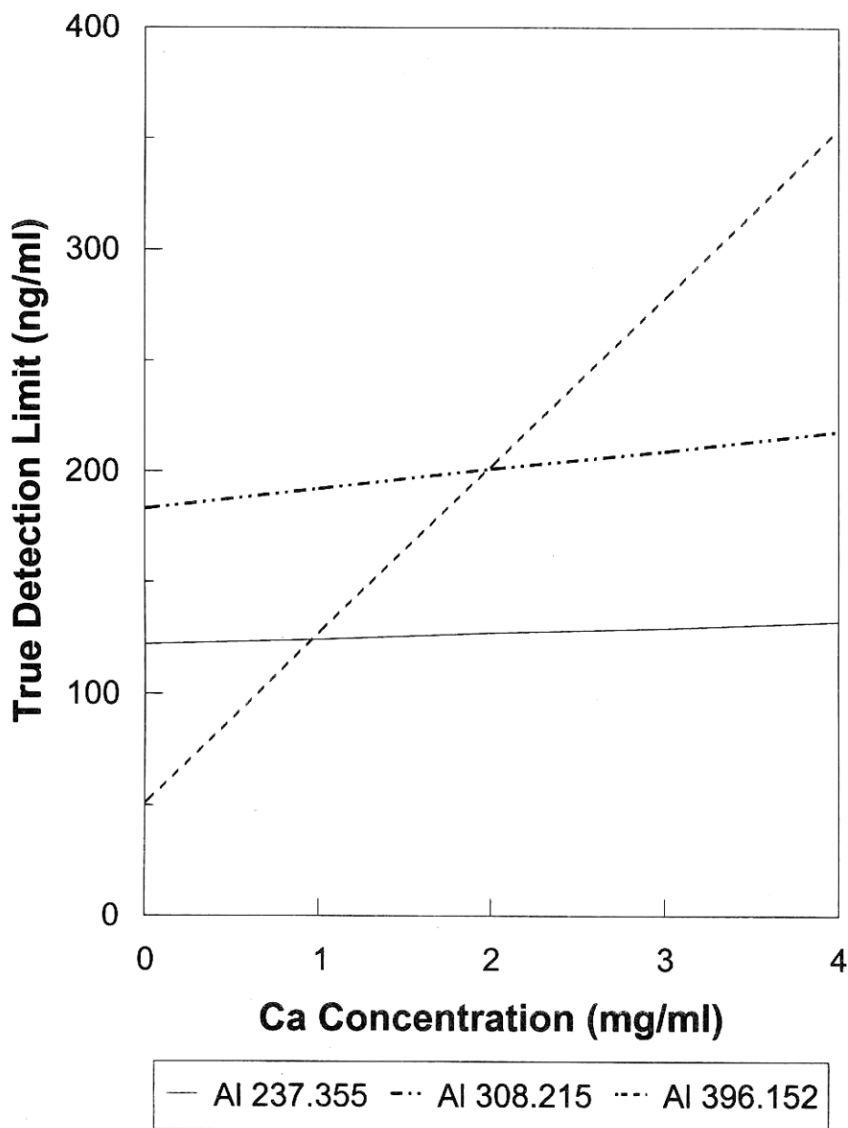


Fig. 4 Plots of true detection limits of three Al prominent lines (nm) as a function of Ca concentration while K, Mg and Na concentrations in the matrix are kept constant at 4mg/ml each.

tion, Al 308.215 nm line becomes more suitable and above 1 mg/ml concentration, Al 237.355 nm line should be chosen for analysis.

In actual practice, samples contain matrix elements in different amounts and the situation is much more complex for analyte line selection. A sample was considered containing K, Mg and Na as

matrix components (4 mg/ml each) and true detection limits for Al lines are plotted as a function of Ca concentration in Fig. 4. The complexity in the selection of best analysis lines is quite evident. Below about 1 mg/ml of Ca concentration, Al 396.152 nm line should be used for analysis while Al 237.355 nm line is more suitable for higher Ca concentration in the sample.

Table-4 :Analyte concentrations determined in synthetic samples; C_{as} : actual concentration; C_0 : concentrations in pure solvent; C_m : concentration in multi-component matrix (Ca, K, Mg and Na 2 mg/ml of each). All concentrations are in $\mu\text{g/ml}$ units.

Analyte	C_{as}	C_0	C_m
Al	1	1.008 (3.56)	0.859 (2.60)
As	1	1.023 (2.80)	0.913 (5.75)
B	2	2.031 (0.88)	1.849 (0.53)
Ba	1	1.018 (0.75)	0.875 (0.59)
Be	0.1	0.099 (0.68)	0.091 (1.16)
Cd	0.1	0.101 (1.75)	0.084 (3.01)
Co	1	0.986 (0.94)	0.809 (1.57)
Cr	0.5	0.500 (0.68)	0.435 (0.81)
Cu	0.5	0.489 (0.97)	0.426 (0.84)
Fe	1	0.993 (0.41)	0.841 (0.53)
Mn	1	1.027 (0.67)	0.827 (0.59)
Ni	0.5	0.508 (1.66)	0.408 (1.42)
Pb	0.5	0.503 (3.71)	0.400 (4.65)
V	1	0.995 (0.65)	0.889 (0.94)
Zn	1	1.038 (0.90)	0.853 (0.70)

Recoveries

Fifteen trace elements were determined in two synthetic samples, one prepared in pure solvent (doubly deionised water) and the other containing Ca, K, Mg and Na (2 mg/ml of each), using the best analysis lines marked in bold face in Table-3. Two-point calibration was assumed to be sufficient for the range of concentrations considered. Doubly deionised water was used as blank and a high standard, covering the range of analyte concentrations in the samples (Table-4), was prepared with aliquots from 1000 mg/l stock solutions in doubly deionised water. The concentrations determined in the samples with off-peak background correction, are shown in Table-4.

The precision and accuracy of the analytical results are related to both the sample preparation step and the analytical performance of the ICP spectrometer. The precision is given in terms of %RSD (in parenthesis) as derived from nine determinations. The recoveries of analytes in the sample with pure solvent as matrix, range from 98% to 104%, while in the sample containing multi-component matrix, recoveries lie in the range of 80% to 93%. Tikkanen *et al.* [13] studied the effect of sodium on 13 trace elements in waste-water by ICP-AES and obtained recoveries from 84% to 116% in a sample containing 10 mg/ml sodium which is contrary to the behaviour of consistent suppression observed in the present work. The low recoveries in the multi-component matrix cannot be explained on the basis of spectral interference. There is a clear indication of non-

spectroscopic matrix interference, which has a depressing effect on analyte intensities [14]. This could arise due to changes in the excitation conditions of the plasma as a result of the presence of high concentrations of concomitants.

Experimental

Apparatus and Operating Conditions

Measurements were performed with an ARL system (model 3410), comprising a 1 m Czerny-Turner monochromator and a 27.12 MHz RF generator. The description of the instrument and the operating conditions are given in Table-5. Compromise operating conditions were obtained by adjusting torch height (9 mm above the load coil) for maximum signal to background ratio (SBR) of the Mn II 257.61 nm line.

Test Solutions

Stock solutions (1 mg/ml) of Johnson Matthey GmbH were used to prepare single element solutions of analytes Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, V, Zn (1 $\mu\text{g/ml}$); As, Hg, Pb (5 $\mu\text{g/ml}$); B (2 $\mu\text{g/ml}$); and Ba, Be (0.5 $\mu\text{g/ml}$) in doubly de-ionized water. The concentrations of analytes for respective solutions were chosen while keeping in mind the permissible limits in environmental samples and also the sensitivities of analyte lines. Solutions of calcium, magnesium, sodium and potassium (2 mg/ml each) were prepared from Specpure $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaNO_3 and KNO_3 (Merck) by dissolution in doubly de-ionized water with 1% nitric acid (GR grade).

Table-5: Apparatus and operating conditions

Spectrometer	1 m, Czerny-Turner, vacuum
Grating	2400 grooves/mm, holographic
bandwidth	13 pm, 1 st order
	7 pm, 2 nd order
slit width	20 μm
PMT	R955 Hamamatsu
RF generator	Crystal controlled solid state exciter, class AB2 amplifier, 27.12 MHz
forward power	650 W
reflected power	1 W
Torch	3-tube minitorch (ARL)
observation height	9 mm above the load coil
Nebulizer	Meinhard concentric glass
spray chamber	conical glass 45 cm ³ volume - impact sphere
Pump	Peristaltic, Ismatic Mini-S-840
sample uptake	2.5 ml/min
outer argon flow	7.5 l/min
intermediate argon flow	0.8 l/min
carrier argon flow	0.72 l/min

Recoveries of analytes were determined using synthetic samples; one containing analytes in pure solvent (doubly de-ionized water), and the other containing analytes and 2 mg/ml each of calcium, magnesium, sodium and potassium.

Conclusions

Trace element analysis in environmental and geological samples containing large quantities of elements like Ca, K, Mg and Na, requires careful analyte line selection. The criterion of "true detection limits", proposed by Boumans and Vrakking [4,5] was used to calculate the Q -values, and conventional and true detection limits of prominent lines of 17 trace elements in the presence of Ca, K, Mg and Na as matrix elements. The Q -values listed in Table-2, suggest that spectral interference in the multi-component matrix is mainly determined by Ca and Mg. The present Q -values were found to be lower than the values determined by Daskalova and Boevski [12]. The detection limits in pure solvent, measured using the mini-torch ICP in the present work, agree favourably with those given by Winge *et al.* [7], but are considerably better than the values of Ref. [12]. Analyte lines having the lowest true detection limits were considered to be most suitable for trace element analysis in samples containing large quantities of Ca, K, Mg and Na. However, it has been shown that the line selection in a multi-component matrix with different relative concentrations of concomitants is much more complex than in a single element matrix. Even in the absence of direct line overlaps, net background intensities are affected by each concomitant in a different manner, thus affecting the SBRs and the detection limits. Therefore, for line selection, prior knowledge of the composition of the multi-component matrix is indispensable. Trace element analysis was carried out in a synthetic sample containing 2 mg/ml of calcium, magnesium, sodium and potassium each. Low recoveries indicate the presence of non-spectroscopic matrix effect, presumably caused by changes in the plasma excitation conditions.

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