

Research Article

Possibilities of High Resolution Inductively Coupled Plasma Optical Emission Spectrometry in the Determination of Trace Elements in Environmental Materials

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This paper presents new quantitative data for the spectral interferences obtained by high resolution 40.68 MHz radial viewing inductively coupled plasma optical emission spectrometry (HR-ICP-OES) in the determination of Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba in environmental materials in the presence of a complex matrix, containing Al, Ca, Fe, Mg, and Ti. The Q-concept for quantification of spectral interferences was used. The optimum line selection for trace analysis of a variety of multicomponent matrices requires the choice of prominent lines, which are free or negligibly influenced by line interference problems. The versatility of Q-concept as basic methodology was experimentally demonstrated in the determination of trace of elements in soil and drinking water. The detection limits are lower in comparison with corresponding threshold concentration levels for soil and drinking water in accordance with environmental regulations. This paper shows the possibilities of present day ICP-OES equipment in the direct determination of trace elements (without preconcentration of impurities) in environmental samples.

1. Introduction

Industrial activities, urban waste treatment, and vehicle exhaust are some of the sources causing large quantities of toxic elements as contamination in atmosphere, water, and soil. In the case of chemical toxicity, elemental analysis of environmental materials such as soil, sediments, natural and waste water, and air particulates can play an important role in the rapid detection and identification of the key element. The health risk of an element is determined by the stability and environmental mobility of the particular species of the element. Toxic effects of large number of elements are well known [1–10].

Due to the adverse health effects of different elements, detection of trace amount of these elements in any environmental sample related to human being is very important. Determination of these elements requires sufficiently sensitive techniques for detection. In the literature, there are many techniques including flame atomic absorption spectrometry (FAAS) [8, 11], electrothermal atomic absorption

spectrometry (ETAAS) [12, 13] inductively coupled plasma optical emission (ICP-OES) [14–21], mass spectrometry (ICP-MS) [22–24], X-ray and total reflection X-ray fluorescence techniques (TXRF), atomic fluorescence spectrometry (AFS), microwave-induced plasma source (MIP-OES and MIP-MS), laser-induced breakdown spectroscopy (LIBS), laser-excited atomic fluorescence spectrometry (LEAFS), and glow discharge mass spectrometry (GD-MS) [25, 26].

Modern environmental science maintains an interest in methods, which ensure the following important characteristics: (a) multielement analysis of a wide variety of environmental sample types; (b) it must be able to detect large number of elements at threshold concentration levels for a different type of samples. Among the modern instrumental methods for determination of trace elements, inductively coupled plasma optical emission spectrometry (ICP-OES) is very powerful [14–21].

At present, accurate ICP-OES analysis of environmental materials, other than natural or waste water, requires dissolution of the samples. The method is influenced by the

blank contribution from all steps during sampling and sample preparation. The blank contribution might be considerable and must be controlled when working at trace concentration [33, 34].

Considerable systematic errors in ICP-OES may arise from different matrix effects (nonspectral and spectral interferences) [35–37]. Nonspectral matrix effects change the sensitivity of the net analyte signals, that is, influence on the slope of the calibration curve [35]. An optimization of the analytical results in inductively coupled plasma with respect to the elimination of nonspectral matrix effects can be achieved by modifying the different operating parameters. Summarizing the investigation on nonspectral matrix effects in the presence of different matrices, the following conclusions can be drawn [16, 17, 38–43]:

- (i) the elimination of nonspectral matrix effects cannot be achieved by the optimization of the operating conditions in most of the cases. The robust plasma conditions are more appropriate when compared to the nonrobust plasma conditions [38–43];
- (ii) by precise matching of the acid and matrix contents in both references and sample solutions, the nonspectral matrix effects can be totally removed, and an accuracy of analytical results can be ensured [16, 18, 44].

Spectral interferences may drastically deteriorate the analytical characteristics of the ICP-OES. The most difficult samples, from this point of view, are the soil and different sediments. These materials normally contain high concentrations of Al, Ca, and Mg, which cause significant background enhancement in many regions of the spectrum, high concentrations of Fe, and to a lesser extent Ti, which can give rise to serious line overlap interferences in the determination of trace elements [14].

The high resolution spectrometers can reduce the number of spectral interferences. However, once the band pass becomes equal to or smaller than the physical line width of the ICP emission lines, no further reduction in interferences will be gained by using higher resolution [45, 46]. Therefore, the use of the high resolution spectrometers does not preclude the occurrence of spectral interferences. In this relation, two different steps can then be taken.

- (i) A line may be chosen which is relatively free of spectral interferences. However, this will involve a tradeoff between spectral interferences and sensitivity, if the most intense line suffers from interference.
- (ii) It may be possible to correct or compensate for the spectral interferences if the interferences can be identified and quantified. The latter approach is possible because of the stability of the ICP emission. However, the identification and quantification of all significant interferences may be a difficult task [46].

Boumans and Vrakking proposed the Q-concept for quantification of spectral interferences and “true detection limit” criterion for quantitative line selection and applied this concept to the determination of trace of rare earth elements in pure rare earth matrices [47, 48]. Background emission

intensity depends on the sample composition. Compared to a continuous background, an interfering line signal in the presence of a given matrix has to be considered as a contribution to the background that can be measured only with a much larger uncertainty. It was this insight that prompted the introduction of the concept of “true detection limits” ($C_{L,true}$) to be distinguished from the “conventional detection limit” ($C_{L,conv}$) and “common detection limit” (C_L) for pure solvent [49–51].

The optimum line selection in the presence of one-component matrices for trace analysis implies the choice of prominent lines with minimum value of the true detection limit [48]. The optimum line selection for the trace analysis of a variety of multicomponent environmental samples requires a choice of the prominent lines, which are free or negligibly influenced by line interference problems [16, 18].

The optimization procedure of experimental conditions in the determination of trace of elements in complex environmental matrix by using 40.68 MHz ICP and ICP-OES spectrometer HORIBA Jobin Yvon ULTIMA is presented in our previous paper. The general conclusions from investigations are that the lowest values for (1) detection limits in pure solvent; (2) line and wing background interferences; and (3) detection limits in the determination of trace of elements in different environmental samples are obtained under the optimal excitation conditions ($T_{exc} \approx 7200$ K) [16, 18]. The excitation temperature was measured by the Boltzmann plot method with ionic titanium lines [52].

The general purpose of the present paper is to show quantitative data for line and wing background spectral interferences in the determination of Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and, Ba in the presence of complex environmental matrix (containing Al, Ca, Mg, Fe, and Ti as interferents) by 40.68 MHz ICP and high resolution spectrometer at optimal excitation conditions ($T_{exc} \approx 7200$ K). The data are needed for analytical atomic spectrometry in the analysis of all types of environmental samples: soil, sediments, water (surface, ground, and drinking), and atmospheric particulate matter.

2. Materials and Methods

2.1. Instrumentation. The experiments were performed with radial viewing ICP-OES system HORIBA Jobin Yvon ULTIMA 2 (Jobin Yvon, Longjumeau, France) equipment. The characteristics of the equipment and operating conditions are specified in Table 1. The quantitative information about the type of spectral interferences was derived from the wavelength scans around the candidate (prominent) analysis lines in the presence of Al, Ca, Mg, Fe, and Ti as interferents.

The practical spectral bandwidth of the spectrometer was determined by measuring the full width at half maximum (FWHM) of Sm II line at 359.260 nm in the 1st order from 320 to 800 nm and of Pb II line at 220.353 nm in the 2nd order from 160 nm to 320 nm. These lines have a physical width of 1.9 pm and 1.4 pm, respectively, [53] and are therefore well suited for the measurement of the practical spectral bandwidth because the contribution of the physical width to

TABLE 1: Specification of ICP-OES spectrometer: HORIBA Jobin-Yvon ULTIMA 2 (France) and ICP operating conditions.

Monochromator	HORIBA Jobin-Yvon ULTIMA 2	
Mounting	Czerny-Turner, focal length 1 m	
Grating	Holographic, 2400 grooves mm ⁻¹	
Wavelength range	first and second order	
Entrance slit	0.015/0.02 mm	
Exit slit	0.02/0.08 mm	
Practical spectral bandwidth	5 pm in the 2nd order from 160 nm to 320 nm; and 10 pm in the 1st order from 320 to 800 nm	
Detectors	High dynamic detectors based on PMT's	
Radio frequency generator	Solid state RF 40.68 MHz	
Frequency power output	40.68 MHz 0.5–1.55 kW	
Nebulizer	Meinhard, concentric glass, type TR 50 Cl	
Spray chamber	JY Glass cyclonic spray chamber	
Plasma torch	Fully demountable torch	
Pump	Peristaltic, two channels, twelve-roller	
Operating conditions		
Incident power, (kW)	1.00	
Outer argon flow rate, (L min ⁻¹)	13	
Nebulizer, pressure, (bar)	3.2	
Carrier gas flow rate, (L min ⁻¹)	0.4	
Sheath gas flow rate, (L min ⁻¹)	0.2	
Sum = carrier gas + sheath gas flow rate, (L min ⁻¹)	0.6	
Liquid uptake rate, (mL min ⁻¹)	1.0	
Observation height, (mm)	10	
Excitation temperature $\approx T_{exc}$, (K)	7200	

the effective width is negligible for the present instrument [54]. In some cases, the practical spectral bandwidth is essentially larger than the resultant spectral slit (theoretical bandwidth, calculated from dispersion and slit width). This is due to aberrations [45, 48].

Here, we will note that the measurements were performed in the 2nd order of the spectrum (practical spectral bandwidth 5 pm) for the prominent lines of Zn, Cd, Sb, Mn, Pb, Sn, and Cr with wavelengths in spectral region 160–320 nm. The wavelengths of the prominent lines of Cu, U, and Ba lie in the spectral region 320–800 nm, and the measurements were made in the 1st order (practical spectral bandwidth 10 pm).

The quantitative data for the spectral interferences were obtained in the presence of 2 mg mL⁻¹ Al, Ca, Mg, Fe, and Ti as interferents, separately. Q values for line interference [$Q_I(\lambda_a)$] and Q values for wing background interference [$Q_w(\Delta\lambda_a)$] were obtained around selected prominent lines of Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba.

An example for the spectral scans over the spectral region around the prominent line of Zn, central wavelength: 213.856 nm (Zn II line), and interferents: Fe 213.858 nm and Ti 213.835 nm is shown in Figure 1.

The scans were used for establishing the type of the spectral interferences as follows.

The total background signal in the presence of a complex environmental matrix is

$$X_{BL} = X_B + X_{WJ}(\Delta\lambda_a) + X_{IJ}(\lambda_a), \quad (1)$$

where X_B is the solvent blank (due to the source and solvent); $X_{WJ}(\Delta\lambda_a)$ is the wing background level with respect to the solvent blank for the interferents ($J = \text{Al, Ca, Mg, Fe, and Ti}$); and $X_{IJ}(\lambda_a)$ is the net interfering signals with respect to the wing background level [$X_{WJ}(\Delta\lambda_a)$] of the interferents ($J = \text{Al, Ca, Mg, Fe, and Ti}$).

The following signals were measured: X_A , X_B , [$X_{WJ}(\Delta\lambda_a)$], and [$X_{IJ}(\lambda_a)$]. The measured signals were then reduced to sensitivities:

- (i) the sensitivity of the analysis line S_A , defined as the net line signal X_A per unit analyte concentration C_A ;
- (ii) the interferent sensitivities [$S_{WJ}(\Delta\lambda_a)$] and [$S_{IJ}(\lambda_a)$], defined as interferent signals [$X_{WJ}(\Delta\lambda_a)$] and [$X_{IJ}(\lambda_a)$], respectively, per unit interferent concentration [C_{IJ}].

Finally, the sensitivities were used for the calculation of the Q -values for wing background interference [$Q_{WJ}(\Delta\lambda_a)$] = [$S_{WJ}(\Delta\lambda_a)$]/[S_A], the Q -values for line

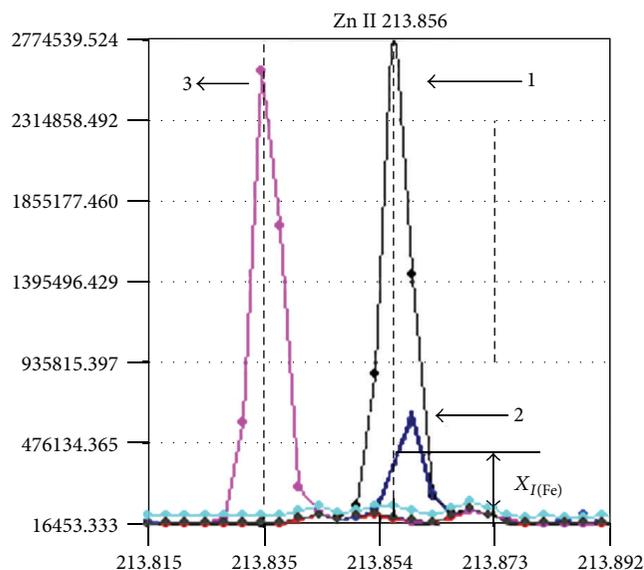


FIGURE 1: Spectral scans over the spectral region around the prominent line of Zn: central wavelength: 213.856 nm (Zn II line); interferents: Fe and Ti. (1) Central wavelength Zn II 213.856 nm, $1 \mu\text{g mL}^{-1}$ Zn in pure solvent; (2) interfering line: Fe 213.858 nm, concentration of Fe 2 mg mL^{-1} ; (3) interfering line: Ti 213.835 nm, concentration of Ti 2 mg mL^{-1} ; $[X_{I(\text{Fe})}(\lambda_a)]$ is the net interfering signals with respect to the wing background level $[X_{W_{\text{Fe}}}(\Delta\lambda_a)]$.

interference $[Q_{IJ}(\lambda_a) = S_{IJ}(\Delta\lambda_a)/S_A]$, and the corresponding background equivalent concentrations $[\text{BEC}_{WJ} = Q_{WJ}(\Delta\lambda_a) \times C_{IJ}]$ and $[\text{BEC}_{IJ}(\lambda_a) = Q_{IJ}(\lambda_a) \times C_{IJ}]$.

2.2. Reagents and Test Solutions. Reagents of highest purity grade were used: 30% HCl and 65% HNO₃, 30% HF, H₃BO₃ (Suprapur, Merck), and tri-distilled water from quartz apparatus. The stock solutions of the analytes Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba (1 mg mL^{-1}) were prepared by using Merck Titrisol. The stock solutions of the matrix components Al, Ca, Fe, Mg, and Ti (10 mg mL^{-1}) were prepared by dissolving the corresponding high purity chlorides with a purity of 99.9999% in hydrochloric acid. The possible presence of impurities causes an uncertainty when the matrix concentration of 2 mg mL^{-1} is used. The Q values were measured by using the following test solutions: $10 \mu\text{g mL}^{-1}$ for each of analytes and 2 mg mL^{-1} for each of interferents, separately. Plastic or PTFE ware was used throughout.

2.3. Certified Reference Materials. The International Atomic Energy Agency (Austria) IAEA/Soil 7—soil reference material, prepared from the fraction which passed through a $70 \mu\text{m}$ sieve; the National Water Research Institute (NWRI) fortified water for trace elements, TMDA-51.2; NWRI, prepared from Lake Ontario water, filtered, diluted, and preserved with 0.2% nitric acid were used.

2.4. Sampling. Soil samples were collected in accordance with ISO 10381-2, soil quality sampling [55]. The samples

were collected from a nonpolluted region which was found at a distance of about 8 km of the metallurgical factory for nonferrous metals in order to show the possibilities of the present ICP-OES method in the determination of low concentration of the pollutants in the presence of Al, Ca, Fe, Mg, and Ti as matrix constituents.

2.5. Digestion Procedures

2.5.1. Extraction of Trace Elements Soluble in Aqua Regia [27]. Extraction of trace elements soluble in *aqua regia* was used as a decomposition method in accordance with ISO 11466. A one g 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 insoluble material has been settled, the supernatant solution was subjected to analysis by ICP-OES. A blank sample containing the acids used for digestion was prepared in the same way. By this procedure, the silicate matrix was separated from the final sample solution.

2.5.2. Digestion Procedure with HCl-HNO₃-HF in a Microwave System [28]. The digestion was performed in a microwave digestion system (Milestone 1200, USA) at 230°C and at pressure of 70 bar. 0.5 g sample was weighed in a PTFE vessel. The digestion procedure in three steps was used: 1st—4 mL nitric acid (65%) and 1 mL hydrochloric acid (30%); 2nd—1 mL hydrofluoric acid (40%) for complete dissolution of the sample; 3rd—10 mL boric acid, saturated at 20°C for complexing insoluble fluorides. Afterwards, boric acid (in excess to HF) was added in order to bind the HF as a HBF₄ complex. HBF₄ solutions do not etch glassware used (volumetric flasks, etc.) as well as the conventional ICP sample introduction system (glass nebulizer, glass chamber, and silica ICP-torch). So a conventional ICP-OES sample introduction system was used for the analysis of such solutions. The duration of one digestion step, including cooling period, was 40 min. The final sample solution was 50 mL. The concentration of boron in the sample solution was $1400 \mu\text{g mL}^{-1}$ and silicon— $1870 \mu\text{g mL}^{-1}$.

3. Results and Discussion

3.1. Database of Q Values and Detection Limits in Pure Solvent Obtained at $T_{exc} \approx 7200 \text{ K}$. Table 2 lists the investigated prominent lines of Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba by 40.68 MHz and spectrometer with high resolution.

TABLE 2: Quantitative values for line interferences [$Q_{IJ}(\lambda_a)$] and wing background interference [$Q_{WJ}(\Delta\lambda_a)$] in the determination of trace of elements Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba. Interferents: Al, Ca, Fe, Mg, and Ti. The data listed under the wavelength of the prominent lines refer to background equivalent concentrations in pure solvent (BEC) and detection limits in pure solvent (C_L).

Analytes, wave lengths, λ nm	Interferents	$Q_{WJ}(\lambda_a)$	$Q_{IJ}(\lambda_a)$
Zn I 213.856 BEC = 0.05 $\mu\text{g mL}^{-1}$ $C_L = 1.4 \text{ ng mL}^{-1}$	Al	8.0×10^{-6}	0
	Ca	2.0×10^{-6}	0
	Fe	0	1.0×10^{-5}
	Mg	0	0
Zn II 202.548 BEC = 0.06 $\mu\text{g mL}^{-1}$ $C_L = 1.7 \text{ ng mL}^{-1}$	Ti	2.0×10^{-6}	0
	Al	2.0×10^{-5}	0
	Ca	1.0×10^{-6}	0
	Fe	1.0×10^{-5}	0
Cd II 226.502 BEC = 0.05 $\mu\text{g mL}^{-1}$ $C_L = 1.4 \text{ ng mL}^{-1}$	Mg	4.0×10^{-6}	0
	Ti	2.0×10^{-5}	0
	Al	0	0
	Ca	1.3×10^{-6}	0
Cd II 214.438 BEC = 0.06 $\mu\text{g mL}^{-1}$ $C_L = 1.7 \text{ ng mL}^{-1}$	Fe	2.0×10^{-5}	8.0×10^{-5}
	Mg	0	0
	Ti	8.0×10^{-5}	0
	Al	0	0
Sb I 206.838 BEC = 0.35 $\mu\text{g mL}^{-1}$ $C_L = 10.0 \text{ ng mL}^{-1}$	Ca	1.3×10^{-6}	0
	Fe	6.2×10^{-6}	2.0×10^{-5}
	Mg	0	0
	Ti	8.0×10^{-5}	0
Cu I 324.754 BEC = 0.045 $\mu\text{g mL}^{-1}$ $C_L = 1.3 \text{ ng mL}^{-1}$	Al	4.0×10^{-4}	0
	Ca	3.0×10^{-4}	0
	Fe	6.0×10^{-5}	0
	Mg	1.0×10^{-4}	0
Mn II 257.610 BEC = 0.0047 $\mu\text{g mL}^{-1}$ $C_L = 0.13 \text{ ng mL}^{-1}$	Ti	4.0×10^{-4}	1.0×10^{-4}
	Al	0	0
	Ca	0	0
	Fe	0	0
Pb II 220.353 BEC = 0.18 $\mu\text{g mL}^{-1}$ $C_L = 5.0 \text{ ng mL}^{-1}$	Mg	0	0
	Ti	0	0
	Al	2.8×10^{-4}	0
	Ca	1.0×10^{-5}	0

TABLE 2: Continued.

Analytes, wave lengths, λ nm	Interferents	$Q_{WJ}(\lambda_a)$	$Q_{IJ}(\lambda_a)$
Sn I 283.999 BEC = 0.30 $\mu\text{g mL}^{-1}$ $C_L = 9.0 \text{ ng mL}^{-1}$	Al	1.7×10^{-5}	0
	Ca	1.7×10^{-5}	0
	Fe	2.8×10^{-5}	0
	Mg	1.8×10^{-4}	0
Cr II 206.149 BEC = 0.14 $\mu\text{g mL}^{-1}$ $C_L = 4.0 \text{ ng mL}^{-1}$	Ti	3.0×10^{-5}	0
	Al	0	0
	Ca	5.2×10^{-5}	0
	Fe	3.0×10^{-5}	0
Cr II 267.716 BEC = 0.08 $\mu\text{g mL}^{-1}$ $C_L = 2.3 \text{ ng mL}^{-1}$	Mg	4.0×10^{-5}	0
	Ti	2.0×10^{-5}	3.0×10^{-5}
	Al	0	0
	Ca	0	0
U II 385.958 BEC = 0.05 $\mu\text{g mL}^{-1}$ $C_L = 1.4 \text{ ng mL}^{-1}$	Fe	7.5×10^{-6}	0
	Mg	0	0
	Ti	0	0
	Al	0	0
U II 367.007 BEC = 0.05 $\mu\text{g mL}^{-1}$ $C_L = 1.4 \text{ ng mL}^{-1}$	Ca	5.0×10^{-5}	0
	Fe	5.2×10^{-4}	6.2×10^{-4}
	Mg	7.0×10^{-5}	0
	Ti	5.5×10^{-5}	0
U II 263.553 BEC = 0.09 $\mu\text{g mL}^{-1}$ $C_L = 2.6 \text{ ng mL}^{-1}$	Al	5.0×10^{-5}	0
	Ca	0	0
	Fe	1.0×10^{-4}	5.0×10^{-4}
	Mg	0	0
U II 409.014 BEC = 0.20 $\mu\text{g mL}^{-1}$ $C_L = 6.1 \text{ ng mL}^{-1}$	Ti	1.0×10^{-4}	5.0×10^{-3}
	Al	1.0×10^{-4}	0
	Ca	0	0
	Fe	0	0
Ba II 455.403 BEC = 0.0042 $\mu\text{g mL}^{-1}$ $C_L = 0.12 \text{ ng mL}^{-1}$	Mg	0	0
	Ti	0	0
	Al	0	0
	Ca	0	0

If the selected analysis line is the most prominent line in accordance with the Boumans ICP Tables [56], this line was investigated only, this refers to the following elements: Sb, Cu, Mn, Pb, Sn, and Ba. If the selected analysis line is not the most prominent line, the lines located before the selected analysis line were listed also, in the cases of Zn, Cd, Cr, and U. The data given underneath the wavelength of the analysis lines

corresponds to detection limits in pure solvent calculated by (2) [48]:

$$C_L = 2\sqrt{2} \times 0.01 \times \text{RSDB} \times \text{BEC}. \quad (2)$$

This equation is written in terms of the background equivalent concentration in pure solvent (BEC) and relative standard deviation of the background (RSDB = 1%) [48]. The selected prominent lines in the presence of complex matrix are printed in bold.

The results show that in the determination of trace of elements in environmental samples by means of 40.68 MHz ICP and spectrometer with high resolution, the prominent lines of the elements Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba, which are free of line interferences, can be selected as analysis lines. The following exceptions are observed in the case of Cd II 214.438 nm where $[Q_{I\text{Fe}}(\lambda_a) > 0]$ and Sb I 206.838 nm where $[Q_{ITi}(\lambda_a) > 0]$. It is well known that the magnitude of spectral interferences depends on the spectral resolution [36], but the selected “best” analysis lines are the same, irrespective of ICP and operating conditions, and therefore, these data can be transferred from one ICP system to another [44].

The magnitude of line and wing background interferences by 40.68 MHz and spectrometer with high resolution are significantly lower in comparison with the corresponding values obtained by 27.12 MHz ICP and spectrometer with middle resolution (practical spectral bandwidth = 15.6 pm) [57]. This result can be expected, but the differences between the magnitudes of the Q -values cannot be predicted in general terms, and consequently, they have to be estimated only by systematic experimental results.

With respect to the “zero” values of the $[Q_{IJ}(\lambda_a)]$, we will note the following in accordance with [48]: if in Table 2 the $[Q_{IJ}(\lambda_a)]$ is listed as “zero,” this implies that $[Q_{IJ}(\lambda_a) \times C_{IJ}]$ is equal to or smaller than the numerical values of the detection limits (in ng mL^{-1}) shown in Table 2 underneath the corresponding prominent line. The database of $[Q$ -values] from Table 2 can be used for the following calculations:

- (i) true detection limits in the case of a multicomponent matrix by using (3) [48]:

$$C_{L,\text{true}} = \frac{2}{5} \sum_j Q_{IJ}(\lambda_a) \times C_{IJ} + C_{L,\text{conv}}, \quad (3)$$

where

$$C_{L,\text{conv}} = 2\sqrt{2} \times 0.01 \times \text{RSDBL} \times [\text{BEC} + \sum_j Q_{IJ}(\lambda_a) \times C_{IJ} + \sum_j Q_{WJ}(\Delta\lambda_a) \times C_{IJ}]. \quad (4)$$

Therefore, the true detection limit ($C_{L,\text{true}}$) is defined by (5):

$$C_{L,\text{true}} = \frac{2}{5} \sum_j Q_{IJ}(\lambda_a) \times C_{IJ} + 2\sqrt{2} \times 0.01 \times \text{RSDB} \times [\text{BEC} + \sum_j Q_{IJ}(\lambda_a) \times C_{IJ} + \sum_j Q_{WJ}(\Delta\lambda_a) \times C_{IJ}]; \quad (5)$$

TABLE 3: Interferent concentration C_{IJ} ($\mu\text{g mL}^{-1}$) for which $[Q_{IJ}(\lambda_a) = 0]$ in the presence of Fe or Ti as interferents for the elements: Zn, Cd, Sb, Cr, and U.

Analytes lines λ , nm	Interferent concentration C_{IJ} , ($\mu\text{g mL}^{-1}$) for which $Q_{IJ}(\lambda_a) = 0$	
	Fe	Ti
Zn I 213.856	140	350
Zn II 202.548	—	—
Cd II 226.502	18	—
Cd II 214.438	85	—
Sb I 206.838	—	100
Cr II 205.552	150	—
Cr II 206.149	—	133
Cr II 267.716	—	—
U II 385.958	2.0	—
U II 367.007	2.0	—
U II 263.553	5.0	1.2
U II 409.014	—	—

- (ii) maximal interferent concentration C_{IJ} for which $[Q_{IJ}(\lambda_a) = 0]$ in the presence of matrix constituents is given by the next equations [48]:

$$S_{IJ}(\lambda_a) \times C_{IJ} = S_A \times C_L. \quad (6)$$

$$C_{IJ} = \frac{C_L}{Q_{IJ}(\lambda_a)}. \quad (7)$$

The maximal interferent concentration C_{IJ} for which $[Q_{IJ}(\lambda_a) = 0]$ in the presence of iron or titanium as interferents (7) for the most prominent lines with $[Q_{IJ}(\lambda_a) > 0]$ is listed in Table 3. These matrix constituents determine line interference levels around the most prominent lines of Zn, Cd, Sb, Cr, and U in accordance with Table 2. The selected prominent lines are printed in bold. If the concentration of the interferents in the sample solution is lower in comparison to the corresponding values shown in Table 3, the most prominent lines can be used as analysis lines.

Therefore, Table 3 can be used for additional line selection. In the determination of pollutants in water samples, the most prominent lines in accordance with Table 3 can be used, regarding the concentrations of iron and titanium in the different type of investigated water sample.

In conclusion of Section 3.1, we have to note that by using the selected analysis lines, the lowest possible detection limits can be achieved in the determination of the above mentioned trace elements in soil and similar materials by using one of the present day ICP-OES equipment. The quantification of all significant interferences for the most prominent lines ensures the accuracy of measurements by ICP-OES. On the other hand, we can use all prominent lines as analysis lines, but the detection limits will be higher. The increasing of the detection limits depends on the magnitude of the line interference levels and the concentration of the matrix elements in the final sample solutions (5).

Here, we have to note that the quantitative information for the spectral interferences in the presence of Al, Ca, Fe, Mg, and Ti as matrix constituents in the determination Hg, As, Se, Tl, Sn, and Bi as well as Pt, Pd, and Rh by 40.68 MHz ICP and optical emission spectrometer with high resolution under the same experimental conditions is given in [16, 18].

3.2. Experimental Demonstration of the Q-Concepts and HR-ICP-OES in the Analysis of Environmental Materials. The focus of this section is on recent applications, illustrating the versatility of the Q-concept and ICP-OES in the determination of toxic elements in environmental samples.

3.2.1. Soil Samples

(1) *Determination of Trace Elements in Certified Reference Materials IAEA/Soil 7.* Both decomposition procedures: extraction of trace elements soluble in *aqua regia* and complex digestion procedure with (HCl-HNO₃-HF) in a microwave system were used as described in (Section 2.5). The present paper offers a methodology which includes two steps.

(i) *Determination of Major Elements in the Final Sample Solutions.*

(a) *Decomposition procedure in the presence of aqua regia (in $\mu\text{g mL}^{-1}$):* Al—660 ± 6; Ca—3160 ± 25, Fe—500 ± 6, Mg—210 ± 5, and Ti—9.6 ± 0.5.

(b) *Decomposition procedure in the presence of (HCl-HNO₃-HF) (in $\mu\text{g mL}^{-1}$):* Al—936 ± 8; Ca—3265 ± 16; Fe—514 ± 6; Mg—225 ± 5; Ti—58 ± 2.

Mean values for statistical confidence $P = 95\%$ and six replicates ($n = 6$) are obtained. The selected prominent lines, which are free of interelement interferences, and OH band are used. The results show that the concentrations of Ca, Fe, and Mg in the certified reference material IAEA/Soil 7 do not depend significantly on the dissolution procedure. The concentration of Al and Ti is lower by using *aqua regia* extraction procedure in comparison with the dissolution procedure with HF. The final sample solutions that contain in both cases high solute matrix concentrations and spectral interferences in the determination of traces of hazardous waste elements by ICP-OES should be taken into consideration, that is, the selected analysis lines can be used as shown in Table 2. The determination of matrix elements is needed for additional line selection in accordance with Table 3 and for calculation of true detection limits (5).

(ii) *Determination of Zn, Cd, Cu, Mn, Pb, Cr, U, and Ba.* The content of Zn, Sb, Cd, Cu, Mn, Pb, Cr, U, and Ba obtained by Jobin Yvon ULTIMA 2 in the analysis of certified reference material IAEA/Soil 7 is presented in Table 4. Both digestion procedures: with *aqua regia* (column 2) and with (HCl-HNO₃-HF) (column 5) described in Section 2.5 are used. The mean values X for $n = 4$ replicates and the confidence interval of the mean value ΔX for statistical confidence $P = 95\%$ and $f = n - 1 = 3$ (columns 2 and 4)

and the relative standard deviations (RSD%) (columns 3 and 5) are calculated. The certified values of the reference material IAEA/Soil 7 are given for comparison (column 6). Using Student's criterion [58], no statistical differences between the experimental values (columns 2 and 4) and certified values (column 6) were registered, and by this way the accuracy can be ensured, independent of the dissolution procedures either by extraction of trace elements soluble in *aqua regia* or dissolution of the sample with HCl-HNO₃-HF in a microwave system. There, we have to note that the final sample solution by using digestion procedure with HCl-HNO₃-HF contains Si and B, but the selected prominent lines of the analytes were free from both line and wing background interferences in the presence of these elements as interferences.

(iii) *Detection Limits with respect to Dissolved Solids and Threshold Concentrations.* Table 5 presents the following data: the threshold concentrations of Zn, Sb, Cd, Cu, Mn, Pb, Cr, U, and Ba in soil ($\mu\text{g g}^{-1}$), in accordance with the regulation Number 3 from the Ministry of Environment and Water of Bulgaria, [29] (column 2); the maximum permissible concentrations of potentially toxic elements in sludge-treated soils ($\mu\text{g g}^{-1}$ for dry soil) in EC member states and US [30] (column 3); the maximum permissible concentrations for uranium [31] (column 4); and the true detection limits ($C_{L,\text{true}}$) obtained by the present ICP-OES method ($\mu\text{g g}^{-1}$), which were calculated by (4) and (5) in the determination of above mentioned elements in the certified reference material IAEA/Soil 7 (column 5).

The results show that the obtained true detection limits by using the selected analysis lines and operating conditions listed in Table 1 are significantly lower in comparison with the maximum permissible limits. Therefore, the level of pollution can be estimated in accordance to the existing maximum permissible limits.

(2) *Determination of Trace Elements in Soil Sample.* As an example in Table 6, the contents of Zn, Cr, Pb, and Cu are presented in soil sample, collected in accordance with Section 2.4 [55] from relatively nonpolluted region in order to show the possibilities of the present ICP-OES method in the determination of low concentration of pollutants in the presence of Al, Ca, Fe, Mg, and Ti as matrix constituents. Extraction of trace elements soluble in *aqua regia* was used as a decomposition method (Section 2.5) [27].

We have to note that *aqua regia* will not totally dissolve soil and similar materials and efficiency of extraction for particular elements can differ for various types of soil. For estimation of the accuracy of results, the direct current arc method (D.C. Arc-OES) was used as an independent method for analysis of solid sample (column 4). The specifications of the spectrograph, D.C. power generator, and operating conditions are shown in [57]. Using Student's criterion [58], statistical differences between the results obtained by the ICP-OES and D.C. Arc-OES are not observed.

(3) *Determination of Cr, Sb, Zn, Pb, Cd, Mn, Cu, U, and Ba in National Water Research Institute (NWRI) Water Certified Standard, TMDA-51.2.* Heavy metal contaminations can pose

TABLE 4: Content of Zn, Sb, Cd, Cu, Mn, Pb, Cr, U, and Ba (in $\mu\text{g g}^{-1}$) obtained by JY ULTIMA 2 in the analysis certified reference material IAEA/Soil 7 by both procedures with *aqua regia* [27] (column 2) and with (HCl-HNO₃-HF) [28] (column 5): mean values X for ($n = 4$ replicates) and the confidence interval of the mean value ΔX for statistical confidence $P = 95\%$ and $f = n - 1 = 3$ (columns 2 and 4) and relative standard deviations (RSD %) (columns 3 and 5), and certified values (column 6).

Selected prominent lines, λ , nm	Procedure with <i>aqua regia</i>		Procedure with (HCl-HNO ₃ -HF)		Certified values. Concentration in ($\mu\text{g g}^{-1}$)
	Concentration in ($\mu\text{g g}^{-1}$) $X \pm \Delta X$	RSD %	Concentration in ($\mu\text{g g}^{-1}$) $X \pm \Delta X$	RSD %	
Zn II 202.548	103.00 \pm 1.4	1.4	104.00 \pm 1.4	1.4	104
Sb I 206.838	1.65 \pm 0.05	3.0	1.72 \pm 0.04	2.3	1.7
Cd II 214.438*	1.27 \pm 0.06	4.7	1.30 \pm 0.06	4.7	1.3*
Cu I 324.754	11.00 \pm 0.4	3.6	10.60 \pm 0.4	3.8	11.0
Mn II 257.610	632.80 \pm 13	2.0	627.60 \pm 13.0	2.0	631
Pb II 220.353	59.80 \pm 1.2	2.0	60.00 \pm 1.0	1.7	60.0
Cr II 267.716	59.00 \pm 1.6	2.6	58.00 \pm 1.8	3.1	60.0
U II 409.014	2.62 \pm 0.1	3.8	2.56 \pm 0.1	3.9	2.6
Ba II 455.403*	162.00 \pm 5.0	3.0	162.00 \pm 5.0	3.0	159*

*Noncertified information value.

TABLE 5: Threshold concentrations in the determination of Zn, Sb, Cd, Cu, Mn, Pb, Cr, U, and Ba in soil ($\mu\text{g g}^{-1}$) [29] (column 2) and the maximum permissible concentrations of potentially toxic elements in sludge-treated soils ($\mu\text{g g}^{-1}$ dry soil) in EC member states and US [30] (column 3), maximum permissible concentrations for U [31] (column 4), and true detection limits obtained by the present ICP-OES method ($\mu\text{g g}^{-1}$) (column 5).

Selected prominent lines, wavelength λ , nm	Threshold concentrations for soils, ($\mu\text{g g}^{-1}$) Bulgarian legislation [29]	Maximum permissible concentrations in sludge-treated soils (in $\mu\text{g g}^{-1}$) in EU member states [30]	Maximum permissible concentration for U (in $\mu\text{g g}^{-1}$) [31]	True detection limits obtained by the present ICP-OES method ($\mu\text{g g}^{-1}$)
Zn II 202.54	88 \div 180	250 \div 300	no data	0.12
Sb I 206.838	no data*	no data	no data	1.5
Cd II 214.438	0.4 \div 1.0	1 \div 3	no data	0.12
Cu I 324.754	34 \div 70	100 \div 140	no data	0.07
Mn II 257.610	no data	no data	no data	0.07
Pb II 220.353	26 \div 50	80 \div 100	no data	0.65
Cr II 267.716	65 \div 130	200	no data	0.12
U II 409.014	34 \div 70	100 \div 140	0.3 \div 11.7	0.75
Ba II 455.403	no data	no data	no data	0.06

*The values are not given in the corresponding documents.

potential health concerns when detected in drinking water and in different aquatic environments [59–62]. The detection limits and the accuracy of analytical results are of prime importance. The European standard EN ISO 11855 “water quality determination of selected elements by inductively coupled plasma optical emission spectroscopy (ICP-OES)” offers a method for the determination of pollutants in drinking water [63]. It should be noted that the line interference level for the most prominent lines of Zn, Cu, Pb, and Mn is determined from iron and titanium (Table 3). By using the information for the matrix interferences from ISO 11855, the chemists cannot decide which of the prominent lines is appropriate as analysis line, without both the quantitative information for line interference level in the presence of iron and the concentration of iron in final sample solutions. The quantification of all significant interferences for selected prominent lines ensures the accuracy of measurements by

a given ICP-OES system. The concentrations of iron in the final sample solution have to be known in advance or have to be determined previously as was mentioned above. If the concentration of iron in the sample solution is lower than the corresponding values shown in column 2 for the most prominent lines (Table 3), then these lines can be used as analysis line and lower detection limits can be achieved.

In the determination of Cr, Sb, Zn, Pb, Cd, Mn, Cu, U, and Ba in TMDA-51.2, the most prominent lines of Cu, Pb, Ba, and Mn were free from line interference (Table 2). The most prominent lines of chromium (Cr II 205.552 nm) and antimony (Sb I 206.838 nm) were influenced by line interference from titanium, but in case of water samples, this element is not common [64, 65]. The most prominent lines of zinc (Zn I 213.856 nm), cadmium (Cd II 226.502 nm), uranium (U II 238.958 nm), and chromium (Cr II 205.552 nm) were influenced by line interference from iron

TABLE 6: Determination of Zn, Cr, Pb, and Cu in soil sample, obtained by ULTIMA 2: mean values $[X]$ for ($n = 4$ replicates) and the confidence interval of the mean value $[\Delta X]$ for statistical confidence $P = 95\%$ and $f = n - 1 = 3$ (column 2); relative standard deviation (RSD %) (column 3). Columns 5 and 6 list the corresponding mean values $[\Delta X]$ for statistical confidence $P = 95\%$ and $f = n - 1 = 3$ (column 5) and RSD, %, obtained by D.C. Arc-OES.

ULTIMA 2, ICP-OES			D.C. Arc-OES		
Selected prominent line, wavelength, λ , nm	Concentration, $X \pm \Delta X$ ($\mu\text{g g}^{-1}$)	RSD, %	Selected prominent line, wavelength, λ , nm	Concentration, $X \pm \Delta X$ ($\mu\text{g g}^{-1}$)	RSD, %
Zn II 202.548	77.5 ± 1.2	1.6	Zn I 328.233	75 ± 4.2	5.6
Cr II 267.716	54.0 ± 1.0	1.9	Cr II 267.716	55.0 ± 3.0	5.5
Pb II 220.353	22.0 ± 0.5	2.3	Pb I 283.563	22 ± 1.0	4.6
Cu I 324.754	15.0 ± 0.4	2.7	Cu I 324.754	12 ± 0.6	5.0

TABLE 7: Detection limits in pure solvent C_L (column 2) obtained by ULTIMA 2 by using the most prominent lines of Cr, Sb, Zn, Pb, Cd, Mn, Cu, U, and Ba (column 1) under optimal experimental conditions (Table 1), threshold concentrations in accordance with Bulgarian Regulation No. 9 on the quality of water intended for human consumption [32] (column 3), mean values $[X]$ for ($n = 4$ replicates), and the confidence interval of the mean value $[\Delta X]$ for statistical confidence $P = 95\%$ and $f = n - 1 = 3$ (column 4) as well as the RSD (column 5) of the analytical results obtained by ICP-OES in the determination of Cr, Sb, Zn, Pb, Cd, Mn, Cu, U, and Ba in NWRI TMDA-51.2 (column 4). Column 6 shows the certified values.

Most prominent lines, wavelength, λ , nm	C_L (ng mL^{-1})	Threshold concentrations, (ng mL^{-1}) in accordance with regulation no. 9 [32]	ICP-OES ULTIMA 2		Certified values, (ng mL^{-1})
			Concentrations, (ng mL^{-1})	RSD, %	
Cr II 205.552	3.0	50	61.9 ± 1.0	1.6	62.5
Sb I 206.838	10	5.0	the element is not detected	—	3.1
Zn I 213.856	1.4	4000	105.5 ± 1.5	1.4	106
Pb II 220.353	5.0	10	73.0 ± 1.0	1.3	72.9
Cd II 226.502	1.4	5.0	25.0 ± 0.5	2.0	25.1
Mn II 257.610	0.13	50	81.8 ± 1.2	1.4	82.0
Cu I 324.754	1.3	2000	90.8 ± 1.2	1.3	91.0
U II 385.958	1.4	30	30.0 ± 1.1	3.3	29.3
Ba II 455.403	0.12	no data	73.0 ± 1.0	1.3	73.3

[64, 65]. The concentration of iron from TMDA-51.2 analysis certificate is $0.111 \mu\text{g mL}^{-1}$, which is lower than $140 \mu\text{g mL}^{-1}$ from Table 3 in the case of Zn I 213.856 nm; $0.111 \mu\text{g mL}^{-1} < 18 \mu\text{g mL}^{-1}$ for Cd II 226.502 nm; $0.111 \mu\text{g mL}^{-1} < 2.0 \mu\text{g mL}^{-1}$ for U II 385.958 nm; $0.111 \mu\text{g mL}^{-1} < 150 \mu\text{g mL}^{-1}$ for Cr II 205.552 nm. Hence, the most prominent lines of Zn, U, Cr, and Cd can be used as analysis lines.

In Table 7, the detection limits are presented in pure solvent C_L (column 2) obtained by ICP-OES, ULTIMA 2 by using the most prominent lines of Cr, Sb, Zn, Pb, Cd, Mn, Cu, U, and Ba under optimal experimental conditions (Table 1), threshold concentrations in accordance with the Bulgarian No. 9 on the Quality of Water Intended for Human Consumption from the Ministry of Environment and Water of Bulgaria [32] (column 3), mean values $[X]$ for ($n = 4$ replicates), and the confidence interval of the mean value $[\Delta X]$ for statistical confidence $P = 95\%$ and $f = n - 1 = 3$ (column 4) as well as the RSD (column 5) of the analytical results obtained by ICP-OES in the determination of Cr, Sb, Zn, Pb, Cd, Mn, Cu, U, and Ba in National Water Research Institute (NWRI) water certified standard, TMDA-51.2. Column 6 shows the certified values for comparison. The results obtained by the present ICP-OES method (column 4) show good agreement with

the corresponding certified values (column 6). By this way, using this pattern, different type of water can be analyzed.

4. Conclusions

The determination of trace of elements in complex environmental materials requires essential information on the spectral interferences because the background under a prominent line cannot be directly measured and, in addition, varies with the sample composition. The correct background correction ensures the accuracy of analytical results.

The present paper presents quantitative new base data for the spectral inferences in the presence of complex matrix containing Al, Ca, Mg, Fe, and Ti around the wavelength λ_a of the prominent lines of ten elements (Zn, Cd, Sb, Cu, Mn, Pb, Sn, Cr, U, and Ba) by using 40.68 MHz ICP. The measurements were performed in the 2nd order of the spectrum (practical spectral bandwidth 5 pm) for the most prominent lines of Zn, Cd, Sb, Mn, Pb, Sn, and Cr with wavelengths in the spectral region 160–320 nm. The wavelengths of the most prominent lines of Cu, U, and Ba lie in the spectral region 320–800 nm, and the measurements were made in the 1st order (practical spectral bandwidth 10 pm). In our

previous paper, was experimentally demonstrated that the selected “best” analysis lines are the same, irrespective of ICP and operating conditions, and therefore, these data can be transferred from one ICP system to another [44].

The versatility of Q-concept as basic methodology was experimentally demonstrated in the determination of trace of elements in certified reference materials: IAEA/Soil 7 and NWRI water certified standard, TMDA-51.2, and a soil sample collected from relatively nonpolluted region. The obtained detection limits satisfy the quality requirements of the practice. In this paper, were shown the possibilities of the present day HR-ICP-OES equipment in the direct determination of trace elements in environmental samples (water and soil) were shown, without preconcentration of trace element of interest.

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