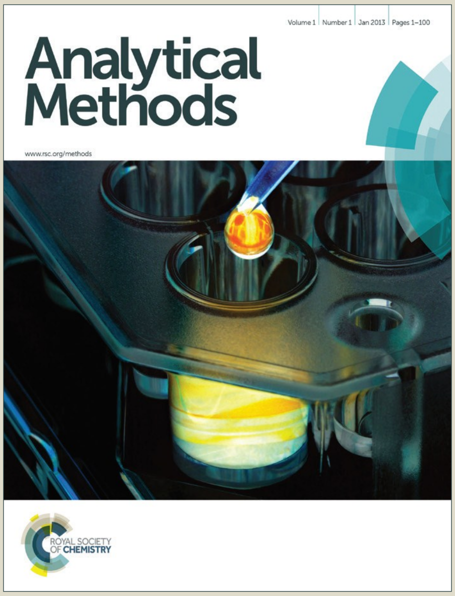
Analytical Methods



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Determination of trace Bi by ICP-OES after magnetic solid phase extraction with fullerene C60 modified γ-Fe_2O_3superparamagnetic iron oxide nanoparticles

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ABSTRACT

In this research, a procedure for the preconcentration of Bi at trace levels in milk samples by inductively coupled plasma optical emission spectrometry (ICP-OES) is proposed. It is based on the batch magnetic solid phase extraction of Bi ions by fullerene C60 modified maghemite (γ-Fe_2O_3superparamagnetic iron oxide nanoparticles-SPION) nanoparticles.Various factors influencing the preconcentration of Bi such as pH, amount of magnetic nanoparticle, initial Bi concentration, sample volume and effects of possible interferic ions were investigated. The analytical curve was achieved as linear in the concentrations range of 0.25-10 ng mL^{-1} with a limit of detection of 0.06 ng mL^{-1}. The precision as RSD was 7.5% for concentration of 0.25 ng mL^{-1}. The method was validated by the analysis of a standard reference material (NIST SRM 1643e). In addition, 96.6–98.7% recoveries were achieved for the spiked samples. Bi concentrations in ten milk samples were successfully determined after developed method was applied. Bi contents ranged in milk samples from 6.5 to 14.3 ng mL^{-1}.

Keywords **:**Bi, preconcentration, magnetic solid phase extraction, ICP-OES, SPION, fullerene

INTRODUCTION

Bismuth (Bi) and its compounds are relatively rare in earth that used in different area of life such as cosmetic industry (e.g. pigments in eye shadow, lipsticks and hair dyes), medicines (such as for treatment of syphilis, peptic ulcers and dermatological disorders), alloys, by- product of copper and tin refining, metallurgical additives, and preparation and recycling of uranium in nuclear fuels, fabrication of catalyst.[1,2] Bi is not accepted as essential element for plants and animals.[3] Extensive usages of Bi and its compounds are main reasons of exposure of this element to organism. Reported toxic effects of Bi and its compounds such as nephrotoxicity, neurophthology, kidney damage symptoms, osteoarthropathy, and hepatitis arerequired to routine determination of Bi in environmental and biological samples. By considering the trace level of Bi, a preliminary preconcentration and separation methods are inevitable prior to its determination.[3,4] These include liquid-liquid extraction (LLE), solid phase extraction (SPE), coprecipitation, cloud point extraction.[4-6]However, only few of them have sufficient sensitivity for Bi. LLE is required the use of toxic organic solvents. The uses of peristaltic pump or manual passing to solution through the column area reason of long analysis time in column SPE method. A complexation ligand should be generally used to provide selectivity.[7] Recently, preconcentration by magnetic solid phase extraction has been attained interest.[8-12] Because problems such as column packing and phase separation in traditional SPE are overcome by the use of magnetic materials.[10] Additionally the use of them in small amount is one of the main advantages. In a recent review, application of magnetic nanoparticles for the preconcentration of metal ions prior to their determination by FAAS, ETAAS, ICP-OES, ICP-MS, CV-AAS, LC-MS/MS, HPLC-ICP-MS, UV-visible were reported in details. By considering the literature survey, it is possible to say that there is no report in literature for preconcentration of Bi by magnetic solid phase extraction method.

Direct determination of elements at trace levels is easy when ICP-MS is used. It is not required a preconcentration step whereas ICP-OES, FAAS. However, ICP-MS could not found in any of laboratory. Because, price of ICP-MS is nearly three times expensive than ICP-OES. So, many of researchers must to use the instruments that already present in their laboratories. From this point of view, preconcentration methods should be applied before measurement by ICP-OES, FAAS and even ICP-MS. Additionally, some regulations and standards for routine analysis are required to use the preconcentration methods for organic and inorganic pollutants and following determination by ICP-OES, UV-VIS or FAAS.

In this study, fullerene C60 modified maghemite (γ-Fe2O3 superparamagnetic iron oxide nanoparticles-SPION) nanoparticles synthesized and characterized in our previous work was used for the prconcentration of Bi prior to its determination by ICP-OES. Important experimental parameters such as pH of the solution, amount of magnetic nanoparticle, initial volume of sample solution, type and volume of the eluent acid were investigated. The developed method was validated through the analysis of standard reference material. Finally, this method was applied for the analysis of Bi in water, drinking and food samples.

EXPERIMENTAL

Instrumentation

Optima 2100 DV inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer, Massachusetts, USA) was used for the determination of Bi at the wavelength of 223.061 nm. The operating conditions of the ICP-OES for determination of Bi were given in our previous study.[13]Mettler Toledo MPC 227 (Polaris Parkway, Columbus) model digital pH meter was used for measurement of acidity of solutions.

Reagents and solutions

All chemicals used in this study were of analytical grade. Ultrapure water was obtained from a maximum ultrapure water system (18.2 M0X ELGA, England). C60 was supplied from Sigma-Aldrich (St Louis, MO, USA). A super magnet (Nd-Fe-B, 1.2 T, 50 × 40 × 20 mm) was used for phase separation.

Stock solution of Bi was prepared from their individual stock solution at the concentration of 1000μg mL^{-1}(High Purity Standards-Charleston, SC.) with ultra pure water. It was diluted for the standards at lower concentrations. All glass materials were washed with 1.0mol L^{-1} of $HNO_3$and then ultra pure water before using. HNO_3(65%) and H_2O_2 (35%) were supplied from Merck and they were used in digestion procedures. Standard reference water sample - NIST 1643e(Gaithersburg, MD) was used to check the accuracy of the method.

General preconcentration procedure

Fullerene C_{60} functionalized γ-Fe_2O_3 magnetic nanoparticles were synthesized and characterized inour previous work.[14] Briefly 100 mL of Bi ion solution (1.0 ng mL^{-1}) was prepared and the pH value was adjusted to 7.0 using phosphoric acid buffer solution, and then, added to 50 mg of magnetic nanoparticles. Under continuous mechanical stirring of the mixture for 10 min, the magnetic adsorbent was isolated easily and quickly with the help of a strong magnet (Nd-Fe-B, 1.2 T, 100 mm 100 mm 20 mm) and the aqueous solution was poured away.

Then the Bi ions retained on the sorbent were elutaed by two times with 1.0 ml of 1 mol L^{-1} HNO_3. The Bi ions in the eluate solution were determined by ICP-OES.

Preparation of samples to magnetic SPE procedure

Milk samples were purchased from a local market in Diyarbakir, Turkey and digested in a microwave oven (Berghof MWS 3, Eningen, Germany). Five bottles from each milk sample from a 200 and/or 500 mL box were mixed, and the homogenized samples were used for the analysis of Bi content. The digestion procedure was reported in our recent manuscript in details.[13]

After digestion in analytical microwave oven, clear digests were transferred to a beaker and acids were evaporated until dryness and then residue was dissolved in 2.0 mL of 1.0 mol L^{-1} HNO_3. After dissolving of the 5.0 mL portion of each of samples, the final volume was 10.0 mL. All of the procedures during the dissolving process were applied to the blank solution. Possible lost of analyte was checked from preliminary experiments and it was observed that there was no loss of analyte from this procedure. For this purpose, one of the samples was spiked with a known amount of Bi (results are given in the following sections).

RESULTS AND DISCUSSION

Effects of pH

Solution pH plays a key role in the magnetic solid phase extraction method. The effect of pH on the preconcentration of Bi by C60-γ-Fe_2O_3 magnetic nanoparticle is presented in Fig. 1. As shown in Fig. 1, the effect of pH of the solution on the extraction of 1.0 ng mL^{-1} ofBi were studied between the pH range of 2.0-9.0. Bi was quantitatively recovered at the pH range of 6.0. When the solution pH increased from 2.0 to 5.0, Bi recovery increased from 28.6% to 76.5% respectively.Subsequent studies were carried out at an initial pH of 6.0.

Fig. 1.

Effect of amount of magnetic nanoparticle

The effect of amounts of magnetic nanoparticle on the magnetic solid phase extraction of Bi ions was investigated in the range of 10–100 mg. The results presented in Fig. 2 showed that Bi ions were quantitatively extracted on 30 mg of the magnetic nanoparticle. Decreasing in the extraction recovery was observed for amount higher than this value. So, 30 mg of C60-γ-Fe_2O_3 magnetic nanoparticle was selected as the optimum amount of magnetic nanoparticle necessary for all subsequent experiments.

Fig. 2.

The effect of contact time

It is well known that sufficient time is required for quantitative interaction between metal ion in aqueous sample and adsorbent in solid phase. Quantitative extraction could not achieve in short extraction time. In the other hand, long time interaction is far of being of practical usefulness. Therefore, the extraction of Bi ions on the magnetic nanoparticle versus time dependence has been investigated with contacttimes of 1–10 min. Results showed that extraction of Bi was quite high on 1.0-5.0 min (Fig. 3). Extraction of Bi ions from the solution reached more than 98% at about 5 min.

Fig. 3.

Effect of sample volume

In preconcentration methods, higher enrichment factor is desired and it depends on the initial sample volume and final volume. Initial sample volume should be higher whereas final volume should be lower. For that reason, the volumes of initial sample solution containing 1.0 ng mL^{-1} of Bi were varied from 10 to 500 mL (Fig. 4.). The results indicated that Bi ions were quantitatively recovered when the sample volume was less than 200 mL and after elution with 2.0 mL of the eluent, an enrichment factor of 100 was achieved. The extraction efficiency decreased on using a larger volume, due to the dilution of the analyte in the initial sample solution.

Fig. 4.

Effect of type and concentration of eluent

It was observed that the type and concentration of the eluent were one of the key factors that influence the magnetic solid phase extraction procedure for the preconcentration of Bi. To choose the most effective eluent acid for quantitative stripping of the Biions on the magnetic nanoparticle, various stripping solutions were tested and results are summarized in Table 1. Acidic eluent was found as suitable to obtain efficient extraction. It was observed that among different cases, the HNO_3 solution admits quantitative stripping of Bi ions. By raising eluting volume from 0.5 to 1.0 mol L^{-1}, the recovery was increased and the recovery of 99.1% was achieved with 2.0 mL eluent. Therefore, 2.0 mL HNO_3(two times elution with 1.0mol L^{-1}) was chosen for elution of Bi ions from magnetic nanoparticle.

Table1

The effect of other ions

It is well known that matrix constituents have an important effect on the preconcentration of trace metals. The effects of possible interferic coexisting ions in water and milk samples were investigated on the extraction recovery of Bi ions. In order to demonstrate the selectivity of the developed method, various metal ions were individually added to 100 mL aqueous solutions containing 1.0 ng mL^{-1} of Bi solution. The tolerance limit was considered if it resulted in a ±5 % variation in the extraction efficiency of Bi. Results presented in Table 2 that the examined cations and their co-anions (chloride, nitrate, sulphate) had no significant effects on the extraction and determination of Bi. So the used sorbent showed high tolerance limit for coexisting ions and the extraction recovery of Bi was almost quantitative in the presence of foreign ions and therefore useful for the analysis of Bi in real samples.

Table 2

Analytical figures of merit

In solid phase extraction studies, the potential regeneration and stability of the column are very important parameters to evaluate the adsorbent that can guarantee its widespread application in industry. The stability of the adsorbent for magnetic solid phase extraction result is shown in Fig.5.The uptake of Bi ion was stable up to at least after 15extraction cycles (total 45 independent experiment by considering the three replicate for each of sample). It was determined that the recoveriesof Biions were lower than 95.0%, respectively after use of 15 times.

Fig. 5.

Analytical characteristics of the developed method are presented in Table 3 with details. A limit of detection (LOD) of the proposed method for the determination of lead was studied under the optimal experimental conditions. The LOD obtained from the equation: $C_{\mathrm{LOD}} = 3S\mathrm{d}/m$, where Sd is the standard deviation of ten consecutive measurements of the blank and m is a slope of the calibration curve, was 0.06 ng mL^{-1}. Limit of quantification (LOQ) values were calculated from $C_{LOQ} = 10Sd\ /m$. The precision was also determined and expressed as a relative standard deviation (RSD).RSD value was found as 7.5%. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

By applying the developed preconcentration method sensitivity of ICP-OES for determination of Bi was improved as 93.3 times. It was calculated from the slope ratio of linear calibration plot of magnetic SPE-ICP-OES method to ICP-OES without SPE method. LOD value was found as 0.06 ng mL^{-1} that was comparable with values reported in literatures. Analytical characteristics of the methods published in literature were presented in comparison with our method (Table 4).

Table 3

Linear range, LOD, RSD and enrichment factor of the developed method with those of other related preconcentration methods for the extraction and determination of Bi are comparatively presented in Table 4. The RSD was 7.5% for 0.25 ng mL^{-1} Bi level, indicating favorable precision of the presented method. From the results it could be concluded that developed magnetic solid phase extraction method for Bi provided excellent precision, selectivity and sensitivity, and has other advantages such as simplicity and environment-friendly.

As seen from these data, the proposed method had a high adsorption capacity, and short extraction procedure (about 5 min) with a sample volume of 200 mL compared to other reported methods. The LOD and preconcentration factor of this method are comparable with other methods. In addition, common interfering ions had no evident interference. The reusability of the C60-γ-Fe_2O_3superparamagnetic iron oxide nanoparticles is the another strong advantages of the method presented here. Finally, Bi at trace level could be successfully determined in real samples before ICP–OES measurement.

Table 4

Method validation and analysis of real samples

To verify the accuracy of the developed method, it was applied to the determination of Bi in a standard reference material (NIST SRM 1643e, trace elements in water). The certified amount of Bi in the SRM is 14.09±0.15ng mL^{-1}. The determined value for Bi by using the presented magnetic solid phase extraction method was 13.96±0.16ng mL^{-1}, (mean of six determinations±standard deviation), which is in good agreement with the certified value. Additionally, the method was applied to milk and water samples to determination of Bi. The analytical results are shown in Table 5. As seen, the recoveries for the Bi were in the range of 96.6–98.7%. Bi concentrations in four milk samples were determined as loer than LOD by a method based on combining Fe_3O_4 nanoparticles accelerated UV Fenton-like digestion and solid phase extraction [23]. Room temperature acid sonication was employed for multielement analysis in milk before ICP-MS. Concentrations of Bi in 28 milk samples were determined in the ranges of 3.6-22.2 ng g^{-1} [24]. Higher concentration of Bi was determined in riverwater versus some literature values whereas itwas not found in tap water [21].

CONCLUSION

Compared with the reported methods, the developed magnetic solid phase extraction method provided environmentally friend procedure, consuming less amount of re-usable sorbent, high enrichment factor, low LOQ, wide linear range, high throughput. Additionally, it has high tolerance to possible interfering ions and quantification of Bi at trace levels in milk samples is satisfactory. Desorption experiments revealed that the C60-γ-Fe_2O_3superparamagnetic iron oxide nanoparticles can be regenerated and reused for 15 consecutive adsorption cycles without loss of its removal efficiency. The accuracy of this method was verified by analyzing the standard reference water sample (NIST 1643e) with satisfactory results.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1. Effect of pH on the magnetic solid phase extraction of Bi

Fig. 2. Effect of amount of magnetic nanoparticle on the magnetic solid phase extraction of Bi

Fig. 3. Effect of contact time on the magnetic solid phase extraction of Bi

Fig. 4. Effect of sample volume on the magnetic solid phase extraction of Bi

Fig. 5. Reusability of C60-γ-Fe_2O_3 superparamagnetic iron oxide nanoparticles for preconcentration of Bi

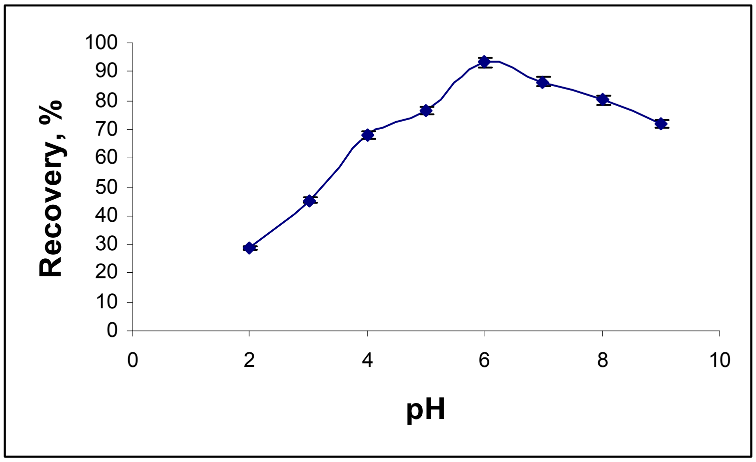


Fig. 1. Effect of pH on the magnetic solid phase extraction of Bi

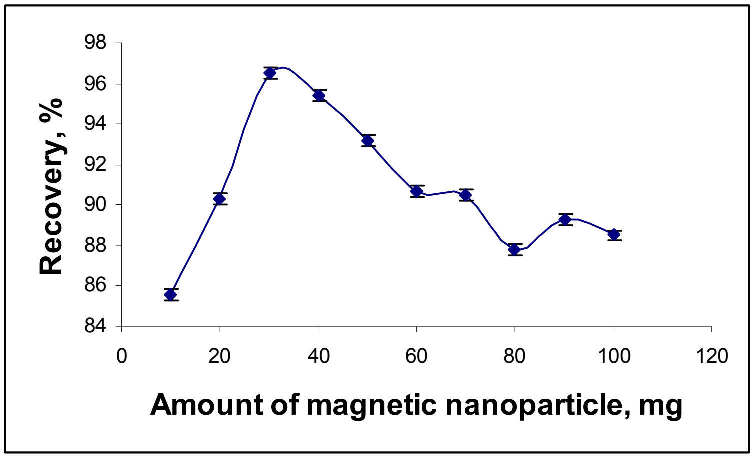


Fig. 2. Effect of amount of magnetic nanoparticle on the magnetic solid phase extraction of Bi

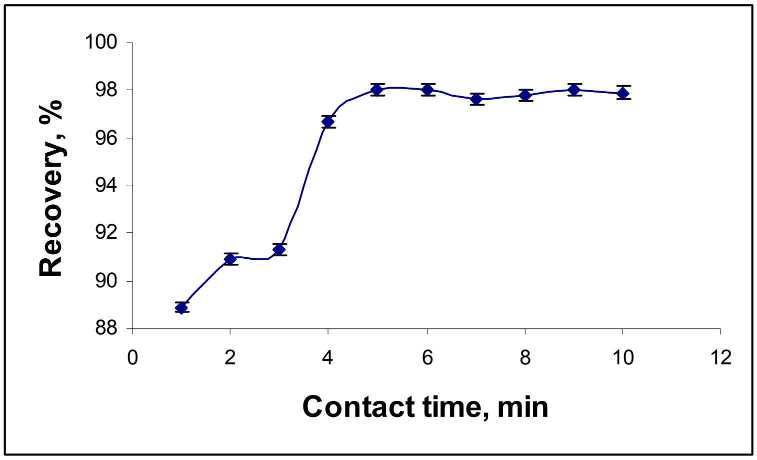


Fig. 3. Effect of contact time on the magnetic solid phase extraction of Bi

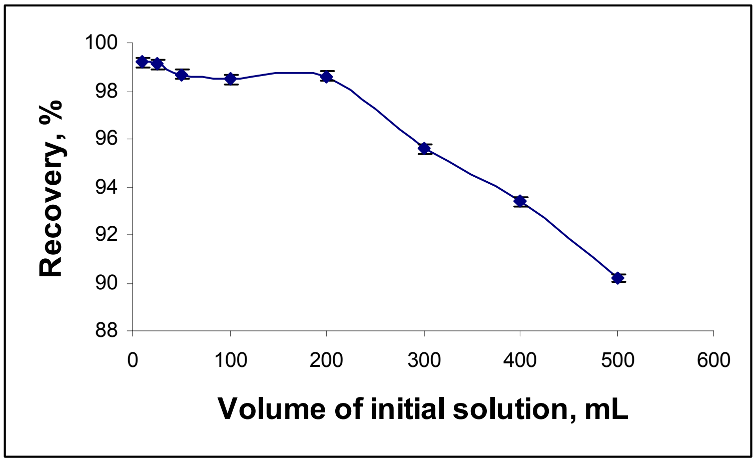


Fig. 4. Effect of sample volume on the magnetic solid phase extraction of Bi

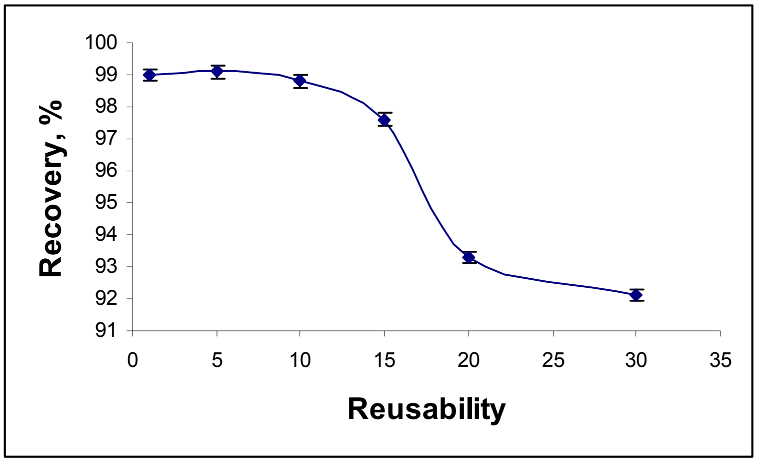


Fig. 5. Reusability of C60-γ-Fe2O3 superparamagnetic iron oxide nanoparticles for preconcentration of Bi

Table 1. Effect of type and concentration of eluent on the magnetic solid phase extraction of Bi

Eluent	**Concentration (mol L^{-1})**	**Recovery (%)**
HCL	0.5	94.5±1.4
	1.0	94.8±2.0
HNO_3	0.5	96.7±1.0
	1.0	99.1±1.2

Table 2. Influences of some foreign ions on the magnetic solid phase extraction of 1.0 ng mL^{-1} of Bi

Ion	Interference/Bi (Weight ratio)	Recovery (%)
Na^+	1000	98.9±0.9
K^+	1000	99.1±1.3
Ca^{2+}	1000	98.9±1.6
Fe^{2+}	750	99.0±2.3
Fe^{3+}	500	99.4±0.9
Zn^{2+}	750	99.4±3.1
Cu^{2+}	500	98.7±2.7
Cd^{2+}	500	98.8±2.6
Ni^{2+}	500	98.9±3.0
Co^{2+}	500	98.0±2.1
Al^{3+}	500	98.4±2.3
Cr^{3+}	5000	98.9±1.9

Table 3. Analytical characteristics of the developed method

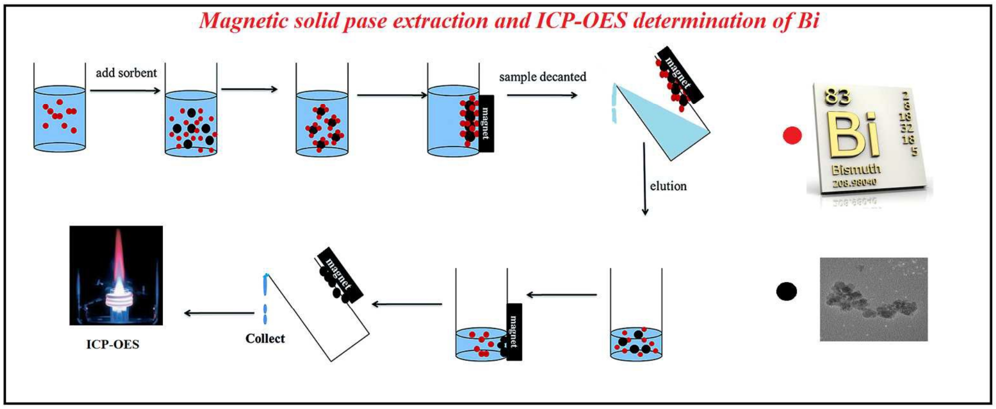
Parameter	**Analytical feature**
Linear range, ng mL^{-1}	0.25-10
r^2	0.9964
LOD, ng mL^{-1}	0.06
LOQ, ng mL^{-1}	0.19
RSD, % (for 0.25 ng mL^{-1})	7.5
Enrichment factor	93.3

Table 4. Comparison of methods for preconcentration of Bi

Method	EF	Linear range	RSD, %	LOD	Instrument	Reference
SPE with MWCNT functionalized with L- proline	160	0.7-75 ng L^{-1}	1.5	0.7 ng L^{-1}	FI-HG-AAS	15
Ion pair based dispersive liquid–liquid microextraction method	125	0.3-8.0 ng mL^{-1}	4.8	0.07 ng mL^{-1}	ET-AAS	16
SPE with octadecyl bonded silica cartridge modified with cyanex 301	20	0.5-10 ng L^{-1}	-	0.01 ng L^{-1}	ET-AAS	17
SPE with ion-imprinted polymer	300	0.035-0.35 ng mL^{-1}	4.1	8.6 ng L^{-1}	ET-AAS	18
Dispersive liquid–liquid microextraction	62.5	5-400 ng L^{-1}	1.14-2.66	1.6 ng L^{-1}	UV-VIS	19
CPE with Diethyldithiophosphate as ligand and	18	0.5-10 ng mL^{-1}	<5	0.063 ng mL^{-1}	ICP-OES	20
Continuous flow hydride generation	12.2	1-50 ng mL^{-1}	3.9	0.16 ng mL^{-1}	ICP-OES	13
SQT-AT	256	7.5-100 ng mL^{-1}	4.0	1.6 ng mL^{-1}	FAAS	21
W coated SQT-AT	613	2.5-25 ng mL^{-1}	7.0	0.51 ng mL^{-1}	FAAS	22
Magnetic solid phase extraction	93.3	0.25-10 ng mL^{-1}	7.5	0.06 ng mL^{-1}	ICP-OES	This study

Table 5. Bi concentrations in real samples

Sample	Spiked, ng mL^{-1}	Detected, ng mL^{-1}	Recovery, %
Tap water	-	-	-
	5.0	4.86±0.25	97.2
Dicle River water	-	10.6±0.6	
	5.0	15.4±0.6	98.7
Mineral water	-	-	-
Energy dring	-	3.5±0.05	-
Milk 1	-	9.8±0.7	-
	5.0	14.3±0.9	96.6
Milk 2	-	10.2±0.8	-
Milk 3	-	11.5±0.6	-
Milk 4	-	10.8±0.6	-
Milk 5	-	10.0±0.8	-
Milk 6	-	6.5±0.4	-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