A METHOD FOR DETERMINATION OF TOXIC AND HEAVY METALS IN SUSPENDED MATTER FROM NATURAL WATERS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES). PART I. DETERMINATION OF TOXIC AND HEAVY METALS IN SURFACE RIVER WATER SAMPLES

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ABSTRACT

This investigation will be carried out in two parts. Part one will be including the determination of toxic and heavy metals in surface river water samples, and part two – on the rainwater samples. Investigations were carried out on the determination of toxic and heavy metals (Ba, Cr, Cu, Zn, Cd, Mn and Pb) of surface river waters. The direct current arc spectrographic method (D.C. arc – AES) was used for semiquantitative analysis to establish the concentration levels of determined elements. The measurements were carried out with Inductively Coupled Plasma Atomic Emission Spectrometry after filtration. The detection limits in ICP – AES for the analysis elements were between 0.12 to 54 ng ml^{-1}. The accuracy of the proposed procedure for 10 replicates calculated as the relative standard deviation (RSD) in sample solution was between 0.8 to 7.5 %. The method was successfully applied for determination of barium, chromium, copper, zinc, cadmium, manganese and lead in surface river water samples.

Keywords: D.C. arc – AES, ICP - AES, environment, toxic and heavy metals, river water samples.

INTRODUCTION

The first of two methods for determination of toxic and heavy metals in surface river water samples is described. During the recent years than 30 elements, considered to be clinically important, have been divided in three groups [1]:

1. Elements substantial for the biological functions of the organisms: Ca, Cr, Cu, F, Fe, I, Mn, Mo, Se, Sr, Sn, V and Zn;

2. Elements, which are not essential, but still they are in the therapy: Al, Au, B, Bi, Co, Ge, Li and Pt;

3. Toxic elements: Ag, As, Ba, Be, Cd, Hg, Ni, Pb, Sb, Te, Tl.

This classification is only loosely defined in view of the fact that some toxic elements (such as As and Pb) are also used for therapeutical purposes. On the other hand grouping the elements into substantial in view of the biological functioning of the organisms is also a subject of discussion [2]. The elements, which are toxic, when present in higher concentrations, could be very useful in smaller amounts. Any essential element in excess could become toxic (for example Cu, Fe and Se). The toxic properties of the elements, studied in the present work, their harmful influence upon the people and on the objects from the surrounding environment, as well as the sources polluting the environment are being widely discussed in the current literature [3-6]. A number of important review papers detailing new approaches for determination of different elements in a wide range of environmental matrices, including information on the analysis of water have been published [7, 8]. The instrumental methods for determination are needed from combine high sensitivity with high accura-

cy, i.e. small risk of systematic errors. For determination of trace elements in environmental materials (natural and waste waters, sediments, air particulate) and in agricultural elemental analysis (soils, plant materials, food, fertilizers, animal tissues) modern science used different instrumental methods: Flame Atomic Absorption Spectrometry (FAAS), Electrothermal Atomic Absorption Spectrometry (ETAAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Instrumental Neutron Activation Analysis (INAA), Cold Vapor Atomic Absorption Spectrometry (CVAAS). Less common techniques such as Glow Discharge and Laser-Induced Breakdown Spectrometry have been used in the analysis of gaseous species [9-14].

ICP-AES is a powerful method for determination of trace levels because of its high sensitivity, selectivity, precision and accuracy. The application of ICP-AES to water quality monitoring is now widespread [14], but the major problems are spectral interferences and their influence on the detection limits and accuracy of analytical results.

A detailed experimental study of spectral interferences in ICP-AES in the analysis of a variety of complex environmental materials has been shown in our previous paper. Spectral data for aluminium, calcium, magnesium, iron, titanium, potassium and sodium as interferens in 400 pm wide windows, centered ($\pm$ 200 pm) around the prominent lines of As, B, Ba, Be, Cd, Cr, Cu, Hg, Mn, P, Pb, Sb, Se, Sn, Tl, U and Zn, and database of Q-values for line interferences [$Q_l(\lambda_a)$] and for wing background line interferences [$Q_w(\Delta\lambda_a)$] were shown [15]. The Q-concept, as proposed by Boumans and Vrakking, was used for the quantification of the spectral interferences [16, 17]. The Direct Current Arc spectrographic method (D.C. arc – AES) was used before ICP – AES for semiquantitative analysis for establishing the levels of determined elements. The purpose of this work is to demonstrate the possibilities of ICP - AES by using a database of Q-values [15] in the determination of Ba, Cr, Cu, Zn, Cd, Mn and Pb in surface river water samples as independent instrumentation method. The experiments show that both methods are simple and convenient to use.

EXPERIMENTAL

Instrumentation

The D.C. arc – AES measurements were performed by a spectrograph model PGS – 2 (Carl Zeiss – Jena), equipped with a ruled grating 650 grooves mm^{-1} and λ - blaze 570 nm. Registered spectra were in the second order. D.C. power generator was used for spectra excitation in electrodes RW – 0, Ringsdorf. Electrode shape: crater 3.5 mm diameter, 4.0 mm depth (the electrode with sample set as anode), half – sphere (upper electrode), Electrode spacing: 4 mm; Amount of sample: 10 mg; Spectral plates: WU – 2 (ORWO). The next wavelengths were used for analysis: Ba I 307 159 pm; Cr II 283 563 pm; Cu I 324 754 pm; Zn I 328 233 pm; Cd I 326 106 pm; Mn II 293 930 pm; Pb I 283 306 pm.

A sequential ICP spectrometer model JY 38 (Jobin Yvon, France) was used. It was equipped with a Czerny – Turner monochromator with a holographic grating 2400 grooves mm^{-1}, wavelength range 170 - 700 nm (first order), dispersion 0,38 nm mm^{-1}, practical spectral bandwidth 15,6 pm; RF generator Plasma - Therm, model HFP, 1500 D with power output of 1.0 kW at 27,12 MHz; Concentric type Meinhard nebulizer. The measurements were carried out under follow conditions: outer argon flow rate 15 l min^{-1}, carrier gas flow rate 0.5 l min^{-1}, liquid uptake rate 1,3 ml min^{-1}, excitation temperature of ICP plasma: 7200 K.

Reagents

Reagents of the highest purity grade were used: Nitric acid (65% HNO_3), Suprapur, Merck; Perchloric acid (70% $HClO_4$), Suprapur, Merck; Sulfuric acid (95% H_2SO_4), Suprapur, Merck; Carbon powder with high purity (RW-0, Ringsdorf - Werke GmbHMehlem); Tridistilled water from a quartz apparatus was used; Polytetrafluorethylen laboratory wares were used throughout.

Sampling

Sampling is the first, very important and the most critical stage of the analysis because it is responsible for the smaller and/or the larger sources of systematic errors [18]. The samples from surface river water were collected in a polytetrafluoroethylene (PTFE) wares, and

Table 1. Contents of the analytes Ba, Cr, Cu, Zn, Cd, Mn and Pb in surface river water samples and relative standard deviation (RSD) % obtained by D. C. arc – AES.

Analysis lines, pm	Concentrations (in %)			RSD, %
	Samples			
	1	2	3	
Ba I 307 159	$n \times 10^{-4}$	$n \times 10^{-4}$	$n \times 10^{-4}$	>6
Cr II 283 563	$n \times 10^{-5}$	$n \times 10^{-5}$	—[a]	>6
Cu I 324 754	$n \times 10^{-5}$	$n \times 10^{-5}$	$n \times 10^{-4}$	>6
Zn I 328 233	$n \times 10^{-5}$	$n \times 10^{-5}$	$n \times 10^{-4}$	>6
Cd I 326 106	—[b]	—[b]	—[b]	
Mn II 293 930	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-6}$	>6
Pb I 283 306	—[c]	—[c]	—[c]	

Where: $n = 1 \div 9$

[a] Element is not found. Detection limit is 1×10^{-5};

[b] Element is not found. Detection limit is 1×10^{-4};

[c] Element is not found. Detection limit is 5×10^{-4}.

filtered immediately after sampling through a cellulose acetate membrane filters with 0.45 µm pore size prior to the measurement by Inductively Coupled Plasma Atomic Emission Spectrometry. Nitric acid was added to the samples in order to hold up pH < 2. Cellulose acetate membrane filters were used because they have very low levels of determined elements, low blank sample and good promising. The filters were carefully washed with nitric acid and rinsed with tridistilled water after their application in according to International Standard ISO 8288:1986 (E). All samples were collected, pretreated and delivered for analysis from Southwest University "N. Rilski" Blagoevgrad.

Sample pretreatment

The subsequent sample pretreatment depends on the type of the natural water and on the purpose of the investigation.

• **Filtration.** To separate the suspended matter from the water, the first step is filtration. To avoid contamination from dust in the ambient atmosphere, a closed system is needed for filtration. A cellulose acetate membrane filter with 0.45 µm pore size is used. Heavy metals retained on the filters are dissolved by the follow schemes:

• **Digestion of suspended matter**. The filtered-off suspended matter is digested together with the filter. The wet digestion procedure can be applied to all types of biological and organic materials.

Procedure 1: The digestion is carried out with 10 ml concentrated nitric (65% HNO_3) and 0.5 ml concentrated perchloric (70% $HClO_4$) acid mixture, heated on a water bath to 80°C for at least 45 min. The solution is removed from the water bath and allowed to cool at room temperature. After cooling the final content is transferred quantitatively to a 25 ml graduated flask and filled up to the mark with 0.5 mol l^{-1} HNO_3. The solutions are introduced for analysis in ICP – AES.

Procedure 2: A cellulose acetate membrane filter was placed in a ZrO_2 crucible and 5 ml of a 9:1 HNO_3/H_2SO_4 acid mixture was added. The sample was heated on a sand bath until white SO_3 vapors and almost to dry. After cooling to room temperature, 0.04 g of powdered carbon (RW-0, Ringsdorf-Werke GmbH-Mehlem) is added and the capped crucible was calcinated in the muffle oven at 480°C. This temperature was maintained of about 90 min. (for chromium determination only). The direct heating of the cellulose acetate membrane filter in the presence of 9:1 HNO_3 / H_2SO_4 up to 480°C leads to losses of chromium. At this tem-

perature chromium Cr (VI) volatilized as CrO_2Cl_2 [19]. The carbon powder was used for both avoiding of the losses and as a collector [20].

The cooled and homogenized samples were analyzed to D.C. arc-Atomic Emission Spectrometry.

Blank samples

In procedure 1 the blank sample containing the acids used for digestion and unused cellulose acetate membrane filter was prepared by the same way.

In procedure 2 the matrix blank containing unused cellulose acetate membrane filter, acid mixture and carbon powdered was prepared by the same way.

Calibration procedure

A stock standard solution of all the analytes Ba, Cr, Cu, Zn, Cd, Mn and Pb with concentration 1000 µg ml^{-1} were prepared from Titrisol (Merck). The single element solutions of each of the analytes Ba, Cr, Cu, Zn, Cd, Mn and Pb with concentrations 1, 5 and 10 µg ml^{-1}, respectively, was prepared from stock solutions by dilution with tridistilled water.

RESULTS AND DISCUSSION

D.C. arc - AES method

The direct current arc spectrographic method with photograph registration of the spectra as a method for analysis of solid samples for the determination of the level concentration semiquantitatively was used. The specifications of the spectrograph, D.C. power generator and operating conditions for the direct spectral determination of Ba, Cr, Cu, Zn, Cd, Mn and Pb in samples 1-3 are listed above. The filters were acid digestions (Procedure 2). The concentrations of the analytes are shown in Table 1. The D.C. arc - AES method is characterized with a relative standard deviation (RSD > 6%).

ICP − AES Method

Spectral interferences

The spectral interferences are a major problem in concentration measurement of toxic and heavy metals by ICP - AES, because the excitation temperature is high and this leads to appearance of many spectral lines. In case of multicomponent matrix it is possible the prominent line of the detected element to be overlapped

with the line and/or wing of line of some of the matrix components. The qualitative information about the type of spectral interferences was derived from wavelength scans centered around the prominent line. The scans were made in a scanning mode of the spectrometer with an x/y recorder, type T5C (Jobin Yvon) [15]. For the quantitative valuation of spectral interferences we applied Q-concept of Boumans and Vrakking [21]. In according to this concept $Q_{Ij}(\lambda_a)$ – values for line interference and $Q_{Wj}(\Delta\lambda_a)$ – values for wing background interference for each of the above mentioned interferents were distinguished.

Measurement of Q − Values

$Q_{Ij}(l_a)$ – values are expressed as the ratio

$$\frac{S_{Ij}(\lambda_a)}{S_A},$$

where:

$S_{Ij}(\lambda_a)$ is the sensitivity of the interfering line defined as the signal per unit interferent concentration;

S_A is the sensitivity of the analysis line (signal per unit analyte concentration).

$Q_{Wj}(Dl_a)$ values are expressed as the ratio

$$\frac{S_{Wj}(\Delta\lambda_a)}{S_A},$$

where: $S_{Wj}(\Delta\lambda_a)$ is the wing sensitivity of the interfering line in the spectral window $\Delta\lambda_a$; S_A is as stated above. The measurement of Q – values was presented in previous our paper [15].

Line selection

The optimum line selection of trace of elements requires the choice of the prominent lines free or negligibly influenced by line interference, i.e. $[Q_{Ij}(\lambda_a) = 0]$. The "best" analysis lines of analytes: Ba, Cr, Cu, Zn, Cd, Mn and Pb in the presence of complex matrix, $Q_{Wj}(\Delta\lambda_a)$ – values for wing background interference and $Q_{Ij}(\lambda_a)$ – values for line interference in the presence of 2 mg ml^{-1} Al, Ca, Fe, Mg and Ti, respectively, as interferents are given in Table 2.

Table 2. $Q_W(\Delta\lambda_a)$ and $Q_I(\lambda_a)$ values in the presence of complex matrix.

Analysis lines, pm	Interferent elements	$Q_W(\Delta\lambda_a)$	$Q_I(\lambda_a)$
Ba II 455 403	Al	0	0
	Ca	9.0×10^{-6}	0
	Fe	0	0
	Mg	4.5×10^{-5}	0
	Ti	2.6×10^{-6}	0
Cr II 267 716	Al	0	0
	Ca	1.2×10^{-5}	0
	Fe	6.7×10^{-5}	0
	Mg	3.7×10^{-5}	0
	Ti	1.2×10^{-5}	2.7×10^{-5}
Cu I 324 754	Al	0	0
	Ca	0	0
	Fe	0	0
	Mg	0	0
	Ti	4.1×10^{-5}	4.3×10^{-5}
Zn II 202 548	Al	1.4×10^{-4}	0
	Ca	2.2×10^{-4}	0
	Fe	9.8×10^{-5}	0
	Mg	3.1×10^{-4}	0
	Ti	1.2×10^{-4}	0
Cd II 214 438	Al	0	0
	Ca	1.3×10^{-4}	0
	Fe	6.0×10^{-4}	0
	Mg	0	0
	Ti	8.5×10^{-4}	0
Mn II 257 610	Al	4.7×10^{-6}	0
	Ca	5.5×10^{-6}	0
	Fe	1.1×10^{-5}	0
	Mg	9.5×10^{-6}	0
	Ti	4.7×10^{-6}	0
Pb II 220 353	Al	9.7×10^{-4}	4.0×10^{-4}
	Ca	5.3×10^{-3}	0
	Fe	4.1×10^{-4}	0
	Mg	4.5×10^{-4}	0
	Ti	5.2×10^{-4}	5.5×10^{-5}

These data can be used for:

a) The determination of the true detection limits by using Eq. (2);

b) Calculation of the interfering background signals [$\sum BEC_{Ij} + \sum BEC_{wj}$] under the prominent analysis lines.

Detection limits

By use of the $Q_{Wj}(\Delta\lambda_a)$ and $Q_{Ij}(\lambda_a)$ values, the conventional detection limits ($C_{L,conv.}$) and the true detection limits ($C_{L,true}$) for a complex matrix obtained by ICP-AES can be calculated according to:

$$C_{L,conv.} = 2\sqrt{2} \times 0.01 \times RSDBL \times [BEC + \sum_J Q_{Ij}(\lambda_a) \times C_{Ij} + \sum_J Q_{Wj}(\Delta\lambda_a) \times C_{Ij} =$$
$$= 2\sqrt{2} \times 0.01 \times RSDBL \times$$
$$\times [BEC + \sum_J BEC_{Ij} + \sum_J BEC_{Wj}] \qquad (1)$$

$$C_{L,true} = \frac{2}{5} \sum Q_{Ij}(\lambda_a) \times C_{Ij} + C_{L,conv} =$$
$$= \frac{2}{5} \sum_J BEC_{Ij} + C_{L,conv} \qquad (2)$$

The detection limit in the pure solvent (or dilute acid) is defined by Eq. (3):

$$C_L = 2\sqrt{2} \times 0.01 \times RSDBL \times BEC \qquad (3)$$

For calculation of the conventional ($C_{L,conv.}$) and the true ($C_{L,true}$) detection limits the determination of matrix elements in the cases of multicomponent matrix is needed. In Table 3 are shown concentrations of the matrix elements. Conventional detection limits $C_{L,conv.}$ (in ng ml^{-1}) and the same detection limits with respect to the dissolved solid (in µg g^{-1}) are shown in Table 4.

Effect of the cellulose acetate membrane filter as the matrix on the analyte line and background intensities

The analytical signal (including the acids used for digestion and unused cellulose acetate membrane filter) is equal with the analytical signal of tridistilled water. Hence, the effect of blank filter is significant on the net signal and background intensities.

Analysis of surface river water samples

Three samples from surface river water from three points in reserve "Parangalitza", Blagoevgrad region (Bulgaria), were collected by the following scheme (Fig 1):

Table 3. Content of Al, Ca, Fe, Mg and Ti in water filtrates (µg ml^{-1}).

Analysis lines, pm	Concentrations (in µg ml^{-1})					
	Sample 1		Sample 2		Sample 3	
	$\overline{X}$	$\overline{X}_1$	$\overline{X}$	$\overline{X}_1$	$\overline{X}$	$\overline{X}_1$
Al I 237 324	70		88		68	
		71		86		71
Al I 394 401	72		84		74	
Ca I 422 673	470		500		480	
		460		495		470
Ca II 315 887	450		490		460	
Fe II 238 204	70		86		78	
		73		83		81
Fe II 239 562	76		80		84	
Mg II 279 806	38		46		50	
		39		49		49
Mg II 285 213	40		52		48	
Ti II 334 941	4.6		5.2		4.0	
		4.5		5.0		4.1
Ti II 336 121	4.4		4.8		4.2	

where $\overline{X}$ is the mean of two replicates; $\overline{X}_1$ is the mean values of two concentrations obtained by using two analysis lines of each analyte.

Table 4. Conventional detection limits $C_{L,conv.}$ (ng ml^{-1}) and the same detection limits with respect to the dissolved solid (in µg g^{-1}).

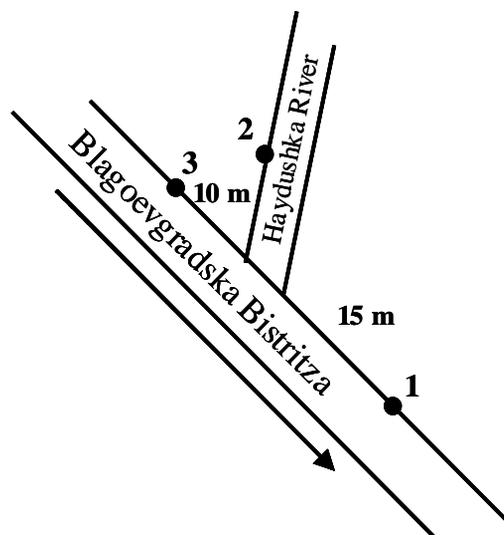| Sample №	"Best analysis lines" pm	$C_{L,conv.}$ (ng ml^{-1})	$C_{L,conv.}$ (µg g^{-1})
1	Ba II 455 403	5.70	0.28
2		6.40	0.32
3		5.90	0.30
1	Cr II 267 716	24	1.20
2		28	1.40
3		26	1.30
1	Cu I 324 754	2.0	0.10
2		2.50	0.125
3		2.20	0.11
1	Zn II 202 548	46	2.30
2		54	2.70
3		48	2.40
1	Cd II 214 438	44	2.20
2		50	2.50
3		46	2.30
1	Mn II 257 610	0.12	0.03
2		0.20	0.01
3		0.18	0.09
1	Pb II 220 353	11	0.55
2		18	0.90
3		13	0.65

Fig.1. Scheme of the points for sampling.
1. River "Blagoevgradska Bistritza" - at the exit of the preserve (at point, situated at 15 m after the flowing of river "Hajdushka");
2. River "Hajdushka", left tributary of river "Blagoevgradska Bistritza" (at point, situated at 10 m before the flowing of river "Hajdushka" into river "Blagoevgradska Bistritza");
3. River "Blagoevgradska Bistritza" (at 10th m. at Nord before the flowing of river "Hajdushka" into river "Blagoevgradska Bistritza").

Table 5. Measurement concentrations for Ba, Cr, Cu, Zn, Cd, Mn and Pb in surface river water samples, standard deviation (SD) and relative standard deviation (RSD) % obtained by ICP – AES (n = 5, P = 95%).

Analysis lines, pm	Concentrations (in ng ml^{-1})			RSD, %
	Samples			
	1	2	3	
Ba II 455 403	100 ± 6.0	100 ± 6.0	100 ± 6.0	6.0
Cr II 267 716	40 ± 7.5	78 ± 5.1	—[a]	$5.1 \div 7.5$
Cu I 324 754	63 ± 4.8	50 ± 6.0	700 ± 0.8	$0.8 \div 6.0$
Zn II 202 548	40 ± 7.8	67 ± 4.5	120 ± 5.0	$4.5 \div 7.8$
Cd II 214 438	—[b]	—[b]	—[b]	
Mn II 257 610	3 ± 3.3	3 ± 3.3	3 ± 3.3	3.3
Pb II 220 353	—[c]	—[c]	—[c]	

[a] Element is not found. Detection limit is 12 ng ml^{-1};

[b] Element is not found. Detection limit is 8 ng ml^{-1};

[c] Element is not found. Detection limit is 37 ng ml^{-1};

The collection was achieved in a polytetrafluorethylen wares. After suitable pretreatment (Procedure 1) the samples were introduce in ICP - AES. Results are shown in Table 5.

CONCLUSIONS

The two procedures of digestion of suspended matter in surface river water samples were experimentally demonstrated by using the both methods D.C. arc – AES and ICP – AES for determination of toxic and heavy metals (Ba, Cr, Cu, Zn, Cd, Mn and Pb). The Q – concept proposed by P. W. J. M. Boumans and J. J. A. M. Vrakking ensures a possibility for quantification of the spectral interferences in the multicomponent samples, as well as calculation of the detection limits.

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