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Short communication

Determination of Cu, As, Hg and Pb in vegetable oils by electrothermal vaporization inductively coupled plasma mass spectrometry with palladium nanoparticles as modifier

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ABSTRACT

The determination of Cu, As, Hg and Pb in vegetable oils by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) was investigated. The oils were injected in the form of emulsions containing 5% m/v vegetable oil, 1.5% v/v Triton X-100 and 50 µg mL^{-1} ascorbic acid. Palladium nanoparticles (Pd-NPs) were used as modifier. The interference of $^{40}Ar^{35}Cl^{+}$ at arsenic mass m/z 75 was reduced significantly using dynamic reaction cell (DRC). Standard addition and isotope dilution methods were used for the quantifications. The method reported has been applied to the determination of Cu, As, Hg and Pb in selected vegetable oil samples purchased from a local market. The analytical results obtained were in good agreement with those of digested samples analyzed by pneumatic nebulization ICP-MS with 95% confidence according to Student *t*-test (except for Cu). Precision between sample replicates was better than 10% with the ETV-ICP-MS method. The detection limits obtained from standard addition curves were 0.4, 0.5, 1.1 and 0.4 ng g^{-1} for Cu, As, Hg and Pb, respectively, in the original oil samples.

1. Introduction

Determination of trace elements in vegetable oils is one of the criteria for the assessment of the quality of oils regarding freshness and storability. Traces of heavy metals in vegetable oils are known to affect the rate of oil oxidation and hence the subject of food legislation [1]. According to the regulations of Taiwan government, the maximum allowable concentration of Cu, As, Hg and Pb in edible oil is 0.4, 0.1, 0.05 and 0.1 µg g^{-1}, respectively.

The determination of trace elements in vegetable oils at sub-ppm levels has been carried out using atomic absorption [2,3], atomic emission [1,4], and ICP-MS [5,6]. Most of the methods require sample pretreatment, including extraction, solubilization, dilution and digestion, are used to destroy the organic material in vegetable oils [1,7,8]. Procedures based on conversion of oil into emulsion have already been published for metal analysis in vegetable oils with ICP-AES and ICP-MS detection systems [1,6].

Electrothermal vaporization (ETV) is currently employed as a sample introduction system in ICP-MS [8–15]. Compared to pneumatic nebulization, this alternative sample introduction presents several advantages, including improved mass transport efficiency, small sample size requirements and also capability for the analysis of suspensions (and/or solids). ETV-ICP-MS is preferred over vapor generation ICP-MS (VG-ICP-MS) because less sample is required and is more widely applicable because not all elements can be converted to gaseous compounds.

Palladium has been used as a chemical modifier to improve the signals of volatile elements in many ETV-ICP-MS applications [16–18]. Huang and Jiang reported determination of Zn, Cd and Pb in vegetable oil by ETV-ICP-MS in which sample was injected as emulsion and Pd solution was used as modifier [19]. Colloidal Pd was reported to be more efficient compared to Pd solutions for ETAAS applications [20,21]. Recently, palladium nanoparticles (Pd-NPs) were used as the modifier for the determination of Zn, As, Cd, Sb, Hg and Pb in biological samples by ultrasonic slurry sampling (USS) ETV-ICP-MS [22]. The effect of addition of another organic modifier to Pd-NPs is of interest.

The aim of the present work is to develop an accurate ICP-MS method with electrothermal vaporization sample introduction

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device for the determination of Cu, As, Hg and Pb in vegetable oils. The analytes selected not only spoil the quality of oil but also not recommended for human consumption due to their toxicity. Moreover, in Taiwan control limits are mentioned only for Cu, As, Hg and Pb. Pd-NPs were tested as modifiers for the analysis. The effect of addition of another modifier to Pd-NPs is also reported. The influences of instrument operating conditions, modifier selection, emulsion preparation and interferences on the ion signals were investigated. This method has been applied to the determination of Cu, As, Hg and Pb in selected oil samples purchased from a local market.

2. Experimental

2.1. Apparatus and conditions

An ELAN 6100 DRCII ICP-MS instrument (Perkin-Elmer SCIEX, Concord, ON, Canada) equipped with an HGA-600MS electrothermal vaporizer was used. Pyrolytic coated graphite tubes with same material platforms were used throughout. The sample introduction system included a Model AS-60 auto sampler equipped with an USS-100 Ultrasonic Slurry Sampler. For solution nebulization, cross flow nebulizer in combination with Scott type spray chamber were used. Polystyrene auto sampler cups were used. In order to increase the homogeneity of the emulsion, the ultrasonic slurry sampling device was employed in this study. The USS-100 was set at 30 W (40% power), and a 5-s mix time was used to mix emulsions before injection of 10-μL sample aliquots for analysis. The vaporized material was carried from the cell to the ICP torch by an 80-cm long polytetrafluoroethylene (PTFE) tubing having an internal diameter of 6 mm.

The ICP conditions were optimized by passing a solution containing 1 ng mL^{-1} each of the elements of interest in 1% HNO_3 was continuously introduced with a pneumatic nebulizer. A 10 ms dwell time was used to ensure proper data collection for the transient signals resulting from the ETV sampling device. The ICP-MS and ETV operating conditions used throughout this work are summarized in Tables 1 and 2, respectively.

Table 1
ICP-MS equipment and operating conditions.

ICP-MS instrument	Perkin-Elmer Sciex ELAN 6100 DRC II
Plasma conditions	
RF power/W	1200
Outer gas flow/L min^{-1}	15.0
Intermediate gas flow/L min^{-1}	1.13
Carrier gas flow/L min^{-1}	0.99
Mass spectrometer settings	
Resolution	0.7 amu at 10% peak maximum
Isotopes monitored	^{63}Cu, ^{65}Cu, ^{75}As, ^{201}Hg, ^{202}Hg, ^{206}Pb,^{208}Pb
Dwell time/ms	10
Sweeps per reading	2
Readings per replicate	300
Peak signal	integrated
Autolens	on
Dynamic reaction cell system	
H_2 reaction gas flow rate/mL min^{-1}	1.8
Rejection parameter *q*	0.6
Rejection parameter *a*	0.0

Table 2
HGA-600MS temperature programming.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow rate (mL min^{-1})	Read
Dry1	80	30	20	300	–
Dry2	200	20	30	300	–
Pyrolysis	500	10	20	300	–
Vaporization	2600	0.3	8	0	ON
Cooling	20	5	5	300	–
Condition	2600	1	10	300	–
Cooling	20	5	5	300	–

2.2. Reagents

Analytical-reagent grade chemicals were used without further purification. Purified water (18.2 MΩ-cm), from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used to prepare all the solutions. Palladium chloride ($PdCl_2$), L-ascorbic acid, HNO_3 (65% m/m), H_2O_2, HCl (30% m/m) and Cu, As, Hg element standard solutions were obtained from Merck (Darmstadt, Germany). Ammonium pyrrolidinecarbodithioate (APDC) and 8-Hydroxyquinolin (8-HQ) used as modifiers were purchased from Sigma-Aldrich (Buchs, Switzerland) and Janssen Chimica (Beerse, Belgium) respectively. Standard solution of lead (1 mg mL^{-1}) was obtained from SPEX CertiPrep (Metuchen, NJ, USA). Triton X-100, antifoam Y-30 and carboxymethyl cellulose sodium salt (CMC, average MW ~90,000) were purchased from Sigma (St. Louis, MO, USA). Standard solution of palladium (1 mg mL^{-1}) was prepared by dissolving suitable amount of $PdCl_2$ in concentrated HCl. Enriched isotopes were procured from the following sources, ^{65}Cu (99.7%) was from the Oak Ridge National Laboratory (Oak Ridge, TN, USA), ^{201}HgO (80.5%) was from Cambridge Isotope Laboratories (Andover, MA, USA) and $^{206}Pb(NO_3)_2$ (99.7%) was from Merck (Darmstadt, Germany).

2.3. Synthesis and characterization of Pd nanoparticles

The synthesis of Pd-NPs was carried out according to the method described by Zhao et al. and Yi et al. [22,23]. The final Pd concentration in the aqueous suspension was 115 μg mL^{-1}. To prepare purified Pd-NPs**,** 1 mL of the suspension was transferred to a centrifuge tube and centrifuged at 31,514 g (MIKRO 22R, Hettich, Germany) for 20 min. The supernatant was decanted and the residual solid material was re-dispersed into pure water to produce a suspension of purified Pd-NPs used for particle characterization and ETV-ICP-MS experiments.

The morphology and size distribution of the Pd-NPs were determined with a JEOL TEM-3010 Analytical Scanning Transmission Electron Microscope at an operating voltage of 200 kV. For TEM analyses, samples of air-dried Pd-NPs were prepared by placing 20 μL of aqueous purified Pd-NPs suspension onto a 100 mesh copper grid with amorphous carbon support film, air-dried under ambient conditions and then heated at 150°C in an oven for 24 h. On the basis of the TEM image, a mean diameter of 11.2 nm was estimated with a standard deviation of 0.9 nm by considering 15 particles.

2.4. Preparation of oil emulsions

The applicability of the method to real samples was demonstrated by analyzing a Mineral Oil Standard (Cat# S23-100Z, ORG AS8-2Z, and ORG HG8-2Z, SPEX CertiPrep, Edison, NJ, USA) and three vegetable oil samples (sunflower oil, olive oil, vegetable oil) purchased from a local market. The oil samples were analyzed by standard addition and isotope dilution methods. Each oil emulsion was prepared according to the following procedure. A 0.5-g portion of the oil was transferred into a 10 mL volumetric flask. Suitable amounts of Triton X-100 and ascorbic acid were added to make the final solution containing 5% m/v vegetable oil, 1.5% v/v Triton X-100 and 50 µg mL^{-1} ascorbic acid. A drop of antifoam Y-30 was also added. After addition of suitable amounts of enriched isotopes or Cu, As, Hg and Pb standard solutions, the emulsified solution was diluted to the mark with pure water. The emulsion was then sonicated for 5 min in an ultrasonic bath, and 1-mL aliquots were transferred into polystyrene auto sampler cups for analysis. To verify the accuracy of the procedure, a Mineral Oil Standard emulsion containing 5 ng mL^{-1} each of Cu, As and Pb and 10 ng mL^{-1} of Hg was prepared and analyzed. A blank solution was also prepared as outlined above. The analysis was carried out using ETV-ICP-MS by injecting 10 µL of the emulsified oil. The concentrations of analytes in the sample were then calculated as described in a previous paper [24] and/or from the standard addition calibration curves.

For the studies on the effect of ETV conditions and emulsion preparations on the ion signals, the oil emulsion was prepared as the procedure described above and spiked with 5 ng mL^{-1} each of As and Hg.

2.5. *Sample mineralization*

Since there is no reference value for the real-world samples, in order to check the accuracy of the determined results, using the present procedure and complete dissolution procedure were compared. For complete dissolution, the oil samples were digested using the following procedure. Oil sample (0.5 g) was weighed into perfluoroalkoxyethylene (PFA) vessel and 10 mL HNO_3 was added. The samples after addition of reagent were heated inside a CEM MARS 5 (CEM, Matthews, NC, USA) microwave digester. The digestion parameters are listed in Table S1 (Supplementary material). The digested solutions were diluted by another 10-fold and directly analyzed by ICP-MS for Cu, As, Hg and Pb. The concentration of the elements studied in the sample was quantified by means of external calibration with 1 ng mL^{-1} of Rh as the internal standard.

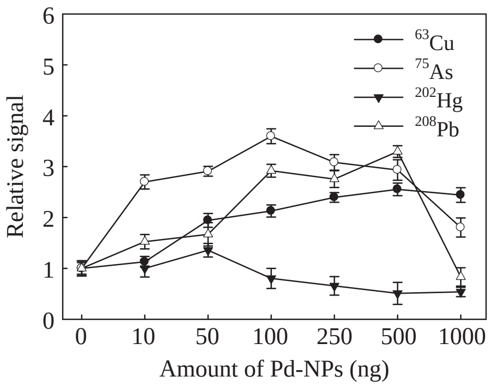

Fig. 1. Effect of the amount of Pd-NPs on ion signals. Injected solution contained 5% m/v of vegetable oil, 2% v/v Triton X-100 and spiked with 5 ng mL^{-1} of As and Hg. Pyrolysis and vaporization temperatures were set at 400 °C and 2600 °C, respectively. Each data point represents the mean of five measurements ± SD. All the data were measured relative to the first point.

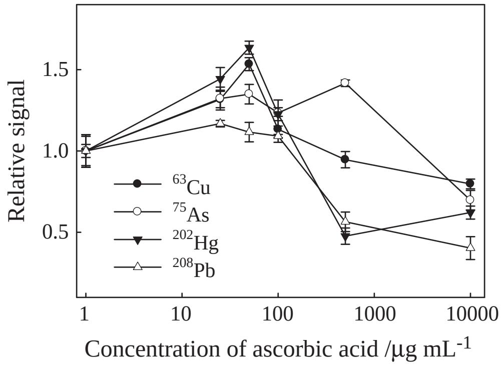

Fig. 2. Effect of the concentration of ascorbic acid on ion signals. Emulsified solution contained 5% m/v vegetable oil, 2% v/v Triton X-100 and spiked with 5 ng mL^{-1} of As and Hg. Pyrolysis and vaporization temperatures were set at 400 °C and 2600 °C, respectively. Each data point represents the mean of five measurements ± SD. All the data were measured relative to the first point (0 µg mL^{-1}).

3. Results and discussion

Certain factors such as the concentration of oil and surfactant, ratio of the concentration of oil to surfactant, analyte partitioning and the homogeneity of emulsion are important for the success of the analysis of oil emulsion by ICP-AES and ICP-MS [1]. In this study Triton X-100 was selected as the surfactant since it has medium hydrophilic–lipophilic balance value [1].

3.1. *Selection of modifier and preparation of emulsion*

Modifiers commonly used in ETV-ICP-MS are believed to work as physical carriers and also generate chemical effects in some specific instances [25]. Pd-NPs have been used as the modifier in a previous ETV-ICP-MS application [22]. In this study Pd-NPs were tested as the modifier for the analysis of oil samples. Effect of concentration of Pd-NPs on ion signal of Cu, As, Hg and Pb is shown in Fig. 1. Optimum concentration for Cu, As and Pb was found to be 1000, 100 and 500 ng, respectively and to analyze all the analytes 500 ng was selected. Mixed modifiers were used in many previous electrothermal vaporization atomic spectroscopic applications [26–30]. Hence, the effect of addition of ascorbic acid [31], 8-HQ [32] and APDC [32] to Pd-NPs was studied. Ascorbic acid was found to increase the signals of elements studied up to a concentration of 50 µg mL^{-1} (Fig. 2). Hence 50 µg mL^{-1} ascorbic acid was selected as the mixed modifier for the analysis. Addition of H_2O_2 and mineral acid (HNO_3) did not yield any benefit and hence were not added.

The addition of TritonX-100 to the emulsion is known to disperse the oil and also can act as modifier. Hence, the effect of the concentration of Triton X-100 in the sample emulsion on the ion signals was also studied. As shown in Fig. S1 (Supplementary material), the ion signals of Cu, Hg and Pb were increased slightly with Triton X-100 concentration up to 1.5% v/v, whereas the ion signal of As decreased. For the simultaneous determination of these elements, 1.5% v/v Triton X-100 was added to all emulsions.

Another important factor in the emulsion method is the concentration of oil the in emulsion. The effect of concentration of oil, in the emulsion, on the ion signals was studied using 2%, 5%, 10% and 20% m/v of oil in the emulsion. The ion signal should increase with decrease in the dilution factor. However, from the experiment it was found that, the sensitivity (counts/mass of oil in emulsion) of the elements studied decreased with the decrease of dilution factor. It could be due to the non-spectral interference caused by the major component of the oil. Furthermore the injected oil emulsion could not be vaporized completely. In order to balance sample homogeneity, analyte signals and complete vaporization of the introduced sample, an oil emulsion containing 5% m/v oil, 1.5% v/v Triton X-100 and 50 µg mL^{-1} ascorbic acid was selected in the following experiments.

3.2. Selection of pyrolysis and vaporization temperature

Figs. S2 and S3 (Supplementary material) show the effect of pyrolysis temperature at constant vaporization temperature and effect of vaporization temperature at constant pyrolysis temperature respectively, on ion signals. Based on the results obtained, for the simultaneous determination of the elements studied, in the following experiments, the pyrolysis temperature was set at 500 °C. However, a higher vaporization temperature was found to be needed for this analysis. In order to evaporate elements studied completely and simultaneously and also considering the life of the graphite tubes, a vaporization temperature of 2600 °C was selected for the following experiments. The operating conditions for ETV are listed in Table 2.

3.3. Interferences study

The presence of chlorides in oils may interfere in the determination of $^{75}As^{+}$ by ICP-MS due to the formation of $^{40}Ar^{35}Cl^{+}$. Though there is a possibility of elimination of Cl during ashing, high background was detected [Fig. 3(a)] at arsenic mass m/z 75 when a sunflower oil emulsion was injected while the ICP-MS was operated in the standard mode. It could be due to the nature of oil matrix. These interferences were reported to be alleviated in the DRC mode with H_2 as the reaction gas [33]. As shown in Fig. 3(b), the background due to $^{40}Ar^{35}Cl^{+}$ was effectively suppressed when H_2 was used as the reaction gas at a flow rate of 1.8 mL min^{-1} and at a rejection parameter (Rpq) of 0.6. In DRC rejection parameters Rpa and Rpq will be selected in such a way that unwanted precursors of interfering species generated in the cell are eliminated. A higher value of Rpq increases the low-mass cutoff which could also decrease the transport efficiency of analyte ion. Rpa value selected is normally zero. At these conditions the signals of Cu, Hg, and Pb were not affected significantly. To achieve accurate results for arsenic, the ICP-MS was operated in the DRC mode for the real sample analysis.

Other possible interferences due to the components of sample are $^{40}Ar^{23}Na^{+}$, $^{40}Ar^{25}Mg^{+}$, $^{40}Ar^{35}Cl^{+}$, $^{186}W^{16}O^{+}$ on the determination of $^{63}Cu^{+}$, ^{65}Cu, $^{75}As^{+}$, $^{202}Hg^{+}$ respectively. The ETV-ICP-MS analysis of emulsions spiked with Cl, Na, Mg and W indicated that the ion signal of As and isotope ratios of Cu and Hg were not affected by the presence of Cl, Na, Mg and W at 1000, 1000, 100 and 10 μg mL^{-1} respectively. These experiments demonstrated that the concentration of As, Cu and Hg in the vegetable oil samples can be determined directly by ETV-ICP-MS without significant interference.

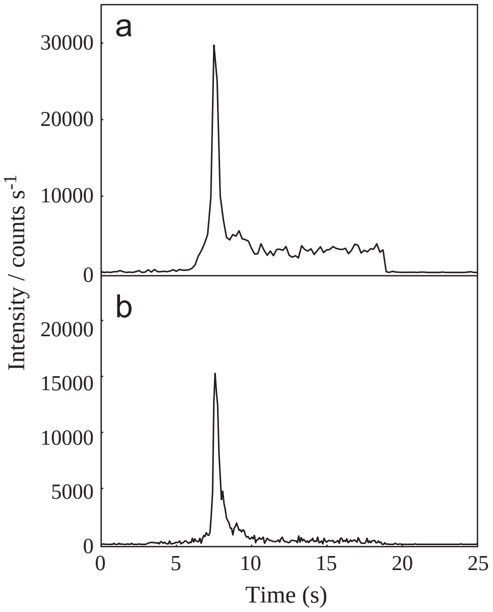

Fig. 3. ETV-ICP-MS ion signal at m/z 75 under (a) standard mode and (b) DRC mode. Emulsified solution contained 5% m/v sunflower oil, 1.5% v/v Triton X-100 and 50 μg mL^{-1} ascorbic acid. For DRC mode, H_2 reaction cell gas flow rate was 1.8 mL min^{-1}; Rejection parameter q and a was 0.6 and 0.0, respectively. ETV-ICP-MS operating conditions are listed in Tables 1 and 2.

3.4. Determination of trace elements in vegetable oil by ETV-ICP-MS

In order to validate the ETV-ICP-MS method, the concentrations of Cu, As, Hg and Pb were determined in three vegetable oil samples. The accuracy of the procedure was verified by analyzing Mineral Oil Standard. The quantifications were carried out using standard addition and isotope dilution methods. Typical element-selective ETV signal (ICP-MS detection) for a solution containing 5% m/v emulsified olive oil solution is shown in Fig. S4 (Supplementary material). The concentration of Cu, As, Hg and Pb in the injected solution was 7.2, 0.06, 1.4 and 1.0 ng mL^{-1}, respectively. Peak area of the flow injection signals were used for quantifications. Analysis results are shown in Table 3. As shown the determined concentrations in the Mineral Oil Standard were in good agreement with the certified values. Moreover, the analytical results of various vegetable oil samples determined by standard addition and isotope dilution methods are in good agreement with those of digested samples using microwaves and analyzed by pneumatic nebulization ICP-MS. The pneumatic nebulization ICP-MS results of copper in various vegetable oil samples are much lower than the ETV-ICP-MS results. The precision between sample replicates is better than 10% for all determinations. The concentration of Hg in the analyzed vegetable oil sample is above the maximum allowable concentration. This experiment indicated that Cu, As, Hg and Pb in vegetable oil could be readily quantified by inductively coupled plasma mass spectrometry with electrothermal vaporization.

Under the selected ETV-ICP-MS operating conditions, standard addition calibration plots for Cu, As, Hg and Pb were linear in the range 0–20 ng mL^{-1} with calibration coefficients (r^2) better than 0.9991. Detection limits were calculated based on the usual

Table 3
Determination of Cu, As, Cd and Hg in vegetable oil by ETV-ICP-MS[a] ($n=3$).

Sample	Method[b]	Concentration[c]/ng g^{-1}			
		As	Cu	Hg	Pb
Element oil Standard	Method 1	1030 ± 81	98.6 ± 8.7	1070 ± 92	106 ± 4.5
	Method 2	NA[d]	99.2 ± 5.5	1010 ± 41	103 ± 3.2
	Certified	1000 ± 10	100 ± 1	1000 ± 10	100 ± 1
Sunflower oil	Method 1	2.28 ± 0.04	93.4 ± 1.5	18.3 ± 0.6	10.1 ± 0.9
	Method 2	NA	94.1 ± 1.3	17.9 ± 0.2	10.3 ± 0.6
	Method 3	2.41 ± 0.28	5.87 ± 4.6	–[e]	14.2 ± 1.1
Olive oil	Method 1	3.16 ± 0.3	143 ± 10	28.2 ± 2.3	20.4 ± 1.2
	Method 2	NA	144 ± 9.2	28.0 ± 1.2	21.1 ± 1.7
	Method 3	3.31 ± 0.08	12.9 ± 0.8	–[e]	21.8 ± 1.6
Vegetable oil	Method 1	7.66 ± 0.05	188 ± 12	126 ± 11	14.4 ± 1.1
	Method 2	NA	183 ± 10	121 ± 9.4	14.6 ± 1.2
	Method 3	8.16 ± 0.3	9.23 ± 0.9	–[e]	15.9 ± 0.4

[a] Values are means of three measurements ± standard deviation.

[b] Method 1: standard addition method. Method 2: isotope dilution method. Method 3: obtained by pneumatic nebulization ICP-MS after complete dissolution. The total dilution factor was 50.

[c] The concentration unit was μg g^{-1} for Mineral Oil Standard.

[d] NA = not available.

[e] Not detectable.

definition as the concentration of the analyte yielding a signal equivalent to three times the standard deviation of the blank signal measurements. Detection limits estimated from standard addition curves were 0.02, 0.02, 0.05 and 0.02 ng mL^{-1} for Cu, As, Hg and Pb, respectively, in prepared emulsified solutions, corresponding to 0.4, 0.5, 1.1 and 0.4 ng g^{-1} for Cu, As, Hg and Pb, respectively, in the original oil samples.

4. Conclusion

Electrothermal vaporization ICP-MS provides a simple, rapid and accurate procedure to determine Cu, As, Hg and Pb in vegetable oils without any complicated sample pretreatment. Compared to traditional sample preparation methods such as acid digestion and dry ashing, emulsified oil sampling offers several benefits including reduced sample preparation time, sample contamination and analyte loss before analysis. The detection limits obtained for Cu, As, Hg and Pb with this system are low enough for the determination of Cu, As, Hg and Pb in many real samples. Precision between sample replicates was better than 10% for all the determinations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.09.013.

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