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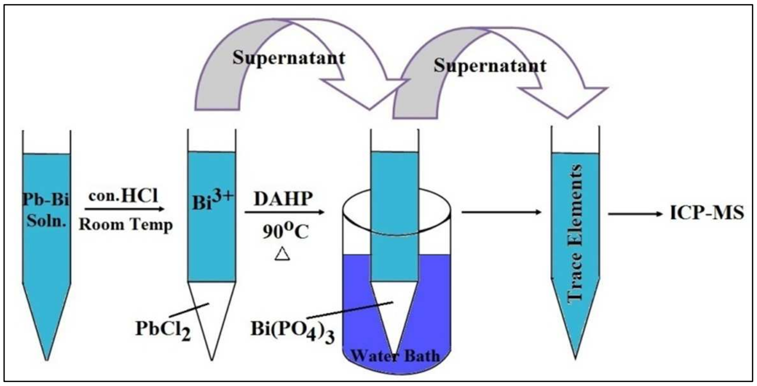

Matrix precipitation for the sensitive determination of impurities in Pb-Bi eutectic by ICP-MS.

Determination of trace elements in Pb-Bi-eutectic by Inductively Coupled Plasma-Quadrupole Mass Spectrometry after sequential removal of matrix by precipitation

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Abstract

A simple method was developed for the separation of trace element impurities in lead-bismuth eutectic (LBE) followed by their determination using inductively coupled plasma mass spectrometry. The matrix components, Pb and Bi, were separated by sequential precipitation. Pb was precipitated as lead (II) chloride followed by Bi as bismuth (III) phosphate. The separation of both the matrix elements (Pb and Bi) was found to be > 99 %. Out of 20 target elements (Rb, Te, Ba, Li, As, Cd, Zn, Ag, Cu, Mg, Co, Ni, Be, Mn, Sr, Se, Cr, Ga, Mo and Tl) spiked into a simulated LBE sample, for 14 elements (Rb, Te, Ba, Li, As, Cd, Zn, Ag, Cu, Mg, Co, Ni, Be and Mn) recoveries in the range 85-100 % were obtained. The developed method was applied to three lead-bismuth alloy samples.

Introduction

Lead and lead–bismuth eutectic (LBE), - an alloy of lead (~ 44.5%) and bismuth (~55.5%), are studied worldwide as spallation targets in accelerator driven system (ADS), in which the neutrons produced can be used either in sub-critical power reactor systems or in the long-lived actinides transmutation system in the framework of nuclear waste management.[1,2]

Lead and lead-bismuth eutectic are considered attractive candidates due to their high atomic weight, low melting points and low vapor pressures. In addition they also show low neutron capture. The lead alloys, though may be used as a primary coolant, unlike sodium which is commonly used as coolant in fast reactors, are not compatible with all categories of steels. Many steels corrode when subjected to the LBE at medium to high temperatures and necessitate strict quality control and specific requirements for corrosion protection in order to ensure adequate and safe operation.[3-6] Solubility of iron, chromium and nickel in lead, bismuth and LBE plays an important role in corrosion phenomena when using such liquid metals/alloys as nuclear coolants. Deposition of impurities in cold parts occurs due to decreasing solubility with decreasing temperature that may cause severe plugging of narrow pipes.

LBE generally shows the impurities Ti, Fe, Cu, Mo, Ag, Cd and Tl, which can lead to the formation of radiotoxic nuclides or may result in difficulties in the operation of the reactor. Likewise, steels used as structural materials coming in contact with the coolant comprise of the transition elements, V, Cr, Mn, Fe, Ni, Cu, Nb and Mo, common alloying elements in high alloy steels. Corrosion products, which enter the coolant, consist of a number of these elements.[7] It is thus essential to determine these elemental contents not only for the suitability of the LBE as a spallation target or coolant but also with regard to nuclear waste classification and disposal.

ICPMS, developed over three decades ago, has several advantages such as rapidity, multi-element capability with a high sensitivity and a wide linear dynamic range of 4–11 orders. However largely being a solution based technique, it often requires a solid sample to be brought into solution form before analysis. Hence LBE needs to be dissolved in a suitable medium.

Direct determination of trace elements in the presence of matrix by ICP-MS is prone to severe spectral and non-spectral interferences. Even sector field mass spectrometers fail to eliminate non-spectral interferences that may occur due to the presence of space charge effects[8] and matrix suppression or enhancement of signals are unpredictable, which not only reduce the sensitivity but compromise the accuracy of results.[9] Especially, it is well-known that heavy mass nuclides, Pb and Bi being such, present as matrix exert large non-spectral interferences on mid and lower mass nuclides. Thus it is of advantage to remove the matrix and preconcentrate the analytes for the determination of a few parts per million to sub-parts per billion range of impurities.

A number of methods such as solvent extraction[10-12], ion-exchange[13] or selective precipitation[14-16] may be employed to remove the matrix. Extraction of Bi(III) from acid or highly acidic solutions of HCl, HBr, HNO_3 and/or H_2SO_4 using Cyanex® 925, Cyanex® 921, 2-bromoalkanoic acid and Cyanex® 302 as extractants has been proposed.[17] Supported liquid membranes have also been employed for the separation and preconcentration of Bi.[18] Horwitz *et al.* developed a resin, 'Pb Spec', which could be used to selectively remove lead.[19] A strong base quaternary amine anion-exchange resin (Dowex 1), was used by Nelson *et al.*[20] for the sorption of Bi and Pb from HNO_3 and HCl media. However, these methods are more appropriate for the separation and preconcentration of Pb and Bi for their analysis. Recently Tindemans *et al.*[21] had used a tandem column setup to remove both Pb and Bi for the determination of trace elements in LBE alloy. The authors made use of a Pb-specific column and an anion exchange column to separate the matrix components, which required the target analytes to be eluted in two fractions, ones that are held along with Pb on the Pb specific column (Ag, Tl and Re) and another fraction that eluted separately after the anion exchange column. These two fractions, thus, needed to be analysed separately. The columns also needed regeneration after each sample passage.

Often in trace analysis of a sample, precipitation of the matrix causes problems due to loss of analytes; processes such as co-precipitation, adsorption, incorporation into the lattice and occlusion result in poor recoveries of trace analytes present in the ppm to sub ppb range. Still, a careful application of precipitation of the matrix can achieve an efficient separation of macro and micro-components of samples. Co-precipitation of large groups of trace elements can often be avoided if the precipitate is composed of regular crystals or if the trace elements can be converted into complexes which show little tendency to co-precipitate.[22] Very good preconcentration of large groups of trace elements from lead materials have been obtained by precipitating lead as $Pb(NO_3)_2$, $PbCl_2$, and $PbSO_4$. Quantitative recoveries, ranging from 90–95 %, have been reported for 25 elements, present at parts per million levels or below.[22] Venkateswarlu *et al.*[23] have recently reported the removal of lead as lead chloride-fluoride precipitate from lead and lead based alloy (PbLi and PbBi) samples for the determination of trace impurities. In their method only Pb was removed but not Bi from LBE sample.

Although papers[22,23] have been published dealing with the removal of lead by precipitation in relation to methods for the chemical characterization of the purity of lead or its compounds, todate no method has been proposed for the precipitation of both Pb and Bi from Pb-Bi alloys, for the analysis of their trace element impurities. We are reporting here a sequential precipitation method for the separation of lead - bismuth matrix from LBE followed by the determination of trace element impurities by ICP-MS. 14 elements – Rb, Te, Ba, Li, As, Cd, Zn, Ag, Cu, Mg, Co, Ni, Be and Mn were determined by the developed method, presented here.

Experimental

Instrumentation

A VG Plasmaquad 3 Inductively Coupled Plasma- Mass Spectrometer (VG Elemental, Winsford, Cheshire, UK) situated in a class 100 laboratory was used in this study. A Meinhard concentric nebulizer and a water cooled (5 °C) Scott type double-pass spray chamber system was used for sample introduction. Parameters such as plasma (rf) power, nebulizer gas flow and lens voltages were optimized daily by aspirating a 10 µg L^{-1} tuning solution containing Be, Co, Rh, In and Bi in 2% (v/v) HNO_3 introduced at a flow rate of 0.7 mL min^{-1} using a peristaltic pump (REGLO Digital MS-4/12, ISMATEC, Switzerland).

Reagents and solutions

All chemicals were of analytical grade unless stated otherwise. Sub-boiled HNO_3 and HCl were prepared in-house in a class 10 clean bench, by sub-boiling in quartz stills using reagent-grade feedstock and used wherever necessary. Ultra-pure water with >18.2 MΩ-cm resistivity, obtained using a Milli-Q Element water system (Millipore, Bedford, MA, USA), located in class 100 area, was used for dilution of standards, for preparing samples and for final rinsing of the acid cleaned vessels. All sample preparations were carried out in a class 10 clean bench. Di-ammonium hydrogen phosphate (EMSURE® ACS, Reag. Ph Eur grade) was procured from Merck, India. An ICP multielement standard VI containing 30 elements in 6% v/v HNO_3, Certipur® Certified Reference Material (Merck, Germany), whose concentrations are traceable to National Institute of Standards and Technology (NIST), USA was used in spiking experiments and for preparation of calibration standards.

Preparation of synthetic sample solution

Stock solutions (50 g L^{-1}) of both lead and bismuth were prepared individually from their respective nitrate salts in nitric acid medium. The concentrations of nitric acid in the Pb and Bi solutions were 0.8 mol L^{-1} and 2.08 mol L^{-1}, respectively. Synthetic LBE sample solutions were prepared by mixing known volumes of Pb and Bi (individual) stock solutions (in 1:1 ratio) and making up to 10 mL with ultrapure water, so that the resulting solutions contained Pb and Bi, each in the range 10,000-20,000 mg L^{-1}. Three solutions of concentrations - (i) 0.5 mg L^{-1} (ii) 1.0 mg L^{-1} and (iii) 2.0 mg L^{-1} of each element - were prepared by spiking known aliquots of a multi-element stock standard into the LBE simulated sample, to study the recovery of target analytes - Rb, Te, Ba, Li, As, Cd, Zn, Ag, Cu, Mg, Co, Ni, Be, Mn, Sr, Se, Cr, Ga, Mo and Tl.

Dissolution of sample

About 0.3 g of the Pb-Bi alloy sample was weighed accurately into a 15 mL centrifuge vial. 500 µL of conc. HNO_3 was added in 100µL installments to the sample, with constant swirling. The Pb-Bi sample dissolves slowly in HNO_3. During the digestion, a white colloidal precipitate is observed. The vial was left overnight for the sample to be completely attacked. Next day, to the white colloidal precipitate, a further 100 µL of conc. HNO_3 and a few drops of ultra pure water were added with shaking. A clear solution was obtained, which was made upto 10 mL with ultrapure water.

Matrix Separation Procedure

To a real/synthetic LBE sample solution (10 mL) containing ca. 15,000 mg L^{-1} of Pb and Bi each, 1 mL conc. HCl was added in 0.2 mL installments at room temperature shaking well after each addition, to precipitate lead as lead (II) chloride. Any further addition did not result in visible precipitation. The resultant solution was centrifuged at 2600 g for 5 min and the supernatant was collected in a separate 50 mL centrifuge vial. The residue (lead chloride precipitate) was washed with 1 mL ultrapure water once and the washings after centrifugation was mixed with the supernatant. The supernatant was then heated on a water bath maintained at a constant temperature of 90 °C, for 10 min with the addition of 6.5 mL of 5 N di-ammonium hydrogen phosphate (DAHP) in installments of 500 µL, shaking the solution thoroughly after each addition. Bismuth precipitated completely as bismuth (III) phosphate and settled to the bottom quickly. Further addition of DAHP did not result in precipitate formation. The solution was centrifuged at 2600 g for 5min and the supernatant was separated. The residue (bismuth phosphate) was washed with 1 mL ultrapure water once and centrifuged. The washings were added to the original supernatant solution before making up to a known volume (20 mL).This solution was diluted further (100 times) before analyzing for the target analytes by ICP-MS using an external calibration method. In real LBE alloy samples, the percentage of Pb present may vary between 45-55 % with the rest being Bi. Hence depending on the weight of the LBE sample taken for analysis, and the percentage of each matrix component, the volume of the precipitants, HCl solution and DAHP required change. The precipitants were added in installments until no further visible precipitation was observed. To check the percentage recovery of target analytes, the sample after complete dissolution, was spiked with a known aliquot of the multi-element stock standard, at different concentration levels (0.5, 1.0 and 2.0 mg L^{-1} of each of the analyte ions) and then the precipitation process described above was carried out to separate the matrix. A process blank was prepared accordingly.

Results and Discussion

The underlying concept of this matrix separation procedure is the principle of solubility product. The solubility product (K_{sp}) of lead(II) chloride, bismuth(III) phosphate and lead (II) phosphate are $1.7 \text{ X } 10^{-5}$, $1.3 \text{ X } 10^{-23}$ and $7.9 \text{ X } 10^{-43}$ respectively. Thus by addition of appropriate reagent the product of the ionic concentration of the respective ions of the salt in solution is made to exceed the solubility product, resulting in precipitating the salt.

Matrix Dissolution

In the present procedure, the LBE alloy sample was treated with concentrated HNO_3. During sample treatment with HNO_3, a white colloidal precipitate formation was observed, due to the lower solubility of lead (II) nitrate in concentrated nitric acid.[22] After overnight dissolution of the sample, when diluted to a known volume (10 mL), the white colloidal matter dissolved completely, to result in a clear homogenous solution.

Matrix Separation by Precipitation

In the method reported by Jackwerth[22] for determination of trace elements in lead, a high nitric acid concentration (~12 mol L^{-1}) resulted in complete precipitation of lead and yielded quantitative recoveries (> 95 %) for most of the trace analytes. Under these conditions bismuth does not precipitate. However, in the present sequential precipitation of lead-bismuth matrix, nitric acid could not be used for precipitating lead first because the concentration of nitric acid in the residual solution would be very high. This would affect the subsequent precipitation of bismuth as phosphate. The amount of DAHP required to be added for precipitating bismuth increases substantially, due to the high acidity of the medium, which needs to be neutralized before bismuth starts precipitating. Hence in the present procedure we have precipitated lead as its chloride followed by precipitating bismuth as its phosphate.

Experiments with LBE simulated sample

A set of four LBE simulated samples containing 15,000 mg L^{-1} each of Pb and Bi with the target elements spiked at concentrations equal to 0.0, 0.5, 1.0 and 2.0 mg L^{-1} each was prepared. Each of these solutions was made in triplicate. The simulated LBE solution without addition of any target analytes was employed as the process blank. The sample solutions after matrix separation were analyzed by ICP-MS after appropriate dilution to study the matrix removal (diluted 1000 times) and the recovery of target elements (diluted 100 times). The recoveries of target elements were calculated based on the amount of spike added to the simulated samples. The percentage recovery was corrected for any blanks resulting from trace element impurities present in the LBE simulated sample and those introduced during the precipitation process.

Initially two different methods of precipitation for separating both Pb and Bi were investigated. In the first method both Pb and Bi were precipitated simultaneously as their phosphates, while in the second method, a sequential precipitation was followed, precipitating Pb as its chloride initially followed by Bi as its phosphate. Significant differences were found in the recovery of various trace elements spiked into the LBE simulated sample, in the above two methods.

(1) Phosphate precipitation (Method 1)

Both lead and bismuth were precipitated as phosphates in a single step. The LBE simulated sample solution was heated to 90 °C in a water bath and DAHP added until further addition resulted in no precipitate formation. After centrifugation, two aliquots of the supernatant were taken and diluted to different dilutions as given above, with 2 % HNO_3, for the determination of both the matrix elements and target analytes by ICP-MS. The results showed that the removal of matrix elements (Pb and Bi) was > 99 %. The percentage recoveries obtained for target elements are given in Table 2 under the head 'Method 1' and discussed below.

(2) Chloride precipitation followed by phosphate precipitation (Method 2)

For a second set of samples, lead was precipitated first as its chloride at room temperature followed by bismuth as its phosphate at 90 °C in a water bath. The supernatant after appropriate dilution and subsequent analysis showed that the removal of lead was > 97 % and that of bismuth was > 99 %. The recoveries of 14 target elements are in the range 85-102 %, as shown in Table 2 under the head 'Method 2'.

Comparison of recovery of target elements by both methods

The recoveries of Li, Rb and Te did not show any marked difference between the two precipitation methods and were in the range 90-105 %. Precipitation of Pb and Bi as their phosphates, method 1, resulted in poor recoveries for the other elements. Except for thallium, there was significant improvement in the recoveries of elements when the matrix precipitation was performed by method 2 in comparison to method 1. In method 2, where Pb was precipitated as its chloride followed by Bi as its phosphate, the recoveries of elements, As, Cd, Zn, Ag and Cu, improved substantially from ~10-50 % (in method 1) to > 95 %. In addition the rest of the elements also showed improved recovery.

The solubility products of phosphates of most of the trace elements being investigated are very low. This explains the poor recovery of the analytes in method 1, involving co-precipitation due to accumulation of excess phosphate anion on the surface of the lead and bismuth phosphates. On the other hand when lead is initially precipitated as its chloride, most of the trace elements, due to excess chloride in the medium, form chloro-complexes that are negatively charged complex ions. The formation of anionic chloro complexes could explain the marked improvement in the recovery of trace elements following Bi precipitation as its phosphate, despite the low solubility products of phosphates of the analytes. This is substantiated by the > 98 % recovery obtained for Ag in the spiked LBE simulated sample. It is a well known fact that Pb and Ag precipitate when chloride ions are added to a solution. Pb being one of the matrix elements present would readily precipitate as lead(II) chloride while Ag present in trace concentration may combine with excess chloride to form $AgCl_2^-$. Jackwerth[22] has reported ~95 % recovery for Ag when Pb matrix was precipitated as its chloride. In the case of thallium, method 1 shows > 94 % recovery in comparison to method 2, where the recovery was only 22 %. In method 2, Tl is most likely undergoing co-precipitation with Pb as its chloride. Thus 14 elements (Rb, Te, Ba, Li, As, Cd, Zn, Ag, Cu, Mg, Co, Ni, Be and Mn) with recoveries in the range of 85-102 % could be determined by method 2.

Analysis of real LBE sample

The optimized matrix separation procedure (method 2) was used to analyze three LBE samples, prepared at BARC, Mumbai. The samples were received in the form of lumps. Each lump was crushed to very small pieces before dissolution, divided into three portions and processed in triplicate. The mean concentration obtained from the triplicate results for each sample is reported in Table 3. The results show that among the elements analyzed for, Ag, Cu, Co, Ni and Cd were the major contaminants. The RSD for Ag and Cu were found to be < 5 % showing that they are homogeneously distributed in the sample, whilst the values were < 10 % for Co, Ni and Cd, exhibiting greater inhomogeneity. The concentration of other elements – Mg, Zn, Te, As, Li, Rb, Mn, Be and Ba in the samples were found to be less than their limit of quantification (LOQ). The value of Li in sample 2 and Ba in sample 1 were higher than the LOQ values and are reported as obtained.

Method Validation

In the absence of a reference material for LBE certified for trace element impurities, the proposed method of matrix dissolution, separation and determination of trace analytes was validated by analyzing simulated LBE samples spiked with target elements at three different concentration levels. The percentage removal of the matrix was > 97 % and the recoveries obtained for target analytes are shown in Table 2 (at 1 mg L^{-1} spike level). The recoveries for 14 elements were > 85 %, while for the rest (Sr, Se, Cr, Ga, Mo and Tl) these were < 80 %. These values are given as information to show an improvement over method 1 (except Tl). Quantification by ICP-MS was based on an external calibration with standards prepared from a certified multielement stock standard from Merck. One of the calibration standards was measured after every ~ 5 samples to ensure that instrumental drift was well corrected for by the internal standard (Rh).

Further, a flow-injection ICP-MS (FI-ICPMS) method was used as an independent method for validating the concentrations of some of the elements (Ag, Cu, Co, Ni and Cd), present at high levels in the real LBE samples. For the FI-ICPMS method, the LBE sample was digested as explained earlier and analyzed directly after diluting 100 times. A 100 µL loop was used for sample/standard injection. Calibration standards were injected similarly and quantification was done based on peak area, obtained using a time resolved data acquisition. Matrix based non-spectral interferences were compensated for by preparing matrix matched calibration standards. For analytes Ag, Cu, Ni, Co and Cd which were found to be at a few tens of ppm the results obtained by the developed method and the direct FI-ICPMS method are in good agreement, as shown in Table 4. Applying the t-test (paired-comparison) with multiple samples showed that the results of the two independent methods did not differ significantly at the 95 % confidence level.

Process Blank

A total of 14 elements among the 20 target analytes gave recoveries in the range 85-102 %. Five solutions without the matrix elements, were prepared and processed through the optimized procedure for method 2, to quantify the concentration of target elements in process blank, introduced during the matrix separation. The method detection limits (MDL), the limit of quantification (LOQ) and the process blank values are given in Table 5. The MDL and LOQ was calculated as concentration equivalent to 3 times and 10 times the standard deviation of the process blank (n = 5) respectively, normalized to 1 g of the LBE sample. The mean of five process blank solutions are reported. The only limitation of the present developed method 2, being the higher process blank values for some of the elements like Mg, As, Li, Ni, Te, Zn and Be. The use of ultrapure DAHP may probably improve the quality of results for the above mentioned elements.

Conclusion

The sequential precipitation method reported here is simple and as it eliminates the Pb and Bi matrix, which are both heavy elements and are thus prone to cause non-spectral interferences in the determination of trace impurities, especially when present at very low levels such as a few tens of parts per billion, and improves the sensitivity of analysis significantly.

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Table1. Instrumental parameters of ICP-MS (VG Plasmaquad 3)

Instrumental Parameters		**Scanning Parameters**	
Coolant gas:	13.4 L min^{-1}	Scanning mode:	Peak jump
Aux. gas:	0.88 L min^{-1}	Number of replicates:	3
Nebulizer gas:	0.92 L min^{-1}	Dwell time:	100 ms/channel
Sampler cone dia:	1.0 mm Ni	Sample uptake time:	50 sec
Skimmer cone dia:	0.7 mm Ni	Washing time:	60 sec
Torch type:	Fassel	Sample uptake rate:	~0.7 mLmin^{-1}
Plasma FW power:	1350 W		
Reflected power:	<0.8 W		

Table 2. Comparison of recoveries obtained for analyte elements spiked in LBE simulated sample, containing 15000 mg L^{-1} of the matrix elements and 1.0mg L^{-1} of analyte elements, by subjecting the sample to both the precipitation methods. (value ± s.d., n = 3)

Element	% Recovery (Method 1)	% Recovery (Method 2)
Rb	99.3 ± 0.5	103.4 ± 1.3
Te	92.4 ± 2.5	102.5 ± 2.4
Ba	71.1 ± 4.8	101.2 ± 4.2
Li	93.9 ± 2.8	100.6 ± 3.6
As	16.5 ± 3.2	98.0 ± 2.6
Cd	47.6 ± 10	98.3 ± 0.1
Zn	53.1 ± 6.8	98.2 ± 3.9
Ag	33.9 ± 1.7	97.0 ± 2.1
Cu	34.6 ± 6.0	97.0 ± 2.7
Mg	85.7 ± 2.4	95.1 ± 3.3
Co	82.5 ± 3.8	94.4 ± 1.3
Ni	62.9 ± 7.8	94.0 ± 3.3
Be	52.3 ± 5.2	92.1 ± 2.5
Mn	52.6 ± 8.2	86.4 ± 3.5
Sr	50.4 ± 7.5	78.6 ± 1.2
Se	< 10	69.5 ± 1.7
Cr	< 10	59.3 ± 3.1
Ga	26.6 ± 5.0	52.4 ± 2.1
Mo	< 5	45.5 ± 4.1
Tl	93.6 ± 1.9	22.4 ± 1.5

Table 3. Concentration of trace elements in real LBE samples after digestion and matrix separation by the proposed method (Method 2)

Element	Sample 1 (µg g^{-1}) ± s.d.[#]	Sample 2 (µg g^{-1}) ± s.d.[#]	Sample 3 (µg g^{-1}) ± s.d.[#]
Ag	138 ± 3	71 ± 4	136 ± 5
Cu	121 ± 4	97 ± 5	110 ± 3
Co	16.2 ± 1.2	10.2 ± 0.6	13.5 ± 0.9
Ni	12.6 ± 0.7	11.0 ± 1.1	12.9 ± 0.5
Cd	8.0 ± 0.5	5.6 ± 0.4	6.8 ± 0.5
Mg	< LOQ	< LOQ	< LOQ
Zn	< LOQ	< LOQ	< LOQ
Te	< LOQ	< LOQ	< LOQ
As	< LOQ	< LOQ	< LOQ
Li	< LOQ	4.8 ± 0.1	< LOQ
Ba	0.24 ± 0.02	< LOQ	< LOQ
Rb	< LOQ	< LOQ	< LOQ
Mn	< LOQ	< LOQ	< LOQ
Be	< LOQ	< LOQ	< LOQ

[#] - s.d. = reproducibility standard deviation (n = 3)

Table 4 Comparison of concentrations obtained (A) by ICP-MS after the matrix separation procedure developed and (B) by FI-ICP-MS directly after sample digestion and dilution.

Element	Sample 1 (µg g^{-1}) ± s.d.[#]		Sample 2 (µg g^{-1}) ± s.d.[#]		Sample 3 (µg g^{-1}) ± s.d.[#]	
	A	B	A	B	A	B
Ag	138 ± 3	135 ± 5	71 ± 4	73 ± 3	136 ± 5	139 ± 4
Cu	121 ± 4	126 ± 6	97 ± 5	94 ± 3	110 ± 3	107 ± 5
Co	16.2 ± 1.2	15.3 ± 2.1	10.2 ± 0.6	11.5 ± 1.0	13.5 ± 0.9	12.7 ± 2.5
Ni	12.6 ± 0.7	13.4 ± 1.5	11.0 ± 1.1	12.4 ± 3.2	12.9 ± 0.5	12.1 ± 2.3
Cd	8.0 ± 0.5	7.8 ± 1	5.6 ± 0.4	4.9 ± 2.4	6.8 ± 0.5	5.8 ± 2.1

[#] - s.d. = measured under repeatability conditions (n = 3)

Table 5 The method detection limits, limit of quantification and the process blank values for elements whose % recovery was > 85% by method-2

Element	Method Detection Limit ($\mu g\ g^{-1}$); n = 5	Limit of Quantification ($\mu g\ g^{-1}$); n = 5	Average Process Blank ($\mu g\ g^{-1}$); n = 5
Ag	0.01	0.03	0.04
As	2.41	8.0	7.2
Ba	0.02	0.1	0.4
Be	0.18	0.6	2.1
Cd	0.02	0.1	0.1
Co	0.01	0.03	0.04
Cu	0.06	0.2	1.0
Li	0.23	0.8	6.5
Mg	2.41	8.0	10.0
Mn	0.25	0.8	1.4
Ni	0.63	2.1	2.4
Rb	0.03	0.1	0.02
Te	0.28	0.9	3.2
Zn	0.7	2.4	2.5