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Preconcentration and Separation of Trace As(III) and Sb(III) by Carbon Nanofibers Loaded With Ammonium Pyrroinedithiocarbamate Prior to ICP-MS Determination

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ABSTRACT

Based on carbon nanofibers (CNFs) loaded with ammonium pyrroinedithiocarbamate (APDC) as an adsorbent, a novel method is described for the preconcentration, separation, and determination of trace As(III) and Sb(III) by inductively coupled plasma mass spectrometry (ICP-MS). The adsorption behavior of the analytes on CNFs-APDC was investigated under dynamic conditions. The effects of pH, sample flow rate and volume, elution solution and interfering ions on the preconcentration and separation of the analytes were examined in detail. The adsorption capacity of CNFs-APDC for As(III) and Sb(III) was 3.6 mg g^{-1} and 2.8 mg g^{-1}, respectively. Under the optimum conditions, the detection limit (3σ) of this method was 0.065 ng mL^{-1} of As(III) and 0.012 ng mL^{-1} of Sb(III), and the relative standard deviation (RSD) was 3.1% and 5.4%, respectively (n=9, c=1.0 ng mL^{-1}). This method was applied to the determination of trace As(III) and Sb(III) in natural water samples with recoveries of 95.3–104%. In order to validate this method, a certified reference material of human hair (GBW 07601) was analyzed, and the determined values were in good agreement with the certified values.

INTRODUCTION

Owing to the rapid growth in technology and the industries, the elemental levels in the environment have received considerable attention in recent years. Arsenic (As) and antimony (Sb) are treated as potential chemical hazards by the World Health Organization (1). There is much epidemiological evidence that shows that arsenic causes diseases such as skin, lung, bladder, and kidney cancers (2, 3). Excessive exposure to antimony may lead to a wide variety of adverse health effects, including respiratory tract irritation, dermatitis, conjunctivities, suppuration of the nasal septum, gastritis, and cellular damage in the lung, heart, and kidneys (4). Consequently, a reliable and accurate analytical procedure is necessary for the determination of trace/ultra-trace arsenic and antimony in environmental and biological samples.

Current analytical techniques for the determination of trace/ultra-trace elements mainly include atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution spark mass spectrometry, neutron activation analysis, and differential pulse anodic strpping voltammetry (5-9). Although some of these techniques are very sensitive, there is still the need for a separation and preconcentration procedure before the measurement step due to matrix effects and low levels of the analytes in real samples. To date, the widely used techniques for the separation and preconcentration of trace/ultra-trace elements include coprecipitation, solvent extraction, cloud point extraction, solid phase extraction (SPE), ion exchange, hydride generation, and chromatography (10-16). Among these techniques, SPE for the preconcentration and separation of trace elements has achieved increasing application because of its simplicity, speed, high enrichment factors, rapid phase separation, and ability to combine with different detection techniques.

In the SPE technique, selection of an appropriate sorbent is of importance for the elaboration of an analytical procedure. Thus, the development of a new adsorbent material with high selectivity and sensitivity is forever of interest to analysts (17, 18). Recently, a nanostructure material as a new adsorbent for the preconcentration and separation of substances has drawn growing attention in the analytical sciences (19-26). As a novel and interesting material, carbon nanofibers (CNFs) have been used for hydrogen storage and the separation/preconcentration of trace elements due to their high chemical stability and large specific surface area (27-30). Some investigations showed that an important strategy for elemental enrichment is the incorporation of complexing reagents in solid supports (31-34). To the best of our knowledge, however, studies on the separation and preconcentration of trace elements have received little attention using CNFs loaded with APDC.

In this study, a novel method was developed for the separation and preconcentration of trace As(III) and Sb(III) by a microcolumn

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packed with immobilized APDC on CNFs before ICP-MS determination. This method validation was performed and applied for the determination of trace As(III) and Sb(III) in environmental and biological samples.

EXPERIMENTAL

Instrumentation

A Thermo Elemental X-7 ICP-MS (Thermo Elemental Corporation, USA), equipped with a standard low-volume glass impact-bead spray chamber, a concentric glass nebulizer and Fassel-type torch, was used in this work. The samples and standards were spiked with 2.0 ng mL^{-1} of indium internal standard before measurement. The ion lens settings, nebulizer flow rate, and torch position of the instrument were optimized daily in order to obtain the maximum ^{115}In count rate. The operating parameters for ICP-MS are listed in Table I.

A Model HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, P.R. China), coupled to a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm × 3.0 mm i.d.) packed with CNFs-APDC, was used for the preconcentration and separation process. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connections. The pH values of the solutions were controlled with a pH meter (Thermo Orion Corporation, USA), supplied with a combined electrode. A Model Ethos T microwave system (Milestone, Italy) was used for sample digestion.

Standard Solutions and Reagents

The As(III) and Sb(III) stock solutions (1.0 mg mL^{-1}) were purchased from the National Analysis Center of Iron & Steel (Beijing, P.R. China). The working solutions of the analytes were prepared by mixing and diluting the stock solutions. All other reagents used were of ultrapure or at least of analytical grade. High-purity water obtained from a Milli-Q®A-10 system (Millipore Corporation, USA) was used throughout this work. The pH values of the solution were adjusted by adding an appropriate amount of HCl. The CNFs were kindly provided by the Shenyang Metal Institute of the Chinese Academy (Shenyang, P.R. China).

Preparation of Microcolumn with APDC

The microcolumn was prepared by placing 20 mg of CNFs into an empty conical column using the dry packing method. To avoid loss of CNFs, a small amount of quartz wool was filled into both ends of the column. The microcolumn was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system.

Before its use, 0.1 mol mL^{-1} HCl solution was passed through the column for cleaning, then it was washed with high purity water to pH 7; and finally, 1.0×10^{-4} mol L^{-1} APDC solution was passed through the column at a flow rate of 0.2 mL min^{-1}. The filtrate was collected and analyzed for un-adsorbed APDC with a UV-vis spectrophotometer at 275 nm. The retained amount of APDC on the CNFs was 0.94 mg g^{-1}.

Sample Decomposition

A 0.1000 g sample of GBW 07601 Human Hair (from the Institute of Geophysical and Geochemical Prospecting, Langfang, P.R. China) was accurately weighed into 100-mL Teflon® vessels, and 3.0 mL of concentrated HNO_3 and 1.0 mL of 35% H_2O_2 (m/V) were added. After about 5 minutes, when the first vigorous reaction had taken place, the digestion vessels were closed and placed into the microwave oven. Then, the samples were digested in the microwave oven at 180 °C (ramp, 10 minutes; hold, 15 minutes) at 1.0 kW power. After cooling and adding 0.5 mL of concentrated $HClO_4$, the solution was transferred into a Teflon beaker and heated to near dryness on a hot plate at 200 °C. The residues were dissolved with 1.0 mL of 0.1 mol L^{-1} HCl, and diluted to 10 mL with deionized water.

The waste sample was collected from Dongxi Lake (Wuhan, P.R. China), filtered through a 0.22-μm membrane filter, and analyzed as soon as possible after collection. The blank was prepared exactly as the samples.

TABLE I
ICP-MS Operating Parameters

Plasma Power	1.3 kW
Plasma Argon Flow Rate	14.5 L min^{-1}
Auxiliary Argon Flow Rate	0.71 L min^{-1}
Nebulizer Argon Flow Rate	0.94 L min^{-1}
Sampler Orifice (nickel)	1.1 mm
Skimmer Orifice (nickel)	0.7 mm
Acquisition Mode	Peak-jumping
Number of Sweep	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotopes	^{75}As, ^{122}Sb, and ^{115}In

Recommended Procedure

Aliquots of 20-mL solutions containing As(III) and Sb(III) were prepared, and the pH was adjusted to the desired value with HCl. The solution was passed through the microcolumn by using a peristaltic pump at a desired flow rate. Afterwards, the retained metal ions were eluted with 0.6 mol L^{-1} NaOH solution. The analytes in the effluents were determined by ICP-MS. The column could be used repeatedly after regeneration with 0.6 mol L^{-1} NaOH solution and high purity water, respectively.

RESULTS AND DISCCUTION

Influence of pH on Adsorption

In the SPE procedure, the pH value of the aqueous sample plays an important role with respect to the adsorption of the analytes on the CNFs-APDC. In order to evaluate the effect of pH, a series of sample solutions was adjusted to the pH range of 1.0–10 with HCl and processed according to the recommended procedure. The effect of pH value on the recoveries of the analytes was investigated. The recoveries were calculated based on the difference between the amounts of the analytes in the starting sample and in the solution flowing out from the column. The results shown in Figure 1 indicate that quantitative recoveries (>90%) for As(III) and Sb(III) were obtained in the pH range of 2.0 to 4.0. Thus, all other experiments in this work were carried out at pH 3.0.

Choice of Eluent

The choice of eluent is very important for the successful coupling of a microcolumn preconcentration system to the ICP-MS. From Figure 1, it can be seen that the adsorption of the analytes on the CNFs-APDC is negligible at pH >10. The reason for this may be that extra NaOH results in the decomposition of the As(III)/Sb(III)-APDC complex and the formation of soluble AsO_3^{3-}/SbO_3^{3-}. Thus, various concentrations of the NaOH solutions were studied for desorption of the retained analytes from the microcolumn. The results in Table II show that 0.4 mol L^{-1} NaOH was sufficient for the quantitative elution of the analytes (>90%). As a result, a 0.6 mol L^{-1} NaOH solution was selected for the elution of As(III) and Sb(III) in the following experiments.

In addition, the effect of eluent volume on the recoveries of the analytes was also investigated with 0.6 mol L^{-1} NaOH solution (Table III). The experimental results demonstrated that quantitative recoveries (>90%) were obtained with 1.5 mL of 0.6 mol L^{-1} NaOH solution. Taking the required sampling volume for ICP-MS into account, a 2.0-mL eluent volume was adopted for this work.

Effect of Flow Rate of Sample Solution

Retention of the analytes on the adsorbent depends on the flow rate of the sample solution. Therefore, the flow rate of the sample solution was optimized in the range of 0.2 and 2.0 mL min^{-1} by passing 20 mL of solution through the microcolumn with a peristaltic pump. The experimental results in Figure 2 show that quantitative recoveries of the studied ions (>90%) were obtained in the flow rate range of 0.2–1.2 mL min^{-1}. However, the recoveries of the analytes will decrease by further increasing the flow rate above 1.2 mL min^{-1} because of a decrease in adsorption kinetics. In this work, a flow rate of 1.2 mL min^{-1} was used for subsequent determination.

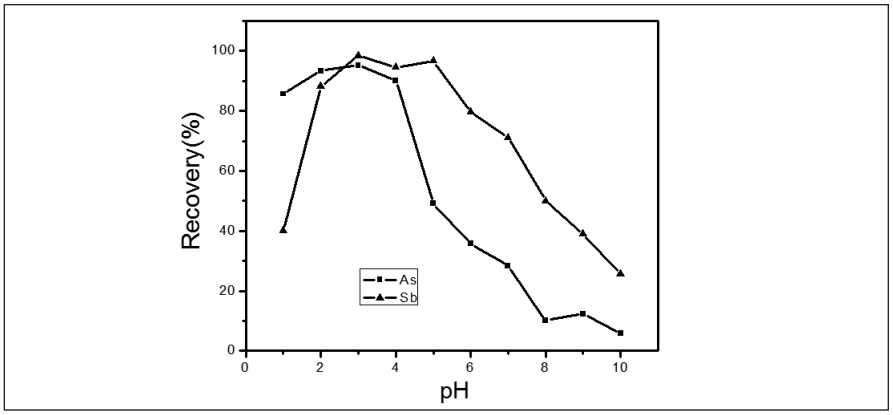

Fig. 1. Effect of pH on the adsorption of As(III) and Sb(III) on CNFs-APDC. As(III) and Sb(III): 5.0 ng mL^{-1}; sample volume: 20 mL.

TABLE II
Effect of Eluent Concentration on the Recovery of Analytes

Concentration (NaOH, mol mL^{-1})	Recovery (%) As(III)	Sb(III)
0.1	42.3	50.2
0.2	68.9	71.3
0.4	90.1	91.4
0.6	98.3	98.7
0.8	96.5	96.5

TABLE III
Effect of Eluent Volume on the Recovery of Analytes

Eluent Volume (NaOH, mL)	Recovery(%) As(III)	Sb(III)
0.5	50.9	45.9
1.0	70.2	75.4
1.5	91.2	92.3
2.0	96.4	94.7
2.5	97.3	98.3
3.0	95.8	95.7

Effect of Sample Volume

High preconcentration factors are neccesary for the determination of lower analyte levels in real environmental and biological samples. Hence, the effect of sample volume on the recovery of the analytes was examined in the range of 20–250 mL sample volume containing 10 ng of the analytes. The above sample solutions were passed through the microcolumn at an optimum flow rate according to the recommended procedure. As can be seen in Figure 3, the analytes could be recovered quantitatively (>90%) up to 150 mL of sample solution. Because the elution volume was 1.5 mL of 0.6 mol L^{-1} NaOH solution, an enrichment factor of 100 was achieved in this work.

Interference Study

The effects of common coexisting ions on the adsorption of the analytes were investigated. The tolerance limit of coexisting ions is defined as the largest amount that makes the recovery of the analyte less than 90%. In the present experiments, 5.0 ng mL^{-1} solutions of the analytes containing the added interfering ions were treated according to the recommended procedure. Table IV shows that the coexisting foreign ions did not interfere in the determination within the range of their amounts tested.

Adsorption Capacity

The adsorption capacity was investigated by a method provided in the literature (35). Aliquots of 100 mL of a series of concentrations (1.0–10 μg mL^{-1}) were adjusted to the appropriate pH, then preconcentrated and eluted. The amount of metal ions adsorbed at each concentration level was determined. Breakthrough curves were obtained by plotting the metal ion concentrations (μg mL^{-1}) versus the milligram of metal ions adsorbed on per gram of adsorbent. The adsorption capacity calculated from the breakthrough curve was 3.6 and 2.8 mg g^{-1} for As(III) and Sb(III), respectively.

TABLE IV
Tolerance Limits of Coexisting Ions

Coexisting Ion	Concentration Ratio[a]
Na^+, K^+	10,000
Ca^{2+}, Mg^{2+}	5000
Al^{3+}, Fe^{3+}	200
SiO_3^{2-}, SO_4^{2-}, PO_4^{3-}	2000

[a] Concentration ratio: Foreign ion/determined ion.

Column Reuse

In order to examine the long-term stability of the microcolumn, it was subjected to successive adsorption and desorption cycles by passing 20 mL of the solutions containing the analytes through the column. The stability and potential regeneration of the column were assessed by monitoring the changes in the recoveries of the analytes. The column can be reused after regeneration with 3.0 mL of 0.6 mol L^{-1} NaOH solution and 20 mL deionized water, respectively, and is stable up to 50 adsorption-elution cycles without any obvious decrease in the adsorption capacity and the recovery for the analytes.

Analytical Performance

The reproducibility of the preconcentration was evaluated by passing 20 mL of standard solution of the analytes through the microcolumn and repeating the procedure nine times. The obtained relative standard deviation (RSD) of As(III) and Sb(III) (c= 1.0 ng mL^{-1}) was 3.1% and 5.4%, respectively. The detection limit, defined as the concentration that produces a signal equivalent to three times the standard deviation of nine measurements of the blank, was 0.065 ng mL^{-1} and 0.012 ng mL^{-1} for As(III) and Sb(III), respectively.

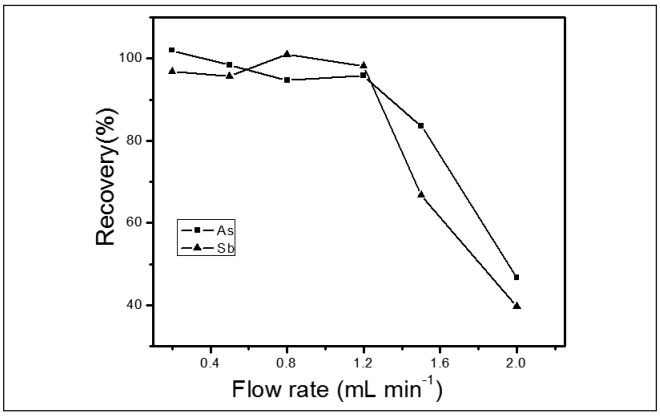

Fig. 2. Effect of sample flow rate on the recovery of As(III) and Sb(III) on CNFs-APDC. As(III) and Sb(III): 5.0 ng mL^{-1}; pH=3.0; sample volume: 20 mL.

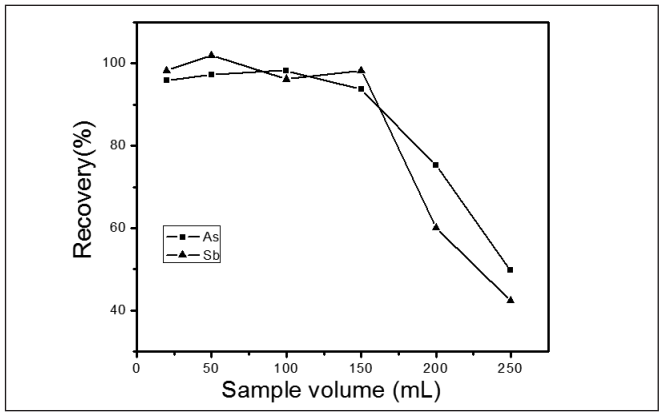

Fig. 3. Effect of sample volume on the recovery of As(III) and Sb(III) on CNFs-APDC. pH: 3.0; sample volume: 20 mL; As(III) and Sb(III): 10 ng.

TABLE V
Analytical Results of the Analytes in Natural Water Sample

Element	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)
As(III)	0	0.38±0.04	-
	2.0	2.31± 0.15	96.5
	3.0	3.51± 0.26	104
Sb(III)	0	0.091± 0.008	-
	2.0	2.13± 0.17	102
	3.0	2.95±0.21	95.3

[a] Mean value ± standard deviation, n=3.

TABLE VI
Analytical Results of the Analytes in Standard Reference Material of Human Hair

Element	Found[a] (μg g^{-1})	Certified (μg g^{-1})
As(III)	0.31±0.02	0.28±0.04
Sb(III)	0.10±0.011	0.095±0.012

[a] Mean value ± standard deviation, n=3.

Sample Analysis

In order to establish the validity of this method, the analytes were determined in a natural water sample and a biological reference material (GBW 07601 Human Hair). The obtained results are summarized in Tables V and VI, respectively. As can be seen, the determined values were in good agreement with the certified values, and the recoveries of the analytes were reasonable for trace analysis and ranged from 95.3–104%.

CONCLUSION

In this work, an effective procedure for the preconcentration and separation of trace As(III) and Sb(III) in environmental and biological samples is described using a microcolumn packed with CNFs-APDC, followed by ICP-MS analysis. The adsorption behavior of the analytes was investigated in detail. The analytes were retained in the pH range of 2.0–4.0, and desorbed quantitatively with 1.5 mL of 0.6 mol L^{-1} NaOH solution. In addition, no carryover was observed in the next analysis. The analytes could be concentrated 100 times within a short time and recovered with high precision. The adsorption capacity for As(III) and Sb(III) was 3.6 mg g^{-1} and 2.8 mg g^{-1}, respectively. The experimental results show that this method is applicable for the determination of trace/ultratrace elements in natural water and hair samples.

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REFERENCES

1. S. Hu, X. Hu, H. Liu, L. Huang, and R. Liu, At. Spectrosc. 35(2), 90 (2014).
2. C. Liao, H.Shen, C. Chen, L. Hsu, T. Lin, S. Chen, and C. Chen, J. Hazard. Mater. 165(1-3), 652 (2009).
3. P.J. Mink, D.D. Alexander, L.M. Barraj, M.A. Kelsh, and J.S. Tsuji, Regul. Toxicol. Pharm. 52(3), 299 (2008).
4. M. Krachler, H. Emons, and J. Zheng, Trac trends Anal. Chem. 20, 79 (2001).
5. K.L. Mandiwana, N. Panichev, and S. Panicheva, Food Chem. 129, 1839 (2011).
6. S. Chen, H. Zhang, and B. Ruan, At. Spectrosc. 30(4), 143 (2009).
7. S. Chen, S. Zhu, Y. He, and D. Lu, Food Chem. 150, 254 (2014).
8. R.E. Sturgeon, S.S. Berman, J.A.H. Desaulniers, A.P. Mykytituk, J.W. Mclaren, and D.S. Russell, Anal. Chem. 52, 1585 (1980).
9. R.R. Barefoot and J. C. Van Loon, Talanta 49, 1 (1999).
10. M. Soylak and N. Kizil, At. Spectrosc. 34(6), 216 (2013).
11. M. Janko and M. J. Herak, Microchim. Acta 60(2), 198 (1972).
12. Y. Yi, S. Wu, S. Jiang, and A.C. Sahayam, At. Spectrosc. 34(2), 39 (2013).
13. S. Chen, S. Zhu, and D. Lu, Microchem. J. 110, 89 (2013).
14. Q. Jia, X. Kong, W. Zhou, and L. Bi, Microchem. J. 89(1), 82 (2008).
15. H. Matusiewicz, M. Ślachciński, and Microchem. J. 82(1), 78 (2006).
16. S.H. Hansen, Microchim. Acta 108(1-4), 47 (1992).
17. F. Augusto, L.W. Hantao, and N.G.S. Mogollón, Trends in Anal. Chem. 43, 14 (2013).
18. L.M. Ravelo-Pérez, A.V. Herrera-Herrera, J. Hernández-Borges, and M.Á. Rodríguez-Delgado, J. Chromatogr. A 1217(16), 2618 (2010).
19. A.C. Sahayam, G. Venkateswarlu, and S.C. Chaurasia, At. Spectrosc. 30(4), 139 (2009).
20. X. Zhang, J. Zhang, and Y. Lee, Microchem. J. 101, 70 (2012).
21. M. Soylak and Y.E. Unsal, Food Chem. Toxic. 48(6), 1511 (2010).
22. Y. Liu, Y. Li, and L. Yang, Microchem. J. 104, 56 (2012).
23. S. Chen, M. Xiao, D. Lu, and Z. Wang, Spectrochim. Acta Part B 62, 1216 (2007).

24. M. Behbahani, A. Bagheri, M. Taghizadeh, M. Salarian, O. Sadeghi, L. Adlnasab, and K. Jalali, Food Chem. 138(2-3), 2050 (2013).

25. S. Chen, X. Guo, Y. Zhang, and D. Lu, Anal. Meth. 6, 3668 (2014).

26. Y. Wu, J. Zhang, J. Liu, Z. Deng, M. Han, F. Jiang, D. Wang, H. Wang, and H. Yuan, At. Spectrosc.32(1), 41 (2011).

27. A. Chambers, C. Park, R. T. K. Baker, and N. M. Rodriguez, J. Chem. Phys. B 102(22), 4253 (1998).

28. Y. He, S. Chen, X. Zhou, and X. Wang, At. Spectrosc. 33(4), 117 (2012).

29. S. Chen, M. Xiao, D. Lu, and X. Zhan, Rapid Comm. Mass Spectrom. 21, 2524 (2007).

30. S. Chen, X. Zhan, D. Lu, and C. Liu, At. Spectrosc. 29(4), 124 (2008).

31. E.M. Soliman, M.B. Saleh, and S.A. Ahmed, Anal. Chim. Acta 523, 133 (2004).

32. M. Tuzen, K.O. Saygi, and M. Soylake, J. Hazard. Mater. 632, 152 (2008).

33. M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A. Pourfarokhi, N. Khanjari, A.S. Mirsadeghi, and M. Soylak, J. Hazard. Mater. 162, 1408 (2009).

34. G. Kaya, I. Akdeniz, and M. Yaman, At. Spectrosc. 29(4), 150 (2009).

35. A. Maqieira, H.AM. Elmahadi, and R. Puchades, Anal. Chem. 66, 3632 (1994).

Application of Wet vs. Microwave Digestion for Trace Element Determination in Soil, Vegetable, Nuts, and Grain Samples by ICP-OES

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ABSTRACT

In this study, the ICP-OES determination of the trace elements Co, Cr, Cu, Fe, Mn, Ni, Se, and Zn in soil, vegetable, nuts and grain samples from Sakarya, Turkey, was evaluated after wet and microwave digestion. Element concentrations found in the soil samples were 0.6–1.7 μg g^{-1} (Co), 4.2–8.5 μg g^{-1} (Cr), 2.5–8.5 μg g^{-1} (Cu), 46.2–69.9 μg g^{-1} (Mn), 4.7–7.6 μg g^{-1} (Ni), and 5.3–9.4 μg g^{-1} (Zn); in the vegetable samples 0.2–1.1 μg g^{-1} (Cu), 27.2–114.6 μg g^{-1} (Fe), 3.8–6.5 μg g^{-1} (Mn), and 2.1–8.9 μg g^{-1} (Zn); and in the dried food samples 0.04–0.94 μg g^{-1} (Co), 0.24–5.64 μg g^{-1} (Cr), 2.55–15.92 μg g^{-1} (Cu), 4.82–37.55 μg g^{-1} (Fe), 1.12–30.17 μg g^{-1} (Mn), 0.43–2.27 μg g^{-1} (Ni), 0.03–0.94 μg g^{-1}, (Se) and 2.93–20.91 μg g^{-1} (Zn). The accuracy of the method was verified using certified reference materials NIST CRM 7001 Light Sandy Soil and NIST SRM 1515 Apple Leaves digested by wet ashing and microwave digestion. The microwave digestion method offered best results and was successfully carried out for all samples. The results agreed well with the literature values.

INTRODUCTION

The trace elements Co, Cr, Cu, Fe, Mn, Ni, Se, and Zn are known to be one of the main sources of environmental pollution and greatly influence ecological quality (1–2). These problems are due to irrigation with contaminated water, application of pesticides and fertilizers, industrial emission, transport, harvesting, storage, and in the distribution process of foods (3–5).

Trace elements are present at low concentrations in most soils, plants, and living organisms and are important for daily nutrition; however, they become hazardous in excess amounts (6–7). For instance, Co, Cu, Fe, Mn, Se, and Zn are essential for the normal growth of plants and the human organism, while Cr and Ni are hazardous when present in excess in soil, water, and foods (8–10).

Fruits and leafy vegetables contain trace elements because of their high water content (11). Nutritional information is of importance to agricultural industries to maintain freshness of produce. Consumers are asking for diversity in their diets and are also aware of the health benefits of fruits and vegetables. Most nutritional requirements can be satisfied by the consumption of fruits and vegetables from 5–13 servings day^{-1} (12). It has also been reported (13–15) that eating more fruits and vegetables (>400 g day^{-1}) is related to a reduced risk of cardiovascular disease and certain cancers.

Different instrumental techniques have been used for the determination of heavy metals in plant and food samples by atomic absorption spectrometry (AAS) (5–16, 17) and inductively coupled plasma optical emission spectrometry (ICP-OES) (18,19). Microwave digestion methods are considered an accomplished sample pretreatment/dissolution procedure in analytical chemistry (8), which is also very fast and reduces sample contamination (20).

The aim of this paper was to determine trace level concentrations of some elements in soil, vegetable, and dried food samples obtained from the area of Sakarya, Turkey. The reliability of the method was verified by using certified (CRM) and standard reference materials (SRM). The analytical parameters show that microwave digestion provided better results than wet digestion. The trace element concentrations of all samples were determined by ICP-OES after microwave digestion.

EXPERIMENTAL

Instrumentation

A Spectro Arcos 165 optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) was used for the determination of all elements. The ICP-OES instrumental operating conditions used were according to the manufacturer's recommendations and are listed in Table I. The Start D microwave closed system (Milestone, Sorisole-Bg, Italy) was used for digestion of the soil, vegetable, and dried food samples (maximum pressure 1450 psi and maximum temperature is 300 °C). The ICP-OES instrumental and operating conditions are listed in Table I.

Reagents and Standard Solutions

The chemicals used for all experiments were of ultra-pure reagents

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(E. Merck, Darmstadt, Germany). The acids HCI (37%), HNO_3 (65%), and H_2O_2 (30%) were of analytical reagent grade (E. Merck, Darmstadt, Germany). All glass utensils were soaked overnight in 10% HNO_3 and cleaned with distilled de-ionized Ultra High Quality (UHQ) water before use, chemical resistivity of 18 MΩ·cm (Millipore Corporation, Bedford, MA, USA). The ranges of the calibration curves were selected to be compatible with conventional concentrations (5–1000 µg L^{-1}) for the elements of the samples studied.

Sample Collection

Soil Samples

The soil samples were collected from agricultural areas in the counties of Sakarya City, Turkey. They were taken from a depth of roughly 0–15 cm, sieved through 230 mesh size (63 µm) (Standard Testing Sieve, New Delhi, India), transferred to clean polyethylene bottles, agitated three times with deionized water, and stored in a refrigerator until analysis.

Vegetable, Fruits, Nuts, and Grain Samples

The vegetables with their green leaves were stored in polyethylene bottles. Dried fruit samples were purchased from local markets selling medicinal herbs. All samples (soils, vegetables, nuts, and grains as listed in Table II) were dried at 105 °C for 24 hours, triturated, homogenized with an agate homogenizer, then stored in polyethylene bottles in a refrigerator until analysis.

Wet Ashing Digestion

Sample Preparation

A mixture of HNO_3/H_2O_2 (6:2) and HCl/HNO_3 (6:2) was added to 1 g of sample, and placed on a hot plate (IKA, KS501D model, Germany) for solubilization at 130 °C for four hours. The residue was filtered through a Whatman filter paper (Whatman Grade 589) and brought to 10-mL volume with distilled deionized water. The element concentrations of the final solutions were determined by ICP-OES. Blanks were prepared in the same way.

Microwave Digestion

Soil Sample Preparation

The soil samples (0.25 g) were placed into reaction vessels (100 mL) and digested with HCl/HNO_3 (6:2) in the microwave digestion system. Digestion conditions for the microwave system are given in Table III. After cooling, the final solutions were brought to 10 mL volume with distilled de-ionized water.

Vegetable Sample Preparation

The vegetable samples (0.25 g) were placed into reaction vessels (100 mL) and digested with HNO_3-H_2O_2 (6:2) in the microwave digestion system. The digestion conditions are given in Table III. After cooling, the final solutions were brought to 10-mL volume with distilled deionized water.

Dried Fruit, Nut, and Grain Sample Preparation

Dried fruit, nut, and grain samples of 1.0 g were placed into reaction vessels, then 100 mL and 8 mL of a freshly prepared mixture of

TABLE I
ICP-OES Operating Parameters for the Determination of Elements

ICP-OES Instrument	SPECTRO ARCOS 165
Viewing Height	12 mm
Wavelengths (nm)	Co: 228.616, Cr: 267.716, Cu: 324.754, Fe: 259.941, Mn:257.611, Ni:231.604, Se:196.090, Zn:213.856
Replicates	3
RF Power	1450 W
Spray Chamber	Cyclonic
Nebulizer	Modified Lichte Model
Nebulizer Flow	0.8 L/min
Plasma Torch	Quartz, fixed, 3.0-mm injector tube
Replicate Read Time	50 sec per replicate
Plasma Gas Flow	13 L/min
Auxiliary Gas Flow	0.7 L/min
Sample Aspiration Rate	2.0 mL/min
Sample Pump Rate	25 rpm

TABLE II
List of Different Foods and Vegetables Used for Analysis in this Study

Scientific Name	English	Turkish
Actinidia	kiwi	kivi
Allium cepaL	green onion	yesil sogan
Allium porrumL.	leek	pirasa
Beta vulgaris L. var. condivitaalef	beetroot	pancar
Corylusavellana	hazelnut	fındık
Cydoniaoblonga	quince	ayva
Erucavesicaria subsp. sativa	arugula	roka
Juglans	walnut	ceviz
Lactuca sativa L.	lettuce	marul
Malusdomestica	apple	elma
Petroselinumhortense	parsley	maydanoz
Prunusdomestica	prune	kuruerik
Solanumlycopersicum	tomato	domates
Spinaciaoleracea L.	spinach	ıspanak
Triticum	wheat	bugday
Zea mays	corn	mısır

concentrated HCl/HNO_3 (6:2) was added and left standing for 10 minutes. The digestion conditions for the microwave system are given in Table III. After cooling, the final solutions were brought to 10-mL volume with 1 M HNO_3. The blanks were prepared in the same way, but without the sample.

Certified (CRM) and Standard Reference Material (SRM)

Recovery, precision, and analytical reproducibility of the proposed method were determined using certified reference material CRM 7001 Light Sandy Soil - Trace Elements (Czech Metrology Institute) and standard reference material NIST SRM 1515 Apple Leaves (National Institute for Standards and Technology, Gaithersburg, MD, USA). Each sample was prepared in duplicate, including the blank. The CRM and SRM analysis results were all within the 95% confidence limit (Tables IV and V) and compared well with the real sample analyses.

TABLE III
Operating Conditions for Samples in Microwave Digestion System

Steps	Time (min)	Power (W)
Soil samples		
1	10	800
2	15	800
Vent	11	-
Vegetable samples		
1	2	250
2	2	0
3	6	250
4	5	400
5	8	600
Vent	11	-
Dried fruit samples		
1	2	250
2	2	0
3	6	250
4	5	400
5	8	550
Vent	8	-

RESULTS AND DISCUSSION

The relative standard deviations were less than 10% for all investigated elements. All of the data were subjected to statistical analysis and correlation matrices were produced to examine the inter-relationship between the trace metal concentrations. The Student's *t*-test was used in this study ($p<0.05$).

A comparison of the results of the wet and microwave digestion methods shows that there are no statistically crucial differences (Table V). However, in comparison to wet digestion, the microwave sample digestion is simple, fast, and accurate for the ICP-OES determination of Co, Cr, Cu, Fe, Mn, Ni, Se, and Zn in soil, vegetable, nut, and grain samples with high recoveries (Table IV). Method validation was performed by the analysis of the means of the certified and standard reference materials.

The recovery values were quantitative for the microwave digestion method. The performance of each digestion method was compared by using two acid mixtures: HNO_3/H_2O_2 (6:2) and HCI/HNO_3 (6:2). The accuracy of the results was verified (Tables IV and V) by analyzing of certified and standard reference materials. The optimized method was carried out for some food samples.

The trace element concentrations of the real samples are listed in Table VI for the soil, Table VII for the vegetable, and Table VIII for the food samples and are discussed below.

Soil Sample Analysis

The element concentrations in the soil samples were 0.6–1.7 (Co), 4.2–8.5 (Cr), 2.5–8.5 (Cu), 46.2–69.9 (Mn), 4.7–7.6 (Ni), and 5.3–9.4 (Zn) μg g^{-1} (Table VI). In accordance with these data, manganese was found to be present at the highest concentration, and selenium below the detection limit. According to E.U. recommendations (21), the maximum allowable concentrations (MAC) for cobalt in soil samples are in the 0.5–65 μg g^{-1} range. Thus, the cobalt levels of this study were within normal limits in all soil samples. The total chromium concentration was 100 μg g^{-1} and is within the accepted limits for all samples. The maximum allowable levels of copper are within the 2–250 μg g^{-1} ranges (22). The maximum allowable concentrations of manganese are within the 164–1330 μg g^{-1} range (23). Thus, the Mn levels in this study are lower than the maximum allowable concentration limits. The nickel levels were within the 100 μg g^{-1} limit, and the zinc levels were also in the accepted limit of 1–900 μg g^{-1} (22).

TABLE IV
Certified and Found Values (μg g^{-1}) of Total Element Concentrations in CRM 7001 Light Sandy Soil - Trace Elements

Elements	Certified value	Found Value	Recovery (%)
Co	9.66 ± 0.61	10.10 ± 1.50	104.6
Cr	71.9 ± 5.9	72.2 ± 3.1	100.4
Cu	28.9 ± 0.8	28.1 ± 0.5	97.2
Mn	479 ± 18	483 ± 10	100.8
Ni	31.8 ± 1.2	32.4 ± 1.3	101.9
Zn	108.0 ± 3.5	109.0 ± 3.6	100.9

Vegetable, Nuts, Grain Sample Analysis

The element concentrations of all vegetable samples were 0.2–1.1 μg g^{-1} (Cu), 27.2–114.6 μg g^{-1} (Fe), 3.8–6.5 μg g^{-1} (Mn), and 2.1–8.9 (Zn) μg g^{-1} (Table VII). While iron was present at the highest concentration, cobalt, chromium, nickel, and selenium were found under the detection limit. The reported acceptable values for copper were within the 2.5–16 μg g^{-1} range (24), but in the samples of this study they were lower. The manganese content varied from 3.8 (parsley) to 6.5 μg g^{-1} (lettuce), while the levels reported in the literature are within the 9–16.6 μg g^{-1} range for all food categories in India (25). Similarly, the Mn levels in the present study were lower than those found in the literature (25).

TABLE V
Comparison of Digestion Conditions of Elemental Concentrations (μg g^{-1}) Using NIST SRM 1515 Apple Leaves (average ± S.D., N=3)

Elements	Certified Value	Microwave Digestion HNO_3/H_2O_2 (6:2)	Recovery (%)	Wet Digestion HNO_3/H_2O_2 (6:2)	Recovery (%)	HCI/HNO_3 (6:2)	Recovery (%)
		Found Value		Found Value			
Co	0.09	0.10 ± 0.01	111	0.12 ± 0.02	133	0.11 ± 0.01	122
Cr	0.30	0.35 ± 0.03	117	0.37 ± 0.02	123	0.36 ± 0.01	120
Cu	5.64	5.58 ± 1.12	99	5.53 ± 1.36	98	5.53 ± 2.10	98
Fe	83	82.17 ± 3.45	99	80.51 ± 2.78	97	81.34 ± 3.10	97
Mn	54	52.92 ± 2.78	98	51.64 ± 3.65	96	53.23 ± 4.12	99
Ni	0.91	0.90 ± 0.13	99	0.92 ± 1.03	101	0.89±0.09	98
Se	0.050	0.048 ± 0.003	96	0.044 ± 0.001	88	0.045 ± 0.002	90
Zn	12.5	12.38 ± 0.69	99	12.25 ± 1.12	98	12.63 ± 2.19	101

TABLE VI
Concentrations (μg g^{-1}) of Trace Metals in Soil Samples (N=3)

Regions	Co	Cr	Cu	Mn	Ni	Se	Zn
Pamukova	0.6±0.1	6.3±1.2	7.4±1.3	48.5±3.8	4.7±0.8	BDL	5.8±0.9
Pamukova	0.6±0.1	7.4±1.3	3.6±0.8	52.3±4.1	5.5±0.9	BDL	6.6±0.9
Ferizli	1.1±0.1	8.5±1.3	2.9±0.6	67.2±4.8	6.8±1.1	BDL	8.4±1.4
Hendek	0.7±0.1	7.4±1.4	2.6±0.4	52..8±3.9	6.5±1.0	BDL	9.4±1.5
Adapazarı	1.1±0.1	5.3±1.3	7.1±1.2	69.9±5.1	6.1±1.2	BDL	7.5±1.4
Pamukova	0.8±0.1	6.2±1.5	2.8±0.6	58.4±4.6	5.8±0.9	BDL	6.3±1.5
Geyve	1.7±0.2	4.2±1.0	3.2±0.9	59.0±4.7	6.1±1.2	BDL	6.7±1.3
Geyve	1.4±0.3	7.6±1.3	3.6±0.9	63.5±5.0	5.3±0.9	BDL	8.9±1.8
Geyve	0.7±0.1	5.3±1.2	8.5±1.2	53.4±4.3	6.5±1.0	BDL	8.6±1.4
Sögütlü	1.5±0.2	8.2±1.6	4.4±1.1	46.2±3.6	6.3±1.1	BDL	5.6±0.9
Sögütlü	1.4±0.2	8.1±1.4	2.5±0.9	60.4±4.7	7.6±1.2	BDL	6.8±1.2

BDL: Below detection limit.

TABLE VII
Concentrations (μg g^{-1}) of Trace Metals in Some Vegetable Samples (N=3)

Sample	Co	Cr	Cu	Fe	Mn	Ni	Se	Zn
Arugula	BDL	BDL	0.5±0.1	27.2±3.1	4.4±0.7	BDL	BDL	3.7±0.3
Lettuce	BDL	BDL	1.1±0.3	114.6±9.3	6.5±1.4	BDL	BDL	2.1±0.1
Parsley	BDL	BDL	0.4±0.1	35.5±4.5	3.8±0.6	BDL	BDL	2.2±0.2
Scallion	BDL	BDL	0.20±0.04	73.1±2.1	4.7±0.3	BDL	BDL	2.4±0.3
Spinach	BDL	BDL	0.6±0.1	53.1±4.7	4.2±0.1	BDL	BDL	8.9±1.6

BDL: Below detection limit.

Iron concentrations ranged (25) from 27.2 (arugula) to 114.6 μg g^{-1} (lettuce) for the vegetables. The iron levels for lettuce were found to be above the accepted limits of 425 μg g^{-1} for soils. In comparison to the suggested levels of the Food and Agriculture Organization (FAO)-World Health Organization (WHO) (26), the zinc levels were below the accepted FAO-WHO limits of 100 mg kg^{-1} (26).

Heavy metals in vegetables are absorbed from the soil, polluted air, and water. It has been reported that higher amounts of heavy metals accumulate mostly in the leaves of leafy vegetables (27).

Food Sample Analysis

The evident toxic and trace elements are very significant for human biology (28-29). Table VIII lists the trace element concentrations of all food samples which were as follows: 0.04–0.94 μg g^{-1} (Co), 0.24–5.64 μg g^{-1} (Cr), 2.55–15.92 μg g^{-1} (Cu), 4.82–37.55 μg g^{-1} (Fe), 1.12–30.17 μg g^{-1} (Mn), 0.43–2.27 μg g^{-1} (Ni), 0.03–0.94 μg g^{-1} (Se), and 2.93–20.91 μg g^{-1} (Zn). In accordance with these data, iron has the highest concentration, followed by manganese, zinc, and iron.

According to the Turkish Food Codex (30), the MAC of cobalt in some food samples is 0.2 mg kg^{-1}. Chromium concentrations in different fruits from Pakistan (31) have been reported to be within the range of 1.48–6.43 mg kg^{-1} wet weight and copper concentrations in dried fruit samples from Pakistan within the range of 3.90–25.0 μg g^{-1} dry weight (32). In fruits sold at Egyptian markets, the Co concentrations ranged from1.22–18.3 mg kg^{-1} (33) and from 1.68–4.52 μg g^{-1} dry weight from fruits sold in Kayseri, Turkey (5).

The concentration of iron was found to be in the 4.82–37.55 μg g^{-1} range for all of the samples in this study. The allowable iron concentration in dried fruits from Pakistan (32) was in the range of 19.0–45.0 μg g^{-1} dry weight. While for dried fruits from Kayseri, Turkey (5), it was found to be 6.76–64.1 μg g^{-1}. For food it was in the 15 mg kg^{-1} range and is in accordance with the Turkish Food Codex (34).

The official allowable manganese values are within the 2.14–17.23 μg g^{-1} range for dried fruits from Pakistan (32) and 4.74–25.5 μg g^{-1} from Turkey (5). In this study, the manganese level was found within the 1.12–30.17 μg g^{-1} range for quince and walnut samples, respectively. The U.S. National Academy of Sciences suggested 2.5–5.0 mg as the daily maximum for manganese, while the WHO recommendations are 2–9 mg daily (35). Nickel allowable values are within the 1.0–8.9 mg kg^{-1} range in fruits from Pakistan (31). The concentration of nickel for samples analyzed in this study was found within the 0.43–2.27 μg g^{-1} range, whereas the MAC of nickel in some food samples was 0.2 mg kg^{-1} (30).

In this study, the concentration of selenium was found within the 0.03–0.94 μg g^{-1} range. The daily MAC intake of selenium in Turkey is 30 μg day^{-1} (36), although the selenium need of adult males and females is computed to be 55 μg day^{-1} (37). According to the Turkish Food Codex (34), the MAC of zinc in food is 5 mg kg^{-1}. The lowest and highest levels of zinc reported were 64.2 and 65.8 μg g^{-1}, respectively, in spices, dried fruit, and nuts from Pakistan (32).

TABLE VIII
Element Concentrations (μg g^{-1}) in Some Food Samples (N=3)

Sample	Co	Cr	Cu	Fe	Mn	Ni	Se	Zn
Bulgur	0.84±0.20	1.16±0.25	3.48±0.07	17.69±3.14	15.32±3.25	1.70±0.05	0.09±0.03	16.51±2.47
Dried kiwi	0.59±0.10	0.83±0.16	7.11±2.10	7.82±2.14	20.29±2.45	1.90±0.10	0.10±0.03	10.87±1.65
Dried tomato	0.31±0.06	3.80±0.36	10.30±2.14	37.55±6.45	4.83±1.12	1.75±0.16	0.31±0.04	12.71±1.45
Hazelnut	0.79±0.18	0.49±0.04	11.49±2.41	18.61±2.78	26.79±3.48	1.41±0.25	0.18±0.04	7.18±1.18
Prune	0.82±0.14	1.73±0.14	2.55±0.16	16.77±3.14	2.69±0.12	0.98±0.14	0.76±0.06	6.94±2.12
Pumpkin shell	0.08±0.02	0.24±0.04	4.48±1.14	4.82±1.13	4.35±0.16	0.46±0.03	0.03±0.01	3.54±0.15
Pumpkin seeds	0.41±0.03	1.40±0.23	15.92±2.36	22.89±4.45	24.15±1.78	1.49±0.14	0.94±0.04	20.91±1.87
Quince	0.04±0.02	1.50±0.17	2.83±0.16	30.41±3.14	1.12±0.02	0.43±0.01	0.07±0.01	2.93±0.08
Tomato	0.57±0.11	5.64±0.42	15.21±3.67	35.54±3.41	5.79±2.54	2.15±0.25	0.36±0.08	15.07±2.65
Walnut	0.94±0.15	1.06±0.07	7.26±1.36	29.72±4.21	30.17±3.65	2.27±0.14	0.04±0.02	9.14±2.10

CONCLUSION

In this study, it was shown that microwave digestion is more accurate, simpler, and faster than wet digestion in the ICP-OES determination of the trace elements Co, Cr, Cu, Fe, Mn, Ni, Se, and Zn in soil, vegetable, nut, and grain samples. The recovery values for these elements using microwave digestion were quantitative. The soil and vegetable samples contained heavy metals at lower than the tolerable levels recommended by the Joint FAO/WHO Expert Committee on Food Additives. The elemental levels of the nut and grain samples were found to be acceptable for human consumption with regard to their nutritional and toxic values. The analytical results were verified by analysis of certified and standard reference materials and were found to be within the 95% confidence limit.

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REFERENCES

1. M. Tuzen, Microchem. J. 74(3), 289 (2003).
2. N. Ozcan and H. Altundag, Bull. Chem. Soc. Ethiopia. 27(2), 205 (2013).
3. M.K. Jamali, T.G. Kazi, M.B. Arain, H.I. Afridi, N. Jalbani, and A.R. Memon, J. Agronomy Crop Sci. 193(3), 218 (2007).
4. H. Altundag, M.S. Dundar, and C.S. Keskin, Eco. Chem. Eng. S. 20(2), 257 (2013).
5. A. Duran, M. Tuzen, and M. Soylak, Inter. J. of Food Sci. Nutr. 59(7-8), 581 (2008).
6. M. Tuzen, and M. Soylak, J. Food Drug Anal. 13(4), 343 (2005).
7. M.S. Dundar, and H. Altundag, Trace. Elem. Electroly. 19(2), 55 (2002).
8. H. Altundag, and M. Tuzen, Food Chem. Tox. 49(11), 2800 (2011).
9. T.G. Kazi, M.K. Jamali, M.B. Arain, H.I. Afridi, N. Jalbani, A. Raja, R.A. Sarfraz, and R. Ansari, J. Hazard. Mater. 161, 1391 (2009).
10. S. Tokalioglu, S. Kartal, and G. Birol, Environ. Monit. Assess. 5(3), 468 (2003).
11. L.A. Sargeant, K.T. Khaw, S. Bingham, N.E. Day, R.N. Luben, S.Oakes, A. Welch, and N.J. Wareham, J. Clin. Nutr. 55(5), 342 (2001).
12. A. Aberoumand, and S.S. Deokule, Food. Anal. Method. 2(2), 116 (2009).
13. L.A. Bazzano, J. He, L.G. Ogden, C.M. Loria, S. Vupputuri, L. Myers, and P.K. Whelton, Amer. J. Clin. Nutr. 76(1), 93 (2002).
14. WHO, World Health Org. Diet Nutr. and Prevent. of Chr. Dis. (2003).
15. P. Ekholm, H. Reinivuo, P. Mattila, H. Pakkala, J. Koponen, A. Happonen, J. Hellstrom, and M.L. Ovaskainen, J. Food Comp. Anal. 20, 487 (2007).
16. H. Altundag, M.S. Dundar, S. Doganci, M. Celik, and M. Tuzen, J. AOAC Int. 96, 166 (2013).
17. M.S. Dundar, and H. Altundag, Environ. Monitor. Assess. 128(1-3), 177 (2006).
18. M. Bettinelli, G.M. Beone, S. Spezia, and C. Baffi, Anal. Chim. Acta. 424, 289 (2000).
19. E. Altintig, H. Altundag, and M. Tuzen, Bull. Chem. Soc. Ethiopia.28(1), 9 (2014).
20. D. Bakircioglu, Y.B. Kurtulus, and G. Ucar, Food Chem. Tox. 49(1), 202 (2011).
21. U. Altinbas, H. Hakerlerler, D. Anac, H. Tuncay and B. Okur, E.U. Rektör. Araş. Fonu Proje No:91 (1994).
22. B.J. Alloway, Record Number: 19901948863, 33 (1990).
23. A. Kabata-Pendias, and H. Pendias, CRC Press. Boca Raton, Florida, USA. 365 (1992).
24. T.E. Bahemuka, and E.B. Mubofu, Food Chem. 66(1), 63 (1999).
25. T.R. Chowdhury, H. Tokunaga, and M. Ando, Sci. Total. Environ. 308(1-3), 15 (2003).
26. WHO, Tech. Report Series No. 683. (1982).
27. D. Demirezen, and A. Aksoy, J. Food Qual. 29, 252 (2006).
28. T.G. Kazi, H.I. Afridi, N. Kazi, M.K. Jamali, M.B. Arain, R.A. Sarfraz, N. Jalbani, R. Ansari, A.Q. Shah, A.R. Memon, and G.A. Khandhro, Clin. Chim. Acta. 389(1-2), 114 (2008).
29. A.R. Memon, T.G. Kazi, H.I. Afridi, M.K. Jamali, M.B. Arain, N. Jalbani, and N. Syed, Clin. Chim. Acta. 379(1-2), 66 (2007).
30. Anonymous, Off. Gazette Iss: 24908 (2002).
31. A. Zahoor, M. Jaffar, and M. Saqib, Nutr. Food Sci. 33(5), 203 (2003).
32. A. Sattar, M. Wahid, and S.K. Durrani, Plant Foods for Human Nutr. 39, 279 (1989).
33. M.A. Radwan, and A.K. Salama, Food Chem. Tox. 44(8), 1273 (2006).
34. S. Saracoglu, M. Tuzen, and M. Soylak, J. Hazard. Mater. 167(1-3), 647 (2009).
35. WHO, World Health Org. Qual. Direct. Pot. Water, 197 (1994).
36. L.H. Foster, and S. Sumar, Crit. Rev. Food Sci. Nutr. 37(3), 211 (1997).
37. RDA, Recom. Diet. Allow. Nation. Acad. Press Washington, DC. (1989).

Coprecipitation of Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) With Ytterbium Hydroxide for Separation and Preconcentration Prior to Determination by FAAS

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ABSTRACT

A coprecipitation procedure for the separation and preconcentratiom of trace amounts of Fe(III), Mn(II), Cu(II), Pb(II), Cot(II), and Ni(II) is described. The analytical parameters including pH, ytterbium amount, centrifugation rate and time for the quantitative recovery of the analyte elements were optimized. The effect of matrix components of highly saline samples was also investigated. The limit of detection of the procedure was in the range of 2.1 µg/L for copper, 8.2 µg/L for nickel, and the preconcentration factor was 80. The accuracy of the method was checked by the addition recovery tests to real samples and by the analysis of the certified reference materials NIST SRM1570a Trace Elements in Spinach Leaves and SPS-WW2 Wastewater Level 2. The application of the method was performed for the determination of analyte elements in food and water samples.

INTRODUCTION

Some trace elements such as copper(Cu) and cobalt (Co) are important nutritional elements for human health in very low quantities (1–3). However, some trace elements like lead (Pb) and cadmium (Cd) can be toxic to humans as well as the environment (3–5). While certain elements such as chromium (Cr) are essential at low levels, when in excess this can result in deleterious effects to human health (6–7). Trace elements are also one of the main sources of environmental pollution resulting from industry, traffic, mining, etc. (8–10). Thus, an accurate and precise determination of trace elements in foods, biological and environmental samples is very important in order to monitor trace element levels in these samples. The instrumental detection systems including UV-Vis spectrometry, atomic absorption spectrometry (AAS), and atomic emission spectrometry (AES) (11–14) are widely used for the determination of trace elements. However, due to the limitation in detection limits of the instruments and the interference effects of the matrix components of the samples, these types of analyses are generally combined with a separation/preconcentration system (15–18). Various sample pretreatment procedures that combine separation and preconcentration include liquid-liquid extraction (19), cloud point extraction (20–22), solid phase extraction (23–25), membrane filtration (26, 27), and electroanalytical systems (28, 29). These methods often require large amounts of high purity organic solvents (30–32).

Coprecipitation is usually considered as a separation/preconcentration method due to its simplicity, speed, and the ability to attain high concentration efficiency for metal ions at trace levels. Coprecipitation with metal hydroxides has been widely used for enrichment/separation of metals at trace levels. Coprecipitation by hydroxide of analyte elements including magnesium, indium, lanthanum, samarium, terbium, erbium, gallium, hafnium, dysprosium, thulium, gadolinium, cerium, europium, neodymium, and iron has been reported for the separation/preconcentration of trace elements (32–35). The use of ytterbium hydroxide in the preconcentration studies is very limited (36–38). Due to its low solubility in water (39), for this work we selected ytterbium hydroxide as the coprecipitant for the separation/preconcentration of trace elements.

For this study, a separation/preconcentration procedure has been established for some metal ions in environmental samples based on coprecipitation. The analytical parameters including pH, amount of reagents, etc., were optimized.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 3110 flame atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used for the analyte measurements in standard and sample solutions. For each metal ion, a hollow cathode lamp and a 10-cm air-acetylene flame atomizer were used. The instrumental settings as recommended by the manufacturer are listed in Table I.

TABLE I
FAAS Instrumental Conditions

Element	Wavelength (nm)	Lamp Current (mA)
Mn	279.5	20
Fe	248.3	30
Pb	283.3	13
Ni	232.0	23
Co	240.7	23
Cu	324.8	15

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For pH measurements, a Nel pH-900 meter (Nel Company, Ankara, Turkey) with a glass electrode was used. Ultrapure deionized water was prepared by reverse osmosis and filtration using a Milli-Q® Direct 16 system (Millipore Australia Pty Ltd., North Ryde, Australia). An ALC PK 120 centrifuge (ALC International, Italy) was used during the centrifugation processes.

Solutions and Reagents

All solutions were made with reverse osmosis purified water. All reagents were of analytical grade. Distilled water was used throughout this work. The chemicals were of analytical reagent grade unless otherwise stated. Plastic and glassware were cleaned by soaking in a 10% HNO_3 solution, then rinsing with distilled water prior to use.

Stock solutions (1000 mg/L) of the analyte ions were diluted daily for obtaining reference and working solutions. The calibration standards were not subjected to the preconcentration procedure. A 0.1% (m/v) ytterbium(III) solution (0.1% mv) was prepared fresh daily by dissolving Yb_2O_3 (No: 1124100005, Merck, Darmstadt, Germany) in small amounts of 1 mol/L HNO_3 and diluting to 100 mL with distilled water.

Two certified reference materials, SRM 1570a - Trace Elements in Spinach Leaves and SPS-WW2 Wastewater Level 2, were purchased from the National Institute of Standards & Technology (NIST, Gaithersburg, MD, USA) and from Spectrapure Standards AS (Oslo, Norway), respectively.

Preconcentration Procedure

In order to optimize the coprecipitation system, 15 mL of deionized water containing analyte elements and 1.0 mL of 0.1% Yb_2O_3 (m/v) solution was used. The pH of the solutions was adjusted to the corresponding pH by the addition of 1 mol/L NaOH solution. The solutions were centrifuged at 4000 rpm for seven minutes. The supernatant was removed. The precipitate adhering to the tube was dissolved with 1 mL of 1 mol/L HNO_3. The final volume was completed to 2.0–10.0 mL with distilled water. The metal concentrations of the final solutions were determined by flame AAS (FAAS).

Application to Real and Certified Samples

A 1.0-g sample amount of certified reference sample (SRM 1570A Spinach Leaves), water, fruit, or spices was digested with 10 mL concentrated HNO_3 at 95 °C. The mixture was evaporated to form a semi-dry mass, mixed with 3 mL of H_2O_2, and then again evaporated to near dryness. After evaporation, 8–9 mL of ultrapure water was added and the sample mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 20 mL with ultrapure water, and the procedure described above was applied. The analytes in the final solution were determined by FAAS.

The certified reference material, SPS-WW2 Wastewater Level 2, was used directly and the coprecipitation procedure listed above applied after adjusting the pH to 11.0 by using 1 mol L^{-1} NaOH solution.

The proposed method was also applied to different water samples which were obtained from the Kayseri area: tap water, bottled mineral water, and wastewater. The samples were collected in pre-washed polyethylene bottles. Before analysis, the pH of the water samples was adjusted to 11.0 by using 1 mol L^{-1} NaOH solution. The preconcentration procedure listed above was applied to the final solutions. All determinations were carried out by FAAS.

RESULTS AND DISCUSSION

The recovery (%) value for the analyte ions of the proposed coprecipitation procedure was calculated using the following equation:

$$\text{Recovery}(\%) = (w_o/w_f) \times 100$$

where w_o (µg) is the amount of analyte in the final solution and w_f (µg) is the amount of analyte in the beginning solution, respectively.

Effect of pH

The influence of pH on the recovery of the analyte elements using coprecipitation with ytterbium(III) hydroxide was investigated in the 8.0–12.0 range. The pH of the working solutions was adjusted by using 1 mol/L NaOH. The results are given in Figure 1. Since the Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) ions were quantitatively (>95%) recovered at pH 11.0, all further studies were performed at this pH.

Effect of Amount of ytterbium(III)

The influence of the amount of ytterbium(III) on the coprecipitation efficiency of Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) was investigated in the 0–200 µg range at pH 11.0 (see Figure 2). It was found that without ytterbium(III), the recovery of the analyte ions was not quantitative (< 80%). Quantitative recovery for the analytes was tested in the range of 100–200 µg of ytterbium(III). The optimum amount of ytterbium(III) selected for further experiments was 100 µg.

Centrifugation Speed and Time

The effect of centrifugation speed on the recovery of the analytes was studied in the 1000–4000 rpm range. Quantitative values were obtained in the range of 2000–4000 rpm. For the present work, 2500 rpm was selected as the optimum centrifugation speed.

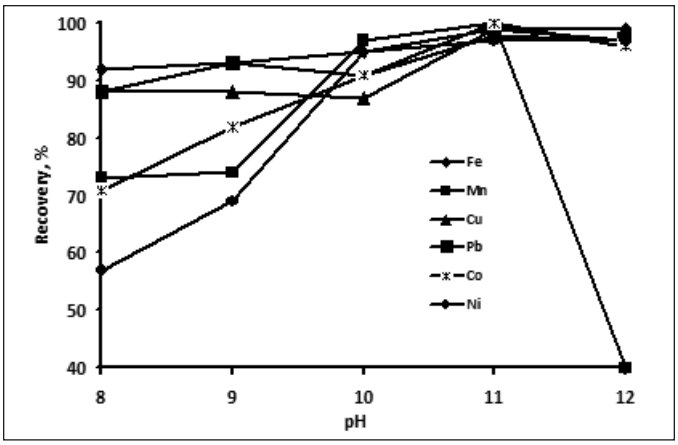

Fig. 1. Recovery(%)–pH relation on the proposed coprecipitation system (sample volume: 15 ml, N=3).

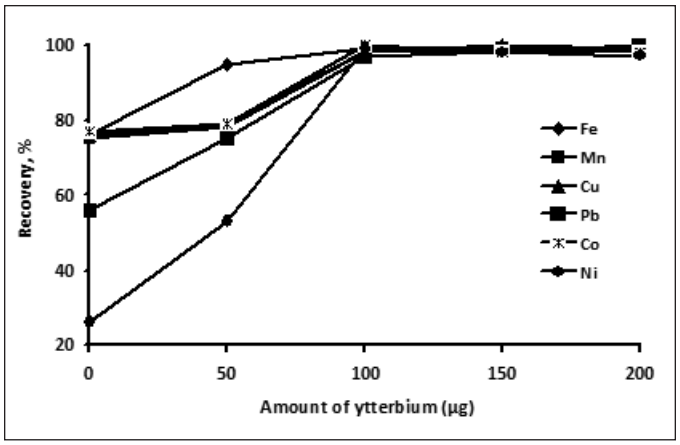

Fig. 2. Relation between amounts of ytterbium and recovery (%), (sample volume: 15 ml, N=3).

The influence of centrifugation time on the present coprecipitation work for the analyte elements was studied from 2–15 minutes. The recovery values were found to be quantitative in the time range of 10–15 minutes. Thus, 10 minutes were selected as the optimum centrifugation time.

Sample Volume

In order to achieve a high preconcentration factor, the sample volume of the working media is a key factor in preconcentration studies (40–45). The influence of sample volume of the aqueous solution on the recovery of the analyte elements was also investigated in the sample volume range of 10–500 mL. The elements were quantitatively (95%) recovered in the sample volume ranging from 10–400 mL. The final volume of the coprecipitation work was 5.0 mL. It was found that a preconcentration factor of 80 can be achieved when the final volume was 5.0 mL.

Effect of Concomitant Ions

Due to the interference effects of alkaline metals and the detection capability of the instrument at trace levels, earth alkaline metal ions and some cations and anions are a big problem for analytical chemists (46–53). The influence of these ions on the proposed coprecipitation procedure was investigated, and the results are listed in Table II. The ions normally present in water do not interfere under the experimental conditions used.

Analytical Performance

The accuracy of the proposed coprecipitation procedure for trace metal ions was checked by using addition/recovery tests for real samples. The results in Table III show that good agreement was obtained between the added and found analyte concentrations. The recovery values calculated for the standard additions were generally > 95%, thus confirming the accuracy of the proposed procedure and the absence of matrix effects.

The relative standard deviations for atomic absorption spectrometric measurements for analyte ions are below 5.0%. The detection limits, defined as the concentration equivalent to three times the standard deviation (n=10) of the reagent blank, are listed in Table IV. The optimum concentration ranges and regression equations for the analytes are also listed in Table IV. The detection limits for the analyte elements ranged from 2.1–8.2 µg/L.

Application

The developed method was applied to certified reference materials: SRM 1570a - Trace Elements in Spinach Leaves and SPS-WW2 Wastewater Level 2 for the determination of analyte metals. The results listed in Table V are based on the average of three replicates for the analytes and show that they are in good agreement with the certified values.

The presented procedure was applied to the determination of analyte elements in water, fruit, and spice samples from Kayseri, Turkey. The results are listed in Table VI.

CONCLUSION

Coprecipitation with ytterbium hydroxide offers a useful separation/preconcentration technique for food and water analysis. The procedure has been successfully applied to the analyte elements Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) with acceptable accuracy and precision. The coprecipitated analyte ions can be sensitively determined by flame atomic absorption spectrometry without any influence caused by ytterbium hydroxide. Accuracy of the method was verified by analysis of the certified reference materials.

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TABLE II
Effects of Matrix Ions on the Recovery of the Analyte Elements (Sample Volume: 15 mL, N=3)

Ion	Added as	Concentration (mg/L)	Recovery(%) Mn	Fe	Pb	Ni	Co	Cu
Na^+	NaCl	20,000	100±2	99±2	98±1	100±1	100±1	96±2
Ca^{2+}	$CaCl_2$	5000	97±1	102±1	98±2	98±1	98±1	99±2
Cl^-	NaCl	35,000	100±1	99±2	98±1	100±1	100±1	96±2
K^+	KCl	6000	96±2	101±1	99±1	97±1	96±1	99±2
SO_4^{2-}	Na_2SO_4	2000	98±1	99±1	98±1	96±1	101±1	99±1
Mn^{2+}	$MnSO_4 \cdot H_2O$	20	–	101±1	97±1	96±1	100±1	99±1
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	20	100±1	99±2	96±1	91±1	97±1	99±1
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	10	97±1	–	100±1	96±1	97±1	100±1
Pb^{2+}	$Pb(NO_3)_2$	20	100±1	101±1	–	99±1	99±1	100±1
Ni^{2+}	$Ni(NO_3) \cdot 6H_2O$	10	96±1	100±1	99±2	–	99±1	99±1
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	10	99±1	100±1	97±2	96±1	–	99±1
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	20	99±1	101±1	98±1	97±1	100±2	–
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	40	97±1	98±1	100±1	98±1	100±1	100±1

TABLE III
Addition/Recovery Test for Real Samples (Sample Volume: 15 ml, N=3)

	Added (µg)	Black Tea Found (µg)	Rec.(%)	Tap Water Found (µg)	Rec.(%)	Bottled Mineral Water Found (µg)	Rec.(%)
Pb	0	BDL	-	BDL		BDL	
	10	9.9±0.0	99	9.8±0	98	9.8±0	98
	20	20.6±0.3	103	20.0±0	100	20.0±0	100
Mn	0	BDL	-	BDL		BDL	
	10	10.2±0.3	102	10.2±0.6	102	10.2±2	102
	20	19.7±0.3	99	19.6±1	98	19.8±1	99
Ni	0	BDL		BDL		BDL	
	10	9.7±0.6	97	10.5±0.6	105	10.5±0	105
	20	20.3±0.0	101	20.5±0.6	103	20.5±1.2	103
Fe	0	BDL		BDL		BDL	
	10	10.3±0.6	103	10.1±0	101	9.6±1	96
	20	20.1±0.6	100	20.1±0.6	100	20.1±0.6	100
Cu	0	BDL		BDL		BDL	
	10	10.2±0.0	102	10.2±1	102	10.4±1	104
	20	20.0±0.0	100	20.2±2	100	20.0±1	100
Co	0	BDL		BDL		BDL	
	10	9.9±0.6	99	9.6±0.6	96	9.6±0	96
	20	19.6±0.3	98	19.6±0.6	98	19.6±1.0	98

Rec.(%) = Recovery(%). BDL : Below the detection limit.

TABLE IV
Analytical Characteristics of Proposed Method

Analyte	Correlation Coefficient	Linear Range (mg/L)	Regression Equation	Limit of Detection (µg/L)
Mn	0.999	0.1-2.0	A=0.058C – 0.0006	2.5
Fe	0.999	0.5-5.0	A=0.024C – 0.0011	7.4
Pb	0.999	1.0-10.0	A=0.006C + 0.0013	3.7
Ni	0.991	0.5-5.0	A=0.024C – 0.0011	8.2
Co	0.998	0.5-5.0	A=0.032C – 0.0040	4.5
Cu	0.999	0.5-5.0	A=0.033C + 0.0020	2.1

A = absorbance, C = concentration of analyte.

TABLE V
Application of Proposed Method to CRMs (Sample Volume: 15 mL)

	SRM 1570a - Trace Elements in Spinach Leaves			SPS-WW2 Wastewater Level 2		
Element	Certified Value (µg/g)	Found Value (µg/g)	Rec.(%)	Certified Value (µg/mL)	Found Value (µg/mL)	Rec.(%)
Cu	12.2	12.1 ±0.6	99	0.4	0.4 ± 0.1	100
Mn	75.9	75.7±0.2	99	0.4	0.4 ± 0.2	100
Co	0.39	0.38±0.04	97	-	-	
Pb	0.2	0.2±0.0	100	-	-	
Ni	2.14	2.1±0.1	98	1.0	1.04 ± 0.02	104
Fe	-	-		1.0	1.02 ± 0.01	102

BDL : below the detection limit.
ND: not determined.

TABLE VI
Levels of Analyte Elements in Real Samples (Sample Volume: 15 mL, N=3)

Sample	Pb (µg/L)	Ni (µg/L)	Mn (µg/L)	Co (µg/L)	Cu(µg/L)	Fe (µg/mL)
Wastewater	21.6 ± 0.04	5.38 ± 0.02	2.48 ± 0.06	3.05 ± 0.01	3.82 ± 0.01	28.8 ± 0.04
	Pb (µg/g)	Ni (µg/g)	Mn (µg/g)	Co (µg/g)	Cu (µg/g)	Fe (µg/g)
Grape	0.31 ± 0.02	2.14 ± 0.06	10.5 ± 0.1	0.43±0.06	11.2± 0.01	25.3±0.02
Cherry	0.31 ± 0.01	1.08 ± 0.02	4.53 ± 0.02	0.49±0.04	13.0±0.02	15.3±0.01
Mulberry	0.15 ± 0.01	1.61 ± 0.04	1.47 ± 0.01	0.31±0.02	18.4±0.04	21.1±0.04
Pepper Flakes	0.23 ± 0.02	1.34 ± 0.02	BDL	0.37±0.06	5.8±0.01	4.6±0.02
Black Pepper	0.31 ± 0.04	1.08 ± 0.04	BDL	0.24± 0.01	7.6±0.02	BDL

BDL: below the detection limit.

REFERENCES

1. G. Tel, H. Cavdar, E. Deveci, M. Ozturk, M.E. Duru, and A. Turkoglu, Food Addit. Contam. 7B, 226 (2014).
2. M. Soylak and L. Elci, J. Trace Microprobe Techn. 18, 397 (2000).
3. H. Cesur and B. Bati, Turk J. Chem. 26, 29 (2002).
4. M. Soylak, L. Elci, S. Saracoglu, and U. Divrikli, Asian J. Chem. 14, 135 (2002).
5. I. Narin, H. Colak, O. Turkoglu, M. Soylak, and M. Dogan, B. Environ. Contam. Tox. 72, 844 (2004).
6. M.Y. Asci, A. Efendioglu, and B. Bati, Turk. J. Chem. 32, 431 (2008).
8. T. Sabudak, G. Seren, G. Kaykioglu, and A.R. Dincer, J. Environ. Prot. Ecol. 8, 101 (2007).
9. M. Soylak, M. Tuzen, A.S. Souza, M.G.A. Korn, and S.L.C. Ferreira, J. Hazard. Mater. 149, 264 (2007).
10. D. Mendil, F. Celik, M. Tuzen, and M. Soylak, J. Hazard. Mater. 166, 1344 (2009).
11. E.I. Adeyeye, F.J. Faleye, and TM. Molaja, B. Chem. Soc. Ethiopia. 21, 23 (2007).
12. N. Sahoo, P.R. Rout, P.C. Samal, G.S. Parida, and K.K. Sardar, Indian Vet. J. 84, 326 (2007).
13. E.E. Ozbas, H.K. Ozcan, N. Balkaya, G. Demir, and C. Bayat, J. Residuals Sci. Tech. 4, 89 (2007).
14. M. Soylak, H. Colak, and O. Turkoglu, Fresen. Environ. Bull. 15, 345 (2006).
15. A.K.M. Atique Ullah, M. Akter, R. Anam, and S.H. Firoz, Am. J. Chem. Eng. 2, 35 (2014).
16. N. Uehara, K. Ozawa, and T. Shimizu, Tetsu To Hagane. 94, 8 (2008).
17. M. Soylak, L. Elci, and M. Dogan, Anal. Lett. 33, 513 (2000).
18. S. Saracoglu and M. Soylak, Food Chem. Toxicol. 48, 1328 (2010).
19. M.R. Jamali, Y. Assadi, and F. Shemirani, Separ. Sci. Technol. 42, 3503 (2007).
20. F. Shemirani, M.R. Jamali, and R.R. Kozani, Chem. Anal-Warsaw 52, 327 (2007).
21. A. Balouch, M.I. Bhanger, and F.N Talpur, Turk. J. Chem. 35, 925 (2011).
22. S. Candir, I. Narin, and M. Soylak, Talanta 77, 289 (2008).
23. M. Soylak, L. Elci, and M. Dogan, Fresen. Environ. Bull. 5, 148 (1996).
24. H. Fazelirad, M.A. Taher, and H. Ashkenani, J. AOAC Int. 97, 1159 (2014).
25. M. Soylak, I. Narin, and M. Dogan, Anal. Lett., 30, 2801 (1997).
26. O. Stroffekova, V. Janosova, M. Sykorova, and E. Havranek, J. Radioanal Nucl. Ch. 275, 659 (2008).
27. M. Soylak and R. Altin, Atom Spectrosc. 35, 79 (2014).
28. K. Zarei, M. Atabati, and M. Karami, J. Hazard. Mater. 179, 840 (2010).
29. R.Y.A. Hassan, I.H.I. Habib, and H.N.A. Hassan, Int. J. Electrochem. Soc. 3, 935 (2008).
30. A.A. Asgharinezhad, H. Ebrahimzadeh, M. Rezvani, N. Shekari, and M. Loni, Food Addit. Contam. 31A, 1196 (2014).
31. P.G. Krishna, J.M. Gladis, U. Rambabu, T.P. Rao, and G.R.K. Naidu, Talanta 63, 541 (2004).
32. J. Ueda, H. Satoh, and S. Kagaya, Anal. Sci. 13, 613 (1997).
33. M. Hiraide, Z.S. Chen, and H. Kawaguchi, Anal. Sci. 7, 65 (1991).
34. D.S.K. Peker, O. Turkoglu, and M. Soylak, J. Hazard. Mater. 143, 555 (2007).
35. M. Soylak, S. Saracoglu, U. Divrikli, and L. Elci, Talanta 66, 1098 (2005).
36. K. Atsumi, T. Minami, and J. Ueda, Anal. Sci. 21, 647 (2005).
37. A. Duran, M. Tuzen, and M. Soylak, Food Chem. Toxicol., 49, 1633 (2011)
38. S. Kagaya, T. Sagisaka, S. Miwa, K. Morioka, and K. Hasegawa, Bull. Chem. Soc. Jpn. 79, 717 (2006).
39. J.A. Dean, Lange's Handbook of Chemistry, fifteenth ed., Mcgraw-Hill, Inc., New York. 1999.
40. G. Venkatesh, and AK. Singh, Separ. Sci. Technol. 42, 3429 (2007).
41. U. Divrikli, M. Soylak, and L. Elci, Anal. Lett. 36, 839 (2003).
42. F.A. Aydin and M. Soylak, Talanta 72, 187 (2007).
43. M. R. Jamali and A. Kazemi, Iran. J. Anal. Chem. 1, 36 (2014).
44. M. Tuzen, K.O. Saygi, and M. Soylak, J. Hazard. Mater. 156, 591 (2008).
45. F. Sabermahani and M.A. Taher, J. AOAC Int. 97, 1713 (2014).
46. M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazerozohori, and M. Soylak, J. Hazard. Mater. 166, 1441 (2009).
47. H. Cesur, Turk. J. Chem. 47, 307 (2013).
48. M. Ghaedi, F. Ahmadi, Z. Tavakoli, M. Montazerozohori, A. Khanmohammadi, and M. Soylak, J. Hazard. Mater. 152, 1248 (2008).
49. M.S. Celebi, H. Ozyoruk, and S. Abaci, Hacettepe J. Biol. Chem. 42, 569 (2014).
50. M. Soylak, S. Saracoglu, and L. Elci, Trace Elemen. Electroly. 20, 160 (2003).
51. M. Ghaedi, K. Mortazavi, M. Montazerozohori, A. Shokrollahi, and M. Soylak, Mater. Sci. Eng. C Mater. Biol. Appl. 33, 2338 (2013).
52. A. Afkhami, H. Ghaedi, T. Madrakiana, and M. Rezaeivala, Electrochim. Acta. 89, 377 (2013).
53. M. Tuzen, I. Karaman, D. Citak, and M. Soylak, Food Chem. Toxicol. 47, 1648 (2009).

GFAAS Determination of Arsenic Levels in Biological Samples of Workers Occupationally Exposed to Metals: An Application in Analytical Toxicology

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ABSTRACT

Arsenic exposure in humans has been associated with adverse health effects such as neurological and cardiovascular effects, diabetes mellitus, skin lesions, skin, lung, kidney and liver cancers. Occupational exposure to arsenic usually occurs with inhalation of arsenic-containing particles in the mining industry. A simple and sensitive method was developed and validated for the determination of arsenic levels in biological samples by graphite furnace atomic absorption spectrometry (GFAAS), equipped with a Zeeman background correction system. Blood, urine, and hair samples are known to be the best biomarkers to assess arsenic exposure in humans. Samples were collected from 95 metal workers who were admitted at the Ankara Occupational Diseases Hospital in Turkey. Prior to analysis, the samples were pre-treated with an acid digestion procedure. The method showed linearity in the range of 0–100 µg/L, with a detection and quantification limit of 0.37 µg/L and 1.1 µg/L, respectively. The calibration curve was characterized by a high correlation coefficient (r=0.9991). Validation of the method was performed in terms of precision and accuracy with the use of reference materials. The method was applied to the analysis of certified reference material samples with satisfactory results (96.77–97.50%). The arsenic levels of the biological samples of the metal workers ranged between 3.83–52.44 µg/L in blood; 1.26–27.54 µg/L in urine; and 0,06–7.90 mg/kg As in hair. The mean arsenic levels in the blood, urine, and hair samples of the silver metal workers were found at 21.25±12.47 µg/L, 6.43±4.99 µg/L, and 1.81±1.79 mg/kg As, respectively.

INTRODUCTION

Arsenic (As) is an extremely poisonous element and has been classified as a human carcinogenic substance, group 1, by the International Agency for Research on Cancer (1). Arsenic exposure in humans is generally associated with the consumption of drinking water contaminated from natural, geological sources of inorganic arsenic. Chronic exposure to arsenic in humans has been related to the development of adverse health effects such as cardiovascular and peripheral vascular diseases, neurological disorders, diabetes mellitus, and various forms of cancer (2–4). Arsenic is found in inorganic and organic forms with different valence or oxidation states in the environment. Unlike inorganic arsenic, organic arsenic compounds in the pentavalent oxidation state are much less toxic because consumption of these organic arsenicals are not immediately accepted into the cells, and meet with limited metabolism (5, 6). Some important arsenic species are listed in Figure 1.

Inorganic arsenic occurs naturally in soil and many kinds of rock, especially in minerals and ores that contain copper, lead, cobalt, silver, and gold. Arsenic trioxide is volatilized during smelting and accumulates in flue dust, which may contain up to 30% arsenic trioxide (8). Thus, inhalation of industrial soil and dust causes arsenic exposure in metal workers. Occupational exposure to chemicals occurs most commonly via inhala-

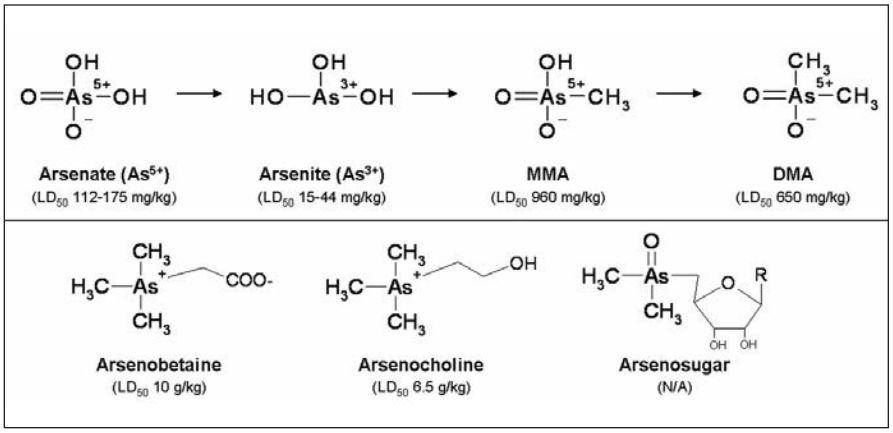

Fig 1. (Yüksel et al.) Some important arsenic species. Common inorganic arsenicals and their metabolites are listed in top row, while organic arsenicals found in seafood are listed in bottom row.

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tion. It can be possible to gather a more accurate prediction of total dose by using biomarkers (9) such as blood, urine, and hair. Since the main route of arsenic excretion takes place in the kidneys, the level of arsenic in urine can be used to predict exposure (10). Blood-arsenic is peculiarly employed only as a sign of very current or comparatively high-level exposure because inorganic arsenic is quickly eliminated from the blood (11). Hair has a unique potential to reveal retrospective information about the exposure of subjects (12). Additionally, once incorporated into keratin, arsenic has limited mobility, so it is known to be deposited in nails and especially in hair (13). Arsenic levels in blood, urine, nail, and hair of unexposed human adults are usually below 1 µg/L, 100 µg/L, 1 mg/kg, and 1 mg/kg, respectively (8).

The determination of arsenic levels in biological samples can be performed by methods such as neutron activation, X-ray fluorescence, atomic absorption and fluorescence spectrometry, and inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS) (14). In recent years, graphite furnace atomic absorption spectrometry (GFAAS), hydride generation atomic absorption spectrometry (HGAAS), and ICP-MS have become the leading techniques. ICP-MS (15-17) is widely used because of its multi-element capabilities, but it is also one of the most expensive instruments (18). Graphite furnace atomic absorption spectrometry is more economical and is a good choice due to its selectivity and sensitivity in the detection of a wide range of metals and non-metals, including arsenic (19).

The Zeeman effect (20) is based on the shift of energy of atoms and molecules in a magnetic field. If a magnetic field is generated at the atomizer (graphite furnace), the absorption lines of the analyte atoms are split into three components. Two of these components (σ–components) are shifted to slightly lower and higher wavelenghts, repectively, whereas the third component (π–component) remains largely unchanged. The π–component can be removed from the spectrum using a polarizer (Figure 2).

The main goal of this study was to develop and validate a sensitive method with graphite furnace atomic absorption spectrometry, equipped with a Zeeman-effect background correction system, to determine arsenic concentrations in biological samples for routine toxicological analytical application. The method developed for the determination of arsenic was applied to blood, urine, and hair samples obtained voluntarily from metal workers. The samples were taken from them at the Ankara Occupational Diseases Hospital, Turkey (21).

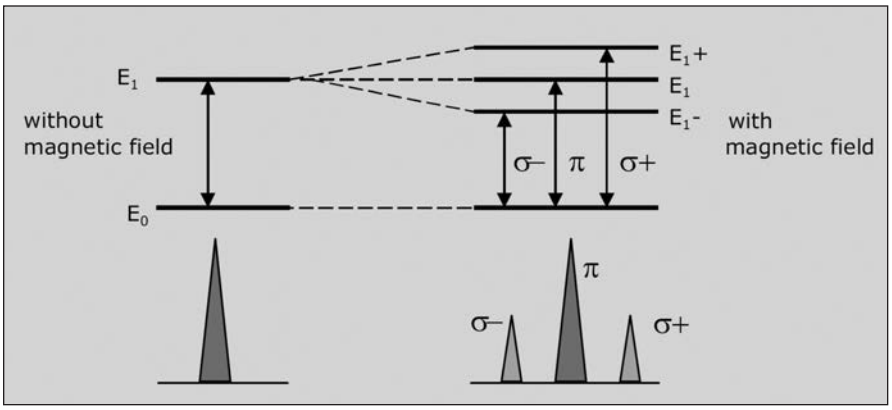

Fig. 2. (Yüksel et al.) Schematic diagram of Zeeman effect.

EXPERIMENTAL

Instrumentation

The measurements for arsenic determination were performed using a Varian AA240Z atomic absorption spectrometer (Varian, Victoria, Australia), equipped with a Zeeman background correction system. A boosted-discharge hollow cathode lamp (Agilent, Australia) was used as the excitation source for arsenic. The digestion procedure for the blood and hair samples was carried out using a Mars Xpress microwave system (CEM, Matthews, NC, USA) with PTFE microwave digestion vessels. The operating parameters for the GFAAS system are listed in Table I.

Standard Solutions and Reagents

A 1000-µg/mL arsenic stock solution was obtained from SCP Science (Courtaboeuf, France). Triton® X-100, polyethylene glycol mono (p-1,1,3,3-tetramethylbutylphenyl) ether, was obtained from Scharlau (Barcelona, Spain). Nitric acid (HNO_3, 65%) was purchased from Merck (Darmstadt, Germany). All chemicals used were of analytical reagent grade unless otherwise specified. Ultrapure water (Human UP 900 Scholar-UV, Korea), with a resistivity of 18 MΩ·cm, was used to prepare the solutions for the experimental process. Argon gas with a purity of 99.999% was purchased from a local supplier (Vasak Gaz, Ankara, Turkey). The reference materials used were BCR-CRM 397 Human Hair Powder (Community Bureau of Reference BCR, Institute for Reference Materials and Measurement, Belgium) and Seronorm™ Trace Elements Whole Blood L-2 (Sero AS, Billingstad, Norway).

Sample Collection

Blood, urine, and hair samples were collected from 95 metal workers (volunteers) at the Ankara Occupational Diseases Hospital, Turkey. The patients ranged in age from 18–61 years. This study was ethically approved by the Research Ethics Committee of the Medical Faculty, Ankara University (Decision Number:11-343-12/25.06.2012). Each volunteer was given a written informed consent form in accordance with the principles as established in The Declaration of Helsinki (World Medical Association, Declaration of Helsinki, 1964). The blood, urine, and hair samples were stored separately at 4 °C in vacutainer blood collection tubes, polypropylene tubes, and polyethylene lock bags, respectively, until the day of analysis.

TABLE I
Operating Parameters for GFAAS System

Element	As
Matrix	Blood, Urine and Hair
Instrument	Zeeman
Concentration Unit	µg/L, µg/kg
Instrument Mode	Absorbance
Sampling	Auto-Mix
Calibration Mode	Concentration
Measurement Mode	Integrated
Replicates Standard	3
Replicate Sample	3
Expansion Factor	1.0
Wavelength	193.7 nm
Slit Width	0.5 nm
Gain	59%
Current	10.0 mA
Background correction	ON
Standard 1	3.0 µg/L
Standard 2	6.0 µg/L
Standard 3	9.0 µg/L
Standard 4	12.0 µg/L
Standard 5	15.0 µg/L
Reslope Standard	Standard 2
Recalibration Rate	50
Calibration Algorithm	Linear

Procedure

In order to prepare calibration standards at the concentrations of 3, 6, 9, 12, and 15 µg/L, a 1000-µg/mL arsenic stock solution was diluted in 5% (v:v) HNO_3. All glassware was kept in 10% (v:v) nitric acid for at least one night prior to each experimental work.

Prior to analysis, the biological samples (except for urine) were pre-treated using the acid digestion procedure. One milliliter of each blood sample was taken into the Teflon® tubes. The microwave system (CEM Mars Xpress) was utilized for digestion of the samples with 5 mL of 65% HNO_3 solution. Similarly, 100-mg amounts of hair samples were taken and washed with Triton®-X, rinsed, and left standing to air-dry. This microwave digestion procedure was also applied to the hair samples. For the urine samples, 1-mL amounts were mixed with 5 mL of 65% HNO_3 (21, 26). All biological samples were diluted with ultra-pure water to 10 mL. The microwave temperature program is listed in Table II.

Optimization and Sample Treatment

Important parameters were adjusted to obtain the best performance from this spectrometric analysis. Selection of the digestion technique, choice of the appropriate wavelength for the biological matrix, calibration concentration range in accordance with element concentration in real samples, assessing the best furnace program and establishing the linearity, were the major criteria for developing and optimizing this atomic absorption spectrometry method. Preliminary studies were performed under these subheadings to establish the best methodology for accurate measurements (22). The graphite furnace temperature program for arsenic determination in biological samples is listed in Table III.

Detection was performed at the 193.7-nm arsenic line. This wavelength was selected due to a higher signal-to-noise ratio in the spectrum of the sample matrices than at the 197.2-nm and 189.0-nm lines. The

TABLE II
Temperature Program For Microwave Digestion

Max. Power (W)	Power (%)	Ramp (min)	Pressure	Temperature (°C)	Hold (min.)
1600	100	10:00	Maximum	210	10:00

TABLE III
Graphite Furnace Temperature Program for Arsenic Determination in Biological Samples

Step	Temperature (°C)	Time (s)	Flow (L/min)	Signal Collection		Reading	
1	85	5	0.3	×	No	×	No
2	95	40	0.3	×	No	×	No
3	120	10	0.3	×	No	×	No
4	800	5	0.3	×	No	×	No
5	800	1	0.3	×	No	×	No
6	800	2	0.0	√	Yes	×	No
7	2450	0.9	0.0	√	Yes	√	Yes
8	2450	2	0.0	√	Yes	√	Yes
9	2450	2	0.3	√	Yes	×	No

proposed method showed linearity in the range of 1–100 µg/L and good repeatability not exceeding 3% for As. On the other hand, the average arsenic levels in the real hair sample solutions without using dilution factors was measured roughly as 2 µg/kg. Hence, for calibration purposes, five calibration standards (namely, 3, 6, 9, 12, and 15 µg/L) were prepared. The calibration graph showed good linearity in the concentration range examined (Figure 3). The correlation coefficient and equation of the calibration curve were, respectively, found to be r=0.9991 and Abs=0.0071C+0.0018, where Abs stands for integrated absorbance and C for the arsenic concentration in µg/L.

Method Validation

In order to validate the method in terms of accuracy and precision, BCR-CRM 397 Human Hair Powder and Seronorm™ Trace Elements Whole Blood L-2 were analyzed for arsenic. Each certified reference material was analyzed 10 times with triplicate measurements. The results were compared with the certified values for accuracy, precision, and reproducibility of the method. The certified arsenic content of BCR-CRM 397 (Hair) was 0.31±0.02 mg/kg, while the measured value was 0.30±0.01 mg/kg, with the successful recovery and relative standard deviation (RSD) as 96.77% and 3.97%, respectively. Similarly, the certified arsenic content of Seronorm™ Trace Elements Whole Blood L-2 was 13.20±1.3 µg/L, while the measured value was 12.87±0.77 µg/L, with a satisfactory recovery and RSD as 97.50% and 5.98%, respectively. The analytical results of the certified reference materials are summarized in Table IV.

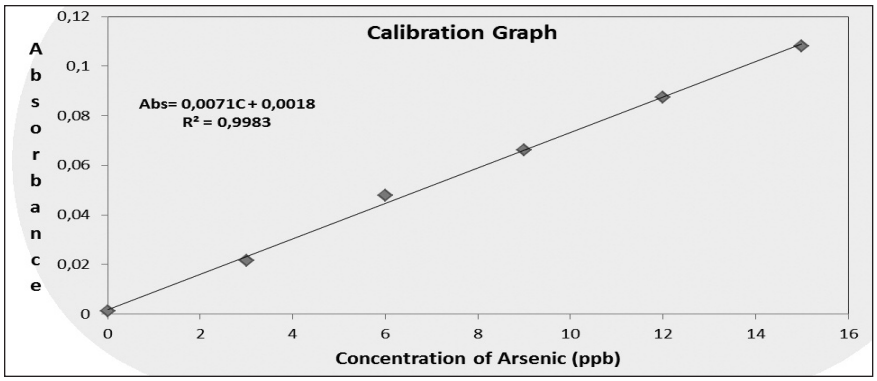

Fig. 3. (Yüksel et al.) Calibration graph of arsenic, performed by graphite furnace atomic absorption spectrometry (GFAAS), equipped with Zeeman-effect background correction.

TABLE IV
Analysis of Certified Reference Materials (CRMs)

CRMs	Number of Analyses (n)	Certified Value	Measured Value	Recovery	RSD
BCR-CRM 397 (Hair)	10	0.31±0.02 mg/kg	0.30±0.01 mg/kg	96.77 (%)	3.97 (%)
Seronorm™ Trace Elements Whole Blood L-2 (Blood)	10	13.20±1.30 µg/L	12.87±0.77 µg/L	97.50 (%)	5.98 (%)

Limit of Detection and Quantification

The limit of detection (LOD) and lowest limit of quantification (LOQ) were determined based on the standard deviation of the response and the slope of the calibration curve, according to ICH guidelines (23, 24) (LOD=3.3σ/S, LOQ=10σ/S, where σ is the standard deviation of the response and S is the slope of the calibration curve). The LOD and LOQ values were calculated for arsenic in the blood samples and found as 0.37 µg/L and 1.1 µg/L, respectively.

RESULTS AND DISCUSSION

Epidemiological studies have provided compelling evidence that inorganic arsenic is carcinogenic to humans. Chronic ingestion of arsenic increases the risk of developing skin, lung, urinary bladder, and liver cancer (25).

The assessed arsenic levels of the biological samples from the metal workers ranged between 3.83 and 52.44 µg/L in blood; 1.26 and 27.54 µg/L in urine; 0.06 and 7.90 mg/kg As in hair. The mean arsenic levels in the blood, urine, and hair samples of the silver metal workers were found as 21.25±12.47 µg/L, 6.43±4.99 µg/L, 1.81±1.79 mg/kg As, respectively, while the acceptable arsenic levels in human biological samples (blood, urine, hair, and nail) were below: 1 µg/L, 100 µg/L, 1 mg/kg, and 1 mg/kg, respectively, and are listed in Table V (8).

According to the results obtained from this toxicological arsenic analysis, 43 of 95 individu-

TABLE V
Normal Arsenic Levels in Human Biological Samples (8)

Blood	Urine	Hair	Nail
<1 µg/L	<100 µg/L	≤1 mg/kg	≤1 mg/kg

als have hair-arsenic concentrations above the safe limits. As for the blood-arsenic and urine-arsenic levels, all individuals have above normal levels of blood-arsenic, but are at safe limits for urine-arsenic levels (21). The evaluated arsenic levels in the biological samples of the metal workers are listed in Table VI.

TABLE VI
Descriptive Statistics of Arsenic Levels in Biological Samples of Metal Workers

N=95	Age (Years)	Body Mass Index	Exposure Time (Year)	Blood Arsenic Level (ppb)	Urine Arsenic Level (ppb)	Hair Arsenic Level (ppm)
Mean	33.22	25.45	3.49	21.25	6.43	1.81
Standard Deviation	8.08	4.22	2.09	12.47	4.99	1.79
Minimum	18	17.34	1.0	3.83	1.26	0.06
Maximum	61	37.50	10	52.44	27.54	7.90

CONCLUSION

A graphite furnace atomic absorption spectrometry (GFAAS) method, using Zeeman background correction, was developed for the determination of arsenic in human blood, urine, and hair. Using the Zeeman-effect for background correction, a strong magnetic field is turned on and off in rapid sequence. Total absorbance (element-specific and non-specific background absorption) is measured with the magnetic field in OFF-position and the background absorption with the magnetic field in ON-position The difference of the two values gives the corrected element-specific absorption. The advantages of the Zeeman-effect technique are as follows:

- Measurement of total and back ground absorption on the same wavelength
- Correction of rapid and structured background
- No special lamp required
- Correction over the entire wavelength range
- Better signal-to-noise ratio

The method developed for arsenic determination in human biological samples is relatively simple, rapid, sensitive, and offers very good precision and accuracy. The method is low-cost since it does not require large amounts of reagents. In addition, the method proposed is quite competitive in relation to other analytical approaches used for toxicological purposes.

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REFERENCES

1. IARC (International Agency for Research on Cancer): Some drinking water disinfectants and contaminants, including arsenic, IARC Monographs on the evaluation of carcinogenic risks to humans, 84 (2004)
2. J.A. Centeno, F.G. Mullick, L. Martinez, N.P. Page, H. Gibb, D. Longfellow, C. Thompson, and E.R. Ladich, Environ. Health Perspect. 110 (5), 883 (2002).
3. World Health Organization (WHO), Diagnosis and treatment of chronic arsenic poisoning. In United Nations synthesis report in drinking water, Geneva, Switzerland, 4, 1 (2000).
4. K. Bailey, Y. Xia, W.O. Ward, G. Knapp, J. MO, J.L. Mumford, R.D. Owen, and S.F. Thai, Toxicol. Pathol. 37(7), 849 (2009).
5. S.M. Cohen, L.L. Arnold,.M. Eldan, A.S. Lewis and B. D. Beck, Crit. Rev. Toxicol. 36, 99 (2006)
6. M.F. Hughes, B.D. Beck, Y. Chen, A.S. Lewis and D.J. Thomas, Toxicol. Sci. 123(2), 305–332 (2011).
7. J. Liu, Y. Lu, Q. Wu, R.A. Goyer and M.P. Waalkes, J. Pharmacol. Exp. Ther. 326(2), 363 (2008).
8. Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for arsenic, Atlanta, GA: US Public Health Service (2007).
9. R.G. Abrefah, D.K. Adotey, E. Mensimah, E. Ampomah-Amoako, R.B.M. Sogbadji and N.S. Opata, Environm. Research, Engineering and Management 2(56), 43 (2011).
10. World Health Organisation (WHO), Environmental Health Criteria (18), Arsenic, Geneva, Switzerland (1981).
11. National Research Council (NRC), Arsenic in drinking water, Washington, DC, USA, National Academy Press (1999).
12. H. Sela, Z. Karpas, M. Zoriy, C. Pickhardt, and J.S. Becker, Int. J. Mass Spectrom, (261), 199 (2007).
13. R.D. Koons and C.A. Peters., J. Anal. Toxicol. 18, 36 (1994).
14. M.F. Hughes, Environ. Health Perspect. 114(11), 1790 (2006).
15. K. Gellein., S. Lierhagen., P.S. Brevik, M. Teigen, P. Kaur, T. Singh, T.P. Falten, and T. Syversen, Biol. Trace. Elem. Res. 123, 250 (2008).

16. D.A. Bass, D. Hickok, D. Quig, and K. Urek, Altern. Med. Rev. 6(5), 472 (2001).

17. A. Unkiewicz-Winiarczyk, A. Bagniuk, K. Gromysz-Kałkowska, and E. Szubartowska, Biol. Trace Elem. Res. 128, 152 (2009).

18. R. Wietecha, P. Kos´cielniak, T. Lech, and T. Kielar, Microchim. Acta 149, 137 (2005).

19. W. Goessler and D. Kuehnelt, Environm. Chem. of Arsenic, Marcel Dekker, New York, USA, 27 (2002).

20. Fundemantals, Instrumentation and Techniques of Atomic Absorption Spectrometry, Analytik Jena AG, Jena, Germany, [http://www.analytik-jena.de], (Access Date: December 20, 2014).

21. B. Yüksel, Z. Kayaalti, V.A., Türksoy, E. Tutkun, and T. Söylemezoglu, Toxicol. Lett., Supplement, 221, 251 (2013).

22. B. Yüksel, G. Mergen, and T. Söylemezoglu, At. Spectrosc. 31(1), 1 (2010).

23. International Conference on Harmonization (ICH) of Technical Requirements for the Registration of Pharmaceuticals for Human Use, Validation of Analytical Procedures: Methodology (ICB-Q2B) (1996).

24. G. Mergen, T. Söylemezoglu, I. Ilhan, and Y.B. Dogan, LC GC Eur. 22(4), 180 (2009).

25. H. Wanibuchi, E.I. Salim, A. Kinoshita, J. Shen, M. Wei, K. Morimura, K. Yoshida, K. Kuroda, G. Endo, and S. Fukushima, Toxicol. Appl. Pharmacol. 198, 366 (2004).

26. B.Yüksel, Ph.D Thesis, Ankara University, Ankara, Turkey (2013).

Determination of Ag and Cd in Soil and Sediment Samples by Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

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ABSTRACT••

An extensive study has been made for the determination of silver (Ag) and cadmium (Cd) in soil and sediment samples using different decomposition procedures. A simple and rapid method has been developed for the accurate determination of Ag and Cd at ppb levels by graphite furnace atomic absorption spectrometry (GFAAS). In the present study, –200 mesh size samples were digested in a 100-mL glass beaker using 1:1 HNO_3 for measurement of Ag and Cd by GFAAS. A bulk calibration standard of 20 ppb of Ag and 10 ppb of Cd was used for the measurement of silver and cadmium, respectively. The method was proposed for the determination of Ag and Cd in soil and sediment samples collected according to the guidelines of the National Geochemical Mapping (NGCM) program and is being followed by the Geological Survey of India with an objective for Geochemical Mapping. The precision of the proposed method was investigated by analyzing 10 soil and sediment samples, and the estimated value of the RSD (%) was found to be <10%. The efficiency of the method was also compared by analyzing 10 international soil and sediment reference samples. Very good agreement and excellent precision were observed for the certified values. The limit of quantitation (10σ) achieved for Ag was 5.0 ng/g and for Cd it was 2.0 ng/g, with a recovery of 95–103%

INTRODUCTION

Silver (Ag) occurs in nature as sulphides, tellurides, arsenides, antimonides, and halides. It also occurs as native state and is associated with native gold and copper. The only oxygen compound of Ag known to occur in nature is argentojarosite, a sulphate of silver and iron. The crustal abundance of silver is 0.070 ppm and of cadmium it is 0.1 ppm. Cadmium (Cd) is a relatively rare metal and found in association with zinc (Zn) (1). It occurs usually as green ockite associated with sphalerite. The Geological Survey of India has taken up the National Geochemical Mapping (NGCM) program and 68 elements are to be determined in soil and sediments at their crustal abundance level or below. The 68 elements are divided into 10 different packages, i.e., from Package A to Package J. The elements Ag and Cd come under Package F and the required detection limits were set as 20 and 100 ppb, respectively. These elements are very useful in geochemical exploration.

Elemental analysis by graphite furnace atomic absorption spectrometry (GFAAS) is normally carried out in the solution phase (2). Geological samples, e.g., soils, sediments, rocks, ores, minerals, etc., are usually brought into solution by mineral acid digestion. Dissolution of geological samples to bring Ag and Cd in solution is an important part of the analysis. Matrix and background absorbance play a vital role for the estimation of elements by GFAAS at such a low level of concentration. Viets et al. (3) determined these elements by flame atomic absorption spectrometry (FAAS) using alkaline fusion, followed by hydrochloric acid dissolution and pre-concentration in an organic solvent resulting in a detection limit of 100 ppb. Zongshou Yu et al. (4) reported different digestion techniques such as $HF/HClO_4$, HF/HNO_3, and HF/H_2SO_4 to dissolve geological samples for trace element determination. Silver and cadmium were also estimated in geological samples with the help of FAAS and GFAAS by several authors using different acid and fusion mixtures (3, 5–8). There are some complete dissolution and some partial decomposition techniques. But an accurate, precise, simple, and rapid method is required to fulfill the requirement as per the National Geochemical Mapping (NGCM) program.

In this paper, a simple and rapid dissolution procedure has been developed for the determination of Ag and Cd in geological samples collected according to the guidelines of the NGCM program. The samples were pulverized to –200 mesh sizes to reduce the probability of leaving the silver trapped in the silicate phase. The proposed method consists of two parts: dissolution and GFAAS measurement.

For geochemical mapping, the total concentration of the elements is required. These data have a multipurpose use, e.g., for mineral exploration and environmental investigative study of basic geology (9). Nitric acid digestion has been most commonly used in exploration

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geochemistry for many years, but it does not always provide a total extraction as reported by Chao and Sanzolone (10). Balaram et al. (11) studied *aqua regia* digestion and extraction for some base metals resulting in 95–99% extraction. Saha et al. (5) reported a comparative study using a different dissolution procedure for the measurement of copper, lead, zinc, nickel, cobalt, silver, and cadmium and concluded that HF-$HClO_4$–HNO_3 digestion is most suitable for the complete extraction of the metals. The present authors observed that complete extraction of Ag and Cd from soil and sediment samples is possible with 1:1 HNO_3. The dilution factor is also very important for low level determination of the elements in geological samples. Flame AAS has been widely used for the trace element determination in geochemical samples (12). However, the detection limits required in NGCM samples for Ag and Cd are very low, and FAAS has not been able to achieve such low detection limits even though some authors have reported such detection limits for one or two elements, e.g., lithium and zinc (13).

Nowadays, GFAAS, inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) are the most commonly used techniques for the determination of trace amounts of Cd and Ag (14–17). GFAAS is simple, sensitive, and cost-effective in comparison to ICP-AES and ICP-MS, but it is a great challenge to achieve the very low detection limits required for Ag and Cd in geological samples. In most cases, detection limits at the ppb level are achieved only using pre-concentration methods such as ion exchange separation, solvent extraction, etc. Sometimes it is required to digest more samples to reach detection limits at the ppb level, but interferences from high concentrations of other elements provide erroneous results. The present dissolution technique overcomes almost all possibilities of error. The limit of quantitation (10σ) achieved for the estimation of Ag and Cd is much less than the crustal abundance level, which is also the required detection level for the NGCM program. The validity of the method was checked with 10 certified reference materials (CRMs).

EXPERIMENTAL

Instrumentation

All analyses were performed using a Varian 220 FS atomic absorption spectrophotometer (Varian, Palo Alto, CA, USA). The analytical parameters used for the determination of Ag and Cd by GFAAS are listed in Table I. The temperature profile for measurement of Ag and Cd is depicted in Tables II and III, respectively.

TABLE I
Instrumental Parameters for GFAAS Measurement of Ag and Cd

	Ag	Cd		Ag	Cd
Sampling Mode	Auto Mix	Auto Mix	Calibration Mode	Concen tration	Concen-tration
Measurement Mode	Peak Height	Peak Height	Wave-length	328.1 nm	228.8 nm
Slit Width	0.5 nm	0.5 nm	Lamp Current*	4.0 mA	4.0 mA
Background Corrector	ON	ON	Conc. Decimal Places	2	2
Sample Volume	20 µL	10 µL	Total Volume	25 µL	15 µL
Bulk Conc.	20 µg/L	10 µg/L	Calibration Standards (µg/L)	2, 10, 20	2, 5,10

* Parameter may change depending on the model of the instrument.

TABLE-II
Temperature Profile for Ag Measurement

Step	Temp. (°C)	Time (sec)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	30.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	700	25.0	3.0	Normal	No	No
5	700	2.9	3.0	Normal	No	No
6	750	2.9	0	Normal	No	Yes
7	2100	0.8	0	Normal	Yes	Yes
8	2100	2.0	0	Normal	Yes	Yes
9	2150	2.0	3.0	Normal	No	Yes

Reagents and Standard Solutions

All reagents used were of analytical reagent (AR) grade. Distilled 1:1 HNO_3 was preferred for the procedure.

Silver and cadmium standards were prepared from silver nitrate and cadmium nitrate (obtained from Johnson and Mathey Chemical Ltd., Royston, U.K).

Stock solutions were made of 100 ppm Ag and 100 ppm Cd solution.

100 ppm Ag: 0.17 g of $AgNO_3$ (SpecPure®) was dissolved in 25 mL 5% HNO_3, and the volume was made up to 1000 mL, maintaining 5% HNO_3 concentration.

100 ppm Cd: 0.236 g of $Cd(NO_3)_2$ was dissolved in 25 mL of 5% HNO_3, and the volume was made up to 1000 mL, maintaining 5% HNO_3 concentration.

Sub-standard solutions: 1.0 and 0.5 ppm solutions of Ag and Cd, respectively, were prepared by successive serial dilution of the 100 ppm stock solution.

Mixed calibration standard (bulk): 20 ppb and 10 ppb mixed standard solutions of Ag and Cd were prepared with 5% HNO_3 by dilution of the 1.0 ppm and 0.5 ppm Ag and Cd solutions, respectively.

High purity Milli-Q® water (18 MΩ·cm) was used for all of the sample and standard preparation procedures. All glassware and digestion vessels were acid-washed and rinsed with Milli-Q water.

Certified Reference Materials (CRMs)

For this study, the authors have selected 10 CRMs obtained from the China National Analysis Centre for Iron and Steel, Beijing, P.R. China. There are five certified soil reference samples (GSS-1, GSS-2, GSS-3, GSS-5, and GSS-8) and five certified sediment reference samples (GSD-3, GSD-4, GSD-5, GSD-6, and GSD-10).

Dissolution Procedure for the Geological Samples and CRMs

A 2.0-g sample (–200 mesh) was taken into a 250-mL glass beaker, and 80 mL (1:1) HNO_3 (AR) was added. The beaker was covered with a glass lid, placed on a hot plate, and boiled gently for 2.0–2.5 hours. The lid was removed and the solution evaporated slowly to a pasty mass. Then, 10 mL of 5% HNO_3 was added, warmed for 5 minutes, removed from the hot plate, and cooled. The contents were transferred to glass-stoppered graduated test tubes, and the volume was made up to 20 mL with demineralized water. The solution was kept aside undisturbed overnight to settle down, and then the appropriate volume of the supernatant solution was taken by auto-pipette for its subsequent measurement by GFAAS using the parameters listed in Tables I, II, and III. A process blank was prepared for each batch of samples, following the same procedure as for the original processed sample solution.

TABLE III
Temperature Profile for Cd Measurement

Step	Temp. (°C)	Time (sec)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	30.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	300	30.0	3.0	Normal	No	No
5	300	2.5	3.0	Normal	No	No
6	400	2.5	3.0	Normal	No	Yes
7	2000	0.8	0	Normal	Yes	Yes
8	2000	2.0	0	Normal	Yes	Yes
9	2100	2.0	3.0	Normal	No	Yes

RESULTS AND DISCUSSION

This study was made using 10 Chinese CRMs of soil and sediments for the determination of Ag and Cd. Excellent agreement was found with the certified values. The results of these 10 CRMs are listed in the Table IV and demonstrate that 1:1 HNO_3 effectively extracts Ag and Cd present in the soil and sediment samples. In order to investigate the precision of the proposed method, six separate sets of each CRM were dissolved using 1:1 HNO_3, and measurement of the solutions was performed by GFAAS taking the mean of three replicates. As can be seen from Table IV, the percentage RSD (relative standard deviation x 100/mean reading) for the determination of Ag and Cd was in the 4–6% range, except for a few cases where it was estimated to be around 8–9%.

Ten soil and stream sediment samples collected under the NGCM program were also analyzed by the proposed methodology, and uniform recovery of Ag and Cd was observed. The results of these 10 samples are listed in Table V. The precision of the proposed method for the analysis of these samples was checked by following the same procedure as for the CRMs. The estimated RSD value was in the range of 3–8%, confirming good precision of the proposed method. The limit of quantitation (LOQ, 10 times the standard deviation of the digestion procedure blank solution) was expressed as the concentration

TABLE IV
Results of Ag and Cd Determination in CRMs by GFAAS

Sample	Ag (ng/g)			Cd (ng/g)		
	Observed	Determined mean ± SD	Certified	Observed	Determined mean ± SD	Certified
GSS-1	366,381,400,389,406,398	390±14.68	350±70	4375,4500, 4213,4555, 4183,4424	4375±150.69	4300±600
GSS-2	53,59,52,56, 57,47	57±4.28	54±10	71,78,76, 82,73,64	74±6.22	71±22
GSS-3	87,93,86,83, 81,80	85±4.77	91±11	49,47,54, 46,53,57	51±4.33	59±20
GSS-5	4200,4486, 4314,4050, 4005,3965	4170± 202.55	4400± 600	460,449,435,443,403,390	430±27.51	450±90
GSS-8	50,46,48,56, 59,53	52±4.94	60±14	122,130,112,103,109,120	116±9.82	130±50
GSD-3	570,560,588,555,612,565	575±21.39	590±70	97,95,92, 87,83,86	90±5.51	100±20
GSD-4	90,98,103, 100,96,89	96±5.55	84±26	177,194,186,173,165,167	178±11.22	190±30
GSD-5	372,350,395,370,365,380	372±15.03	360±40	820,840,828,808,780,784	810±24.10	820±70
GSD-6	355,378,375,336,341,346	355±17.70	360±40	409,435,402,416,390,420	412±15.50	430±30
GSD-10	261,252,240,287,280,246	261±18.89	270±30	1174,1067, 1140,1096,1125,1130	1122±36.88	1120±120

SD = standard deviation of six determinations.

TABLE V
Results of Ag and Cd Determination of 10 Soil and Sediment Samples by GFAAS

Sample ID		Sample Type	[a]Determined mean ± SD [b]RSD(%)	
			Ag (ng/g)	Cd (ng/g)
1.	14935-1	Soil	21 ± 1.34 (6.38)	59 ± 2.13 (3.61)
2.	14935-10	Soil	26 ± 1.55 (5.96)	63 ± 1.98 (3.14)
3.	14935-21	Soil	44 ± 1.87 (4.25)	125 ± 1.87 (1.49)
4.	14935-31	Soil	20 ± 1.42 (7.10)	50 ± 1.74 (3.48)
5.	14935-41	Soil	5 ± 0.46 (9.20)	9 ± 0.43 (4.78)
6.	14849-1	Stream Sediment	24 ± 1.43 (5.96)	41 ± 1.21 (2.95)
7.	14849-4	Stream Sediment	33 ± 1.63 (4.94)	49 ± 1.33 (2.71)
8.	14849-11	Stream Sediment	27 ± 1.59 (5.89)	46 ± 1.56 (3.39)
9.	14849-18	Stream Sediment	23 ± 1.26 (5.48)	42 ± 1.37 (3.26)
10.	14849-19	Stream Sediment	11 ± 0.78 (7.09)	27 ± 1.19 (4.41)

[a] Mean of six determinations.
[b] %RSD = relative standard deviation values listed in parentheses..

in the samples, thereby accounting for the dilution factor used. The standard calibration curves obtained for the measurement of Ag and Cd are shown in Figures 1 and 2. The absorbance value of a 10-ppb Ag solution was 0.1974, whereas for a 4-ppb Cd solution it was 0.2253. The characteristic concentration for Ag and Cd was 0.222 ng/mL and 0.0781 ng/mL, respectively. Thus, a solution containing 0.222 ng/mL Ag and 0.0781 ng/mL Cd will give 1% absorption. The LOQ (10σ) observed for the quantification of Ag was 5 ng/g and for Cd 2 ng/g, which is below the crustal abundance level; the RSD was <10%. These results confirm that this methodology may be used very effectively for the determination of Ag and Cd in soil and sediment samples for geochemical exploration work.

CONCLUSION

The proposed method is very simple and rapid in comparison to other dissolution techniques followed by preconcentration, it uses

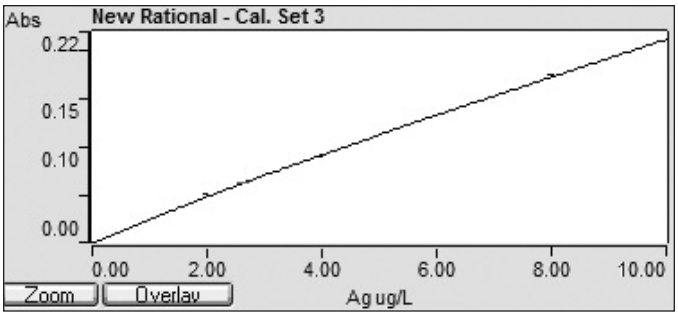

Fig.1: Calibration Curve of Silver by GF-AAS.

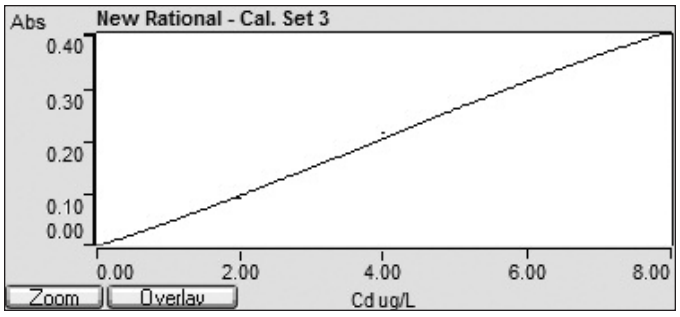

Fig.2: Calibration Curve of Cadmium by GF-AAS.

a single acid decomposition procedure, and allows complete extraction of Ag and Cd. The most striking advantages of the nitric acid decomposition method are simplicity, smaller background value, and direct injection of the aqueous solution into the graphite tube with the auto-injection procedure. The method is less hazardous in comparison to the *aqua regia* and HF-$HClO_4$ dissolution processes which produce harmful chlorine and hydrogen fluoride gases. There is no probability of loss of the analyte element during evaporation using the proposed dissolution procedure since no volatile chlorides are formed, which is a common phenomenon in the case of *aqua regia* digestion methods. The crustal abundance of Ag is 70 ppb and of Cd it is 100 ppb. The limit of quantification achieved by the proposed method is much below the crustal abundance for these elements. Due to its simplicity, rapid estimation, low cost, and achievement of a much lower detection limit, this method is routinely followed by the Geological Survey of India for the quantitative determination of Ag and Cd in soil and sediment samples collected under the NGCM program. The limit of quantitation (10σ) achieved for Cd was 2.0 ng/g and for Ag 5.0 ng/g, with a recovery of 95–103%.

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REFERENCES

1. K.H. Wedepohl, Geochem. et Cosmochem. Acta 59(7), 1217 (1995).
2. H.M. Kingston and S.J. Haswell (Eds.), Microwaves enhance chemistry. Fundamentals, sample preparation and applications, AES, Washington, DG, USA (1997).
3. John G. Viets, Richard M. O'Leary and J. Robert Clark, Analyst 109, 1589 (1984).
4. Zongshou Yu, Philip Robinson, and Peter McGoldrick, Geostd. Newsl. 25(2-3), 199 (2001).
5. M.C. Saha, T. Bhattacharya and N.K. Roy, Indian Minerals 59, 123 (2005).
6. Anindya Das and Manik C. Saha, At. Spectrosc. 34(2), 60 (2013).
7. J.G Sengupta and J.L Bouvier, Talanta 42(2), 269 (1995).
8. Zhongxi Li, Liping Zhou, and Feng Tan, Microchim. Acta 156, 263 (2007).
9. X. Xueijing, Analyst 120, 1497 (1995).
10. T. T. Chao and R. F. Sanzolone, J. Geochem. Expl. 44, 65 (1992).
11. V. Balaram, P.V.S. Raju, S.L. Ramesh, K.V. Anjaiah, B. Dasaram, C. Manikyamba, V.R. Mohan, and D.S. Sarma, At. Spectrosc. 20(4), 155 (1999).
12. John G. Viets, J. Geochem. Expl. 42, 107 (1992)
13. P.J. Potts, A Handbook of Silicate Rock Analysis, Blackie Academy and Professional, London, U.K., 187 (1987).
14. M.A. Rahman, S. Kaneco, and M. Amin, Talanta 62, 1047 (2004).
15. J.B. Borba da Silva, M.A. Mesquita da Silva, A.J. Curtius, and B.J. Welz, Anal. At. Spectrom. 14, 1737 (1999).
16. A. Vaisanen, R. Suontamo, J. Silvonen, and J. Rintala, Anal. Bioanal. Chem. 373, 93 (2002).
17. L.P. Zhou and Z. Li, Chin. J. Anal. Lab. 24(9), 20 (2005).

Determination of Lead in Plastic Food Packaging by Graphite Furnace Atomic Absorption Spectrometry

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ABSTRACT

Lead sulfate and lead stearate are commonly used as additives or stabilizers to protect plastic material from chemical degradation. Moreover, lead chromate is used in pigments. Considering that the presence of Pb in plastic material used for food and beverage packaging may cause deleterious effects to the human body, a simple and fast analytical method for Pb monitoring in plastic food packaging is proposed.

Direct solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (DSS HR-CS GFAAS) was used as the analytical technique and calibration against aqueous standards was employed. A mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ was used as the chemical modifier. The developed method was applied to different plastic containers. For comparison, some samples were also analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The concentration of Pb in the evaluated samples varied from 16 to 793 μg kg^{-1}. A paired *t*-test at a 95% confidence level showed that the DSS HR-CS GFAAS method provided similar results as those obtained by ICP-MS. The proposed method resulted in a characteristic mass of 5.0 pg of Pb and a limit of detection of 4.9 μg kg^{-1}. The relative standard deviation ranged from 2.7 to 18.8% for the determinations by DSS HR-CS GFAAS and from 2.1 to 13.3% when using ICP-MS.

INTRODUCTION

The global plastics consumption is estimated to reach 297 million tons by 2015 with an expressive fraction being used in food and beverage packaging (1). In this sense, quality control of plastic material for food and beverage represents an increasingly important concern. Besides organic compounds, plastic materials may also hold inorganic species, some of them considered potentially harmful (2,3). The presence of Cu, Cr, Ni, and Pb in polyethylene (4), Sn and Sb in polyvinyl chloride (5,6), Ag in polypropylene (7), and Hg in polyethylene, polystyrene, and polyvinyl chloride (8) have been described.

Some toxic metals are frequently added to plastics during the manufacturing process, while others are present as contaminants of raw materials. Lead sulfate and lead stearate are commonly used as additives or stabilizers to protect plastic materials from chemical degradation. Moreover, pigments containing lead chromate are used to color the coating of plastics (9,10). Considering that the presence of lead (Pb), an extremely toxic metal, in plastic material for food and beverage packaging may cause deleterious effects to human health, the development of a simple and fast method for the determination of this element in different types of plastic materials sounds interesting and promising.

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Flame or electrothermal atomic absorption spectrometry (4,9,10) inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) (11) are among the main spectroscopic analytical techniques used for elemental determination in plastic materials. These techniques are commonly applied for liquid samples, requiring a previous conversion of the solid material into a solution by acid digestion. Dissolution of plastic polymers by conventional wet decomposition procedures is difficult, unless closed vessels, concentrated acids, high temperatures, and high pressures are involved. Regarding plastic polymer digestion for inorganic analysis, microwave-assisted sample preparation provides several methods based on wet digestion and induced combustion (11). Alternatively, direct solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (DSS HR-CS GFAAS) seems to be an attractive option for elemental determinations since it does not require previous dissolution of plastic materials. This technique provides low detection limits and offers improved background correction (12,13). Nevertheless, DSS HR-CS GFAAS has been underexplored for the determination of Pb in plastic materials for packaging food and beverage, only one paper reports the determination of Pb in plastic material from electro-electronic waste (14).

This study reports the development of a simple and fast DSS HR-CS GFAAS method for the determination of Pb in plastic material

for food and beverage such as high density polyethylene (HDPE), polystyrene (PS), and polyethylene terephthalate (PET). Accuracy of the proposed method was checked by analyzing two polyethylene (PE) certified reference materials. The method was then applied to the Pb determination in samples of different plastic polymers, and the results were compared with those obtained by ICP-MS after sample digestion.

EXPERIMENTAL

Instrumentation

For the determination of Pb by direct solid sampling, an Analytik Jena ContrAA 700 high-resolution atomic absorption spectrometer was used (Analytik Jena, Germany). This spectrometer is equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) as a continuum radiation source, a compact high-resolution monochromator comprising a prism and an Echelle grating with a spectral bandwidth lower than 2 pm per pixel in the far ultraviolet range and a charge-coupled device (CCD) array detector. An automatic microbalance (Sartorius WZ2PW, Göttingen, Germany) with a precision of 0.001 mg was used to weigh the samples directly onto the solid sampling graphite platforms. The sample weight was automatically transmitted to the instrument's computer to calculate the normalized integrated absorbance since it is impossible to always introduce exactly the same sample mass. A previously adjusted pair of tweezers, part of the SSA 600 automatic solid sampling accessory, was used to transfer the solid sampling platforms to the atomizer. Pyrolytic graphite-coated solid sampling tubes without a dosing hole were used. High-purity argon was used as the purge and protective gas.

An Anton Paar Multiwave® microwave oven (Graz, Austria), equipped with a 6-position rotor and 50-mL PFA vessels (minimum filling volume of 6 mL), was used to digest the samples for subsequent determination of Pb by ICP-MS.

An ELAN® DRC™ II inductively coupled plasma mass spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used as the comparative technique for Pb determinations. The operating conditions for the ICP-MS determinations are summarized in Table I.

Reagents, Standards, and Samples

Deionized water (18 MΩ·cm resistivity), obtained with a Millipore® Rios 5® reverse osmosis and a Millipore Milli-Q® Academic deionizer system (Millipore Corporation, Bedford, MA, USA), was used to prepare all solutions. All glassware and polypropylene flasks were washed with Extran® laboratory detergent, soaked in 10% (v/v) HNO_3 for 24 hours, and rinsed with deionized water prior to use. Nitric acid (69%, J.T. Baker, Deventer, Holland) and H_2O_2 (30%, Merck, Darmstadt, Germany) were used for sample digestion.

Chemical modifier solutions containing 1000 mg L^{-1} $Pd(NO_3)_2$ and 500 mg L^{-1} $Mg(NO_3)_2$ were prepared by appropriate dilution of 10 g L^{-1} $Pd(NO_3)_2$ and dissolution of $Mg(NO_3)_2 \cdot 6H_2O$ (Suprapur®, Merck, Darmstadt, Germany). These solutions were prepared in 0.05% (m/v) Triton® X-100 (Mallinckrodt Baker, Paris, KY, USA).

For DSS HR-CS GFAAS and ICP-MS calibration, the Pb standard solutions were prepared by appropriate dilutions of the standard stock solution of 1000 mg L^{-1} (Spex Sample Preparation, Metuchen, NJ, USA).

The certified reference materials (CRMs) ERM-EC680 Trace Elements in Polyethylene (high level) and ERM-EC681 Trace Elements in Polyethylene (low level) from the Institute for Reference Materials and Measurements (Geel, Belgium) were cryogenically ground and used for method validation.

TABLE I
Operating Conditions of the ICP-MS Determinations

Instrumentation	PerkinElmer® ELAN® DRC™ II ICP-MS
Spray Chamber	Cyclonic
Nebulizer	Meinhard® Model
RF power	1100 W
Ar nebulizer gas flow	0.86 - 0.98 L min^{-1}
Interface	Pt sampler
Sampling cone	1.1 mm
Skimmer	0.9 mm
Measurement Parameters	
Scan mode	Peak hopping
Resolution	0.7 μ
Replicate time	1 s
Dwell time	50 s
Sweeps	20 reading
Integration time	1000 ms
Replicates	3
Isotopes	^{208}Pb

Sample Preparation

Plastic materials for packaging food (white HDPE, white and brown PS) and for packaging beverage (green, yellow, red, and colorless PET) were chosen for analysis. These samples were ground using a cryogenic mill (Spex, model 6750, USA). The grinding program consisted of a pre-cooling time of 4 minutes, followed by three cycles of 3-minute grinding with re-cooling intervals of 2 minutes.

Samples were also analyzed by ICP-MS after microwave-assisted acid digestion. For sample digestion, a mass of 150 mg was accurately weighed and transferred to microwave PFA vessels, followed by the addition of 2.0 mL of concentrated nitric acid, 1.0 mL of hydrochloric acid, and 3.0 mL of deionized water. The mixture was submitted to the following heating program: (a) 0-800 W, 15 minutes ramp time; (b) 800 W, 40 minutes hold; (c) 0 W, and 20 minutes ventilation. The maximum temperature reached was 220 ºC. The final digests were transferred to polypropylene flasks and diluted to 50-mL volume with deionized water.

RESULTS AND DISCUSSION

Method Development for the Determination of Lead

Due to the high concentration of Pb in the CRMs ERM-EC680 and ERM-EC681 in relation to the samples, the proposed method optimization was carried out using a green PET sample. The concentration of Pb in this sample (81 μg kg^{-1}) was previously determined by ICP-MS after sample digestion. The main Pb analytical line at 217.001 nm was used during all of the optimization experiments.

Initial experiments without a chemical modifier indicated that the pyrolysis curve exhibited thermal stability up to 700 °C. However, double transient signals were observed during the atomization step fixed at 2000 ºC. In the present case, the double peak indicates the presence of two different forms of atomization mechanisms. In order to increase the thermal stability of the analyte and avoid double transient signals, pyrolysis and atomization curves were established using the chemical modifier $Pd(NO_3)_2 + Mg(NO_3)_2$ in the presence of Triton® X-100. This strategy was previously used by Duarte et al. (14).

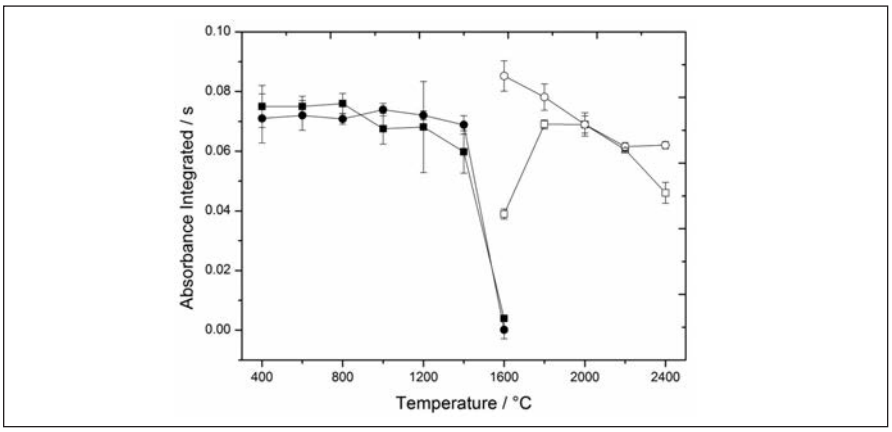

Fig. 1. Pyrolysis (using a T_{at} of 2000 ºC) and atomization (using a T_{pyr} of 1400 ºC) curves for Pb: (■□) Integrated absorbance normalized to 0.6 mg of the green PET sample, and (●○) 100 pg of Pb in 10 μL of aqueous standard solution.

To evaluate the effect of the modifier on the thermal stability of Pb, 5 μL of a solution containing 5 μg Pd and 2.5 μg Mg in 0.05% (m/v) Triton X-100 were dispensed over aliquots of analytical solutions and solid samples in the graphite platform. A mass of 0.6 – 0.8 mg of the sample was used to evaluate the thermal behavior of Pb in the solid material. The effects of pyrolysis and atomization temperatures on Pb sensitivity in an aqueous standard solution and in the solid green PET sample using a chemical modifier are presented in Figure 1. A pyrolysis temperature of 1400 ºC was adequate to eliminate the matrix. An atomization temperature of 2000 ºC was chosen because it provided a single sharp peak for the atomic absorption signal, better precision, and fast return of the signal to the baseline. Also, at 2000 °C the analytical signal of Pb presented similar profiles for both media (Figure 2). The optimized temperature program used for the determination of Pb in plastic material for food beverage by DSS HR-CS GFAAS is presented in Table II. An additional pyrolysis step at 600 °C for 30 seconds assisted by air improved matrix removal.

Studies on minimum mass and homogeneity (15) were then conducted by analyzing different masses (0.05–1.0 mg) of sample with intervals of 0.1 mg. The most accurate and precise results were obtained for sample masses in the 0.6–0.8 mg range. Therefore, 0.6–0.8 mg of sample mass was used for all further investigations.

Figures of Merit

The limit of detection (LOD) and quantification (LOQ), the characteristic mass (m_0) and the correlation coefficient (r) for the proposed method determined at 217.001 nm and 205.328 nm are presented in Table III. The LODs and LOQs were calculated as the concentration corresponding to 3- and 10-fold the

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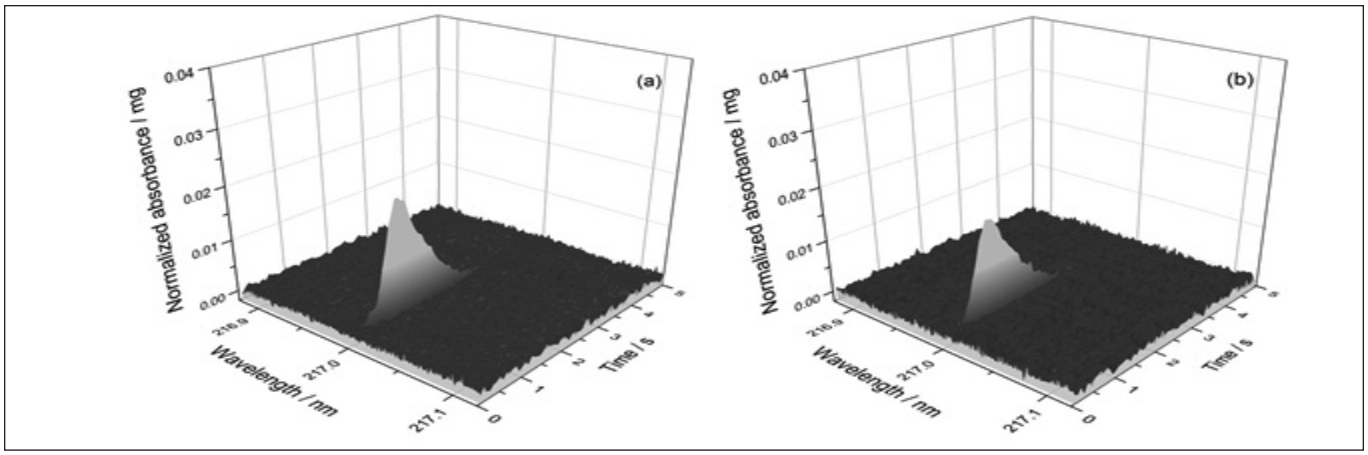

Fig. 2. Absorbance-time profile for Pb determination. Signals correspond to 100 pg Pb in 0.1% (v/v) HNO_3 (a) and Pb in 0.6 mg of PET sample (b) using 5 µg Pd and 2.5 µg Mg in 0.05% (m/v) Triton X-100 as the modifier.

TABLE II
Optimized Heating Program for Lead Determination in Plastic Material Used for Food and Beverage Packaging by DSS HR-CS GFAAS

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold Time (s)	Argon Flow Rate (L min^{-1})
Drying 1	110	10	10	2.0 (Ar)
Drying 2	130	5	10	2.0 (Ar)
Ash	600	50	30	2.0 (air)
Cooling	100	-	20	2.0 (Ar)
Pyrolysis	1400	100	10	2.0 (Ar)
Auto-zero	1400	0	5	0
Atomization	2000	3000	4	0
Cleaning	2500	500	5	2.0 (Ar)

TABLE III
Figures of Merit for Lead Determination in Plastic Material Used for Food and Beverage Packaging by DSS HR-CS GFAAS

Parameters	Wavelength 217.001 nm	205.328 nm
LOD*	4.9 µg kg^{-1}	0.5 mg kg^{-1}
LOQ*	16 µg kg^{-1}	1.65 mg kg^{-1}
m_o	5.0 pg	0.4 ng
r	0.9998	0.9996

* Calculated for 0.6 mg sample.

standard deviation of the blank divided by the slope of the analytical curve (16). The standard deviation of the blank was calculated by repeatedly inserting an empty solid sampling platform containing only the modifier and running the temperature program (15). The characteristic mass (m_0) was obtained as the mass of analyte corresponding to an integrated absorbance of 0.0044 s.

Determination of Lead in Samples and Certified Reference Materials

The DSS HR-CS GFAAS method with calibration against aqueous standards was applied for the determination of Pb in 9 samples using the most sensitive analytical line at 217.001 nm. The concentration of Pb in the samples varied from 16 to 793 µg kg^{-1}. In order to compare the results obtained by DSS HR-CS GFAAS, the samples were analyzed by ICP-MS after microwave-assisted acid digestion. All of the results are summarized in Table IV. A paired *t*-test at a 95% confidence level showed that the proposed method provided similar results as those obtained by ICP-MS. The precision, expressed as the relative standard deviation (RSD, n=3), varied from 2.7 to 18.8% for the determinations by DSS HR-CS GFAAS and from 2.1 to 13.3% when using ICP-MS.

The proposed method for Pb determination was then applied for two CRMs, and the results obtained are presented in Table V. Due to the high concentration of Pb in both CRMs, a less sensitive analytical line at 205.328 nm was used with the same temperature program developed for the most sensitive line. The proposed method provided accurate results based on an unpaired *t*-test at the 95% confidence level.

Duarte et al. (14) developed a method for the determination of Pb in plastic material from waste electric and electronic equipment using line source GFAAS and direct solid sampling analysis with deuterium background correction; the LOQ obtained was 72 µg kg^{-1}. Obviously, the method with line source GFAAS

TABLE IV
Results (mean ± standard deviation, μg kg^{-1}) for Lead Determination (n= 3) in Plastic Material Used for Food and Beverage Packaging by the Proposed Method (DSS HR-CS GF AAS) and by the Comparative Technique (ICP-MS)

Sample	DSS HR-CS GF AAS	ICP – MS
Green PET	82 ± 8	81 ± 9
Blue PET	27 ± 4	25 ± 3
Red PET	51 ± 4	54 ± 4
Colorless PET	44 ± 4	42 ± 3
Brown PS	793 ± 51	776 ± 20
White PS	735 ± 20	731 ± 15
White HDPE 1	16 ± 3	17 ± 2
White HDPE 2	24 ± 4	24 ± 3
White HDPE 3	17 ± 3	15 ± 2

(14) is not adequate to analyze the samples used in this study because the concentrations of Pb are below 72 μg kg^{-1} in 67% of the samples. However, the DSS HR-CS GFAAS method could perform this task because the LOQ obtained (16 μg kg^{-1}) was 4.5 times lower than the line source GFAAS method.

CONCLUSION

The developed DSS HR-CS GFAAS method provided accurate results and adequate LOQ (16 μg kg^{-1}) for the determination of Pb in plastic material used for food and beverage packaging by applying calibration against aqueous standards. That LOQ found is about 4.5 times lower than the LOQ described in a published work dealing with the determination of Pb in plastic material from waste electric and electronic equipment using line source GFAAS and direct solid sampling analysis with deuterium background correction. The proposed method is also characterized by a low consumption of reagents and minimum generation of laboratory residues in relation to ICP-MS detection after sample digestion.

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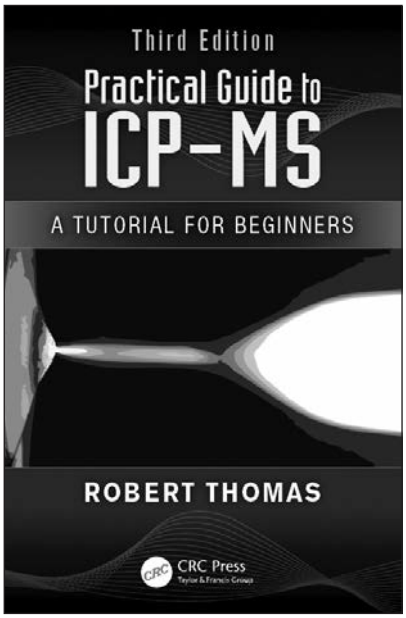
REFERENCES

1. Plastics: A Global Outlook. Available at: <http://www.prweb.com/releases/plastics_bioplastics/engineered_plastics/prweb9194821.htm>. [Accessed 30 October 2014].
2. W. Romão, M.A.S. Spinacé and M. De Paoli, Polímeros 19, 121 (2009).
3. F. Welle, Resour. Conserv. Recy. 55, 865 (2011).
4. A. Janssen, B. Bruckner, and U. Kurfürst, Fresenius 322, 713 (1985).

TABLE V
Lead Concentration (mean ± standard deviation, mg kg^{-1}) in Certified Reference Materials Determined (n= 3) by DSS HR-CS GF AAS

CRM	Pb (mg kg^{-1})	
	Certified	Determined
ERM-EC680	107.6 ± 2.8	98.6 ± 6.3
ERM-EC681	13.8 ± 0.7	12.2 ± 2.8

5. M.A. Belarra, M. Resano, S. Rodríguez, J. Urchaga and J.R. Castillo, Spectrochim. Acta B 54, 787 (1999).
6. M.A. Belarra, I. Belategui, I. Lavilla, J.M. Anzano and J.R. Castillo, Talanta 46, 1265 (1998).
7. M. Resano, M. Aramendía, E. García-Ruiz, C. Crespo and M.A. Belarra, Anal. Chim. Acta 571, 142 (2006).
8. M. Resano, J. Briceno and M.A. Belarra, Spectrochim. Acta B 64, 520 (2009).
9. S. Cadore, E. Matoso and M.C. Santos, Quím. Nova 31, 1533 (2008).
10. S. Waheed, N. Siddique, S. Rahman and S.M. Husnain, J. Radioanal. Nucl. Chem. 292, 937 (2011).
11. J.S.F. Pereira, C.L. Knorr, L.S.F. Pereira, D.P. Moraes, J.N.G. Paniz, E.M.M. Flores and G. Knapp, J. Anal. At. Spectrom. 26, 1849 (2011).
12. R. Lemaire, D. Del Bianco, L. Garnier and J. L. Beltramo, Anal. Lett. 46, 2265 (2013).
13. I.N.B. Castilho, E.R. Pereira, B. Welz, A.A. Shaltout, E. Carasek and I.B. Gonzaga Martens, Anal. Methods 6, 2870 (2014).
14. A.T. Duarte, M.B. Dessuy, M.M. Silva, M.G.R. Vale and B. Welz, Microchem. J. 96, 102 (2010).
15. U. Kurfürst, Solid Sample Analysis, Springer, Berlin, Germany (1998).
16. A. Gustavo González and M. Angeles Herrador, Trends Anal. Chem. 26, 227 (2007).



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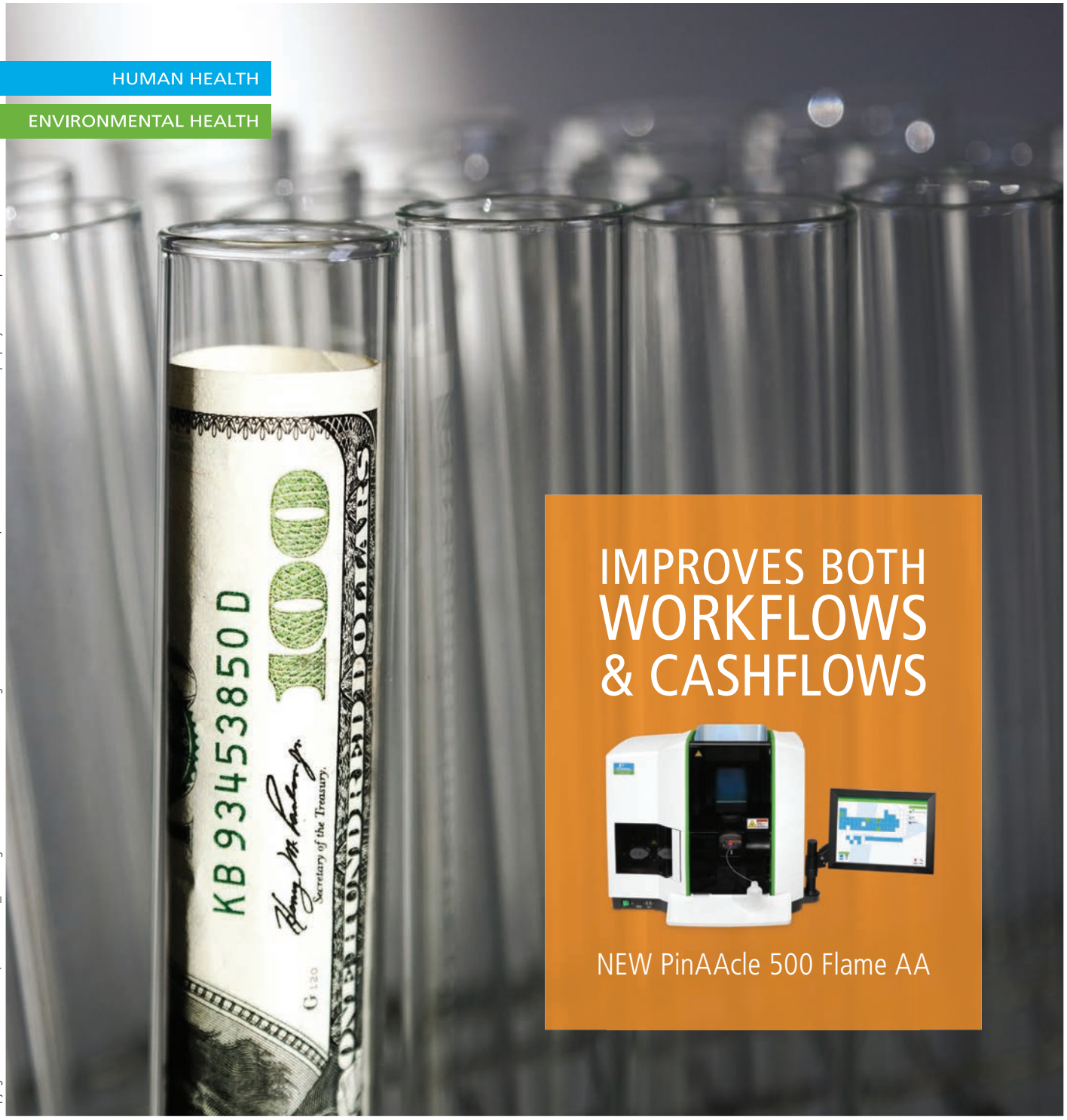

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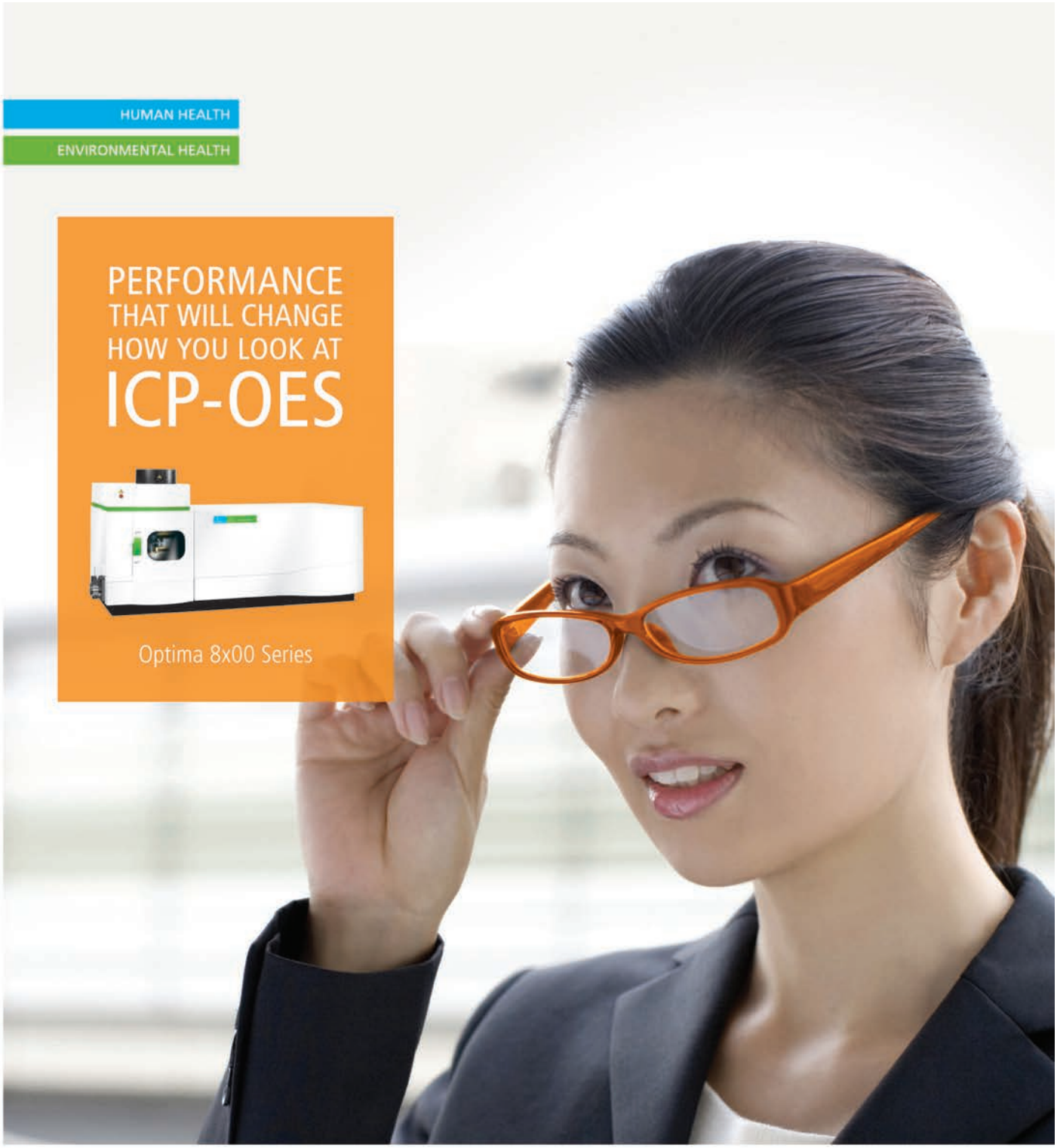

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