Quantitation of Toxic Elements in Various Water Samples by Multi-element Graphite Furnace Atomic Absorption Spectrometry

Zsolt Ajtony^a, Nikoletta Laczai^b, Norbert Szoboszlai^c, and László Bencs^{a,b}

^a Institute of Food Science, University of West Hungary,
H-9200 Mosonmagyaróvár, Lucsony utca 15-17, Hungary

^b Institute for Solid State Physics and Optics, Wigner Research Centre for Physics,
Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

^c Laboratory of Environmental Chemistry and Bioanalytics, Department of Analytical Chemistry, Institute of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

ABSTRACT

A simultaneous, multi-element graphite furnace atomic absorption spectrometric method was developed for the determination of several toxic elements (As, Cd, Cr, Cu, Pb, and Se) in various water samples (snow, tap, well, and highly mineralized). The transversely heated graphite atomizer (THGA) with Zeeman-effect background (BG) correction was applied throughout the study. Two sets of analytes, i.e., Cr-Cu and As-Cd-Pb-Se, were simultaneously determined by using standard and end-capped THGA tubes, respectively. During the drying and pyrolysis stages of the furnace heating program, 5% H₂ was added to the internal furnace gas (Ar) in order to assist the action of the chemical modifiers, and to provide a prolonged lifetime of the THGA tubes.

The effect of chloride and sulfate interferents as well as the composition/amount of the Pd-Mg modifier was studied. Addition of SO₄²⁻ matrix even at a relatively low concentration (500 mg/L) caused a more significant decrease in recovery than with the Cl⁻ matrix, for instance, for As, Pb and Se, by applying low modifier amounts (5 µg Pd + 0.5 µg Mg).

The best limit of detection (LOD) values acquired for As, Cd, Cr, Cu, Pb, and Se were 0.85, 0.05, 0.22, 0.21, 0.35, and 0.44 µg/L, respectively. Each of these LOD data is at least one order of magnitude lower than the maximum allowable concentration of these elements in drinking water (as legislated by WHO). The correlation coefficients obtained from linear fits to the calibration points were always better than 0.999 for each analyte. The upper limit of the linear range of calibration for As, Cd, Cr, Cu, Pb, and Se was 100, 5, 20, 50, 100, and 100 µg/L, respectively. The characteristic mass (*m*₀) values were 21 pg As, 1.5 pg Cd, 3.8 pg Cr, 12 pg Cu, 28 pg Pb, and 36 pg Se.

The concentrations of As, Cd, Pb, and Se in the water/snow samples ranged from non-detectable up to 14.8, 0.07, 6.3, and 1.9 µg/L, respectively, with averages of 2.1, 0.037, 2.3 and 0.71 µg/L, respectively. The Cu and Cr content of the samples was in the range of 0.7–249 and 0.035–1.7 µg/L, respectively, with averages of 26.6 and 0.24 µg/L, respectively. In the snow samples, strong correlations of As, Cr, Cu, Pb, and SO₄²⁻ were found, but weak/anti-correlation with Cd and Se. The chloride content of snow was correlated with Se. These results show at least two sources of the studied elements in the atmosphere.

INTRODUCTION

Exact measurement of the elemental content of natural and industrial wastewater samples is of general concern and has been studied in analytical laboratories worldwide (1-10). The release/presence of toxic elements in natural waters, and the subsequent uptake and accumulation in aquatic biological systems as well as in the food chain, supports this need (11,12). Analytical problems arise from the fact that tracers/contaminants in waters vary over a large concentration range, i.e., from pg/L (e.g., fresh Arctic snow) to g/L (e.g., seawater) levels (11,12). This widely varying matrix constitution requires the application of instrumental analytical techniques with high sensitivity and selectivity for the determination of the elemental content in waters at trace/ultra-trace levels.

Current analytical techniques used for this particular analytical task include inductively coupled plasma atomic emission spectrometry (2,13), isotope dilution spark mass spectrometry (2), inductively coupled plasma mass spectrometry (10,14), and differential pulse anodic stripping voltammetry (15). Most of these techniques possess properly high sensitivity. However, they suffer from interferences and/or salt-out effects during the analysis of high saline water samples and, therefore, often require coupling to efficient separation techniques, such as ion exchange (2), chelation and solvent extrac-

* Corresponding author.
E-mail: bencs.laszlo@wigner.mta.hu
Tel.: +36 1 392 2222/1684
Fax: +36 1 392 2768

tion (2), flow injection mini-column pre-concentration (10,13-15). On the other hand, graphite furnace atomic absorption spectrometry (GFAAS) offers a unique alternative to solve this analytical task by providing the possibility of selective evaporation of matrix constituents whose presence could, otherwise, cause interference effects (16). Chemical modifiers can also assist in the evaporation of the matrix/sample components (17).

On the other hand, highly saline/mineralized waters with excessive chloride and/or sulfate content can cause an analytical challenge in GFAAS due to physical and chemical interference effects frequently encountered during the determination of analytes of low/medium volatility, even with a transversely heated graphite atomizer (THGATM) system by condensation at cooler sites of the atomizer and/or on matrix components (aerosols) in the gas phase (18,19). In order to overcome these interferences, application of the stabilized temperature platform furnace (STPFTM) conditions (20) is recommended as a general GFAAS method for trace element determinations in a heavy matrix. For instance, the STPF concept is reported for use with the GFAAS determination of As, Cd, Pb, and Se in highly mineralized waters (7) but is also used in connection with other matrices/analytes as is described below.

Several chemical modifiers were applied to the GFAAS determination of tracers in natural (21), drinking (22,23), surface (24), and highly mineralized (3-9,25,26) waters. For example, the Cr determination was performed using HNO₃ (9), NH₄VO₃ (25), Na₂MoO₄ (25,26), Na₂WO₄ (25,26), Pd(NO₃)₂ (5,25), Mg(NO₃)₂ (1,3,5,26), NH₄H₂PO₄ (8), ascorbic acid (5), oxalic acid (8), and for the Cd and/or Pb determination, NH₄H₂PO₄ (1,3,8),

Mg(NO₃)₂ (8). For volatile analytes (As, Se), Ir-Ru-W permanent modifier (21) and also various combinations of them were used. However, the universal modifier, Pd+Mg, applied as nitrate, has mostly been utilized and reported in connection with water analysis (4-7).

It is to be noted that due to the excellent sensitivity and the multi-element capability of some commercially available GFAAS systems (27-30), several papers report simultaneous GFAAS methods for the quantitation of trace elements in complex matrices, for instance, foodstuff (31), wine (32-34), honey (35), mineral water (36), seawater (37-40), aerosol (41), human brain (42), blood (43,44), and urine (45-48), Al-alloy (49), and optical crystal (50) samples.

The aim of the present work is to study the possibilities for the simultaneous, multi-element determination of a set of trace elements (As, Cd, Cr, Cu, Pb, and Se, most of them being toxic in biological systems) in various waters, such as tap, well, snow, and highly mineralized waters from Hungary. Another aim of this investigation is to study the chemical/physical interferences, which can often occur in connection with the GFAAS determination of the set of analytes concerned.

EXPERIMENTAL

Instrumentation

The GFAAS measurements were performed on a PerkinElmer® SIMAATM 6000 (PerkinElmer, Inc., Shelton, CT, USA) simultaneous atomic absorption spectrometer, equipped with a transversely heated graphite tube atomizer (THGATM), longitudinal Zeeman-effect background (BG) corrector, and a PerkinElmer AS-72 autosampler. This system along with the application of chemical modifiers provides STPFTM conditions. For the concurrent determination of As,

Cd, Pb, and Se, end-capped THGA graphite tubes (PerkinElmer Part No. B3 000653) were used, while for the simultaneous determination of Cu and Cr, standard THGA tubes (PerkinElmer Part No. B3 000641) were applied, each tube type is fit with an integrated, pyrolytically coated L'vov graphite platform. Sample and chemical modifier aliquots of 20 µL and 5 µL, respectively, were dispensed onto the platform. In general, high purity argon (5N) was applied as a furnace gas. In some experiments, 5% H₂ was added to the internal furnace gas (Ar) during the drying and pyrolysis stages of the furnace heating program in order to assist the decomposition of the matrix and the action of the chemical modifiers, and moreover, to provide a prolonged lifetime of the THGA tubes. The optimized graphite furnace heating program is listed in Table I.

For the determinations, the resonant lines of As 193.6 nm, Cd 228.8 nm, Cr 357.9 nm, Cu 324.8 nm, Pb 283.3 nm, and Se 196.0 nm were chosen to attain maximum sensitivity, each with a common spectral bandpass of 0.7 nm. The electrodeless discharge lamps (EDLs) of As, Cd, Pb, and Se were operated with a 380, 200, 450, and 290 mA working point current, respectively, in accordance with the manufacturer's recommendations (51). The hollow cathode lamp of Cr, which also served as a line source for Cu determination, was operated at 15 mA. The integrated absorbance (A_{int}) signals of As, Cd, Cr, Cu, Pb, and Se were measured with signal integration times set to 5, 3, 6, 5, 5, and 5 seconds, respectively. Each signal was corrected for non-specific BG absorption, i.e., the specific line absorption is used for data processing. Triplicate determinations ($n=3$) were performed for each sample/standard, and the data were used to calculate the average value and the

standard deviation (SD). Classic Student's *t*- and F-tests were applied for statistical evaluation of the analytical results. Bivariate correlation analysis at a two-tailed significance level (*p*) was applied using the IBM® SPSS Statistics software package (Version 20, IBM, USA) for calculating Pearson's correlation coefficients of the elemental concentrations.

Chemicals

All chemicals used were of analytical grade or better quality. Each standard/sample dilution was made in calibrated volumetric flasks by ultrapure, deionized Milli-Q™ water (Milli-Q RG, Millipore Corporation, USA) having a conductivity of 18 MΩ cm. Suprapur® grade. (65%) HNO₃ (Merck, Darmstadt, Germany) was applied to acidify and preserve the samples/standards at pH 2 until sample processing/analysis. All volumetric flasks, pipette tips, autosampler cups, and sample containers were washed in 1:1 dilution of HNO₃ and then rinsed several times with ultrapure water.

Preparation of Samples and Standards

Freshly and earlier deposited snow samples were collected from the top and middle sections of a 25-30 cm deep snow layer around the KFKI Campus (N 47°29'14.62" E 18°57'15.86", elevation: 417 m

ASL) and the nearby road, and at Normafa in the woods (N 47°30'09.36" E 18°57'56.16", elevation: 478 m ASL). Both sites are located on the Buda hills on the outskirts of Budapest (Hungary), at a distance of around 3.5 km from each other. From each site, three simultaneous, independent samples were taken. Tap water was collected in Budapest and Emőd (a town situated near the city of Miskolc, North Hungary, at N 47°56'17.11" E 20°48'56.21", elevation: 113 m ASL) by sampling in the morning and evening hours, each after running the cold tap at least for 5 minutes. Well water samples were drawn at Emőd, located in a valley near the slopes of the Bükk hills. Both wells are 10 m deep. One of them is a pumping well with iron piping, while the other is a regular, hand-dug well, cased with concrete rings. The samples were taken in mid-February, 2013. After sampling in pre-cleaned bottles, each sample was preserved at pH 2, being adjusted with addition of Merck Suprapur HNO₃ and preserved in a refrigerator at 4 °C until GFAAS analysis.

Standards were prepared by dilution of a PerkinElmer® GFAAS Mixed Standard stock solution containing 5 µg/mL Be and Cd; 10 µg/mL Ag; 20 µg/mL Cr, Fe, and Mn; 50 µg/mL Ba, Co, Cu, and Ni; and 100 µg/mL Al, As, Pb, Sb, Se, and Tl.

Chemical modifiers with various amounts were prepared via dilution of a PerkinElmer palladium modifier and/or Merck magnesium modifier stock solution, which contains 1.0 ± 0.02% (m/v) Pd in ca. 15% HNO₃ and 1.0 ± 0.02% (m/v) Mg in ca. 17% HNO₃, respectively. For recovery studies, each sample/standard was spiked with solutions of chloride and sulfate. The stock solutions of the interfering ions were prepared by weighing appropriate amounts of their corresponding sodium salts on a Model Sartorius TE214S (Sartorius AG, Göttingen, Germany) electronic analytical balance at a precision of ±0.001 g, then dissolving them in Milli-Q™ water and bringing to volume in calibrated volumetric flasks. The chloride and sulfate content of each water sample was determined by regular ion chromatography (IC) as described in detail elsewhere (52). The TMDA-51 fortified water sample (National Water Research Institute, Burlington, Ontario, Canada) was obtained through LGC Standards (Teddington, Middlesex, UK).

RESULTS AND DISCUSSION

Optimization of Graphite Furnace Program

The simultaneous GFAAS determination of analytes with diverse volatility requires the selection of compromise pyrolysis temperature (*T*_{pyr}) and atomization temperature (*T*_{at}). The most volatile analyte determines the maximum permissible *T*_{pyr}, while the most refractory analyte determines the minimum *T*_{at} required for complete vaporization of the set of analytes concerned. Chemical modifiers are generally used in GFAAS for matrix removal and thermal stabilization of analytes in the pyrolysis step (17). Moreover, the amount of modifier also has an influence on GFAAS sensitivity (53). Consequently, as a first step of this study, various composi-

TABLE I
Graphite Furnace Heating Program

Step	Temp. (°C)	Ramp Time	Hold Time	Internal Furnace Flow Rate (cm ³ min ⁻¹)	Furnace Gas Composition
Drying 1	130	1	50	250	Ar + 5% H ₂
Drying 2	200	10	20	250	Ar + 5% H ₂
Pyrolysis	700/800	1	20	250	Ar + 5% H ₂
Cooling	200	1	30	250	Ar
Atomization	2100/2200	0	5	0	Ar
Cleaning	2450	1	3	250	Ar

tions/amounts of chemical modifiers were tested. As an example, Figure 1 shows that Cd is not stabilized by 5 μg Pd modifier, nor 5 μg Pd + 0.5 μg Mg at T_{pyr} of higher than 700 $^{\circ}\text{C}$. Conversely, the addition of 16 μg Pd, or more addition of 1.6 μg or 10 μg Mg, exhibits an optimal T_{pyr} at 800 $^{\circ}\text{C}$. Similarly, the other volatile analytes were also tested over a wide T_{pyr} range of 200 to 1000 $^{\circ}\text{C}$ in order to find optimal (compromise) pyrolysis conditions for each analyte. It was found that for the rest of the analytes the pyrolysis curves developed a plateau section in the T_{pyr} range of 200-800 $^{\circ}\text{C}$ (curves not shown here). The optimized T_{pyr} and T_{at} values along with the applied composition/amount of chemical modifier are listed in Table II. For the medium volatile Cr and Cu, the pyrolysis and atomization curves are plotted in Figure 2. As can be seen, the maximum allowable T_{pyr} for Cu is 1100 $^{\circ}\text{C}$, while for Cr it is 1400 $^{\circ}\text{C}$ without using a chemical modifier. Consequently, for this set of analytes, the compromise T_{pyr} at 1100 $^{\circ}\text{C}$ was selected for the determinations as seen below. This T_{pyr} appeared to be high enough for the selective vaporization of interfering matrix constituents, i.e., chloride and sulfate salts, and is thus considered

optimal for the determinations even in highly mineralized waters.

Interference and Modifier Effects in Highly Mineralized Matrices

The effect of increasing the chloride concentrations and various compositions/amounts of the chemical modifiers on the absorbance signal of As and Se were studied (Figure 3). In these experiments, optimized T_{pyr} and T_{at} values were applied, i.e., 700/800 $^{\circ}\text{C}$ and 2200 $^{\circ}\text{C}$, respectively. As can be seen, the A_{int} signal of As does not change considerably within the error of the determinations. Only a slight increase of absorbance can

be spotted with the use of the highest amounts of Mg (i.e., 10 μg) added along with 5 μg Pd, which might be due to a highly structured BG absorption arising from the vaporization of excess amounts of MgO and/or MgCl. On the other hand, the A_{int} signal of Se shows a stepwise decrease at chloride concentrations higher than 100 mg/L. This chloride interference effect can be completely eliminated by increasing the amount of Mg modifier in the Pd-Mg mixture (Figure 3).

The effect of an increase in sulfate concentration and various compositions/amounts of chemical modifiers on the absorbance signal of As and Se was also studied (Figure 4). In these determinations, the same optimized T_{pyr} and T_{at} values were used as in the chloride interference studies noted above. Generally, the A_{int} signals of As and Se considerably decrease at increasing sulfate concentrations in the presence of low amounts of Mg modifier (0.5 μg). For Se, the trend is clear, i.e., a decreasing matrix effect with an increase in the amount of Mg is experienced. On the other hand, for the A_{int} signals of As, the change is not so obvious. The Pd-Mg modifier at low amounts (5 μg + 1.6 μg , respectively)

TABLE II
Optimal Pyrolysis and Atomization Temperatures Applied With Various Compositions of Chemical Modifiers for the Determination of As, Cd, Pb and Se

Chemical Modifier	T_{pyr} ($^{\circ}\text{C}$)	T_{at} ($^{\circ}\text{C}$)
5 μg Pd	600	2100
5 μg Pd + 0.5 μg Mg	700	2100
16 μg Pd	800	2200
16 μg Pd + 1.6 μg Mg	800	2200
16 μg Pd + 10 μg Mg	800	2200

Fig. 1. The effect of pyrolysis temperature on the integrated absorbance signal of 50 pg Cd with various compositions of chemical modifiers (T_{at} 2200 $^{\circ}\text{C}$).

Fig. 2. Pyrolysis curves for 320 pg Cu and 128 pg Cr without application of any chemical modifier (T_{at} 2300 $^{\circ}\text{C}$).

does not result in any decrease in the extent of interference. However, applying higher amounts of Mg (e.g., 1.6 μg) lead to the elimination of matrix interference up to 100 mg/L sulfate concentration. Above this concentration, the sulfate interference becomes significant, i.e., the signal decrease is larger than 10%.

Application of an increase in the amount of chemical modifier may also cause enhancement in the extent of BG absorption (53). Thus, a study is needed to estimate the increase in the non-specific BG on the concerned analytical lines of the analytes. Moreover, due to the higher matrix amount, introduced

even by “chemically inert” modifiers, physical interference effects can be encountered and amplified (18,19). The integrated BG absorption (BG_{int}) was measured with various modifier amounts and compositions (Figure 5). Here, we refer to the addition of 5 μg Pd or 5 μg Pd plus 0.5 μg Mg as the base case, where these modifier amounts only insignificantly increase the level of BG absorption ($BG_{\text{int}}=0.02\text{--}0.04$ s) on the resonant lines of the analytes. However, by using around triplicate amounts of Pd (16 μg) alone, or even adding it with low amounts of Mg (1.6 μg), can lead to an already 2–3 times higher BG absorption signal. In addition, the steepest increase of BG absorption (~ 50 -fold) is obtained by the addition of 10 μg Mg plus 16 μg Pd for each analyte. The highest BG increase is certainly experienced with As and Se, whose analytical lines are below 200 nm, being more close to the absorption edge of scattered solid particles.

Calibration and Analytical Performance

Calibration of the method was performed with the application of aqueous standards and addition of Pd-Mg modifier. By this method, the non-linearity problem of the calibration curves, encountered in the determination of volatile elements (Cd and Pb) (29) and medium volatile elements (e.g., Cu and Cr) (30) with standard THGA, can be effectively overcome. The use of end-capped THGAs also assists in the elimination of such double sloping anomaly of calibration (30).

The calibration data with various chemical modifier compositions/amounts are listed in Table III. As can be seen, the correlation coefficients (R) obtained from linear fits to the calibration points ($m=5$, $n=3$) are always better than 0.999 for each analyte. The upper limit of the linear range of calibration for

Fig. 3. Effect of the chloride concentration on the integrated absorbance signal of 1 ng As and 1 ng Se in the presence of 5 μg Pd + 0.5 μg Mg (T_{pyr} : 700 $^{\circ}\text{C}$, T_{ar} : 2100 $^{\circ}\text{C}$), 5 μg Pd + 1.6 μg Mg and 5 μg Pd + 10 μg Mg modifier (T_{pyr} : 800 $^{\circ}\text{C}$, T_{ar} : 2200 $^{\circ}\text{C}$).

Fig. 4. Effect of the sulphate concentration on the integrated absorbance signal of 1 ng As and 1 ng Se in the presence of 5 μg Pd + 0.5 μg Mg (T_{pyr} : 700 $^{\circ}\text{C}$, T_{ar} : 2100 $^{\circ}\text{C}$), 5 μg Pd + 1.6 μg Mg and 5 μg Pd + 10 μg Mg modifier (T_{pyr} : 800 $^{\circ}\text{C}$, T_{ar} : 2200 $^{\circ}\text{C}$).

As, Cd, Cr, Cu, Pb, and Se is 100, 5, 20, 50, 100, and 100 µg/L, respectively. The characteristic mass (m_0) values were also calculated for different chemical modifier compositions. As can be seen, an increase in modifier amount added to the standards does not considerably

influence the m_0 data. Slight improvement of m_0 can only be seen for As, Pb, and Se with the use of higher modifier amounts. On the other hand, for Cd the higher modifier amount increases (worsens) the m_0 values. These data are in line with those reported for the perfor-

mance of the SIMAA™ 6000 spectrometer fitted with end-capped THGA™ (51,54). Mini-flow conditions increased the m_0 values 1.2–1.6-fold, which is element dependent, i.e., 34 pg As, 2.1 pg Cd, 4.7 pg Cr, 15 pg Cu, 41 pg Pb, and 50 pg Se.

The limits of detection (LOD), corresponding to 3σ confidence, were obtained from replicate determinations ($n=11$) of acidified blanks also containing various modifier compositions and amounts (Table IV). It can be seen that the general trend for the chemical modifier amount is to slightly increase (worsen) the LOD values, which is possibly due to the higher fluctuations of the blank measurements in the presence of higher amounts of chemical modifier. Accordingly, the LOD values for As, Cd, Pb, and Se ranged between 0.85–1.9, 0.065–0.11, 0.35–0.9, and 0.44–1.3 µg/L, respectively, while they were around 0.2 µg/L for Cu and Cr. All these LOD data are well below the maximum allowable concentration of the studied elements in drinking water (Table IV) as legislated by WHO (1993).

The recovery data of water samples spiked with chloride and sulfate salts and various chemical modifier compositions and amounts are compiled in Table V. It can be seen that by increasing the chloride content, the recovery of the determinations worsened for some analytes, e.g., for Se significantly lower recoveries were found at 1000 mg/L Cl^- matrix than with 500 mg/L Cl^- . Interestingly, the recovery for Cd is also higher at lower matrix concentrations. However, the increase in the amount of Pd+Mg modifier decreases the recovery, likely due to physical interferences induced by co-vaporization of the higher amounts of chemical modifier. In general, recovery is considerably increased by the addition of higher modifier amounts.

Fig. 5. Effects of various chemical modifier compositions/masses on the integrated background absorbance signal of 50 pg Cd and 1 ng As, Pb and Se.

TABLE III
Analytical Performance Data
With Various Compositions of Chemical Modifiers

Analyte	Dynamic Range (µg/L)	Slope (s L/µg)	R	m_0 (pg)	Modifier Mass (Pd+Mg in µg)
As	100	0.00385	0.999	22.9	5 + 0.5
		0.00420	0.999	21.0	16 + 1.6
		0.00413	0.999	21.3	16 + 10
Cd	5	0.0589	0.999	1.49	5 + 0.5
		0.0540	1.000	1.63	16 + 1.6
		0.0541	1.000	1.63	16 + 10
Pb	100	0.00239	0.999	36.8	5 + 0.5
		0.00244	1.000	36.1	16 + 1.6
		0.00244	1.000	36.1	16 + 10
Se	100	0.00234	0.999	37.6	5 + 0.5
		0.00244	1.000	36.1	16 + 1.6
		0.00236	0.999	37.3	16 + 10
Cr	20	0.0229	0.9993	3.8	-
Cu	50	0.0074	0.9990	12	-

R - correlation coefficient of linear fitting; m_0 - characteristic mass.

Addition of SO_4^{2-} matrix even at relatively low concentrations (e.g., 500 mg/L) caused a more significant decrease in recovery than the Cl^- matrix, i.e., for As, Pb, and Se, by applying low modifier amounts (5 μg Pd + 0.5 μg Mg). A slight improvement in recovery was only experienced for Pb and Se when applying higher modifier amounts (16 μg Pd + 10 μg Mg). For the reference TMDA-51 fortified water samples, the recovery generally ranged where it is expected, e.g., for As, Pb, and Se between 103-115%, 97-100%, and 101-107%, respectively. Similarly, good recoveries were obtained for Cu and Cr (34) ranging from 93-106%.

Analysis of Water Samples

Typical water and snow samples with their quantified trace element, chloride and sulfate content are listed in Table VI. The chloride and sulfate concentrations in the samples cover a wide concentration range, i.e., from 0.9 to 501 mg/L and 0.7 to 465 mg/L, respectively. Specifically, the snow samples show rather fluctuating chloride content, between 0.7 and 501 mg/L, while their sulfate content is less fluctuating, i.e., near the 1-3 mg/L level. The tap water samples have fairly similar chloride and sulfate content, i.e., 24 and 30 mg/L, respectively. Not unexpectedly, the well water samples were found to have the highest mineral content with chloride and sulfate concentrations as high as 105-125 mg/L and 370-465 mg/L, respectively. These samples are the most challenging from the viewpoint of GFAAS analysis. Therefore, in order to verify the accuracy of the GFAAS determinations, the most saline samples (ST4, SM4, W1, and W2) were spiked with known amounts of the analytes (Table VII). Accordingly, the recovery for As, Cd, Cr, Cu, Pb, and Se ranged between 82-102, 85-93, 92-109, 87-93, 96-102, and 80-87%, respectively, all of

TABLE IV
Limit of Detection Data With the Application of Various Modifier Compositions

Modifier	LOD ($\mu\text{g/L}$)					
	As	Cd	Pb	Se	Cu	Cr
No modifier	-	-	-	-	0.21	0.22
5 μg Pd + 0.5 μg Mg	0.85	0.065	0.35	0.70	-	-
16 μg Pd + 1.6 μg Mg	1.8	0.050	0.9	0.44	-	-
16 μg Pd + 10 μg Mg	1.9	0.11	0.52	1.3	-	-
Max. allowable conc. ^a	10	3	10	10	2000 ^b	50

^a Guidelines for drinking water quality, WHO, April 1993.

^b WHO, Copper in drinking water, Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/88, 2004.

TABLE V
Recovery Data of As, Cd, Pb and Se in the Presence of Chloride and Sulfate Matrix With Various Modifier Compositions and in a Certified Reference Water Sample

Matrix	Recovery (%)				Modifier Mass (Pd+Mg in μg)
	As	Cd	Pb	Se	
500 mg/L Cl^-	100	97	101	90	5 + 0.5
	97	95	100	96	16 + 1.6
	100	91	102	98	16 + 10
1000 mg/L Cl^-	102	94	100	84	5 + 0.5
	98	94	98	96	16 + 1.6
	104	97	104	103	16 + 10
500 mg/L SO_4^{2-}	95	99	89	79	5 + 0.5
	98	89	82	76	16 + 1.6
	90	97	88	83	16 + 10
1000 mg/L SO_4^{2-}	91	99	79	68	5 + 0.5
	101	89	78	72	16 + 1.6
	92	96	86	80	16 + 10
TMDA-51 ^a	115	-	97	101	5 + 0.5
	115	-	99	107	16 + 1.6
	103	-	100	101	16 + 10

^a TMDA-51: certified reference water sample for elemental content (As: 14.4, Cd: 36.1, Pb: 66.6, Se: 9.86, all in $\mu\text{g/L}$); informative values (in mg/L): Cl^- : 5.8 ± 0.12 , SO_4^{2-} : 4.2 ± 0.01 determined by means of conventional IC as described in detail elsewhere (52).

which are acceptable results for the present analytical instrumentation and method.

The concentrations of As, Cd, Pb, and Se in the samples ranges from not detectable (n.d.) up to 14.8, 0.07, 6.3, and 1.9 $\mu\text{g/L}$,

respectively, with averages of 2.1, 0.037, 2.3, and 0.71 $\mu\text{g/L}$, respectively. A considerably increased As level was obtained only from one of the well water samples, with a concentration around 1.5 times higher than the maximum allowable As content of potable water (WHO,

TABLE VI
Average Concentration ($\pm$ SD) Data of As, Cd, Cr, Cu, Pb, Se, Cl⁻ and SO₄²⁻ in Various Water Samples

Sample I.D.	Sampling Site	Concentration (in $\mu\text{g/L}$ for Elements, in mg/L for Cl ⁻ and SO ₄ ²⁻) ^{a, b}							
		As	Cd	Pb	Se	Cu	Cr	Cl ⁻	SO ₄ ²⁻
ST1	Normafa (woods)	0.81 $\pm$ 0.06	0.034 $\pm$ 0.069	2.92 $\pm$ 0.2	n.d.	3.14 $\pm$ 0.07	1.48 $\pm$ 0.19	0.92 $\pm$ 0.04	1.4 $\pm$ 0.01
SM1	Normafa (woods)	0.73 $\pm$ 0.58	0.074 $\pm$ 0.009	2.08 $\pm$ 0.0	0.93 $\pm$ 0.82	2.59 $\pm$ 0.85	0.85 $\pm$ 0.12	0.70 $\pm$ 0.006	0.76 $\pm$ 0.05
ST4	Road, Buda-hills	2.26 $\pm$ 0.57	n.d.	2.40 $\pm$ 0.06	1.19 $\pm$ 0.32	3.99 $\pm$ 0.20	0.39 $\pm$ 0.02	341 $\pm$ 1	3.3 $\pm$ 0.03
SM4	Road, Buda-hills	1.76 $\pm$ 0.27	0.013 $\pm$ 0.026	2.15 $\pm$ 0.18	1.50 $\pm$ 0.27	2.64 $\pm$ 0.01	0.15 $\pm$ 0.01	501 $\pm$ 1.2	2.1 $\pm$ 0.005
ST9	KFKI Campus	0.92 $\pm$ 0.22	n.d.	2.11 $\pm$ 0.31	n.d.	3.20 $\pm$ 0.01	0.17 $\pm$ 0.00	14 $\pm$ 0.05	1.7 $\pm$ 0.005
SM9	KFKI Campus	0.38 $\pm$ 1.1	n.d.	1.42 $\pm$ 0.28	n.d.	1.68 $\pm$ 0.01	0.26 $\pm$ 0.00	5.9 $\pm$ 0.02	1.2 $\pm$ 0.003
TAMo1	Budapest, district VIII.	1.53 $\pm$ 3.19	0.017 $\pm$ 0.045	0.36 $\pm$ 0.35	n.d.	249 $\pm$ 8	0.17 $\pm$ 0.01	24 $\pm$ 0.05	29 $\pm$ 0.07
TAE1	Budapest, district VIII.	3.21 $\pm$ 1.0	0.011 $\pm$ 0.008	0.97 $\pm$ 0.12	1.90 $\pm$ 0.98	249 $\pm$ 6	0.22 $\pm$ 0.02	24 $\pm$ 0.02	31 $\pm$ 0.09
TAMo2	Emőd, N Hungary	2.79 $\pm$ 0.37	0.050 $\pm$ 0.02	0.53 $\pm$ 0.31	0.84 $\pm$ 0.76	64 $\pm$ 1	0.24 $\pm$ 0.01	24 $\pm$ 0.02	29 $\pm$ 0.07
TAE2	Emőd, N Hungary	2.73 $\pm$ 0.00	0.031 $\pm$ 0.003	1.11 $\pm$ 0.04	n.d.	147 $\pm$ 1	0.21 $\pm$ 0.01	24 $\pm$ 0.03	30 $\pm$ 0.08
W1	Emőd, N Hungary	14.8 $\pm$ 0.3	n.d.	n.d.	n.d.	7.6 $\pm$ 0.3	0.14 $\pm$ 0.01	125 $\pm$ 0.5	465 $\pm$ 0.2
W2	Emőd, N Hungary	2.95 $\pm$ 1.34	0.032 $\pm$ 0.013	0.11 $\pm$ 0.24	n.d.	3.67 $\pm$ 0.03	0.35 $\pm$ 0.01	105 $\pm$ 0.7	370 $\pm$ 0.12

Abbreviations: S – snow, T – top, M – middle, TA – tap, Mo – morning, E – evening, W – well.

^a – The As, Cd, Pb, and Se content of the samples was determined with the application of 5 μg Pd + 3 μg Mg, while the Cr and Cu content was determined without any modifier.

^b – Chloride and sulfate content was quantitated by conventional IC as described elsewhere (52).

TABLE VII
Spike Recovery Data for the most Saline Samples

Sample ^a	Recovery $\pm$ SD (%) ^b					
	Pb	As	Se	Cd	Cu	Cr
SM4	102.0 $\pm$ 2.9	100.9 $\pm$ 2.3	84.6 $\pm$ 7.1	93.2 $\pm$ 3.0	91.6 $\pm$ 2.9	94.0 $\pm$ 3.6
W2	96.2 $\pm$ 3.9	82.2 $\pm$ 5.9	80.4 $\pm$ 4.3	89.1 $\pm$ 3.2	87.3 $\pm$ 4.0	102.9 $\pm$ 2.9
ST4	100.3 $\pm$ 3.1	101.8 $\pm$ 3.4	87.3 $\pm$ 5.3	84.5 $\pm$ 3.5	90.6 $\pm$ 4.1	91.9 $\pm$ 4.3
W1	98.2 $\pm$ 3.0	82.7 $\pm$ 3.8	82.5 $\pm$ 4.5	91.8 $\pm$ 4.2	93.0 $\pm$ 4.3	109.4 $\pm$ 3.9

^a – Explanation and data on samples is indicated in Table VI.

^b – Spike concentrations: As, Pb, and Se: 10 $\mu\text{g/L}$; Cd: 0.5 $\mu\text{g/L}$; Cr: 2 $\mu\text{g/L}$; Cu: 5 $\mu\text{g/L}$.

see Table IV). This increased As concentration is due likely to the higher abundance of As in the upper layer of soil for this region. The outstandingly high As content in natural (well) waters is a general problem for several regions of Eastern Hungary, especially, in the plains where the soil is of high salinity. Though its compounds are hardly soluble in water, As can be easily mobilized, for instance, by acidic precipitation.

The Cu and Cr content of the studied water samples was in the range of 0.7-249 and 0.035-1.7 µg/L, respectively, with averages of 26.6 and 0.24 µg/L, respectively. An outstandingly high concentration was observed in the tap water samples, most likely due to the use of copper pipes. As it follows from Table VI, the As, Pb, Cr, and Cu content is generally higher at the top layer of snow, while the Se and Cd content frequently shows fluctuations, but they usually reach higher levels in the middle layer. The former set of elements likely originate from local traffic emissions, which exhibits their enrichment in the top snow layer through dry deposition of atmospheric particulates. On the other hand, Se and Cd also come from atmospheric pollution, but these elements may have other anthropogenic emission source(s). They possibly precipitate along with snow, but for sure, their lower enrichment on the top of the snow-pack is apparent and implies a lower degree of dry deposition rather than those of the other four elements studied. The bivariate correlation data of elements also support this assumption (Table VIII). It shows fairly strong correlations of As, Cr, Cu, and Pb, but their weak anti-correlation with Cd and Se, which points toward at least two sources of these sets of elements in the atmosphere. This assumption is also supported by the correlation data obtained between elements and ionic species of snow samples

TABLE VIII
Pearson's Correlation Coefficients Between Elements for Snow Samples (right-upper side) and the Number of Concentration Values Applied for the Calculations (left-bottom side)

	Pb	Cd	As	Se	Cu	Cr	Cl ⁻	SO ₄ ²⁻
Pb	1	-0.155	0.574 ^b	-0.129	0.776 ^b	0.714 ^b	0.049	0.731 ^b
Cd	14	1	-0.134	0.170	-0.323	-0.339	-0.525	-0.418
As	23	14	1	0.075	0.431 ^a	0.456 ^a	0.258	0.440 ^a
Se	10	7	10	1	-0.028	-0.182	0.652 ^a	-0.084
Cu	24	14	23	10	1	0.927 ^b	0.247	0.966 ^b
Cr	24	14	23	10	24	1	0.163	0.932 ^b
Cl ⁻	24	14	23	10	24	24	1	0.291
SO ₄ ²⁻	24	14	23	10	24	24	24	1

Note: ^a - correlation is significant at p=0.05 level,

^b - correlation is significant at p=0.01 level.

(Table VIII). For instance, the sulfate concentration of snow was fairly strongly correlated with As, Cr, Cu, and Pb, while the chloride content was correlated with Se. On the other hand, Cd was weakly anti-correlated with both ionic species.

CONCLUSION

The fast, simultaneous determination of two sets of elements, i.e., (a) Cr, Cu, (b) As, Cd, Pb, and Se, in highly mineralized waters can be accurately performed using the SIMAATM 6000 spectrometer with THGA furnace, Zeeman-effect background correction, and chemical modification, e.g., the application of all STPF conditions. Problems arise only during the analysis of waters with high salt content (e.g., chloride and/or sulfate), which considerably influences recovery of the analytes. An increase in Pd+Mg modifier amount can help to eliminate or at least decrease these negative effects on recovery, but in some instances reverse effects can be experienced, i.e., worsened recovery for some of the analytes and improvement for others. Nevertheless, the limit of detection of the method is well below the strictest limiting values of the European Union for potable waters, thus it provides a rugged method for

water analysis. The developed method can be adapted to the novel continuum source GFAAS, which is a multi-element technique for present day applications.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support from the Hungarian Scientific Research Fund (OTKA) under the project of K111635. The authors thank Willemien Anaf (Department of Chemistry, University of Antwerp) for her assistance in the IC measurements.

Received June 6, 2013.

REFERENCES

1. M.J. Fishman, G.R. Perryman, and L.R. Schroder, J. Assoc. Off. Anal. Chem. 69, 704 (1986).
2. R.E. Sturgeon, S.S. Berman, J.A.H. Desaulniers, A.P. Mykytiuk, J.W. McLaren, and D.S. Russell, Anal. Chem. 52, 1585 (1980).
3. Z. Grobowski, R. Lehmann, B. Radziuk, and U. Völlkopf, At. Spectrosc. 5, 87 (1984).
4. B. Welz, G. Schlemmer, and J.R. Mudakavi, J. Anal. At. Spectrom. 3, 695 (1988).

5. S.D. Huang, W.R. Lai, and K.Y. Shih, *Spectrochim. Acta Part B* 50, 1237 (1995).
6. G. Bozsai, and M. Melegh, *Microchem. J.* 51, 39 (1995).
7. G. Bozsai, G. Schlemmer, and Z. Grobowski, *Talanta* 37, 545 (1990).
8. U. Völlkopf, Z. Grobowski, and B. Welz, *At. Spectrosc.* 4, 165 (1983).
9. J.Y. Cabon, and A. Le Bihan, *Spectrochim. Acta Part B* 50, 1703 (1995).
10. K. Ndung'u, R.P. Franks, K. W. Buland, and A.R. Flegal, *Anal. Chim. Acta* 481, 127 (2003).
11. A. Vercruyse, (Ed.) *Hazardous Metals in Human Toxicology*, Elsevier, Amsterdam, The Netherlands, 1984, p. 337.
12. D.L. Tsalev, Z.K. Zaporinov, *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice: Determination of Individual Elements* (Ed. D.L. Tsalev), CRC Press, FL, USA, 1984. p. 252.
13. S. Hirata, Y. Umezaki, and M. Ikeda, *Anal. Chem.* 58, 2602 (1986).
14. D.B. Taylor, H.M. Kingston, D.J. Nogay, D. Koller, and R.J. Hutton, *J. Anal. At. Spectrom.* 11, 187 (1996).
15. H.E. Taylor, *A Summary of Methods for Water-quality Analysis of Specific Species*, In: (Eds. R.A. Minear and L.H. Keith), *Water Analysis*, Vol. 1. *Inorganic Species*, Part 1. Academic Press, New York, NY, USA, pp. 235-237 (1982).
16. B. Welz, M. Sperling, *Atomic Absorption Spectrometry*, 3rd edition, Wiley-VCH Verlag GmbH, Weinheim, Germany (1998).
17. D.L. Tsalev, V.I. Slaveykova, and P.B. Mandjukov, *Spectrochim. Acta Rev.* 13, 225 (1990).
18. W. Frech, N.P. Romanova, and B.V. L'vov, *Spectrochim. Acta Part B* 47, 1461 (1992).
19. W. Frech, and B.V. L'vov, *Spectrochim. Acta Part B* 48, 1371 (1993).
20. W. Slavin, D.C. Manning, and G.R. Carnrick, *At. Spectrosc.* 2, 137 (1981).
21. G.P.G. Freschi, C.D. Freschi, and J.A.G. Neto, *At. Spectrosc.* 27, 1 (2006).
22. V.R.A. Filho, K.G. Fernandes, M. de Moraes, and J.A.G. Neto, *At. Spectrosc.* 23, 7 (2002).
23. C.S. Nomura, P.R.M. Correia, P.V. Oliveira, and E. Oliveira, *J. Braz. Chem. Soc.* 15, 75 (2004).
24. M. Feuerstein and G. Schlemmer, *At. Spectrosc.* 20, 149 (1999).
25. J.L. Manzoori, and A. Saleemi, *J. Anal. At. Spectrom.* 9, 337 (1994).
26. S.C. Apte, S.D.W. Comber, M.J. Gardner, and A.M. Gunn, *J. Anal. At. Spectrom.* 9, 337 (1994).
27. B. Radziuk, G. Rödel, H. Stenz, H. Becker-Ross, and S. Florek, *J. Anal. At. Spectrom.* 10, 127 (1995).
28. B. Radziuk, G. Rödel, M. Zeiher, S. Mizuno, and K. Yamamoto, *J. Anal. At. Spectrom.* 10, 415 (1995).
29. M. Hoenig and A. Cilissen, *Spectrochim. Acta Part B* 52, 1443 (1997).
30. L. Bencs, O. Szakács, N. Szoboszlai, Zs. Ajtony, and G. Bozsai, *J. Anal. At. Spectrom.* 18, 105 (2003).
31. P.R.M. Correia, E. Oliveira, and P.V. Oliveira, *Anal. Chim. Acta* 405, 205 (2000).
32. G.P.G. Freschi, C.S. Dakuzaku, M. de Moraes, J.A. Nóbrega, and J.A.G. Neto, *Spectrochim. Acta Part B* 56, 1987 (2001).
33. K.G. Fernandes, M. De Moraes, J.A.G. Neto, J.A. Nóbrega, and P.V. Oliveira, *Analyst* 127, 157 (2002).
34. Zs. Ajtony, N. Szoboszlai, E.K. Suskó, P. Mezei, K. György, and L. Bencs, *Talanta* 76, 627 (2008).
35. Zs. Ajtony, L. Bencs, R. Harasz, J. Szigeti, and N. Szoboszlai, *Talanta* 71, 683 (2007).
36. V.R.A. Filho, K.G. Fernandes, M. de Moraes, and J.A.G. Neto, *J. Braz. Chem. Soc.* 15, 28 (2004).
37. P.G. Su and S.D. Huang, *Spectrochim. Acta Part B* 53, 699 (1998).
38. P.G. Su and S.D. Huang, *J. Anal. At. Spectrom.* 13, 641 (1998).
39. C.L. Chen, K.S.K. Danadurai, and S.D. Huang, *J. Anal. At. Spectrom.* 16, 404 (2001).
40. P.H. Lin, K.S.K. Danadurai, and S.D. Huang, *J. Anal. At. Spectrom.* 16, 409 (2001).
41. J.P. Pancras, J.M. Ondov, and R. Zeisler, *Anal. Chim. Acta* 538, 303 (2005).
42. E. András, S. Igaz, N. Szoboszlai, É. Farkas, and Zs. Ajtony, *Spectrochim. Acta Part B* 54, 819 (1999).
43. A. Viksna and E.S. Lindgren, *Anal. Chim. Acta* 353, 307 (1997).
44. P.R.M. Correia, P.V. Oliveira, J.A.G. Neto, and J.A. Nóbrega, *J. Anal. At. Spectrom.* 19, 917 (2004).
45. B.S. Iversen, A. Panayi, J.P. Cambor, and E. Sabbioni, *J. Anal. At. Spectrom.* 11, 591 (1996).
46. M.C. Hsiang, Y.H. Sung, and S.D. Huang, *Talanta* 62, 791 (2004).
47. P.V. Oliveira, and E. Oliveira, *Fresenius J. Anal. Chem.* 371, 909 (2001).
48. T.W. Lin and S.D. Huang, *Anal. Chem.* 73, 4319 (2001).
49. N. Carrión, A.M. Itriago, M.A. Alvarez, and E. Eljuri, *Talanta* 61, 621 (2003).
50. L. Bencs, O. Szakács, T. Kántor, I. Varga, and G. Bozsai, *Spectrochim. Acta Part B* 55, 883 (2000).
51. SIMAA 6000. *Simultaneous Multielement Atomic Absorption Spectrometer. Setting up and Performing Analysis*, PerkinElmer, Inc. Shelton, CT, USA, Publication B3119, 20 (1995).
52. L. Bencs, K. Ravindra, J. de Hoog, E.O. Rasoazanany, F. Deutsch, N. Bleux, P. Berghmans, E. Roekens, A. Krata, and R. Van Grieken, *J. Environ. Monit.* 10, 1148 (2008).
53. W. Frech, K. Li, M. Berglund, and D.C. Baxter, *J. Anal. At. Spectrom.* 7, 141 (1992).
54. G. Schlemmer, H. Schulze, and C. Gönner, *Atomic Absorption Technical Summary*, No. TSAA-46 (B050-4288), PerkinElmer, Inc., Shelton, CT, USA (1995).