



Determination of Arsenic(III) and Total Arsenic at Trace Levels in Baby Food Samples via a New Functionalized Magnetic Graphane Oxide Nanocomposite

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Abstract

Baby food safety is an essential issue in health policy. For this reason, a simple, cheap, and fast analytical procedure to developed arsenic(III) and total arsenic determination in baby food samples using functionalized magnetic graphane oxide nanocomposite. A new nanocomposite anchored of tiopronin (TSH) magnetic graphane oxide (GO-PG4@Fe₃O₄-TSH) was first synthesized/characterized and used as an adsorbent to determine arsenic(III) and total arsenic for baby food samples. Arsenic(III) was directly determined on GO-PG4@Fe₃O₄-TSH nanocomposite at pH 4.5. The determination of total arsenic used KI and L(+) ascorbic acid solution as reducing reagents. The parameters influential on arsenic(III) determination in the baby food samples including the sample's pH, adsorption time, amount of GO-PG4@Fe₃O₄-TSH, eluent type, sample volume, reducing reagent type and amount, and also foreign ion effect were investigated. The GO-PG4@Fe₃O₄-TSH carrying As(III) could easily be separated from baby food samples via applying an external magnetic field. The detection limit for arsenic(III) was found as 0.11 µg L⁻¹, while the limit of quantification values was computed as 0.37 µg L⁻¹. The precision of results, expressed as relative standard deviation, was always lower than 1.6% at 1 mg L⁻¹ As(III) levels. The accuracy of this method was confirmed by analysis of certified reference material. The method was successively applied to determine arsenic(III) and total arsenic in baby food samples.

Keywords Magnetic graphane oxide · Nanocomposite · Arsenic(III) · Total arsenic · Baby food samples

Introduction

Chemical food safety, especially baby food safety, is a topic of increasing concern within the community. However, due to modern risk management procedures, harmful chemicals' acute threat is very uncommon. It has been postulated that chemical contaminants found in foods might be etiological factors behind several diseases (e.g., cancer), the causes of which are mostly unknown. In addition to the environmental and agrochemical residues and natural toxins, contaminants

produced during food processing or storage, such as trace metals and arsenic, are becoming an issue [1].

Babies and persons with allergies are the most sensitive population groups, and special attention should be paid to the food products consumed by these groups. Food for babies used to be carefully and safely prepared at home daily; however, due to modern lifestyles, the increase in the quality and variety of commercial baby food has considerably increased the production and consumption of this ready-made baby food. These products typically contain vegetables and meat (turkey, chicken, and beef) with oil, salt, and, sometimes, pasta or rice [2].

Exposure to toxic inorganic forms of arsenic, including arsenite (As(III)) and arsenate (As(V)), has been linked to an increased risk of cancer [3]. Methylated forms of arsenic such as methylarsonic acid (MMA) and dimethylarsinic acid (DMA) are significantly less toxic than inorganic arsenic. Still, they have been identified as potential cancer promoters [4]. Dietary intake and drinking water are the major routes of arsenic exposure for most people [5]. The

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predominant forms of arsenic found in drinking water are inorganic; however, dietary arsenic sources may contain several different arsenic species [6–8]. By contrast because of this anionic nature, arsenic can be found in relatively greater concentrations in aqueous environments than divalent trace metals [9].

The arsenic concentrations in most foods are generally at much lower levels (ng g^{-1}) than those found in finfish, shellfish, and seaweed (mg g^{-1}) [10]. Arsenic is found in all beverages, vegetables, cereals, milk products, meat, and seafood. The highest concentrations (over 100 mg kg^{-1} of arsenic) are found in seafood living at the bottom of the sea, especially shrimps and lobsters [11]. It has been reported that ultra-trace levels of arsenic have a potential nutritional value and apparent beneficial effects. However, arsenic compounds were restricted worldwide after reports of diseases and death caused by the ingestion of arsenic substances or contaminated food. Several arsenic surveys in total diet food composites and baby foods have been published because of growing interest in trace element concentrations in baby foods and the need to establish infant exposure to such elements from the diet [12].

It is known that even the elongated intake of low concentrations of arsenic can cause severe toxic effects to appear [13]. Since other species of the same element may have different chemical and toxicological properties, the total concentration of an element may not provide information about the element's actual physicochemical forms, required for understanding its toxicity, biotransformation, etc. On the other hand, some studies indicate this trace element's potential to induce skin lesions when individuals are exposed to high arsenic content from water or nonmelanoma skin carcinoma for individuals exposed to increased environmental arsenic levels as a consequence of a coal-burning power plant [13, 14]. Thus, to obtain information on toxicity and biotransformation of elements in aquatic systems, quantification of individual species of an element is needed [15].

Different analytical methods for the analysis of inorganic arsenic in food products can be found in the literature. Therefore, the development of sensitive analytical methods for determining residue levels of As(III)/(V) baby food products is required. Nowadays, a variety of analytical techniques based on high-performance liquid chromatography (HPLC) [16], mass spectrometry detection [17], chemiluminescence [18], capillary electrophoresis [19], atomic absorption spectrometry (AAS) [20], atomic fluorescence spectrometry (AFS) [21], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [22], and inductively coupled plasma mass spectrometry (ICP-MS) [23] have been developed for the inorganic arsenic determination in food samples. However, to the best of our knowledge, no methods have been reported to date to determine the presence of total arsenic and inorganic arsenic(III) in baby food.

The aims of this study were (i) to synthesize/characterize a new nanoparticle anchored of tiopronin (TSH) magnetic graphane oxide ($\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$); (ii) to develop and validate a zetasizer measurement system—a rapid, simple, and reliable method for the determination of arsenic species in baby foods; (iii) to apply the developed method to study the concentration levels of arsenic species in different kind of baby food samples purchased from the local markets (Kayseri, Turkey); and (iv) to estimate the exposure of Kayseri infants to arsenic, based on the levels detected. Finally, the new $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ nanocomposite was used to determine arsenic(III) and total arsenic in different baby food samples.

Materials and Methods

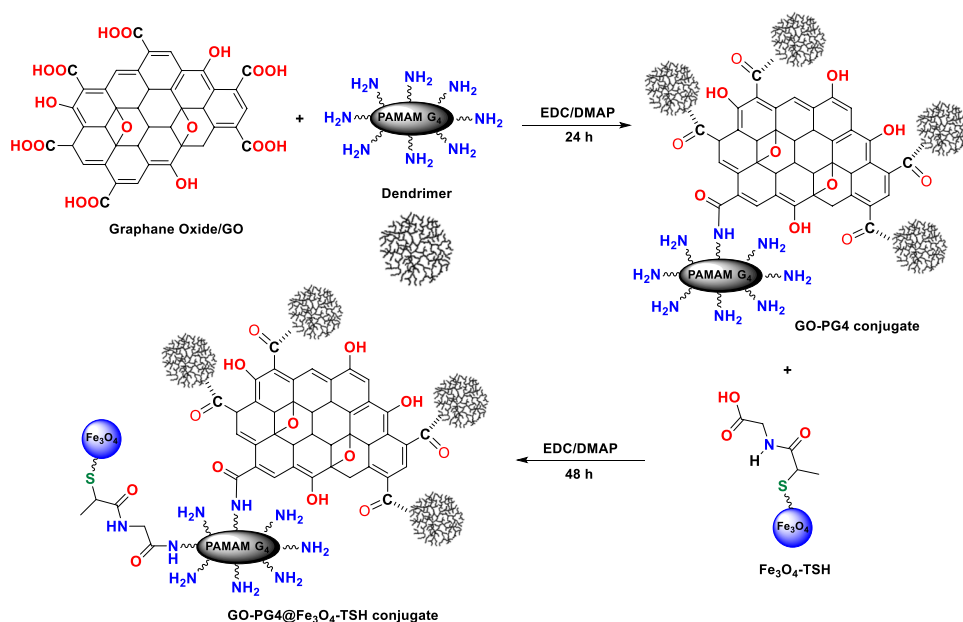
Reagents and Instruments

The chemical reagent used in this work was all of the analytical purity and used without further purification. Ultrapure water was also used in all the experiments. The stock solution of arsenic(III) (1000 mg L^{-1}) was purchased from Merck (Darmstadt, Germany). Graphite powder (particle size $< 20 \mu\text{m}$) was purchased from Samchun Pure Chemical Co., Ltd. (Pyeongtaek, Korea). Sulfuric acid (H_2SO_4 , 99.8%), hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (HCl, 37%), ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25%), potassium permanganate (KMnO_4 , 99%), ferric chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, 99%), and ferrous chloride tetrahydrate ($\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, 99%) were obtained from Merck Chemicals (Darmstadt, Germany). PAMAM G4 dendrimer (PG4), N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC·HCl), and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich (St Louis, MO). Tiopronin (TSH) was procured from Sigma-Aldrich (Germany).

The certified standard reference material (SRM) (INCT-TL-1, tea sample) was obtained from the Institute of Nuclear Chemistry and Technology (Warsaw, Poland). Laboratory glassware was kept overnight in a 5% (v/v) HNO_3 solution and then rinsed with ultrapure water. Working solutions were prepared from these stock solutions daily at 1.0 mol L^{-1} of HNO_3 . The $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ nanocomposite (Fig. 1) was first synthesized/characterized and then used as a magnetic dispersive solid-phase adsorbent to analyze arsenic(III) and total arsenic.

The chemical composition and morphology of $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ nanocomposite was investigated using scanning electron microscopy (field emission-environmental scanning electron microscope-energy distribution spectrometry, FE-ESEM-EDS, Model No. FEI Quanta 450 FEG) set an accelerating voltage of 10 kV. Raman spectrum was recorded on Renishaw in a via Raman microscope

Fig. 1 Representation route for preparation of GO-PG4@Fe₃O₄-TSH nanocomposite



spectrophotometer with 0.5 cm⁻¹ resolution, in the range 4000–100 cm⁻¹. The diode laser beam (785 nm) was focused on the sample with 5% laser power using 50× objective during 10 s. Raman has –70 °C cooled CCD (charge-coupled device) detector. IR spectra were recorded on a Perkin Elmer Spectrum Two Model FT-IR spectrophotometer using the ATR method. Homogeneous stirring was done by using the ultrasonic model HD 2070 Bandelin Sonopuls Ultrasonic Homogenizer (Germany).

Fabrication of GO-PG4@Fe₃O₄-TSH Nanocomposite

Preparation of Graphene Oxide

Oxidation of graphite was carried out by a modified Hummer's method [24, 25]. In a typical reaction, 20 mg of graphite was allowed to react with 10 mL of H₂SO₄ (99.8%) for 18 h at room temperature, followed by simultaneous cooling in an ice bath and the addition of 120 mg of KMnO₄. The reaction mixture was then stirred at 80 °C for 30 min, and subsequently at 85 °C for 2 h. The reaction was then performed at an elevated temperature of 95 °C for 30 min and 1 mL of ultrapure water was added. The reduction was completed with the addition of 2.8 mL of ultrapure water and 0.2 mL H₂O₂ (30%). The activated graphite was washed repeatedly with HCl and ultrapure water to yield graphene oxide.

Synthesis of GO-PG4 Conjugate

GO-PAMAM-G4 conjugate was synthesized as reported previously [26]. For this reason, 20 mg of PG4 dendrimer was added to a solution of GO (2 mg, 10 mL ultrapure

water). The mixture was continuously stirred for 24 h at room temperature. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC·HCl) was used as a coupling agent along with 4-dimethylaminopyridine (DMAP) as a catalyst. The modified GO was collected and washed with ultrapure water by ultracentrifugation to remove unbound PG4 along with the excess of EDC·HCl and DMAP collected and dried at room temperature to obtain GO-PG4 conjugate.

Anchoring of Tiopronin (TSH) on Fe₃O₄ Surfaces

Fe₃O₄ nanoparticles were prepared by coprecipitation of Fe(II)/Fe(III) ions with ammonia solution and treating under hydrothermal conditions according to the literature [27]. Fe₃O₄ (0.25 g) was dispersed in 10 mL ultrapure water and 5 mL of methanol and sonicated for 15 min. TSH (0.30 g) dissolved in 5 mL of ultrapure water was added to this solution and again sonicated for 3 h. The tiopronin functionalized nanomaterial (Fe₃O₄-TSH) was then isolated by centrifugation, washed with water and methanol, and dried under vacuum at 50 °C.

Fabrication of GO-PG4@Fe₃O₄-TSH Nanocomposite

For the fabrication of GO-PG4@Fe₃O₄-TSH nanoparticle, 0.5 g of Fe₃O₄-TSH was dispersed in 20 mL MeOH and 15 mL solution of GO-PG4 (0.5 g, 10 mL ultrapure water) was added to the reaction media with EDC·HCl/DMAP as a catalyst, and was ultrasonicated for 3 h. The reaction was allowed to stand for 48 h at room temperature. The product was then collected by an external magnet and washed several times in distilled water and methanol. Then, it was dried in an oven at 50 °C for 24 h.

Analytical Procedure for As(III)

The pH of 5.0 mL of a solution containing 1 mg L^{-1} of arsenic(III) was set at pH 4.5 using $\text{NaCH}_3\text{COO}/\text{CH}_3\text{COOH}$ buffer in a 15-mL polyethylene centrifuge tube. Then, 0.5 mL of ultrapure water containing 0.2 mg of synthesized $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ was dispersed to the sample solution. After the adsorption was carried out by the batch sorption technique, the extracted arsenic(III) was eluted using 0.2 mL of 0.1 mol L^{-1} HCl. For this purpose, the mixture of nanocomposite and eluent was vortexed for 2 min. Subsequently, two phases were separated using an external magnetic field, and the eluent containing arsenic(III) was diluted to 5 mL using ultrapure water. After that, arsenic (III) concentration was measured using a zetasizer system as an electrical charge on their surfaces.

Zeta potential is a physical property which is exhibited by any particle in suspension. For transdermal vaccination, the particles need to remain stable in the suspension buffer before it is delivered. For good suspendability, a potential of $\pm 25 \text{ mV}$ is ideal. Hence, the zeta potential was used in this study to evaluate arsenic(III) and total arsenic in baby food samples [28].

Blank determinations were carried out the same way as the measurements made for the sample and calibration standards.

Determination of Total Arsenic

For the determination of total arsenic, the procedure given in the literature was applied to model solutions and then to the baby food samples. One milliliter of the sample solution containing 0.1 mL of 2% KI and 0.1 mL of 1% of L(+) ascorbic acid was added to the sample solution containing 1.0 mg L^{-1} of As(III)/As(V) and 6 mol L^{-1} of 0.2-mL of HCl [28]. After reducing As(V) to As(III), the method given in section “Analytical procedure for As(III)” was applied to determine the total arsenic. The zeta potential analyzer determined the levels of total arsenic as the surface charge.

Pretreatment of Samples

Baby food samples (baby biscuits, baby fruit puree, baby yogurt, baby milk powder, etc.) were purchased from local markets in Kayseri (Turkey). After that, the samples were dried at a temperature of $105 \text{ }^\circ\text{C}$ for 24 h in an oven. The dried samples were homogenized using an agate homogenizer and stored in polyethylene bottles until analyzed. The performance of digestion procedures, including dry-ashing and wet-ashing digestion, was compared in the presented work. The reliability of the developed method for estimating

trace arsenic(III) and total arsenic in samples was checked by analyzing certified reference material (INCT-TL-1).

For comparison purposes, for digestion with dry-ash, 0.2 mg from the baby food samples was used. All samples were dry-ashed in a furnace at a temperature of $600 \text{ }^\circ\text{C}$ and time of 12 h. The ashed sample was then treated with 1 mL of concentrated HNO_3 (65% w/w) for ash whitening, and this mixture was ashed again for 4 h. The residue was then dissolved in 1–2 mL of concentrated HNO_3 (65% w/w) and filtered through blue band filter paper. The sample was diluted to 25 mL with ultrapure water.

Then, 0.2 mg of each of the dried samples and 0.2 mg of INCT-TL-1 was precisely weighed and transferred into beakers. Ten milliliters of concentrated HNO_3 (65% w/w) was then added to each beaker, and they were heated on a hot plate at $100 \text{ }^\circ\text{C}$ until dryness (wet-ash). After cooling to ambient temperature, the heating process was repeated after the addition of 5 mL of a mixture containing concentrated HNO_3 and H_2O_2 (1 mL). The residue was filtered through blue band filter paper. The developed procedure was used to determine arsenic(III) levels and total arsenic in digested samples after diluting to 25 mL with ultrapure water. These sample solutions were treated according to the proposed procedure described in sections “Analytical procedure for As(III)” and “Determination of total arsenic”. The final measurement volume of the sample solutions was 1 mL. Blank digestions were also carried out in the same way. The investigated arsenic concentration in the final measurement solution was determined by the zetasizer system as surface charge (Table 1).

Results and Discussion

Characterization of $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$

The size and morphology of the $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ nanocomposite were studied by field emission scanning electron microscopy (FESEM). The FESEM image in Fig. 2 reveals that the $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ were formed consisting of many spherical-like nanocomposites with diameters of about 20–50 nm.

The chemical composition of the $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ nanocomposite was studied by EDX analysis and confirmed the presence of Fe, S, O, N, and C in the sample. In EDX analysis, Fe, O, and S are the dominant elements throughout the surface of the $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ with weight percentages of 28%, 57%, and 6%, respectively. The EDX mapping of $\text{GO-PG4@Fe}_3\text{O}_4\text{-TSH}$ is presented in Fig. 3 to investigate their localized elemental information. It is worth noting that the elemental Fe, O, and S were well dispersed on the adsorbent's surface. It can easily be seen that

Table 1 The determination of arsenic(III) and total arsenic in various baby food samples by using the presented procedure ($n=3$)

Sample (Central Kayseri)	Dry-ash digestion ($\mu\text{g g}^{-1}$)		Wet-ash digestion ($\mu\text{g g}^{-1}$)	
	Arsenic(III)	Total arsenic	Arsenic(III)	Total arsenic
Baby biscuits 1	- ^a	0.19 ± 0.02	-	-
Baby biscuits 2	-	-	-	-
Baby fruit puree 1	0.28 ± 0.02^b	0.43 ± 0.06	0.31 ± 0.02	0.48 ± 0.11
Baby fruit puree 2	0.17 ± 0.03	-	0.18 ± 0.02	-
Baby yogurt 1	-	-	-	-
Baby yogurt 2	-	-	-	-
Baby yogurt 2	-	-	-	-
Baby milk powder 1	-	-	-	-
Baby milk powder 2	-	-	-	-
Baby milk powder 3	-	0.21 ± 0.03	-	0.18 ± 0.02
Baby cereal 1	3.18 ± 0.08	3.81 ± 0.18	3.17 ± 0.11	3.37 ± 0.15
Baby cereal 2	4.08 ± 0.06	4.68 ± 0.24	4.05 ± 0.04	4.77 ± 0.32

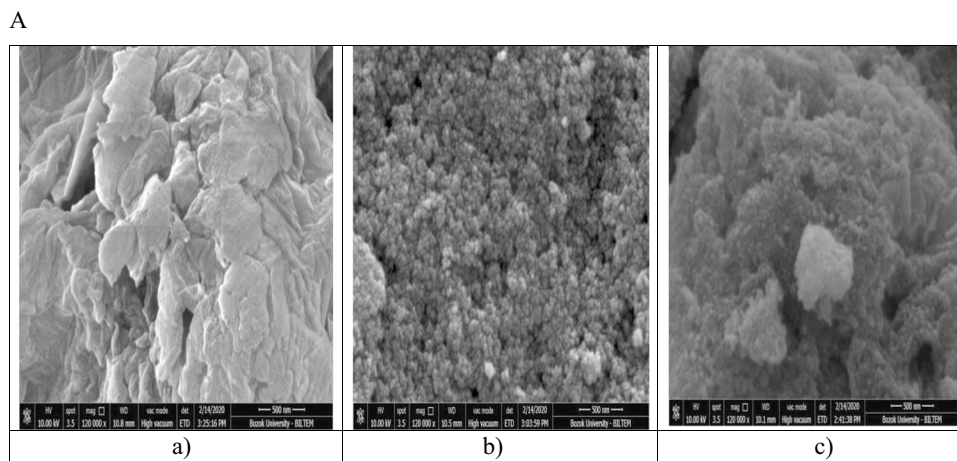
^aBelow detection limit^bAverage \pm standard deviation

homogenous surface structures were achieved after the synthesis of the magnetic nanocomposite.

The typical characteristic IR peaks of GO, GO-PG4, Fe_3O_4 -TSH, GO-PG4@ Fe_3O_4 -TSH, and TSH nanocomposite were depicted in Fig. 4. After incorporation of PG4 to GO, the spectrum of GO-PG4 showed characteristic O-H ($\sim 3443 \text{ cm}^{-1}$), as well as NH stretching of primary amine ($\sim 3176 \text{ cm}^{-1}$) and anti-symmetric substituted primary amine ($\sim 3054 \text{ cm}^{-1}$), C=C ($\sim 1558 \text{ cm}^{-1}$), C-N ($\sim 1357 \text{ cm}^{-1}$) in the amide group, C-OH ($\sim 1214 \text{ cm}^{-1}$), together with carbonyl ($\sim 1722 \text{ cm}^{-1}$) peaks, which confirmed the formation of carboxyl and hydroxyl groups. This further confirms that the PAMAM G4 dendrimer was successfully synthesized by GO (curve B). The anchoring of tiopronin (TSH) on the surface of magnetic nanoparticles (Fe_3O_4) was examined by IR spectroscopy. Fe_3O_4 -TSH shows the absorption peaks of C=O ($\sim 1628 \text{ cm}^{-1}$), C=C ($\sim 1540 \text{ cm}^{-1}$), C-O-C ($\sim 1391 \text{ cm}^{-1}$), C-O ($\sim 1017 \text{ cm}^{-1}$), Fe-O ($\sim 558 \text{ cm}^{-1}$) NH

($\sim 3157 \text{ cm}^{-1}$), as well as O-H ($\sim 3379 \text{ cm}^{-1}$). All the characteristic bands confirmed the attachment of tiopronin on nano-ferrite surfaces (curve C). On the other hand, the characteristic peaks at 3398 cm^{-1} (\sim O-H), 3148 cm^{-1} (\sim N-H), $3020\text{--}2884 \text{ cm}^{-1}$ (\sim CH), 1716 cm^{-1} (\sim C=O), 1558 cm^{-1} (\sim C=N), and a strong absorption band at 556 cm^{-1} (\sim Fe-O) were observed in GO-PG4@ Fe_3O_4 -TSH nanocomposite (curve D).

The Raman spectra of GO, GO-PG4, Fe_3O_4 -TSH, and GO-PG4@ Fe_3O_4 -TSH are shown in Fig. 5. As shown in Fig. 5, the Raman spectrum of GO and GO-PG4 exhibited D-band peaks at 1348 and 1300 cm^{-1} that correspond to the breathing mode of κ -point phonons of A_{1g} symmetry and G-band peaks 1605 and 1599 cm^{-1} due to the first-order scattering of the E_{2g} phonons [29]. Generally, the D-band assigned to the sp^3 carbons in graphane sheets and the D mode of GO are relatively weak due to the symmetry breaking at the edge [30]. Compared with GO and GO-PG4, the

Fig. 2 SEM images of a GO-PG4, b Fe_3O_4 -TSH, and c GO-G4@ Fe_3O_4 -TSH

B

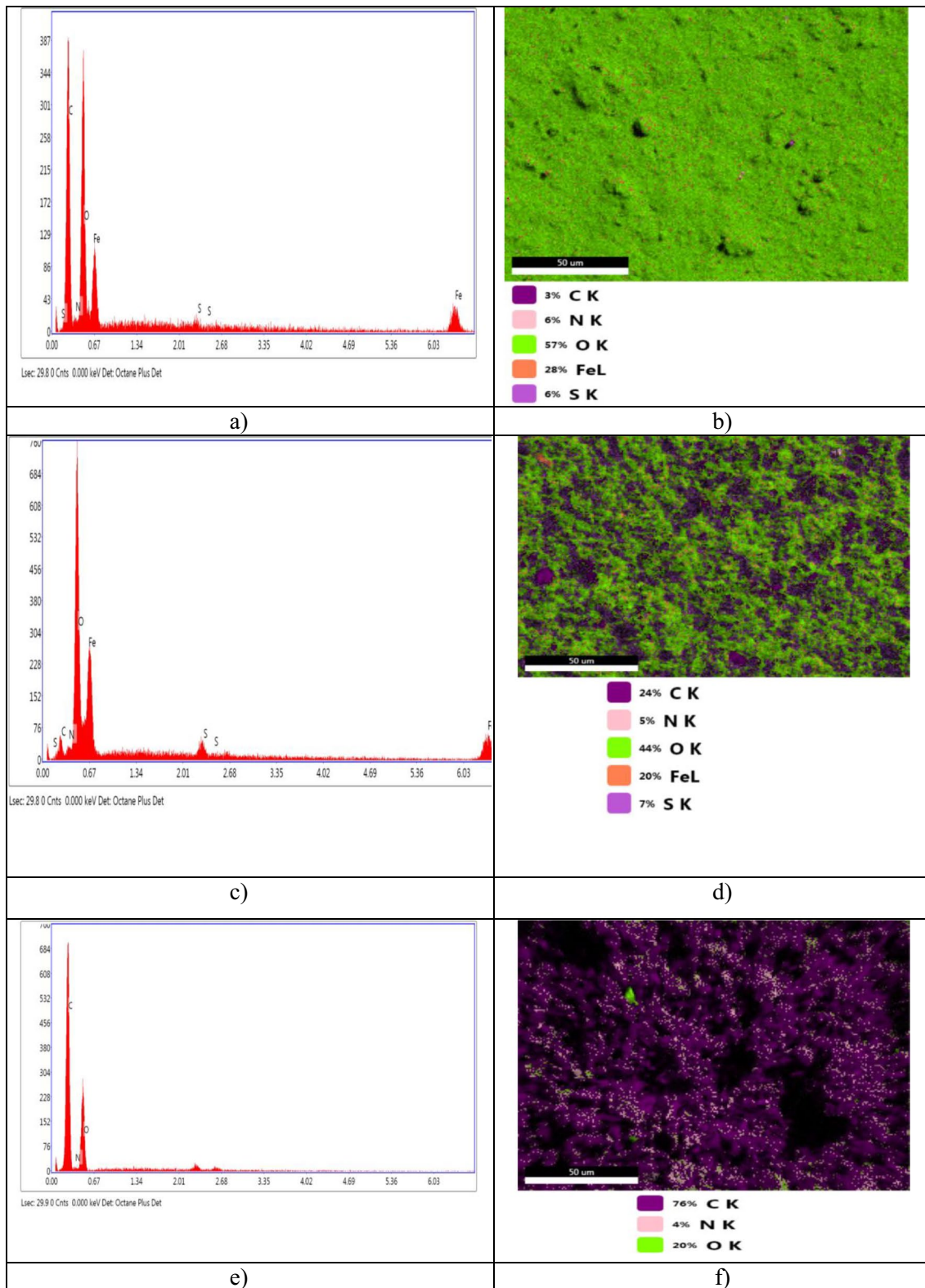


Fig. 3 EDX spectra and element maps of a, b GO-G4@Fe₃O₄-TSH, c, d Fe₃O₄-TSH, and e, f GO-PG4

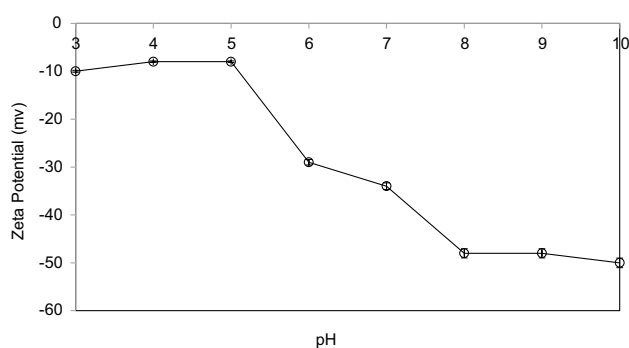


Fig. 6 Effect of solution pH on arsenic(III) uptake by GO-PG4@Fe₃O₄-TSH ($n=3$)

adsorption. The adsorption efficiency was found to decrease in MDSPE at pH values higher than pH 6.0. The optimal pH for arsenic(III) was determined to be 4.5, and the results are shown in Fig. 6. It was determined that when the pH values were higher than 6.0, the adsorption efficiency decreased in this study. After that, pH 4.5 was used for magnetic solid-phase extraction of arsenic(III).

The Adsorption Capacity of GO-PG4@Fe₃O₄-TSH Nanocomposite

To study the maximum adsorption capacity of the GO-PG4@Fe₃O₄-TSH nanocomposite for arsenic(III), 10 mL of the solution was prepared and its pH value was set at 4.5. Then, 2 mg GO-PG4@Fe₃O₄-TSH nanocomposite was added to this solution, including arsenic(III). After shaking for 2 min, the phase separation was performed using the magnetic field. After elution with 2 mL of 0.1 mol L⁻¹ HCl, 1 mL of the aqueous phase was diluted to 100 mL and determined by the zetasizer. The capacity of synthesized sorbent was calculated as 54.3 mg g⁻¹ for arsenic(III).

Eluent Type, Volume, and Concentration of Eluent

The eluent type, volume, and concentration used to recover arsenic(III) from the GO-PG4@Fe₃O₄-TSH nanocomposite surface were other important factors in MDSPE studies. HCl and HNO₃ (0.01, 0.1, 0.5, 1, 2, and 3 mol L⁻¹) were used as eluent in this study in different volumes (0.1, 0.2, 0.35, 0.5, and 1 mL). According to these results, 0.2 mL 0.1 mol L⁻¹ HCl solution was most suitable for studied MDSPE. In subsequent studies, 0.2- mL 0.1 mol L⁻¹ HCl was used as eluent.

Effect of Sample Volume

To achieve high preconcentration factors and determine the optimum sample volume, 2, 5, 10, 25, 40, and 50 mL

containing 1 mg L⁻¹ As(III) was investigated through MDSPE under optimum conditions. The sample volume efficiency decreased arsenic(III) recovery at values higher than 25 mL sample volume. Therefore, the most suitable sample volumes for the recovery of arsenic(III) were 25 mL. As the optimal elution volume was found to be 0.2 mL, the preconcentration factors for As(III) were determined as 125.

Effect of the Amount of GO-PG4@Fe₃O₄-TSH Nanocomposite

The amount of GO-PG4@Fe₃O₄-TSH nanocomposite is an essential factor for adsorption and selective arsenic(III) determination. To observe the influences of GO-PG4@Fe₃O₄-TSH nanocomposite, the procedure given in section “Analytical procedure for As(III)” was performed with different amounts of GO-PG4@Fe₃O₄-TSH nanocomposite, and then the preconcentration procedure was applied. The recoveries of arsenic(III) were increased with the increased amounts of GO-PG4@Fe₃O₄-TSH nanocomposite. Quantitative recovery values for As(III) were obtained after 0.1 mg of GO-PG4@Fe₃O₄-TSH nanocomposite. In all subsequent works, 0.2 mg of GO-PG4@Fe₃O₄-TSH nanocomposite was used to satisfy arsenic(III) recoveries.

Effect of Contact Time

The equilibrium time was measured from 0 to 60 min, and the effect of contact time was determined by plotting the percentage uptake of arsenic(III) against contact time. It was observed that the removal rate was very fast for the first 10 min, but it gradually became slower after 10 min. Thus, 10 min was selected for the subsequent experiments.

Effect of Foreign Ions

The effect of foreign ions on the recovery of As(III) was investigated to determine the developed methods’ selectivity. The effect of various concentration of foreign ions such as Na(I), K(I), Ca(II), Mg(II), Fe(II), Fe(III), Cd(II), Cu(II), Ni(II), Zn(II), Mn(II), Pb(II), and Al(III) was added to a solution containing 1 mg L⁻¹ arsenic(III) solutions and the test procedure given in section “Analytical procedure for As(III)” was applied. The tolerance limit was set as the diverse ion amount required to cause $\pm 5\%$ error in arsenic(III) determination. Under these optimized conditions, most of the probable concomitant cations and anions remained in the first phase (Table 2).

Applications

The developed method was applied to various baby foods (from Kayseri, Turkey) to determine arsenic(III) and total

Table 2 Tolerable levels of some foreign ions on the retentions of As(III) ions ($n=3$)

Foreign ions	Added as	Concentration (mg L ⁻¹)	Recovery (%)
Cl ⁻	NaCl	5000	99 ± 2 ^a
SO ₄ ²⁻	Na ₂ SO ₄	1000	97 ± 2
PO ₄ ³⁻	NaH ₂ PO ₄ · 2H ₂ O	1000	97 ± 1
Ca ²⁺	Ca(NO ₃) ₂ · 4H ₂ O	1000	96 ± 1
K ⁺	KNO ₃	1000	98 ± 1
Na ⁺	NaNO ₃	5000	99 ± 1
Fe(II)	FeCl ₂ · 4H ₂ O	5	96 ± 1
Fe(III)	Fe(NO ₃) ₃ · 9H ₂ O	5	98 ± 2
Cd(II)	Cd(NO ₃) ₂ · 4H ₂ O	5	97 ± 3
Cu(II)	Cu(NO ₃) ₂ · 3H ₂ O	5	99 ± 2
Ni(II)	Ni(NO ₃) ₆ · 6H ₂ O	5	98 ± 2
Zn(II)	Zn(NO ₃) ₂ · 6H ₂ O	5	99 ± 1
Mn(II)	Mn(NO ₃) ₂ · 4H ₂ O	5	97 ± 2
Pb(II)	Pb(NO ₃) ₂	5	96 ± 1
Al(III)	Al(NO ₃) ₃ · 9H ₂ O	5	96 ± 1

^aAverage of three measurements ± standard deviation

arsenic. According to the results presented in Table 1, this method is reliable for measuring arsenic(III) in the studied baby food samples. Therefore, this technique was successfully applied to the determination of µg L⁻¹ levels of arsenic(III) and total arsenic with good accuracy and good reproducibility (Table 1).

The suggested method's accuracy was validated using arsenic(III) determination in certified reference material of INCT-TL-1 tea sample. The outcomes shown in Table 3 are in good agreement with the certified values.

Also, to validate the optimized procedure's accuracy, different amounts of arsenic(III) were added to the baby food samples. The resulting solutions were applied to the proposed preconcentration/separation procedure in section "Analytical procedure for As(III)." The obtained results are

shown in Table 3. A good agreement was obtained between the added and the measured analyte amounts.

Analytical Features

Under optimal experimental conditions, the calibration graphs are linear in the concentration range of 0.01–5 mg L⁻¹ arsenic(III). The equations of the curves are $V = -18.14C - 0.021$ ($R^2 = 0.998$) for arsenic(III).

The limit of detection of the MDSPE was calculated under optimal experimental conditions (pH: 4.5, eluent volume: 0.2 mL) after application of the developed preconcentration procedure to blank reagent solutions. The limit of detections was arsenic(III): 0.11 µg L⁻¹ ($n = 21$). The quantification limit, according to the signal-to-noise ratio of 10Sb/m, was about 0.37 µg L⁻¹.

The analytical performance of arsenic(III) ions was calculated for the results from zetasizer measurements. The method's reproducibility was investigated with a sample solution containing arsenic(III) through the batch procedure and repetition of this procedure ($n = 9$). The relative standard deviations (RSD) were below 1.6%. It was found that the recovery of arsenic(III) was 95% confidence level.

Conclusions

In the present study, GO-PG4@Fe₃O₄-TSH nanocomposite has been synthesized as a new adsorbent. Its application for MDSPE and the separation/preconcentration of arsenic(III)/total arsenic before their measurements with zetasizer were studied.

The MDSPE recovery of applying the developed method on baby food samples and certified reference material was above 95%, which shows this method's reasonable ability to determine arsenic(III) without being affected by their complex matrix nature. The proposed method is cost-effective and fast, and it is green because no toxic solvent has been

Table 3 Recovery analysis for the As(III) in the spiked some baby food samples ($n=3$)

Sample	Added (µg g ⁻¹)	Wet-ash digestion (µg g ⁻¹)	Recovery (%)
Baby biscuits 1	- ^a	-	-
	5.0	4.97 ± 0.09 ^b	99 ± 1
	10.0	9.97 ± 0.32	100 ± 1
Baby cereal 1	-	3.17 ± 0.11	-
	5.0	8.08 ± 0.18	8.08 ± 0.18
	10.0	13.09 ± 0.43	97 ± 1
INCT-TL-1 tea sample	Certified value (mg g ⁻¹)	Our value (mg g ⁻¹)	Recovery (%)
	0.106 ± 0.021	0.103 ± 0.025	97 ± 1

^aBelow detection limit

^bAverage ± standard deviation

used during this developed procedure. Furthermore, this new GO-PG4@Fe₃O₄-TSH nanocomposite compared to similar nano-adsorbents used for arsenic(III) preconcentration showed a better or comparable limit detection, preconcentration factor, and adsorption capacity for arsenic(III).

The experimental results for the certified standard material (INCT-TL-1) for wet digestions agreed with the certified values. The proposed digestion methods were precise and accurate. The analytical parameters obtained make this method suitable for the determination of arsenic in various baby foods.

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Declarations

Ethics Approval This research did not contain any studies involving human or animal subjects.

Competing Interests The authors declare no competing interests.

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