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Inductively Coupled Plasma Atomic Emission Spectrometry – Accuracy of Analytical Results and Detection Limits in the Determination of Trace Elements in Soils and Sediments

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Abstract

A radial viewing 40.68 MHz ICP equipped with a 1 m Czerny-Turner monochromator (practical bandwidth 5 pm in the 2-nd order from 160 to 320 nm) was used for the determination of As, Mn, Cu, Pb, Zn, Cr and Ba in soils and sediments. The quantification of spectral interferences in the presence of Al, Ca, Mg, Fe and Ti as matrix constituents was made by the Q-concept, as was proposed by Boumans and Vrakking. New spectral data with the above mentioned equipment were obtained.

The *aqua regia* extraction procedure (ISO 11466) is widely used for most environmentally important heavy metals. In the present paper it was shown that the certified reference materials IAEA/Soil 7 and Lake Sediment IAEA/ SL-1 can be used for the experimental demonstration of the accuracy of analytical results obtained with the *aqua regia* dissolution procedure only for As, Mn, Cu and Pb. The elements Zn, Cr and Ba were silicate-bound species.

Keywords: ICP-AES, spectral interferences, certified reference materials, soils, sediments

Introduction

A number of instrumental approaches has been developed to solve environmental analysis problems: flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry (ICP-MS), X-ray and total reflection X-ray fluorescence techniques (TXRF), atomic fluorescence spectrometry (AFS), microwave-induced plasma source MIP-AES and MIP-MS, laser induced breakdown spectroscopy (LIBS), laser excited atomic fluorescence (LEAFS) and glow discharge mass spectrometry (GD-MS) [1].

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The determination of trace metals in the environmental samples such as soils and sediments is currently performed in order to designate the level of pollution as the number of ecological and health problems associated with environmental contamination continues to rise. Modern environmental science maintains a great interest in techniques for the multi-element analysis of different materials: natural and waste waters, soils, sediments and air particulates [2]. Inductively coupled plasma atomic emission spectrometry (ICP–AES) is the preferred technique among the modern analytical methods for determination of trace elements [2, 3].

The demands on analytical trace element determination are continually increasing. Environmental scientists require analytical results with high precision and accuracy for a large number of analytes. Systematical errors in ICP-AES may result from different steps in the analytical procedure or from spectral interferences [3].The most difficult samples from the point of view of spectral interferences and selection of an appropriate digestion procedure are the soils and the sediments. These materials normally contain Al, Ca, Mg, Fe and Ti as matrix components, which can give rise to strong line overlap interferences in the determination of trace elements. In our previous papers the quantitative spectral data for spectral interferences in the presence of the above mentioned complex matrix were published as follows:

(i) Determination of Ba, Be, Cd, Cr, Cu, Hg, Mn, P, Pb, Sb, Se, Sn, Tl, U and Zn using 27.12 MHz ICP and spectrometer with practical bandwidth 15.6 pm [4];

(ii) Determination of As, Hg, Se, Tl, Sn and Bi at wavelengths below 200 nm and up to 320 nm using 40.68 MHz and spectrometer with practical bandwidth 5 pm [5].

It is well known that the magnitude of spectral interferences depends on the spectral resolution [6]. The prominent lines selected as the “best” analysis lines in the presence of a given matrix remain in force independent of the frequency of the ICP, spectral bandwidth of spectrometers and the operating conditions [7].

ICP-AES analyses of solid environmental materials require dissolution of the samples. The choice of an appropriate procedure is complicated by the following:

(i) The original sample should be diluted as little as possible so that the maximum number of trace elements can be determined;

(ii) Total dissolved solid concentrations (t.d.s.) higher than 1-2 % in the solution introduced into the ICP should be avoided [4].

The dissolution of environmental materials can be accomplished by a variety of techniques that fall into two major categories: acid digestion and fusion [2, 8-11]. The acid digestion procedures have definite advantages over the fusion methods because excess acids can be easily removed from the samples by evaporation [3].

It is always an advantage to have standard methods for the decomposition of soil samples and sediments. Two standard methods were available:

(i) Extraction of trace elements soluble in *aqua regia* in accordance with ISO 11466 [12];

(ii) Determination of total trace element content by digestion with hydrofluoric and perchloric acids in accordance with ISO 14869-1[13].

The *aqua regia* extraction procedure is widely used for most environmentally important heavy metals. The efficiency of extraction with *aqua regia* differs from element to element. The hard grinding of a soil, from < 2 mm to < 63 μm, introduces relevant changes of extractability of the heavy metals. The direction and magnitude of the change depend on the metal and on the extracting solutions [14]. Therefore, the solubility of different elements cannot be predicted in general terms. Only detailed experimental data can reveal the situation for each element and sample type separately.

The use of reference materials is an essential requirement for quality control of measurement in environmental chemistry [15]. For this purpose an appropriate digestion procedure, ensuring the total dissolution of the trace elements in different type of soils and sediments can be used (ISO 14869-1).

The purposes of the present paper were to obtain:

(i) New data for Al. Ca, Mg, Fe and Ti as interferents separately by radial- viewing 40.68 MHz ICP equipped with a spectrometer with spectral bandwidth (BW) 5 pm around selected “best” analysis lines of Mn, Pb, Zn, Cr, Cu and Ba. The “best” prominent lines were selected in our previous paper by radial-viewing 27.12 MHz ICP and spectrometer with spectral bandwidth 15.6 pm [4];

(ii) Comparative data for the magnitude of spectral interferences using 27.12 MHz ICP with radial-viewing and spectrometer with spectral bandwidth 15.6 pm [4];

(iii) Quantitative data for the content of As, Mn, Pb, Zn, Cr, Cu and Ba in the certified reference materials: IAEA/Soil 7 and IAEA/Lake sediment SL1 and comparison with the corresponding certified values by using two digestion procedures: ISO 11466 (Extraction of trace elements soluble in *aqua regia*) [12] and ISO 14869-1 (Determination of total trace element contents: digestion with hydrofluoric and perchloric acids) [13];

(iv) Detection limits depending on the concentration of matrix elements in the final solutions using both digestion procedures. The detection limits were obtained using the "true detection limit "criterion. Comparative detection limits were obtained by two ICP systems.

As a result, an experimental demonstration of the possibility of ICP–AES and Q concept as a basic methodology for the determination of analytes in two certified reference materials was made. It was noted that the digestion procedure can be selected according to both the solubility of analytes and analytical task.

2. Experimental

2.1. Instrumentation

The experiments were performed with the Jobin Yvon (France) High Resolution ICP-AES equipment JY ULTIMA 2. The instrument was equipped with a 1 m Czerny-Turner monochromator (practical bandwidth 5 pm in the 2nd order from 160 to 320 nm, 10 pm in the 1st order from 320 to 800 nm), a 40.68 MHz radial viewing ICP and vacuum ultraviolet region (a nitrogen generator LabCraft, 220 V, 50/60 MHz, nitrogen flow 3 L min^{-1}), ICP generator power =1.3 kW, plasma gas flow rate = 12 L min^{-1}, sample uptake rate = 0.8 mL min^{-1}. Comparative data of $Q_{WJ}(\lambda_a)$, $Q_{IJ}(\lambda_a)$ values, and detection limits in pure solvent C_L were obtained with JY 38 (27.12 MHz ICP, 1 m Czerny-Turner monochromator with practical bandwidth 15.6 pm) and approximately the same operating conditions [4]. The System JY 38 was without vacuum ultraviolet region.

2.2. Reagents and test solutions

Reagents of highest purity grade (Merck) were used: 30 % HCl, 65 % HNO_3, 40 % HF, 70 % $HClO_4$, and tri-distilled water from a quartz apparatus.

Stock solutions of the analytes (1 mg mL^{-1}) were prepared using Merck Titrisols. The stock solutions of the matrix components (10 mg mL^{-1}) were prepared by dissolving the corresponding high purity chlorides in hydrochloric acid. Q-values were measured by using the test solutions with concentration 10 μg mL^{-1} of each of the analytes. The procedure of measurements was described in details in Ref. [5]. Plastic or PTFE ware was used throughout.

2.3. Certified reference materials:

IAEA / Soil 7 - the material is prepared from fraction which passed through a 70 μm sieve;

IAEA/ Lake Sediment SL -1 - the material is prepared from fraction which passed through a 100 μm sieve.

2.4. Dissolution procedures

2.4.1. Dissolution procedure No 1 (ISO 11466):

Extraction of trace elements soluble in *aqua regia* was used as a decomposition method in accordance with ISO 11466.

1g sample was weighed accurately in a reaction vessel; 0.5 mL of tri-distilled water was added to obtain slurry, followed by 9 mL of HCL (12 mol. L^{-1}) and 3 mL nitric acid (15.8 mol. L^{-1}). Then 10 mL of 0.5 mol. L^{-1} nitric acid was added to the reaction vessel which was connected to the reflux condenser. The apparatus was placed on the top of the reaction vessel. The samples were allowed to stay for 16 h at room temperature for slow oxidation of the organic matter and reduction of the gases produced during the subsequent heating cycle. They were boiled under reflux for 2 h and allowed to cool slowly to room temperature. The content of the reaction vessel was transferred quantitatively to a 50 mL graduated flask and filled up to the mark with nitric acid (0.5 mol. L^{-1}). After the undissolved material has settled, the supernatant solution was subjected to analysis by ICP-AES. A blank sample containing the acids used for digestion was prepared in the same way.

2.4.2. Dissolution procedure No 2 (ISO 14869-1):

0.5 g of the material was transferred into a 100 ml PTFE beaker. 5 mL of 65 % HNO_3 were added. The beaker was heated on a water bath. Evaporate to dryness, the reaction vessel was cooled. 9 mL of 40 % HF and 1 mL of 70 % $HClO_4$ were added and the beaker was heated on a sand bath almost to dryness. This procedure was repeated three times. The solution was evaporated at 200 ^{o}C almost to dryness on a sand bath. The residue obtained was then dissolved in 10 mL of 3 mol L^{-1} HCl. The resulting solution was transferred to a 25 mL graduated flask, brought up to the mark with 3 mol L^{-1} HCl and was subjected to analysis by ICP-AES. The silicate matrix was separated as insoluble residue from the soluble elements.

3. Results and discussion

3.1. Spectral interferences

Spectral data for Al, Ca, Mg, Fe and Ti as interferents around the prominent lines of the investigated elements (Ba, Cr, Cu, Zn, Cd, Mn and Pb) were obtained using radial viewing 40.68 MHz ICP. The information for the equipment was given in Section 2.1. The quantitative data bases of $Q_{WJ}(\Delta\lambda_a)$-values for wing background interference and $Q_{IJ}(\lambda a)$-values for line interference were obtained in accordance with Boumans and Vrakking [16,17].

3.2. Selected analysis lines

The most prominent lines in pure solvent [18] cannot be considered as the most prominent lines in the presence of complex soil or sediment matrices. Optimum line selection for trace analysis of multi-component environmental materials without information regarding the concentration of the matrix constituent (Al, Ca, Fe, Mg and Ti) requires the choice of prominent lines free or negligibly influenced by line interference [4, 5]. Table 1 lists the selected analysis lines in the presence of a complex environmental matrix, the corresponding $Q_{WJ}(\lambda_a)$, $Q_{IJ}(\lambda_a)$ values in the presence of matrix constituents and detection limits in pure solvent C_L (columns 1. 2. 3) obtained in the present paper by JY ULTIMA 2 (columns 1, 2, 3). The comparative data were taken from Ref. [4] (columns 5, 6, 7).

Table 1. Values of $Q_{WJ}(\lambda_a)$, $Q_{IJ}(\lambda_a)$ for the selected analysis lines of analytes and the detection limits in pure solvent obtained by the two ICP systems

Selected analysis lines, nm	Q_{WJ} $(\Delta\lambda_a)$	Q_{IJ} (λ_a)	Interferent	**Selected analysis lines, nm**	Q_{WJ} $(\Delta\lambda_a)$	Q_{IJ} (λ_a)
JY ULTIMA 2 40.68 MHz ICP, BW=5 pm				**JY 38 27.12 MHz ICP, BW =15.6 pm [4]**		
AsI 189.042*	4.4×10^{-4}	0	**Al**	As I 200.334	5.0×10^{-3}	0
	0	0	**Ca**		1.0×10^{-2}	0
C_L= 3.0 ng ml^{-1}	0	0	**Fe**	C_L=260ng m1^{-1}	1.8×10^{-3}	0
	0	0	**Mg**		6.4×10^{-3}	0
	0	0	**Ti**		5.3×10^{-3}	0
MnII257.610	0	0	**Al**	MnII257.610	4.7×10^{-6}	0
	0	0	**Ca**		5.5×10^{-6}	0
C_L= 0.13 ng ml^{-1}	0	0	**Fe**	C_L= 1.2 ng ml^{-1}	1.1×10^{-5}	0
	0	0	**Mg**		9.5×10^{6}	0
	0	0	**Ti**		4.7×10^{-3}	0
Cu I 324.754	0	0	**Al**	Cu I 324.754	0	0
	0	0	**Ca**		0	0
C_L= 1.3 ng ml^{-1}	0	0	**Fe**	C_L= 7.4 ng ml^{-1}	0	0
	0	0	**Mg**		0	0
	0	0	**Ti**		4.1×10^{-5}	0
Pb II 220.353	2.8×10^{-4}	0	**Al**	Pb II 220.353	9.7×10^{-4}	4.0×10^{-4}
	4.0×10^{-5}	0	**Ca**		5.3×10^{-4}	0
C_L= 5.0 ng ml^{-1}	1.2×10^{-4}	0	**Fe**	C_L= 37 ng ml^{-1}	4.1×10^{-4}	0
	0	0	**Mg**		4.5×10^{-4}	0
	0	0	**Ti**		5.2×10^{-4}	5.5×10^{-5}
Zn I 202.548	0		**Al**	Zn I 202.548	0	0
	6.0×10^{-6}		**Ca**		8.3×10^{-5}	0
C_L= 0.35 ng ml^{-1}	0		**Fe**	C_L= 8.5 ng ml^{-1}	0	0
	1.7×10^{-4}		**Mg**		1.9×10^{-3}	0
	0		**Ti**		1.5×10^{-4}	4.2×10^{-4}

Table 1 (Continued)

Selected analysis lines, nm	QWJ (Δλa)	QIJ (λa)	Interferent	**Selected analysis lines, nm**	QWJ (Δλa)	QIJ (λa)
JY ULTIMA 2 **40.68 MHz ICP, BW=5 pm**				**JY 38** **27.12 MHz ICP, BW =15.6 pm [4]**		
Cr II 267.716	0	0	**Al**	Cr II 267.716	0	0
	0	0	**Ca**		1.2×10^{-5}	0
C_L= 0.7 ng ml^{-1}	7.5×10^{-6}	0	**Fe**	C_L= 5.7 ng ml^{-1}	6.7×10^{-5}	0
	0	0	**Mg**		3.7×10^{-5}	0
	0	0	**Ti**		1.2×10^{-5}	2.7×10^{-5}
Ba II 455.403	0	0	Al	Ba II 455.403	0	0
	0	0	Ca		9.0×10^{-6}	0
C_L= 0.12 ng ml^{-1}	0	0	Fe	C_L=0.65 ng ml^{-1}	0	0
	0	0	Mg		4.5×10^{-5}	0
	0	0	Ti		2.6×10^{-6}	0

The detection limits in pure solvent are listed under the wavelength of the selected analysis lines using both ICP systems. The detection limits in pure solvent were calculated by equation (1) which is written in terms of background equivalent concentration (BEC) and relative standard deviation of the background (RSDB = 1%] [4]:

$$C_L = 2\sqrt{2} \times 0.01 \times \text{RSDB} \times \text{BEC} \qquad (1)$$

Our investigations show the following:

(i) The different analysis lines were selected only for arsenic, because JY 38 was not prepared for the vacuum ultraviolet region. The detection limit in pure solvent by As I 189.042 nm (JY ULTIMA 2, column 1) was 86 times lower in comparison with the corresponding value by As I 200.334 nm (JY 38, column 5). For the selected analysis lines of Mn, Cu, Pb, Zn, Cr and Ba , the detection limits in pure solvent obtained by JY ULTIMA 2 are from 6 to 20 times lower in comparison with the detection limits from Ref [4] obtained by JY 38 equipment. The outcome can be attributed partly to difference between both ICP sources and the spectral bandwidths of the spectrometers. This result is in accordance with literature data [6].

(ii) The comparison between $Q_{WJ}(\lambda_a)$ and $Q_{IJ}(\lambda_a)$ shows that the Q–values strongly depend on the spectral resolution of the spectrometer. This is the reason why the $Q_{WJ}(\lambda_a)$ and $Q_{IJ}(\lambda_a)$ values obtained in the present paper (columns 2, 3) are significantly lower in comparison with the corresponding values derived in Ref. [4] (columns 6, 7). In some cases (Pb II 220.353nm, Zn I 202.548 nm, Cr II 267.716 nm) $Q_{IJ}(\lambda_a)$-values > 0 using JY38 ICP system, but for ULTIMA 2 equipment these $Q_{IJ}(\lambda_a)$-values are equal to zero.

(iii) Using JY ULTIMA 2 equipment all selected analysis lines were free of line interferences. In this case the background correction can be accomplished using simple off-peak background measurement, i.e. without using a matrix blank. Some of the selected analysis lines are influenced by wing background interferences [$\Sigma Q_{WJ}(\lambda a) > 0$].

3.3. Experimental demonstration of the Q-concept in the analysis of reference materials

Two digestion procedures were used: dissolution procedure No 1 (ISO 11466) described in section 2.4.1; dissolution procedure No2 (ISO 14869-1) described in section 2.4.2. The resulting solutions were introduced into the ICP for the determination of major and trace elements.

3.3.1. Determination of major elements

The reliability of major component determination is mainly related to the accuracy and precision of the ICP-AES. For improving accuracy and precision of the results we have used two analysis lines, which are characterized with different sensitivities in ICP [18] in order to eliminate the differences in acidity and solid sample concentration between the samples and calibration solutions. In this case the analytical results cannot depend on the selected analysis lines. The selected analysis lines, free of inter-element interferences, are listed in Tables 2 and 3. The mean values were obtained in μg mL^{-1} for reference materials IAEA/Soil 7 (Table 2) and IAEA/ Lake Sediment SL 1 (Table 3), respectively, by using two dissolution procedures. The mean values were obtained using two analysis lines of each analyte (mean of three replicates). The sample solutions were diluted (dilution factor 5) in order to eliminate the multiplicative interferences [19]. The reference solutions were prepared on the basis of an acid blank.

Table 2. Determination of major elements in solution (μg mL^{-1}) in reference material IAEA/Soil 7.

Analysis lines (nm)	Concentrations, in μg mL^{-1} Dissolution procedure 1 Mean values	Concentrations, in μg mL^{-1} Dissolution procedure 2 Mean values
Al II 237. 324 Al II 394. 401	660	926
Ca I 422. 673 Ca II 315. 887	3160	3173
Mg II 279. 806 Mg II 285. 213	210	204
Fe II 238. 204 Fe II 239. 562	500	511
Ti II 334. 941 Ti II 336. 121	9.6	44.5

Table 3. Determination of major elements in solution (μg mL^{-1}) in reference material IAEA/ Lake Sediment SL 1

Analysis lines (nm)	Concentrations, in μg mL^{-1} Dissolution procedure 1 Mean value	Concentrations, in μg mL^{-1} Dissolution procedure 2 Mean value
Al II 237. 324 Al II 394. 401	1200	1820
Ca I 422. 673 Ca II 315. 887	40	42
Mg II 279. 806 Mg II 285. 213	89	113
Fe II 238. 204 Fe II 239. 562	1257	1350
Ti II 334. 941 Ti II 336. 121	14.7	80

The data from Tables 2, 3 and the Q-values, listed in Table 1 were used for calculation of the true detection limits ($C_{L,\ true}$) by equation 2 [4] as follows:

$$C_{L,\ true} = 2/5\Sigma_J\ Q_{IJ}(\lambda_a) \times C_{IJ} + C_{L,\ conv} \qquad (2)$$

Equation 3 presents the conventional detection limits ($C_{L,conv}$):

$$C_{L,\ conv} = 2\sqrt{2}\ 0.01\times RSDBL\times[BEC + \Sigma_J\ Q_{IJ}(\lambda_a)\times C_{IJ} + \Sigma_J\ Q_{WJ}(\Delta\lambda_a)\times C_{IJ}] \qquad (3)$$

where :

RSDBL is the relative standard deviation of blank samples; C_{IJ} – matrix concentration; J –Al. Ca, Mg, Fe, Ti. The background equivalent concentrations in pure solution are shown in Table 4.

Table 4. BEC (in μg mL^{-1}) in pure solvent

Analysis lines, nm	BEC, μg mL^{-1}
As I 189.042	0.10
Mn II 257.610	0.0047
Cu I 324.754	0.045
Pb II 220.353	0.18
Zn II 202.548	0.0124
Cr II 267.716	0.025
Ba II 455.403	0.0042

Table 5 lists the content of Al, Ca, Fe, Mg, and Ti with respect to the t.d.s. in the solution (in %) in certified reference material IAEA / Soil 7 using the two digestion procedures (Section 2.4.1 and Section 2.4.2). Table 6 lists the corresponding concentrations in certified reference material IAEA/ Like sediment SL -1. Table 5 and Table 6 (columns 3) show also the corresponding certified values.

Table 5. Content of matrix component Al, Ca, Mg, Fe and Ti (in %) in certified reference material IAEA / Soil 7, obtained by ICP-AES (columns 2 and 4). Column 3 lists the corresponding certified values

Element	Concentration, % Dissolution procedure No1	Concentration, % Certified values	Concentration, % Dissolution procedure No2
Al	3.30	4.70	4.72
Ca	16.4	16.336	16.23
Fe	2.5	2.57	2.56
Mg	1.05	1.13	1.02
Ti	0.048	0.30	0.22

From the results (Tables 5 and 6) the following conclusions may be drawn:

(i) The concentrations of Ca, Fe and Mg in the certified reference material IAEA / Soil 7 (Table 5) do not depend on the dissolution procedure. The total dissolution of these elements was achieved (columns 2 and 3 versus column 2). The concentration of Al and Ti is lower by using *aqua regia* extraction procedure in comparison with the dissolution procedure (HF + $HClO_4$) - column 2 versus column 5.

(ii) Magnesium in certified reference material IAEA/ Lake sediment SL -1 (Table 5) cannot be dissolved neither by procedure 1 nor by procedure 2 (columns 2 and 4 versus column 3). For this certified material the concentrations of Ca and Fe do not depend on the dissolution procedure (column 2 versus column 4). The concentrations of Ca and Fe were equal in the solutions from both procedures (columns 2 and 4 versus column 3).

(iii) The concentration of Ti in the sample solutions using procedure 1 is significantly lower in comparison with that using procedure 2.

Table 6. Content of matrix components Al, Ca, Mg, Fe and Ti (in %) in certified reference material IAEA/ Like sediment SL -1, obtained by ICP-AES (columns 2 and 4). Column 3 lists the corresponding certified values

Element	Concentration, % Dissolution procedure No1	Concentration, % Certified values	Concentration, % Dissolution procedure No2
Al	6.0	8.9	9.10
Ca	0.20	0.25	0.22
Fe	6.30	6.74	6.75
Mg	0.45	2.90	0.59
Ti	0.074	0.517	0.40

In general the final solutions contain high matrix concentrations (Tables 2, 3). Hence, the interference level cannot be eliminated and the selected analysis lines have to be used as the “best” analysis lines (Table 1).

3.3.2. Determination of trace elements

The certified reference materials IAEA / Soil 7; IAEA/ Lake sediment SL1 were used for experimental demonstration of the accuracy of the analytical results. The materials were dissolved by two digestion procedures (Sections 2.4.1, 2.4.2). The results obtained for As, Mn, Cu, Pb, Zn, Cr and Ba by the ICP-AES method are presented in Tables 7 and 8. The confidence interval of the mean values for three replicates for statistical confidence P = 95% is also shown. Using Student’s criterion, no statistical differences between the experimental values for As, Mn, Cu and Pb and the certified values of the standard reference materials IAEA / Soil 7 and IAEA/ Lake sediment SL-1 were registered, independent of the dissolution procedures by extraction of trace elements soluble in *aqua regia* (Tables 7 and 8, column 2) or dissolution with hydrofluoric acid and perchloric acids (Tables 7 and 8, column 5). The data for these elements in Tables 7 and 8 are printed in bold.

Table 7. Content of As, Mn, Cu, Pb, Zn, Cr and Ba (in μg g^{-1}) in certified reference material IAEA / Soil 7 using two decomposition procedures

Element	Concentration, μg g^{-1} Dissolution procedure No1	RSD	Concentration, μg g^{-1} Certified values	Concentration, μg g^{-1} Dissolution procedure No2	RSD
As	**13.1 ± 0.5**	**3.8**	**13.4 (12.5 -14.2)**	**13.1 ± 0.5**	3.9
Mn	**637.8 ± 13**	**2.0**	**639 (604 -650)**	**637.8 ± 13**	**1.0**
Cu	**11.0 ± 0.4**	**3.6**	**11 (9 – 13)**	**11.0 ± 0.4**	3.8
Pb	**59.8 ± 1.2**	**2.0**	**60 (55 -71)**	**59.8 ± 1.2**	**2.0**
Zn	75.0. ± 1.4	2.0	104 (101 -113)	102 ± 1.4	1.4
Cr	40.9 ± 1.2	2.9	60 (49 – 74)	58.0 ± 1.2	2.0
Ba	59.2 ± 1.2	2.0	159 (131 -196)*	162 ± 5.0	3.0

*Non-certified information value

Table 8. Content of As, Mn, Cu, Pb, Zn, Cr and Ba in certified reference material IAEA/ Lake sediment SL-1

Element	Concentration, $\mu g\ g^{-1}$ Dissolution procedure No1	RSD	Concentration, $\mu g\ g^{-1}$ Certified values	Concentration, $\mu g\ g^{-1}$ Dissolution procedure No2	RSD
As	**25.6 ± 1.0**	**3.9**	**27.5 (24.6 -30.4)**	**25.6 ± 1.0**	3.9
Mn	**3473 ± 38**	**1.0**	**3460 (3300 – 3620)**	**3473± 32**	**1.0**
Cu*	**32.0 ± 1.2**	**3.8**	**30 (25 – 35)**	**32.0 ± 1.2**	**3.8**
Pb*	**37.6 ± 1.4**	**3.7**	**37.7 (30.3 – 45.1)**	**37.6 ± 1.4**	3.7
Zn	183.0 ± 2.4	1.3	223 (213 -233)	225 ± 2.4	1.0
Cr*	70.8 ± 1.4	2.0	104 (95 -113)	102 ± 1.6	1.6
Ba	388.2± 9.0	2.3	639 (586 -692)	635 ± 12.0	2.0

* Non-certified information value

The *aqua regia* procedure cannot quantitatively extract Zn, Cr and Ba. The accurate results were obtained using the second digestion procedure for both reference materials IAEA / Soil 7 and IAEA/ Lake sediment SL -1. The precision is expressed in terms of relative standard deviation (RSD) (Tables 7 and 8, columns 3 and 6).

3.3.3. Detection limits

Tables 2 and 3 list the concentrations of major elements in the final solutions (in $\mu g\ mL^{-1}$) using the two digestion procedures and certified reference materials. These data and Q-values (Table 1) were needed for estimation of the true detection limits by using Eqs. 1 and 2. In this case all selected analysis lines are free of line interferences (Table 3), $Q_{IJ}(\lambda_a) = 0$, $Q_{WJ}(\Delta\lambda_a) > 0$. Hence, $C_{L,\ true} = C_{L,\ conv}$, i.e. the detection limits were estimated by Eq. 3. In Table 9 and Table 10 the conventional detection limits are listed.

Table 9. Detection limits in the determination of As, Mn, Cu, Pb, Zn, Cr and Ba in certified reference material IAEA / Soil 7 obtained by JY ULTIMA 2 (in brackets for JY 38), using the two digestion procedures.

Element	Detection limits (in $\mu g\ g^{-1}$)	
	Dissolution procedure No1	Dissolution procedure No2
As	0.52 (56.5)	0.72 (61.8)
Mn	0.0065 (0.096)	0.0065 (0.1)
Cu	0.0065 (0.24)	0.0065 (0.24)
Pb	0.80 (11.2)	0.9 (14.2)
Zn	0.095 (1.45)	0.095 (1.76)
Cr	0.035 (0.40)	0035 (0.42)
Ba	0.006 (0.085)	0.006 (0.086)

The detection limits obtained by JY ULTIMA 2 depend insignificantly on the matrix concentrations in the final sample solution because $Q_{IJ}(\lambda_a) = 0$ and $C_{L,\,true} = C_{L,\,conv}$ (Eq. 2).

Table 10. Detection limits obtained by JY ULTIMA 2 (in brackets for JY 38) in the determination of As, Mn, Cu, Pb, Zn, Cr and Ba in certified reference material IAEA/ Lake sediment SL-1

Element	Detection limits (in μg g^{-1})	
	Dissolution procedure No1	Dissolution procedure No2
As	0.8 (17.6)	1.1 (22.4)
Mn	0.0065 (0.086)	0.0065 (0.092)
Cu	0.0065 (0.24)	0.0065 (0.25)
Pb	0.95 (17.4)	1.2 (21)
Zn	0.04 (0.8)	0.045 (1.5)
Cr	0.035 (0.42)	0.035 (0.47)
Ba	0.006 (0.040)	0.006 (0 0.40)

The detection limits obtained by JY ULTIMA 2 were over one order of magnitude lower because of the weaker spectral interferences levels around the analysis lines (Table 1, columns 2 and 3 versus columns 6 and 7).

Conclusion

In this work the Q concept was used for quantification of the spectral interferences in the presence of Al, Ca, Fe, Mg and Ti as interferents in a complex environmental matrix. Q-values, obtained using a radial viewing 40.68 MHz ICP and monochromator with high spectral resolution (practical bandwidth 5 pm in the 2nd order from 160 to 320 nm) were significantly lower in comparison with the corresponding values derived using radial viewing 27.12 MHz ICP and monochromator with practical bandwidth 15.6 pm (Table 1, columns 2, 3 versus columns 6, 7). As a result, the detection limits derived by JY ULTIMA 2 were significantly lower (Tables 9 and 10). New quantitative data for spectral interferences, obtained in the present paper are listed in Table 1, columns 2, 3.

The experimental demonstration of ICP–AES and Q-concept as appropriate methodology was presented. Our results show that in the determination of As, Mn, Cu and Pb in certified reference materials (IAEA/Soil 7 and Lake Sediment IAEA/ SL-1) using *aqua regia* dissolution procedure (ISO 11466), the accuracy of the analytical results can be ensured (Tables 7, 8). Using Q-values (Table 1, columns 2, 3), the concentration of matrix elements in the final solutions (Tables 2 and 3) and background equivalent concentrations (Table 4) the true detection limits (Equation 3) were calculated (Tables 9, 10). The concentration of matrix elements was different (Tables 2, 3) but the detection limits were approximately the same, on account of an appropriate line selection and utilization of equipment with high spectral resolution.

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