

## Determination of As, Zn, Pt, B, Hg, Cd, Tl and U in environmental materials by high resolution radial viewing 40.68 MHz inductively coupled plasma optical emission spectrometry (ICP - OES)

N. Velitchkova<sup>1</sup>, O. Veleva<sup>1</sup>, S. Velichkov<sup>2</sup>, P. Markov<sup>2</sup>, N. Daskalova<sup>2\*</sup>

<sup>1</sup> Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bontchev Street, bl. 24, 1113 Sofia, Bulgaria

<sup>2</sup> Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bontchev Street, bl. 11, 1113, Sofia, Bulgaria

Received September 24, 2012; revised February 10, 2013

The possibilities and limitations of high resolution radial viewing 40.68 MHz inductively coupled plasma optical emission spectrometry (ICP - OES) were shown in the determination of As, Zn, Pt, B, Hg, Cd, Tl and U in environmental materials. Improvement of the detection limits was achieved by optimization of the operating conditions. The lowest detection limits were obtained under robust conditions (excitation temperature  $\approx 7200$  K in pure solvent and in presence of Al, Ca, Fe, Mg and Ti as a complex environmental matrix). The detection limits in the determination of As, Zn, B, Hg, Cd, Tl and U satisfy the requirements for maximum permissible concentrations in soils and drinking waters. In the determination of Pt in road dust an improvement of the detection limit was achieved by the development of a new column method with *2-mercaptobenzimidazole* immobilized on activated carbon for separation of the matrix elements Al, Ca, Fe, Mg and Ti and pre-concentration of platinum.

**Keywords:** ICP - OES, Environmental materials, Spectral interferences, Line selection, Detection limits

### INTRODUCTION

Matrix effects in ICP - OES include non-spectral and spectral interferences [1, 2]. A large number of research groups have investigated the non-spectral matrix effects by optimization of excitation in order to suppress or eliminate this type of interferences [3 – 6]. Summarizing the investigation of non-spectral matrix effects in the presence of different matrices, the conclusion can be drawn that the robust plasma conditions are more appropriate when compared to the non-robust plasma conditions, but elimination of non-spectral matrix effects cannot be achieved [7, 8]. Our investigations show that non – spectral matrix effects can be totally removed by precise matching of the acid and matrix contents in both reference and sample solutions [9 – 11]. In the present paper the non-spectral matrix effects were totally removed by precise matching of the acid and matrix contents in both reference and sample solutions and are not subject of the present investigation.

Spectral interferences may drastically deteriorate the analytical characteristics of ICP–OES [1, 2]. Analysis of a variety of complex environmental matrices ensures that all possible

types will encounter soon or later. The most difficult samples from this point of view are the soils and the sediments. Such materials normally contain high concentrations of Al, Ca and Mg, which cause significant background enhancement in many regions of the spectrum; they also contain 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 [12].

In our previous papers the possibilities of ICP – OES and Q-concept as a basic methodology for improvement of the true detection limits by using different excitation conditions in ICP were shown:

(i) in the determination of traces of rare earth elements in line-rich rare earth matrices at  $T_{exc} \approx 6000$  K [13];

(ii) in the determination of a large number of dopants with different characteristics (charge and ionic radius) (Na, Rb, Al, Fe, Cr, Ga, Nb, Ni, Mn, Yb, Tm, Er, Ho, Tb, Nd, Ge, Zr and Ce) in single crystals of potassium titanylphosphate (KTiOPO<sub>4</sub>). The lowest detection limits were obtained at different excitation temperatures for analytes with different spectral characteristics:

$T_{exc} \approx 6200$  K for Na, Rb, Al, Ga, Tm, Er, Ho, Tb, Nd and Ce;

\* To whom all correspondence should be sent:  
E-mail: das15482@svr.igic.bas.bg

$T_{exc} \approx 7200$  K for Fe, Cr, Nb, Ni, Ge and Zr [14].

The general purpose of the present paper was to investigate the possibilities of a radial 40.68 MHz ICP and spectrometer with high resolution (spectral bandwidth = 5 pm) in the determination of As, Zn, Pt, B, Hg, Cd, Tl and U in the presence of a complex matrix containing Al, Ca, Fe, Mg and Ti in environmental materials. The optimization procedure of the experimental conditions in the determination of traces of elements in complex matrices will be presented. Quantification of spectral interferences is made by Q-values for line interference  $Q_{IJ}(\lambda_a)$  and Q-values for wing background interference  $Q_{WJ}(\Delta\lambda_a)$ , for each of the interferents [15].

## 2. EXPERIMENTAL

### 2.1. Instrumentation

The experiments were performed with a radial viewing ICP - OES system Horiba Jobin Yvon ULTIMA 2 (Longjumeau, France) equipment, whose characteristics are specified in Table 1. The operating conditions were modified by varying the incident power and the sheathing gas flow rate, whereas the carrier gas flow rate was kept constant ( $0.4 \text{ l min}^{-1}$ ) (Table 2). This is the optimal value of the carrier gas flow rate in accordance with the recommendations for the Meinhard nebulizer in the user manual to the JY ULTIMA 2 equipment. The prominent lines with wavelengths below 200 nm were measured by a nitrogen-purged spectrometer in accordance with the recommendation of the manufacturer. The quantitative information about the type of the spectral interferences was derived from wavelength scans around the candidate

(prominent) analysis lines in the presence of Al, Ca, Mg, Fe and Ti as interferents. The quantitative data for the spectral interferences were obtained in the presence of  $2 \text{ mg ml}^{-1}$  Al, Ca, Mg, Fe, and Ti as interferents, separately. Q-values for line interferences  $Q_I(\lambda_a)$  and Q-values for wing background interference  $Q_w(\Delta\lambda_a)$  were obtained around the selected prominent lines of As, Zn, Pt, B, Hg, Cd, Tl and U. The total background signal in the presence of a complex environmental matrix is [15]:

$$X_{BL} = X_B + X_{WJ}(\Delta\lambda_a) + X_{IJ}(\lambda_a) \quad \text{where:}$$

–  $X_B$  is the solvent blank (due to source and solvent);

–  $X_{WJ}(\Delta\lambda_a)$  - the wing background level with respect to the solvent blank for the interferents ( $J = \text{Al, Ca, Mg, Fe or Ti}$ );

–  $X_{IJ}(\lambda_a)$  - the net interfering signals with respect to the wing background level  $X_{WJ}(\Delta\lambda_a)$  of the interferents ( $J = \text{Al, Ca, Mg, Fe or Ti}$ ).

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:

- the sensitivity of the analysis line  $S_A$  (defined as the net line signal  $X_A$  per unit analyte concentration  $C_A$ ;

- 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  $Q_{WJ}(\Delta\lambda_a) = S_{WJ}(\Delta\lambda_a) / S_A$  and the Q-values for line interference  $Q_{IJ}(\lambda_a) = S_{IJ}(\lambda_a) / S_A$ .

**Table 1.** Specification of HORIBA Jobin - Yvon ULTIMA 2 (France) ICP system

Monochromator	HORIBA Jobin - Yvon ULTIMA 2
Mounting	Czerny - Turner, focal length 1 m
Grating	Holographic, 2400 grooves $\text{mm}^{-1}$
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 2 <sup>nd</sup> order from 160 nm to 320 nm and 10 pm in the 1 <sup>st</sup> order from 320 to 800 nm
Detectors	High Dynamic Detectors based on PMT's
Rf generator	Solid state RF 40.68 MHz
Frequency	40.68 MHz
Power output	0.5 - 1.55 kW
Nebulizer	Meinhard, concentric glass
Spray chamber	JY Glass cyclonic spray chamber
Plasma torch	Fully demountable
Pump	Peristaltic, two channels, twelve-roller

**Table 2.** Operating conditions with the 40.68 MHz ICP HORIBA JY ULTIMA 2 (France)

Variable parameters	$T_{exc} \approx 6200$ K,	$T_{exc} \approx 7200$ K,
	Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio = 4.0	Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio = 11.4
Incident power, (kW)	1.00	1.00
Outer argon flow rate, (l min <sup>-1</sup> )	13	13
Nebulizer, Meinhard, type TR 50 C1, pressure, bar	3.2	3.2
Carrier gas flow rate, (l min <sup>-1</sup> )	0.4	0.4
Sheath gas flow rate, (l min <sup>-1</sup> )	1.0	0.2
Sum = Carrier gas + Sheath gas flow rate, (l min <sup>-1</sup> )	1.4	0.6
Liquid uptake rate, (ml min <sup>-1</sup> )	1.0	1.0
Observation height, (mm)	10	10

The true detection limits ( $C_{L, true}$ ) were calculated by Eq. 1 [13]:

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

where:

$$C_{L, conv} = 2\sqrt{2} \times 0.01 \times RSDBL \times [BEC + \sum_j Q_{II}(\lambda_a) \times C_{II} + \sum_j Q_{WI}(\Delta\lambda_a) \times C_{II}] \quad (2)$$

Therefore, the ( $C_{L, true}$ ) is obtained by Eq. 3:

$$C_{L, true} = 2/5 \sum_j Q_{II}(\lambda_a) \times C_{II} + 2\sqrt{2} \times 0.01 \times RSDB \times [BEC + \sum_j Q_{II}(\lambda_a) \times C_{II} + \sum_j Q_{WI}(\Delta\lambda_a) \times C_{II}] \quad (3)$$

The detection limit of the analytes in pure solvent (or dilute acid) is defined by Eq. 4 [13]:

$$C_L = 2\sqrt{2} \times 0.01 \times RSDB \times BEC \quad (4)$$

This equation (4) is written in terms of the background equivalent concentration in pure solvent (BEC) and relative standard deviation of the background (RSDB=1%) [15].

### 2.2. Reagents and test solutions

Reagents of highest purity grade were used: 30 % HCl, 65 % HNO<sub>3</sub>, 47 % HBr (Suprapur, Merck), bi-distilled water from a quartz apparatus, activated carbon GAS 1240 (Norit N.V. Netherlands) with specific surface area of 1240 m<sup>2</sup>g<sup>-1</sup> and buffer solutions (Merck): pH = 1 (0.1 M HCl). Plastic or PTFE ware was used throughout.

Stock solutions of the analytes (1 mg ml<sup>-1</sup>) were prepared from Merck single element standard solutions. Stock solutions of the matrix components Al, Ca, Mg, Fe and Ti (10 mg ml<sup>-1</sup>) were prepared by dissolving the corresponding chlorides with a purity of 99.9999% in hydrochloric acid. The possible presence of impurities causes an

uncertainty when matrix concentration of 2 mg ml<sup>-1</sup> is used. Q-values were measured by using the following test solutions: 10 µg ml<sup>-1</sup> for each analyte and 2 mg ml<sup>-1</sup> for each interferent, separately.

### 2.3. Certified reference materials

1. International Atomic Energy Agency IAEA / Soil 7;
2. Certified reference material BCR-723 - road dust;
3. National Water Research Institute certified standard, TMDA-51.2, certified standard for trace elements in diluted Lake Ontario water.

## 3. RESULTS AND DISCUSSION

### 3.1. Optimization of the operating conditions

**3.1.1. Pure solvent.** The results presented in Table 3 lists the sensitivities of the analysis line  $S_A$  – values for the atomic and the ionic prominent lines with different excitation potentials ( $E_q$ ) for elements with various ionization potentials ( $V_i$ ) at  $T_{exc} \approx 6200$  K where the Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio is equal to 4 and at  $T_{exc} \approx 7200$  K ( Mg II / Mg I = 11.4), as well as the detection limits in pure solvent derived by the above mentioned operating conditions (Table 2). The ionization and excitation potentials were taken from [16]. The detection limits in pure solvent were calculated by using Eq.4. The change in  $T_{exc}$  was achieved by varying the sheath gas flow rate (Table 2) and was measured by the Boltzmann plot method with titanium lines [17]. The main outcome from the investigations was:



**Table 3.** Values of  $S_A$  for the atomic and ionic prominent lines for  $T_{exc} \approx 6200$  K (1) and  $T_{exc} \approx 7200$  K (2)

Atomic prominent lines, $\lambda$ , nm	Ionization potential, V [16]	$T_{exc} \approx 6200$ K (1) $S_{A(1)} \times 10^6$	$T_{exc} \approx 7200$ K (2) $S_{A(2)} \times 10^6$	$S_{A(2)}/S_{A(1)}$ ratio	$C_{L(1)}$ , ng ml <sup>-1</sup>	$C_{L(2)}$ , ng ml <sup>-1</sup>
As I 193.695	9.81	330	1000	3.0	8.4	3.0
Zn I 213.856	9.39	342	990	2.9	13.0	4.5
Pt I 265.945	9.00	326	880	2.7	37.8	14.0
B I 249.773	8.30	480	960	2.0	10.2	5.1
Ionic prominent lines, $\lambda$ , □nm	Sum = ionization + excitation potentials	$T_{exc} \approx 6200$ K (1) $S_{A(1)} \times 10^6$	$T_{exc} \approx 7200$ K (2) $S_{A(2)} \times 10^6$	$S_{A(2)}/S_{A(1)}$ ratio	$C_{L(1)}$ , ng ml <sup>-1</sup>	$C_{L(2)}$ , ng ml <sup>-1</sup>
Hg II 194.277	16.83	375	1200	3.2	6.5	2
Cd II 214.338	14.77	520	1670	3.2	6.0	1.7
Tl II 190.852	12.60	420	1260	3.0	11.2	7.0
U II 385.958	9.44	450	1260	2.8	4.0	1.4

**Table 4.** Identification of matrix lines which influence the platinum prominent lines

Analytes, Wavelengths, $\lambda$ , □nm	Interferents, wavelength of interfering line, $\lambda$ , nm	$\Delta\lambda_{ka}^*$ , nm	$Q_{WJ}(\Delta\lambda_a)$	$Q_{IJ}(\lambda_a)$
Pt II 203.646 BEC = 0.23 $\mu\text{g ml}^{-1}$ $C_L = 7.0 \text{ ng ml}^{-1}$	Al II 203.993 [19]	+0.347	$7.2 \times 10^{-4}$	0
	Ca	-	0	0
	Fe 203.643 [20]	-0.003	$9.6 \times 10^{-5}$	$8.5 \times 10^{-3}$
	Mg	-	0	0
	Ti 203.681	+0.035	$2.4 \times 10^{-5}$	$6.6 \times 10^{-5}$
Pt II 214.423 BEC = 0.26 $\mu\text{g ml}^{-1}$ $C_L = 8.0 \text{ ng ml}^{-1}$	Al I 214.539 [19]	+0.116	$1.9 \times 10^{-4}$	$2.3 \times 10^{-4}$
	Ca	-	0	0
	Fe 214.445 [19, 20]	+0.022	$1.9 \times 10^{-5}$	$3.7 \times 10^{-5}$
	Mg	-	0	0
	Ti 214.361 [19, 20]	-0.062	$1.9 \times 10^{-5}$	0
Pt I 217.467 BEC = 0.43 $\mu\text{g ml}^{-1}$ $C_L = 12.0 \text{ ng ml}^{-1}$	Al I 217.403 [19, 20]	-0.064	$7.1 \times 10^{-4}$	$2.0 \times 10^{-3}$
	Ca	-	0	0
	Fe I 217.486 [19, 20]	+0.019	$5.1 \times 10^{-5}$	$5.7 \times 10^{-5}$
	Mg	-	0	0
	Ti	-	0	0
Pt I 193.670 BEC=0.44 $\mu\text{g ml}^{-1}$ $C_L = 13.0 \text{ ng ml}^{-1}$	Al 193.564	+ 0.106	$2.4 \times 10^{-3}$	$6.0 \times 10^{-3}$
	Ca	-	0	0
	Fe 193.657 [19, 20]	- 0.015	$3.1 \times 10^{-5}$	$2.1 \times 10^{-5}$
	Mg	-	0	0
	Ti 193.657	- 0.013	$2.7 \times 10^{-5}$	$3.0 \times 10^{-6}$
Pt I 265.945 BEC= 0.48 $\mu\text{g ml}^{-1}$ $C_L = 14.0 \text{ ng ml}^{-1}$	Al I 266.039 [19, 20]	+ 0.094	$1.7 \times 10^{-5}$	0
	Ca	-	0	0
	Fe 265.924 [19, 20]	- 0.021	$7.1 \times 10^{-6}$	$7.0 \times 10^{-6}$
	Mg	-	0	0
	Ti	-	0	0

\*  $\Delta\lambda_{ka}$  is the wavelength distances between the analyte and interfering lines

(i) The sensitivities of all atomic and ionic prominent lines are higher at  $T_{exc} \approx 7200$  K in comparison with the corresponding values at  $T_{exc} \approx 6200$  K (column 3 versus column 4). The enhancement factors decrease with decreasing ionization potentials of the analytes for atomic prominent lines or with decreasing of the sum =

ionization potential + excitation potentials of elements for ionic prominent lines (column 5). The atomic lines of elements with low to medium ionization potentials ( $V_i \leq 8$  eV) were denoted as “soft” lines. All other atomic and ionic lines were denoted as “hard” lines [1, 18].



**Table 5.** Values of  $S_{\text{IFe}}(\lambda_a)$  and  $S_{\text{WFe}}(\Delta\lambda_a)$  for the prominent lines of Zn, Pt, B, Hg, Cd, Tl and U for  $T_{\text{exc}} \approx 6200$  K (1) and  $T_{\text{exc}} \approx 7200$  K (2). Interferent:  $2 \text{ mg ml}^{-1}$  Fe

Prominent lines, $\lambda$ , nm	$T_{\text{exc}} \approx 6200$ K (1)		$T_{\text{exc}} \approx 7200$ K (2)		$S_{\text{IFe}}(2)(\lambda_a) / S_{\text{IFe}}(1)(\lambda_a)$ ratio	$S_{\text{WFe}}(2)(\Delta\lambda_a) / S_{\text{WFe}}(1)(\Delta\lambda_a)$ ratio
	$S_{\text{IFe}}(1)(\lambda_a) \times 10^6$	$S_{\text{WFe}}(1)(\Delta\lambda_a) \times 10^6$	$S_{\text{IFe}}(2)(\lambda_a) \times 10^6$	$S_{\text{WFe}}(2)(\Delta\lambda_a) \times 10^6$		
Zn I 213.856	0.003	-	0.0099	-	3.3	-
Pt I 265.945	0.003	0.003	0.006	0.006	2.0	2.0
B I 249.773	0.025	0.003	0.048	0.0058	1.9	1.9
Hg II 194.277	0.004	0.005	0.012	0.0168	3.0	3.4
Cd II 214.338	0.011	0.004	0.0334	0.0104	3.2	2.8
Tl II 190.852	0.290	0.280	0.870	0.850	3.0	3.0
U II 385.958	0.270	0.220	0.780	0.650	2.9	3.0

**Table 6.** Values of  $Q_{\text{IFe}}(\lambda_a)$  and  $Q_{\text{WFe}}(\Delta\lambda_a)$  for the prominent lines of Zn, Pt, B, Hg, Cd, Tl and U for  $T_{\text{exc}} \approx 6200$  K (1) and  $T_{\text{exc}} \approx 7200$  K (2). Interferent:  $2 \text{ mg ml}^{-1}$  Fe

Prominent lines, $\lambda$ , nm	$T_{\text{exc}} \approx 6200$ K (1)		$T_{\text{exc}} \approx 7200$ K (2)		$Q_{\text{IFe}}(2)(\lambda_a) / Q_{\text{IFe}}(1)(\lambda_a)$ ratio	$Q_{\text{WFe}}(2)(\Delta\lambda_a) / Q_{\text{WFe}}(1)(\Delta\lambda_a)$ ratio
	$Q_{\text{IFe}}(1)(\lambda_a)$	$Q_{\text{WFe}}(1)(\Delta\lambda_a)$	$Q_{\text{IFe}}(2)(\lambda_a)$	$Q_{\text{WFe}}(2)(\Delta\lambda_a)$		
Zn I 213.856	$9.0 \times 10^{-6}$	0	$1.0 \times 10^{-5}$	0	1.10	-
Pt I 265.945	$9.2 \times 10^{-6}$	$9.2 \times 10^{-6}$	$6.8 \times 10^{-6}$	$6.8 \times 10^{-6}$	0.74	0.74
B I 249.773	$5.2 \times 10^{-5}$	$6.25 \times 10^{-6}$	$5.0 \times 10^{-5}$	$6.0 \times 10^{-6}$	0.96	0.96
Hg II 194.277	$1.1 \times 10^{-5}$	$1.3 \times 10^{-5}$	$1.0 \times 10^{-5}$	$1.4 \times 10^{-5}$	0.91	1.10
Cd II 214.338	$2.1 \times 10^{-5}$	$7.7 \times 10^{-6}$	$2.0 \times 10^{-5}$	$6.2 \times 10^{-6}$	0.95	0.81
Tl II 190.852	$6.9 \times 10^{-4}$	$6.7 \times 10^{-4}$	$6.9 \times 10^{-4}$	$6.8 \times 10^{-4}$	1.00	1.00
U II 385.958	$6.0 \times 10^{-4}$	$4.9 \times 10^{-4}$	$6.2 \times 10^{-4}$	$5.2 \times 10^{-4}$	1.00	1.10

**Table 7.** Values of  $S_{\text{IAI}}(\lambda_a)$  and  $S_{\text{WAI}}(\Delta\lambda_a)$  for the prominent lines of As, Pt and Tl for  $T_{\text{exc}} \approx 6200$  K (1) and  $T_{\text{exc}} \approx 7200$  K (2). Interferent:  $2 \text{ mg ml}^{-1}$  Al

Prominent lines, $\lambda$ , nm	$T_{\text{exc}} \approx 6200$ K (1)		$T_{\text{exc}} \approx 7200$ K (2)		$S_{\text{IAI}}(2)(\lambda_a) / S_{\text{IAI}}(1)(\lambda_a)$ ratio	$S_{\text{WAI}}(2)(\Delta\lambda_a) / S_{\text{WAI}}(1)(\Delta\lambda_a)$ ratio
	$S_{\text{IAI}}(1)(\lambda_a) \times 10^6$	$S_{\text{WAI}}(1)(\Delta\lambda_a) \times 10^6$	$S_{\text{IAI}}(2)(\lambda_a) \times 10^6$	$S_{\text{WAI}}(2)(\Delta\lambda_a) \times 10^6$		
As I 193.695	1.5	0.9	3.7	1.8	2.5	2.0
Pt I 193.670	4.2	1.2	5.8	2.3	1.4	1.9
Tl II 190.852	0.3	0.24	1.0	0.71	3.3	3.0

**Table 8.** Values of  $Q_{\text{IAI}}(\lambda_a)$  and  $Q_{\text{WAI}}(\Delta\lambda_a)$  for the prominent lines of As, Pt and Tl for  $T_{\text{exc}} \approx 6200$  K (1) and  $T_{\text{exc}} \approx 7200$  K (2). Interferent:  $2 \text{ mg ml}^{-1}$  Al

Prominent lines, $\lambda$ , nm	$T_{\text{exc}} \approx 6200$ K (1)		$T_{\text{exc}} \approx 7200$ K (2)		$Q_{\text{IAI}}(2)(\lambda_a) / Q_{\text{IAI}}(1)(\lambda_a)$ ratio	$Q_{\text{WAI}}(2)(\Delta\lambda_a) / Q_{\text{WAI}}(1)(\Delta\lambda_a)$ ratio
	$Q_{\text{IAI}}(1)(\lambda_a)$	$Q_{\text{WAI}}(1)(\Delta\lambda_a)$	$Q_{\text{IAI}}(2)(\lambda_a)$	$Q_{\text{WAI}}(2)(\Delta\lambda_a)$		
As I 193.695	$4.6 \times 10^{-3}$	$2.7 \times 10^{-3}$	$3.7 \times 10^{-3}$	$1.8 \times 10^{-3}$	0.80	0.70
Pt I 193.670	$1.1 \times 10^{-2}$	$3.1 \times 10^{-3}$	$5.8 \times 10^{-3}$	$2.3 \times 10^{-3}$	0.53	0.74
Tl II 190.852	$7.1 \times 10^{-4}$	$5.6 \times 10^{-4}$	$7.9 \times 10^{-4}$	$5.6 \times 10^{-4}$	1.10	1.00

It follows therefore that all prominent lines shown in Table 3 are “hard” lines and by adjusting the operating conditions it is possible to obtain the optimum temperatures for the emission of distinct lines of analytes.

(ii) The detection limits in pure solvent decrease at  $T_{\text{exc}} \approx 7200$  K in comparison with the detection limits at  $T_{\text{exc}} \approx 6200$  K (column 6 versus column 7).

**3.1.2 Complex environmental matrix.** The optimization of experimental conditions in the determination of traces of elements in complex matrices requires a procedure consisting of the following three steps:

**3.1.2.1. Identification of all matrix lines which influence the prominent lines of the analytes.** The identification requires a detailed study of the spectrum of the interferents. The interfering lines were identified by measuring their position with respect to that of the relevant analysis lines in a separate scan of the analyte in the presence of 2 mg ml<sup>-1</sup> Al, Ca, Fe, Mg and Ti as interferents separately. Table 4 shows, as an example, the identification of the spectrum of Al, Ca, Fe, Mg and Ti as interferents around five prominent lines of platinum by using 40.68 MHz ICP and spectrometer with high resolution (practical spectral bandwidth = 5 pm). The following special features should be noted:

(i) Known from the existing spectral tables [19 – 21] is the line of Al II 203.993. This matrix line is far away from the most prominent line of platinum Pt II 203.646 ( $\Delta\lambda_{\text{ka}} = + 0.347$  nm), but even though it influences the line and wing background interference level;

(ii) The wide lines Al I 214.539 nm [53] and Al I 217.403 nm [19, 20] determine  $Q_{\text{IAI}}(\lambda_a) > 0$  around the prominent lines of Pt II 214.423 nm and Pt I 217.467 nm, respectively;

(iii) The Al 193.564 nm is not listed in the existing spectral tables [19 – 21]. At a practical spectral bandwidth = 5 pm this line was registered as a wide complex line (Al 193.588 nm, Al 193.573 nm, Al 193.570 nm, Al 193.564 nm, Al 193.554 nm and Al 193.547 nm), which influenced the background intensity in the investigated spectral window up to 193.757 nm;

(iv) The following four matrix lines: Ti 203.681 nm (in the spectral window of Pt II 203.646 nm) and Al 193.564 nm, Fe 193.655 nm, Ti 193.657 nm (in the spectral window of Pt I 193.670 nm) were register. These lines are not noted in the existing spectral tables [19 – 21], but they determine the line

interference and wing background interference levels around Pt II 203.646 and Pt I 193.670 nm.

In addition, Pt I 265.945nm (the fifth prominent line, in accordance with the detection limits in pure solvent) was chosen as analysis line. This prominent line is relatively free of line interference (only  $Q_{\text{IFe}} = 7.0 \times 10^{-6}$ ). However, this involves a trade-off between spectral interferences and sensitivity, if the most intense lines suffer from interference.

It may be than concluded that the type and the magnitude of the spectral interferences are specific for a given matrix and cannot be predicted in general terms. The data presented in Table 4 shows that there are unknown matrix lines, very wide known matrix lines, in some cases out of the spectral window of the corresponding prominent lines, but just these matrix lines determine the line and wing background level. Therefore, only detailed experimental study can reveal the situation for each matrix type.

**3.1.2.2. Quantification of type of spectral interferences under different experimental conditions.** The spectral interferences in the presence of 2 mg ml<sup>-1</sup> Al, Ca, Fe, Mg or Ti separately around the selected prominent lines of elements with different ionization potentials at  $T_{\text{exc}} \approx 6200$  K and 7200 K were studied by 40.68 MHz ICP and spectrometer with high resolution. The change in  $T_{\text{exc}}$  was affected by varying the sheath gas flow rate (Table 2) and was measured by the Boltzmann plot method with titanium lines [17]. The investigations show that the line interference level using a spectrometer with high resolution is determined by aluminium, iron and titanium.

The magnitudes of the sensitivities of interfering signals are presented in Tables 5 and 6.  $S_{\text{IJ}}(\lambda_a)$  and  $S_{\text{WJ}}(\Delta\lambda_a)$  values (Table 5) and the magnitudes of  $Q_{\text{IJ}}(\lambda_a)$  and  $Q_{\text{WJ}}(\Delta\lambda_a)$  values (Table 6) in the presence of 2 mg ml<sup>-1</sup> iron as interferent for the prominent lines of Zn, Pt, B, Hg, Cd, Tl and U. Tables 7 and 8 list the magnitudes of sensitivities of interfering signals (Table 7) and the magnitudes of Q-values (Table 8) in the presence of 2 mg ml<sup>-1</sup> aluminium as interferents for the prominent lines of As, Pt and Tl. The prominent lines, which are influenced by line interferences in the presence of iron (Tables 5, 6) or aluminium (Tables 7, 8) are included in Tables 5 – 8. Here we would like to illustrate the cases of variation of Q-values as a function of  $T_{\text{exc}}$ . The following comes to a conclusion:



**Table 9.** Line selection in the determination of As, Zn, Pt, B, Hg, Cd, Tl and U in environmental materials. Interferents: Al, Ca, Fe, Mg and Ti

Analytes, wavelengths, $\lambda$ , nm	Interferents	$Q_{WJ}(\Delta\lambda_a)$	$Q_{II}(\lambda_a)$
As I 193.695 BEC = 0.1 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 3.0 ng ml <sup>-1</sup>	Al	$1.8 \times 10^{-3}$	$3.7 \times 10^{-3}$
	Ca	0	0
	Fe	$5.9 \times 10^{-5}$	0
	Mg	0	0
	Ti	$2.6 \times 10^{-5}$	0
<b>As I 189.042</b> BEC = <b>0.15 <math>\mu\text{g ml}^{-1}</math></b> C <sub>L</sub> = <b>4.3 ng ml<sup>-1</sup></b>	<b>Al</b>	<b><math>4.4 \times 10^{-4}</math></b>	<b>0</b>
	<b>Ca</b>	<b>0</b>	<b>0</b>
	<b>Fe</b>	<b>0</b>	<b>0</b>
	<b>Mg</b>	<b>0</b>	<b>0</b>
	<b>Ti</b>	<b>0</b>	<b>0</b>
Zn I 213.856 BEC = 0.05 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 1.4 ng ml <sup>-1</sup>	Al	$8.0 \times 10^{-6}$	0
	Ca	$2.0 \times 10^{-6}$	0
	Fe	0	$1.0 \times 10^{-5}$
	Mg	0	0
	Ti	$2.0 \times 10^{-6}$	$4.0 \times 10^{-6}$
<b>Zn II 202.548</b> BEC = <b>0.06 <math>\mu\text{g ml}^{-1}</math></b> C <sub>L</sub> = <b>1.7 ng ml<sup>-1</sup></b>	<b>Al</b>	<b><math>2.0 \times 10^{-5}</math></b>	<b>0</b>
	<b>Ca</b>	<b><math>1.0 \times 10^{-6}</math></b>	<b>0</b>
	<b>Fe</b>	<b><math>1.0 \times 10^{-5}</math></b>	<b>0</b>
	<b>Mg</b>	<b><math>4.0 \times 10^{-6}</math></b>	<b>0</b>
	<b>Ti</b>	<b><math>2.0 \times 10^{-5}</math></b>	<b>0</b>
Pt II 203.646 BEC = 0.23 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 7.0 ng ml <sup>-1</sup>	Al	$7.2 \times 10^{-4}$	0
	Ca	0	0
	Fe	$9.6 \times 10^{-5}$	$8.5 \times 10^{-3}$
	Mg	0	0
	Ti	$2.4 \times 10^{-5}$	$6.6 \times 10^{-5}$
Pt II 214.423 BEC = 0.26 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 8.0 ng ml <sup>-1</sup>	Al	$1.9 \times 10^{-4}$	$2.3 \times 10^{-4}$
	Ca	0	0
	Fe	$1.9 \times 10^{-5}$	$3.7 \times 10^{-5}$
	Mg	0	0
	Ti	$1.9 \times 10^{-5}$	0
Pt I 217.467 BEC = 0.43 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 12.0 ng ml <sup>-1</sup>	Al	$7.1 \times 10^{-4}$	$2.0 \times 10^{-3}$
	Ca	0	0
	Fe	$5.1 \times 10^{-5}$	$5.7 \times 10^{-5}$
	Mg	0	0
	Ti	0	0
Pt I 193.670 BEC = 0.46 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 13.0 ng ml <sup>-1</sup>	Al	$2.4 \times 10^{-3}$	$6.0 \times 10^{-3}$
	Ca	0	0
	Fe	$3.1 \times 10^{-5}$	$2.1 \times 10^{-5}$
	Mg	0	0
	Ti	$2.7 \times 10^{-5}$	$3.0 \times 10^{-6}$
<b>Pt I 265.945</b> BEC = <b>0.50 <math>\mu\text{g ml}^{-1}</math></b> C <sub>L</sub> = <b>14.0 ng ml<sup>-1</sup></b>	<b>Al</b>	<b><math>1.7 \times 10^{-5}</math></b>	<b>0</b>
	<b>Ca</b>	<b>0</b>	<b>0</b>
	<b>Fe</b>	<b><math>7.1 \times 10^{-6}</math></b>	<b><math>7.0 \times 10^{-6}</math></b>
	<b>Mg</b>	<b>0</b>	<b>0</b>
	<b>Ti</b>	<b>0</b>	<b>0</b>
B I 249.773 BEC = 0.18 $\mu\text{g ml}^{-1}$ C <sub>L</sub> = 5.1 ng ml <sup>-1</sup>	Al	0	0
	Ca	0	0
	Fe	$6.0 \times 10^{-6}$	$5.0 \times 10^{-5}$
	Mg	$1.0 \times 10^{-5}$	0
	Ti	$1.2 \times 10^{-5}$	0

**Table 9** (continued)

Analytes, wavelengths, $\lambda$ , nm	Interferents	$Q_{WJ}(\Delta\lambda_a)$	$Q_{II}(\lambda_a)$
B I 249.678 BEC = 0.20 $\mu\text{g ml}^{-1}$ $C_L = 5.6 \text{ ng ml}^{-1}$	Al	0	0
	Ca	0	0
	Fe	$6.0 \times 10^{-6}$	$5.0 \times 10^{-5}$
	Mg	$4.0 \times 10^{-6}$	0
	Ti	$1.2 \times 10^{-5}$	0
<b>B I 208.959</b> <b>BEC = 0.23 <math>\mu\text{g ml}^{-1}</math></b> <b><math>C_L = 6.5 \text{ ng ml}^{-1}</math></b>	<b>Al</b>	<b><math>6.0 \times 10^{-5}</math></b>	<b>0</b>
	<b>Ca</b>	<b>0</b>	<b>0</b>
	<b>Fe</b>	<b>0</b>	<b>0</b>
	<b>Mg</b>	<b>0</b>	<b>0</b>
	<b>Ti</b>	<b>0</b>	<b>0</b>
Hg II 194.277 BEC = 0.07 $\mu\text{g ml}^{-1}$ $C_L = 2.0 \text{ ng ml}^{-1}$	Al	$4.7 \times 10^{-4}$	0
	Ca	0	$1.0 \times 10^{-5}$
	Fe	$1.4 \times 10^{-5}$	0
	Mg	$3.4 \times 10^{-6}$	$1.9 \times 10^{-5}$
	Ti	$1.0 \times 10^{-5}$	0
<b>Hg I 253.652</b> <b>BEC = 0.07 <math>\mu\text{g ml}^{-1}</math></b> <b><math>C_L = 2.0 \text{ ng ml}^{-1}</math></b>	<b>Al</b>	<b>0</b>	<b>0</b>
	<b>Ca</b>	<b><math>7.7 \times 10^{-6}</math></b>	<b>0</b>
	<b>Fe</b>	<b><math>2.0 \times 10^{-4}</math></b>	<b>0</b>
	<b>Mg</b>	<b><math>5.1 \times 10^{-5}</math></b>	<b>0</b>
	<b>Ti</b>	<b><math>8.7 \times 10^{-5}</math></b>	<b>0</b>
Cd II 226.502 BEC = 0.05 $\mu\text{g ml}^{-1}$ $C_L = 1.4 \text{ ng ml}^{-1}$	Al	0	0
	Ca	$1.3 \times 10^{-6}$	0
	Fe	$2.0 \times 10^{-5}$	$8.0 \times 10^{-5}$
	Mg	0	0
	Ti	$8.0 \times 10^{-5}$	0
<b>Cd II 214.438</b> <b>BEC = 0.06 <math>\mu\text{g ml}^{-1}</math></b> <b><math>C_L = 1.7 \text{ ng ml}^{-1}</math></b>	<b>Al</b>	<b>0</b>	<b>0</b>
	<b>Ca</b>	<b><math>1.3 \times 10^{-6}</math></b>	<b>0</b>
	<b>Fe</b>	<b><math>6.2 \times 10^{-6}</math></b>	<b><math>2.0 \times 10^{-5}</math></b>
	<b>Mg</b>	<b>0</b>	<b>0</b>
	<b>Ti</b>	<b><math>8.0 \times 10^{-5}</math></b>	<b>0</b>
Tl II 190.852 BEC = 0.14 $\mu\text{g ml}^{-1}$ $C_L = 4.0 \text{ ng ml}^{-1}$	Al	$3.6 \times 10^{-4}$	$4.3 \times 10^{-4}$
	Ca	0	0
	Fe	$2.0 \times 10^{-5}$	$5.3 \times 10^{-4}$
	Mg	0	0
	Ti	$2.6 \times 10^{-4}$	$8.8 \times 10^{-4}$
Tl II 190.876 BEC = 0.24 $\mu\text{g ml}^{-1}$ $C_L = 7.0 \text{ ng ml}^{-1}$	Al	$5.6 \times 10^{-4}$	$8.4 \times 10^{-4}$
	Ca	0	0
	Fe	$4.0 \times 10^{-4}$	$6.9 \times 10^{-4}$
	Mg	0	0
	Ti	$4.0 \times 10^{-4}$	$1.5 \times 10^{-3}$
<b>Tl I 276.787</b> <b>BEC = 0.54 <math>\mu\text{g ml}^{-1}</math></b> <b><math>C_L = 15.0 \text{ ng ml}^{-1}</math></b>	<b>Al</b>	<b><math>1.0 \times 10^{-5}</math></b>	<b>0</b>
	<b>Ca</b>	<b><math>1.0 \times 10^{-5}</math></b>	<b>0</b>
	<b>Fe</b>	<b><math>1.4 \times 10^{-4}</math></b>	<b>0</b>
	<b>Mg</b>	<b><math>2.5 \times 10^{-4}</math></b>	<b>0</b>
	<b>Ti</b>	<b><math>4.5 \times 10^{-5}</math></b>	<b>0</b>
U II 385.958 BEC = 0.05 $\mu\text{g ml}^{-1}$ $C_L = 1.4 \text{ ng ml}^{-1}$	Al	0	0
	Ca	$5.0 \times 10^{-5}$	0
	Fe	$5.2 \times 10^{-4}$	$6.2 \times 10^{-4}$
	Mg	$7.0 \times 10^{-5}$	0
	Ti	$5.5 \times 10^{-5}$	0

**Table 9** (continued)

Analytes, wavelengths, $\lambda$ , nm	Interferents	$Q_{WJ}(\Delta\lambda_a)$	$Q_{IJ}(\lambda_a)$
U II 367.007 BEC = 0.05 $\mu\text{g ml}^{-1}$ $C_L = 1.4 \text{ ng ml}^{-1}$	Al	0	0
	Ca	$5.0 \times 10^{-5}$	0
	Fe	$5.0 \times 10^{-5}$	$6.0 \times 10^{-4}$
	Mg	$7.0 \times 10^{-5}$	0
	Ti	$5.5 \times 10^{-5}$	0
U II 263.553 BEC = 0.09 $\mu\text{g ml}^{-1}$ $C_L = 2.6 \text{ ng ml}^{-1}$	Al	$5.0 \times 10^{-5}$	0
	Ca	0	0
	Fe	$1.0 \times 10^{-4}$	$5.0 \times 10^{-4}$
	Mg	0	0
	Ti	$1.0 \times 10^{-4}$	$5.0 \times 10^{-3}$
<b>U II 409.014</b> <b>BEC = 0.2 <math>\mu\text{g ml}^{-1}</math></b> <b><math>C_L = 6.1 \text{ ng ml}^{-1}</math></b>	<b>Al</b>	<b><math>1.0 \times 10^{-4}</math></b>	<b>0</b>
	<b>Ca</b>	<b>0</b>	<b>0</b>
	<b>Fe</b>	<b>0</b>	<b>0</b>
	<b>Mg</b>	<b>0</b>	<b>0</b>
	<b>Ti</b>	<b>0</b>	<b>0</b>

(i) The  $S_{IJ}(\lambda_a)$  and  $S_{WJ}(\Delta\lambda_a)$  values increase with increasing  $T_{exc}$  in the presence of iron or aluminium as interferents (Tables 5 and 7);

(ii) The magnitude of  $Q_{IJ}(\lambda_a)$  and  $Q_{WJ}(\Delta\lambda_a)$  values (Tables 6 and 8) depends on the enhancement factor of  $S_A$  (Table 3) and  $S_{IJ}(\lambda_a)$  or  $S_{WJ}(\Delta\lambda_a)$ , respectively (Tables 5 and 7):

- if  $S_{A(2)}(\lambda_a) / S_{A(1)}(\lambda_a) > S_{IJ(2)}(\lambda_a) / S_{IJ(1)}(\lambda_a)$  and  $S_{A(2)}(\lambda_a) / S_{A(1)}(\lambda_a) > S_{WJ(2)}(\Delta\lambda_a) / S_{WJ(1)}(\lambda_a)$ ,

then  $Q_{IJ(2)}(\lambda_a) / Q_{IJ(1)}(\lambda_a) < 1$  and  $Q_{WJ(2)}(\Delta\lambda_a) / Q_{WJ(1)}(\Delta\lambda_a) < 1$  in the case of Tables 6 for Pt I 265.945 nm, B I 249.773 nm and Cd II 214.338 nm and Table 8 for As I 193.695 nm and Pt I 193.670 nm.

- if  $S_{A(2)}(\lambda_a) / S_{A(1)}(\lambda_a) \approx S_{IJ(2)}(\lambda_a) / S_{IJ(1)}(\lambda_a)$  and  $S_{A(2)}(\lambda_a) / S_{A(1)}(\lambda_a) \approx S_{WJ(2)}(\Delta\lambda_a) / S_{WJ(1)}(\lambda_a)$ ,

then  $Q_{IJ(2)}(\lambda_a) / Q_{IJ(1)}(\lambda_a) \approx 1$  and  $Q_{WJ(2)}(\Delta\lambda_a) / Q_{WJ(1)}(\Delta\lambda_a) \approx 1$  in the case of Table 6 for Tl II 190.852 nm and U II 385.958 nm and Table 8 for Tl II 190.852 nm.

- if  $S_{A(2)}(\lambda_a) / S_{A(1)}(\lambda_a) < S_{IJ(2)}(\lambda_a) / S_{IJ(1)}(\lambda_a)$  and  $S_{A(2)}(\lambda_a) / S_{A(1)}(\lambda_a) < S_{WJ(2)}(\Delta\lambda_a) / S_{WJ(1)}(\lambda_a)$ ,

then  $Q_{IJ(2)}(\lambda_a) / Q_{IJ(1)}(\lambda_a) > 1$  and  $Q_{WJ(2)}(\Delta\lambda_a) / Q_{WJ(1)}(\Delta\lambda_a) > 1$  presented in Table 6 for Hg I 194.277 nm and Zn I 213.856 nm.

It should be noted that the increase of Q-values at  $T_{exc} \approx 7200 \text{ K}$  is insignificant. This factor is equal to 1.1 in Table 6 for Zn I 213.856 nm and U II 385.958 nm and Table 8 for Tl II 190.852 nm.

The main result from the investigations is that  $T_{exc} \approx 7200 \text{ K}$  is an appropriate excitation

temperature for determination of traces of elements in environmental samples. The results show that the lowest detection limits in the determination of traces of elements in environmental materials can be obtained under robust operating conditions (Mg II / Mg I = 11.4, which corresponds to  $T_{exc} \approx 7200 \text{ K}$ ).

*3.1.2.3. Line selection at  $T_{exc} \approx 7200 \text{ K}$ .* The prominent lines of analytes, which are investigated in the present paper, are listed Table 9 (column 1). The data presented under the wavelength of the analysis lines refer to detection limits in pure solvent calculated in accordance with Eq. (4). Column 2 gives matrix elements, columns 3 and 4 show  $Q_{WJ}(\Delta\lambda_a)$  values for wing background interference and  $Q_{IJ}(\lambda_a)$  values for line interference, respectively. It should be noted that  $Q_{WJ}(\Delta\lambda_a)$  values do not enter into the selectivity term in Eq. (3) and affect the true detection limits only via the conventional detection limits (Eq. 2). This implies that the influence of  $Q_{WJ}(\Delta\lambda_a)$  values is minor or negligible, as long as  $C_{L, true}$  is dictated by line interference, i.e. by the magnitude of  $Q_{IJ}(\lambda_a)$  values in the presence of a complex matrix. Hence, the optimum line selection for trace analysis in a variety of multi-component environmental materials without information regarding the concentration of the matrix constituents (Al, Ca, Fe, Mg and Ti) requires the choice of prominent lines free or negligibly influenced by line interference. The selected prominent lines in the presence of complex matrix are printed in bold.



Discussing the results shown in Table 9 it can be seen that in the case of a multi-component matrix containing Al, Ca, Fe, Mg and Ti in the determination of As, Zn, Pt, B, Hg Cd, Tl and U it is not possible to choose the most prominent lines in accordance with the detection limits in pure solvent as analysis lines because these lines are influenced by line interferences, i.e.  $\Sigma Q_{II}(\lambda_a) > 0$ . In this case the second prominent lines of mercury, arsenic and zinc were free of line interferences, i.e.  $\Sigma Q_{II}(\lambda_a) = 0$  for Hg I 253.652 nm, As I 189.042 nm and Zn II 202.548 nm and were selected as analysis lines. The fourth prominent line of uranium U II 409.014 nm and the third thallium Tl I 276.787 nm were free of line interferences. These lines were selected as analysis lines. For cadmium and platinum no prominent lines free of line interference could be selected. For these elements the following prominent lines were selected as analysis lines: the second prominent line of cadmium (Cd II 214.438) for which  $\Sigma[Q_{IAI}(\lambda_a) + Q_{ICa}(\lambda_a) + Q_{IMg}(\lambda_a) Q_{ITi}(\lambda_a)] = 0$ , but  $Q_{IFe}(\lambda_a) > 0$  - and the fifth prominent line of platinum Pt I 265.945 nm for which  $\Sigma[Q_{IAI}(\lambda_a) + Q_{ICa}(\lambda_a) + Q_{IMg}(\lambda_a) Q_{ITi}(\lambda_a)] = 0$  and  $Q_{IFe}(\lambda_a) > 0$ .

With respect to “zero” values of  $Q_{II}(\lambda_a)$  values, we will note the following in accordance with [13]: if in Table 3  $Q_{II}(\lambda_a)$  are listed as “zero”, this implies that  $Q_{II}(\lambda_a) \times C_{II}$  is equal to or smaller than the numerical values of the detection limits (in ng ml<sup>-1</sup>) shown in Table 3 under the corresponding prominent line.

By using  $Q_{II}(\lambda_a)$  values and detection limits in pure solvent (Table 9) the maximal interferent concentration  $C_{II}$  for which  $Q_{II}(\lambda_a) = 0$  in the presence of matrix constituents can be calculated by equation (5) [13]:

$$C_{II} = C_L / Q_{II}(\lambda_a) \quad (5)$$

Table 10 lists the maximal interferent concentrations  $C_{II}$  for which  $Q_{II}(\lambda_a) = 0$  in the presence of aluminium, iron or titanium as interferents (Eq. 5). These matrix constituents determine line interference levels around the most prominent lines of the analytes in accordance with Table 9. The “best” prominent lines are printed in bold. If the concentration of interferents in the sample solution is lower in comparison with the corresponding values shown in Table 10, the most prominent lines can be used as analysis lines. Therefore, Table 10 can be used for additional line selection.

**Table 10.** Maximum interferent concentration  $C_{II}$  ( $\mu\text{g ml}^{-1}$ ) for which  $Q_{II}(\lambda_a) = 0$

Analysis lines, $\lambda$ , nm	Maximum interferent concentration $C_{II}$ ( $\mu\text{g ml}^{-1}$ ) for which $Q_{II}(\lambda_a) = 0$		
	Al	Fe	Ti
As I 193.695	0.80	-	-
<b>As I 189.042</b>	-	-	-
As I 197.198	0.34	24.0	-
<b>As I 200.334</b>	-	-	-
Zn I 213.856	-	140	350
<b>Zn II 202.548</b>	-	-	-
Pt I 203.646	-	0.82	106
Pt II 214.423	35	216	-
Pt I 217.467	6	210	-
Pt I 193.670	2	620	4330
<b>Pt I 265.945</b>	-	2000	-
B I 249.773	-	100	-
B I 249.678	-	112	-
<b>B I 208.959</b>	-	-	-
Hg II 194.277	-	200	105
<b>Hg I 253.652</b>	-	-	-
Cd II 226.502	-	18	-
<b>Cd II 214.438</b>	-	<b>85</b>	-
Tl II 190.852	5.0	6.0	5.0
Tl II 190.876	8.0	10.0	5.0
<b>Tl I 276.787</b>	-	-	-
U II 385.958	-	2.0	-
U II 367.007	-	2.0	-
U II 263.553	-	5.0	1.2
<b>U II 409.014</b>	-	-	-

In conclusion it should be noted that the “best” analysis lines can be used in the determination of the above mentioned trace elements in environmental materials. The optimal operating conditions are shown (Table 2). By using the “best” analysis lines the lowest possible detection limits can be achieved in the presence of the above mentioned matrix constituents. If the concentration of interferents in the sample solution is lower in comparison with the corresponding values shown in Table 10, the most prominent lines in pure solvent can be used as analysis lines in the determination of As, Zn, Pt, B, Hg, Cd, Tl and U in environmental materials with various matrix constituents. Quantification of all significant interferences for the prominent lines ensures the accuracy of measurements by ICP - OES.

### 3.2. Application of ICP-OES in the determination of As, Zn, Pt, B, Hg, Cd, Tl and U in environmental materials

3.2.1. Determination of As, Zn, Hg, Cd and U in the certified reference material IAEA/ Soil 7. a) Digestion procedure. Extraction of trace elements soluble in *aqua regia* was used as a decomposition method in accordance with ISO 11466 [22]. 1 g sample was dissolved and the final solution was

collected in 50 ml volume. After the undissolved material has settled, the supernatant solution was subjected to analysis by ICP - OES. The blank sample contains the acids used for digestion.

b) Determination of matrix elements. The concentrations of Al, Ca, Fe, Mg and Ti are as follows: Al – 660 ± 6 (in µg ml<sup>-1</sup>), Ca – 3160 ± 25 (in µg ml<sup>-1</sup>), Fe – 500 ± 6 (in µg ml<sup>-1</sup>), Mg – 210 ± 5 (in µg ml<sup>-1</sup>) and Ti – 9.6 ± 0.5 (in µg ml<sup>-1</sup>). Mean values for statistical confidence P = 95 % and six replicates (n =6) are obtained.

c) Determination of As, Zn, Hg, Cd and U. Table 11 shows the contents of As, Zn, Hg, Cd and U obtained by ULTIMA 2 ICP - OES in the analysis of the certified reference material IAEA /

Soil 7, as well as the relative standard deviation (RSD %) and the corresponding certified values. Using Student's criterion [25], no statistical differences between the experimental values and certified values were registered. In this way the accuracy of the analytical results can be ensured.

The “best” analysis lines of As, Zn, Hg and U are free of line interferences and true detection limits are equal to conventional detection limits ( $C_{L, true} = C_{L, conv}$ ) (column 3). The conventional detection limits were calculated in the presence of the matrix constituents Al, Ca, Fe, Mg and Ti in the final sample solution by Eq. 2. In case of Cd, the “best” line was influenced by line interference  $Q_{II}(\lambda_a) > 0$  and  $C_{L, true}$  was calculated by Eq.3.

**Table 11.** Contents of As, Zn, Cd, Hg and U (µg g<sup>-1</sup>) obtained in the analysis of certified reference material IAEA / Soil 7: 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); detection limits in the presence of above mentioned matrix constituents (µg g<sup>-1</sup>) (column 3); relative standard deviation (RSD %) (columns 4); certified values (column 5); maximum permissible concentrations for soils (column 6)

Selected prominent lines, λ, nm	Concentration µg g <sup>-1</sup> X ± ΔX	True detection limits, µg g <sup>-1</sup>	RSD, %	Certified values, µg g <sup>-1</sup>	Maximum permissible concentrations for soils in µg g <sup>-1</sup>
As I 189.042 BEC = 0.15 µg ml <sup>-1</sup> C <sub>L</sub> = 4.3 ng ml <sup>-1</sup>	13.2 ± 0.4	C <sub>L, true</sub> = C <sub>L, conv</sub> = 1.58	4.2	13.4	15 ÷ 22 [23]
Zn II 202.548 BEC = 0.06 µg ml <sup>-1</sup> C <sub>L</sub> = 1.7 ng ml <sup>-1</sup>	103 ± 1.4	C <sub>L, true</sub> = C <sub>L, conv</sub> = 0.23	1.8	104	150 ÷ 300 [23]
Hg I 253.652 BEC = 0.07 µg ml <sup>-1</sup> C <sub>L</sub> = 2 ng ml <sup>-1</sup>	The element is not detected.	C <sub>L, true</sub> = C <sub>L, conv</sub> = 0.58	-	0.04	1 ÷ 1.5 [23]
Cd II 214.438 BEC = 0.06 µg ml <sup>-1</sup> C <sub>L</sub> = 1.7 ng ml <sup>-1</sup>	1.27 ± 0.06	C <sub>L, true</sub> = 0.62	4.7	1.3	1 ÷ 3 [23]
U II 409.014 BEC = 0.2 µg ml <sup>-1</sup> C <sub>L</sub> = 6.1 ng ml <sup>-1</sup>	2.62 ± 0.1	C <sub>L, true</sub> = C <sub>L, conv</sub> = 0.75	3.8	2.6	0.3 ÷ 11.7 [24]

### 3.2.2. Determination of platinum in certified reference material BCR-723 (road dust).

a) Digestion procedure: Extraction of traces of Pt by acid mixture (HBr /HNO<sub>3</sub>) in an apparatus, described in [ISO 11466:1995 (E)] was used for digestion of the certified reference material BCR-723 (road dust). 1 g sample was dissolved and the final solution was collected in 100 ml volume.

b) Determination of matrix elements. The concentrations of Al, Ca, Fe, Mg and Ti are as follows: Al – 220 ± 6 (in µg ml<sup>-1</sup>), Ca – 550 ± 10 (in µg ml<sup>-1</sup>), Fe – 350 ± 8 (in µg ml<sup>-1</sup>), Mg – 250 ± 6 (in µg ml<sup>-1</sup>) and Ti – 9.0 ± 0.5 (in µg ml<sup>-1</sup>). Mean

values for statistical confidence P = 95 % and six replicates (n =6) are shown.

c) Determination of platinum. The true detection limit for Pt was 19 times higher in comparison with the certified value in the certified reference material BCR-723 - road dust (Table 12). Hence this concentration cannot be detected by direct ICP-OES (without separation or pre-concentration procedure).

The improvement of the detection limits in the determination of Pt in environmental materials by ICP - OES was achieved by developing a new column method with 2-mercaptobenzimidazole immobilized on activated carbon for separation of the matrix elements Al, Ca, Fe, Mg and Ti and pre-concentration of platinum. The interest in activated

carbons is determined by their unique properties such as large specific surface area, strongly

developed micro porosity and the possibility to modify their surface and texture [26 – 32].

**Table 12.** Contents of Pt ( $\mu\text{g g}^{-1}$ ) obtained in the analysis certified reference material BCR-723 mean values [X] for ( $n = 4$  replicates) (column 2); detection limits in the presence of above mentioned matrix constituents ( $\mu\text{g g}^{-1}$ ) (column 3); and certified values (column 5)

Selected prominent lines, $\lambda$ , nm	Concentration $\mu\text{g g}^{-1}$ $X \pm \Delta X$	True detection limits, $\mu\text{g g}^{-1}$	RSD, %	Certified values, $\mu\text{g g}^{-1}$
Pt I 265.945 BEC = $0.50 \mu\text{g ml}^{-1}$ $C_L = 14.0 \text{ ng ml}^{-1}$	The element is not detected	$C_{L \text{ true}} = 1.54$	–	0.0813

**Table 13.** Detection limits with respect to the dissolved solid sample, in  $\mu\text{g g}^{-1}$  in the determination of Pt in certified reference material BCR-723, concentration of Pt in  $\mu\text{g g}^{-1}$ , RSD of the analytical results and certified values in  $\mu\text{g g}^{-1}$

Analysis line, $\lambda$ , nm	Detection limits, $\mu\text{g g}^{-1}$	Concentration, in $\mu\text{g g}^{-1}$	RSD, %	Certified values, $\mu\text{g g}^{-1}$
Pt II 203.646	0.0033	$0.0809 \pm 0.005$	3.0	0.0813

*2-mercaptobenzimidazole* modified activated carbon was prepared by the following steps: first step: the activated carbon was heated in a furnace at  $600^\circ\text{C}$  for 3 h in inert atmosphere. Then the sample was cooled down to room temperature in argon; second step: 3 g of activated carbon were heated for 1 h at  $200^\circ\text{C}$  in vacuum, whereupon 10 ml of a 2 wt % solution of *2-mercaptobenzimidazole* in ethanol were added and the mixture was allowed to stand at  $20^\circ\text{C}$  for 2 h to facilitate better penetration of the modifier into the pores of the activated carbon. Then the solvent was evaporated at  $90 - 100^\circ\text{C}$ . This procedure was repeated three times. The modified carbon was washed with distilled water and 1M HCl until attaining a constant pH value of the washing water, and then dried at  $100^\circ\text{C}$  for 6 h.

The optimal parameters of the new column method were: column with bore = 3 mm, length = 9 mm, amount of activated carbon = 0.4 g, flow rate of the solution =  $4 \text{ ml min}^{-1}$ , pH = 1, concentrations of matrix elements were 10 times lower in comparison with the corresponding values shown in Table 4. The column was washed with 0.1 HCl. The experiments were carried out at room temperature. Under these experimental conditions, 100 % of platinum was sorbed on the activated carbon immobilized with *2-mercaptobenzimidazole*. The column with activated carbon was dried in a drying-oven at  $90^\circ\text{C}$ . The activated carbon was transferred to a quartz crucible and the sample was heated at  $450^\circ\text{C}$  (1 h) and  $850^\circ\text{C}$  (1 h) in a furnace; the quartz crucible was allowed to cool slowly at room temperature and after that the

crucible was put into the reaction flask of an apparatus, described in ISO 11466:1995 (E); an acid mixture  $\text{HNO}_3/\text{HBr}$  (3 ml  $\text{HNO}_3 + 3 \text{ ml HBr}$ ) was used for dissolution of the so prepared residue; the sample was heated under reflux until boiling for 1 h and allowed to cool slowly at room temperature. The final sample solution was 10 ml.

The column method with *2-mercaptobenzimidazole* immobilized on activated carbon was applied for pre-concentration/ separation in the determination of Pt in the certified reference material BCR - 723 (road dust.) The final sample solution was introduced into the ICP using an ultrasonic nebulizer (Courtesy of Cetac Technologies, Omaha, Nebraska, USA). Table 13 shows the detection limits in the determination of Pt with respect to the dissolved solid sample, in  $\mu\text{g g}^{-1}$  (column 2) by using the above pre-concentration/separation procedure, the content of Pt in the certified reference material BCR-723, obtained by ICP - OES (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 3), as well as the RSD of the analytical results (column 4). Column 5 lists the certified values for comparison. By using the above mentioned pre-concentration/separation procedure the spectral interferences were totally eliminated and the most prominent line Pt II 203.646 nm in pure solvent was used as analysis line. The results obtained by the present pre-concentration / separation method and following ICP-OES determination agree well with the certified values of the reference material BCR-723

and can be successfully used in the determination of platinum in environmental materials.

3.2.3. Determination of As, Zn, Cd, Tl and U in National Water Research Institute (NWRI) certified standard, lake water TMDA-51.2.

**Table 14.** Determination of As, Zn, Cd, Tl and U in National Water Research Institute (NWRI) certified standard, lake water TMDA-51.2

Selected prominent lines, $\lambda$ nm	Concentration $\text{ng ml}^{-1}$ $X \pm \Delta X$	Detection limits in pure solvent, $\text{ng ml}^{-1}$	RSD, %	Certified values, $\text{ng ml}^{-1}$	Maximum permissible concentrations for drinking waters ( $\text{ng ml}^{-1}$ ) [33]
As I 193.695	$15.4 \pm 0.4$	3.0	2.6	15.3	10
Zn I 213.856	$107 \pm 3$	1.4	2.8	106	5 000
Cd II 226.502	$24.8 \pm 0.5$	1.4	2.0	25.1	5
Tl II 190.852	$19.8 \pm 0.6$	4.0	3.0	20.0	No data
U II 385.958	$30 \pm 1.0$	1.4	3.3	29.3	60
Al	-	-	-	96.0	-
Fe	-	-	-	111.0	-

The concentrations of As, Zn, Cd, Tl and U in NWRI certified standard, lake water - TMDA-51 are collected in Table 14: the results are obtained by ICP - OES, JY ULTIMA 2 equipment (column 2) ( $n = 6$  replicates); detection limits for the analytes in pure solvent (column 3); relative standard deviation (RSD, %) (column 4) and corresponding certified reference values (column 5). It should be noted that the line interference level for the most prominent lines of As, Zn, Cd, Tl and U is determined by aluminium and iron as interferents (Table 9). The concentrations of the interferents in the NWRI certified standard are  $C_{\text{Al}}$  (certificate) =  $0.096 \mu\text{g ml}^{-1}$  and  $C_{\text{Fe}}$  (certificate) =  $0.111 \mu\text{g ml}^{-1}$ , respectively. These concentrations are lower than the corresponding values for which  $Q_{\text{I Al}}(\lambda_a) = 0$  and  $Q_{\text{I Fe}}(\lambda_a) = 0$  (Table 9). Therefore, the most prominent lines of As, Zn, Cd, Tl and U with  $Q_{\text{II}}(\lambda_a) = 0$  can be used for determination of these elements and the detection limits are equal to the values obtained in pure solvent (column 3). The background can be corrected by a simple off-peak background measurement.

The results obtained by the present ICP-OES method agree well with the corresponding certified values. The detection limits obtained by JY ULTIMA 2 satisfy the requirements from the point of view of maximum permissible concentrations for drinking waters [33].

## CONCLUSIONS

This work shows that in the analysis of complex environmental materials, quantitative information on the spectral interferences is

essential. The Q-concept, as proposed by Boumans and Vrakking [15], was used for quantification of the spectral interferences in the presence of Al, Ca, Fe, Mg and Ti as interferents. By using a spectrometer with a practical spectral bandwidth of 5 pm it is possible to select the “best” analysis lines for As, Zn, B, Hg, Tl and U, which are free of line interferences in the presence of a complex environmental matrix. The “best” prominent lines for Pt and Cd were influenced by line interference (Table 9). The results of Table 11 illustrate the correct background subtraction in the determination of As, Zn, Cd, Hg and U in the analysis of the certified reference material IAEA / Soil 7. Extraction of trace elements in *aqua regia* was used as a dissolution method.

Comparison of the detection limits (Table 11, column 3) by using 40.68 MHz ICP JY ULTIMA 2 with the corresponding maximum permissible concentrations for soils in  $\mu\text{g g}^{-1}$  shows that the detection limits are significantly lower in comparison with the given threshold levels. Therefore, this method can be successfully used for real contaminations in soil samples.

The determination of platinum in road dust requires the application of a separation / pre-concentration procedure for improvement of the detection limit. In the present paper a new column method with 2-mercaptopbenzimidazole immobilized on activated carbon was developed for separation of matrix elements Al, Ca, Fe, Mg, Ti and pre-concentration of platinum. The results obtained by the present pre-concentration/separation method and following ICP - OES determination show that this method can be successfully used in the determination of platinum in environmental materials (Table 13).



The detection limits obtained by JY ULTIMA 2 satisfy the requirements from point of view of maximum permissible concentrations for drinking waters [33] (Table 14).

#### REFERENCES

1. P.W.J.M. Boumans, Basic concepts and characteristics of ICP - AES, in: Boumans (eds.), Inductively Coupled Plasma Emission Spectroscopy - Part 1, Methodology, Instrumentation, and Performance, John Wiley & Sons, New York, US, 1987, p. 100, Chapter 4.
2. P.W.J.M. Boumans, *Fresenius Z. Anal. Chem.*, **324**, 394 (1986).
3. J. Dennaud, A. Howes, E. Poussel, J.M. Mermet, *Spectrochim. Acta Part B*, **56**, 101 (2001).
4. M. Stepan, P. Musil, E. Poussel, J.M. Mermet, *Spectrochim. Acta Part B*, **56**, 443 (2001).
5. G.C.Y. Chan, W.T. Chan, X. Mao, R.E. Russo, *Spectrochim. Acta Part B*, **56**, 77 (2001).
6. G.C.Y. Chan, G.M. Hieftje, *Spectrochim. Acta Part B*, **61**, 642 (2006).
7. P. Razpotnik, B. Budić, M. Veber, *Appl. Spectrosc.*, **56**, 1000 (2002).
8. G.C.Y. Chan, W.T. Chan, *Spectrochim. Acta Part B*, **58**, 1301 (2003).
9. I. Kolibarska, S. Velichkov, N. Daskalova, *Spectrochim. Acta Part B*, **63**, 603 (2008).
10. P. Petrova, S. Velichkov, I. P. Havezov, N. Daskalova, *Bulg. Chem. Commun.*, **41**, 65 (2009).
11. P. Petrova, S. Velichkov, N. Velitchkova, I. Havezov, N. Daskalova, *Spectrochimica Acta Part B*, **65**, 130 (2010).
12. J.W. McLaren, Applications: Environmental, in: P.W.J.M. Boumans (ed.), Inductively Coupled Plasma Emission Spectroscopy, Part 2: Applications and Fundamentals, Chapter 3, Wiley, New York, 1987, p. 48.
13. N. Velitchkova, S. Velichkov, N. Daskalova, *Spectrochim. Acta Part B*, **62**, 386 (2007).
14. N. Daskalova, L. Aleksieva, G. Gentsheva, S. Velichkov, *Spectrochim. Acta Part B*, **57**, 755 (2002).
15. P.W.J.M. Boumans, J.J.A.M. Vrakking, *Spectrochim. Acta Part B*, **43**, 69 (1988).
16. P.W.J.M. Boumans, Introduction to atomic emission spectrometry, in: P.W.J.M. Boumans (eds.) - Inductively Coupled Plasma Emission Spectroscopy - Part 1, Methodology, Instrumentations and Performance, John Wiley & Sons, New York, US, 1987, Chapter 1, p. 1
17. J.M. Mermet, Spectroscopic diagnostics: basic concepts, in: P.W.J.M. Boumans (eds.), Inductively Coupled Plasma Emission Spectroscopy - Part 1, Methodology, Instrumentation and Performance, John Wiley & Sons, New York, US, 1987, Chapter 10, p. 353.
18. M.W. Blades, G. Horlick, *Spectrochim. Acta Part B*, **36**, 861 (1981)
19. G.R. Harrison, M.I.T. Wavelength Tables, M.I.T. Press, Cambridge, MA, 1969.
20. A.N. Zaidel, V.K. Prokofëv, S.M. Raiskii, V.A. Slavnyi, E.Ya. Shreider, Tables of spectral lines, IFI / Plenum, New York, 1970.
21. P.W.J.M. Boumans, Line Coincidence Tables for inductively coupled plasma atomic emission spectrometry, Pergamon, Oxford, 1980.
22. International Organization for Standardization, Soil Quality, Extraction of Trace Elements Soluble in Aqua Regia, ISO 11466, 1995.
23. Maximum permissible concentrations of potentially toxic elements in sludge-treated soils (mg kg<sup>-1</sup> dry soil) in EC Member States and US, Millieu, WRC and RPA, 2010.
24. S.C. Sheppard, M.I. Sheppard, M. Gallerand, B. Sanipelli, *J. Environ. Radioactivity*, **79**, 55 (2005).
25. K. Doerffel, Statistik in der Analytischen Chemie, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1960.
26. K.Jankowski, A. Jackowski, P.Łukasiak, *Analytica Chimica Acta*, **540**, 197 (2005).
27. H.H. Someda, R.R. Sheha, *Radiochemistry*, **50**, 56 (2008).
28. B. Miķuła, B. Puzio, *Talanta* **71**, 136 (2008).
29. M.Ghaedi, A. Shokrollahi, A.H. Kianfar, A.Pourfarokhia, N. Khanjaria, A.S. Mirsadeghia, M. Soylak, *Journal of Hazardous Materials*, **162**, 1408 (2009).
30. A.A. Ensafi, T. Khayamian, M. Karbasi, *Analytical Sciences* **19**, 953 (2003).
31. A.C. Ferreira, M.A. Korn, S.L.C. Ferreira, *Microchim. Acta*, **146**, 271 (2004).
32. G. Gentsheva., P. Vasileva, P. Tzvetkova, L. Lakov, O. Peshev, E. Ivanova, *J. Porous Mater.*, **15**, 331 (2008).
33. Regulation No. 9, /2001, Quality Requirements for Drinking waters.

## ОПРЕДЕЛЯНЕ НА As, Zn, Pt, V, Hg, Cd, Tl И U В ПРОБИ ОТ ОКОЛНАТА СРЕДА ЧРЕЗ ОПТИЧНА ЕМИСИОННА СПЕКТРОМЕТРИЯ С ИНДУКТИВНИ СВЪРЗАНА ПЛАЗМА С РАДИАЛНО НАБЛЮДЕНИЕ И ВИСОКО РАЗДЕЛЯНЕ

Н. Величкова<sup>1</sup>, О. Велева<sup>1</sup>, С. Величков<sup>2</sup>, П. Марков<sup>2</sup>, Н. Даскалова<sup>2\*</sup>

<sup>1</sup> *Геологически институт, Българска академия на науките, Акад. Г. Бончев, бл. 24, 1113 София*

<sup>2</sup> *Институт по обща и неорганична химия, Българска академия на науките, Акад. Г. Бончев, бл. 11, 1113 София*

Постъпила на 24 септември 2012 г.; приета на 10 февруари 2013 г.

(Резюме)

Показани са възможностите и ограниченията на оптичната емисионна спектроскопия с радиална 40.68 МНz индуктивно свързана плазма и спектрометър с високо разделяне при определяне на As, Zn, Pt, V, Hg, Cd, Tl и U в проби от околната среда. Подобряване на границите на откриване е постигнато чрез оптимизирането на работните условия. Най-ниски граници на откриване бяха получени при твърди работни условия (температура за възбуждане около 7200 К) както в присъствие на чист разтворител, така и в присъствие на Al, Ca, Fe, Mg или Ti като комплексна матрица за пробите от околната среда. Границите на откриване за As, Zn, V, Hg, Cd, Tl и U задоволяват изискванията за максимално допустими концентрации за почви и питейни води. Подобряването на границите на откриване при определяне на платина в пътен прах беше постигнато чрез разработване на нов колонен метод с активен въглен, имобилизиран с 2-меркаптобензимидазол за отделяне на матричните компоненти и концентриране на платината.