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Analytical Methods

A new pre-concentration procedure based on poly(styrene-*co*-maleamide and imide) copolymers modified with 2-hydrazinobenzothiazole prior to spectrophotometric monitoring of inorganic as (as As(III)) in edible vegetable oils

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ABSTRACT

This study describes the development of 2-hydrazinobenzothiazole modified-amide/imide co-polymers for the extraction/pre-concentration of trace As(III), from edible vegetable oils. Their characterization was realized by help of instrumental techniques. The method is based on pH-dependent complexation between As(III) and co-polymeric chelators in presence of 35-fold excess As(V), their selective extraction into the mixed micellar phase, and detected at pH 2.0 and 6.0 by UV–vis spectrophotometer. The variables affecting extraction efficiency were optimized. From pre-concentration of 20-mL sample, the good linear relationships were obtained in range of 1–40 and 3–75 μg/L with DLs of 0.32 and 1.00 μg/L. The accuracy was verified by analysis of a certified sample without and with spiking. The method was applied into the analysis of iAs levels of samples. The results show that the functional co-polymers are efficient chelators, and exhibit great potential for the selective extraction of As(III) from edible vegetable oils.

1. Introduction

Arsenic (As) exists both in inorganic and organic forms and also in different valence states. Inorganic arsenic (iAs), comprising As(III) (pK$_a$ 9.2) and As(V) (pK$_{a1}$ 2.2), is significantly more toxic than organic arsenic compounds such as dimethylarsinic acid (DMA, pKa 6.2), mon-omethylarsonic acid (MMA, pK$_{a1}$ 4.1), zwitterionic arsenobetaine (AsB, pK$_a$ 2.2) and cationic arsenocholine (AsC), and in turn the pH-dependent trivalent forms of As, AsO(OH), As(OH)$_3$ or As(OH)$_4^-$, are more toxic than the pentavalent arsenates. The latter are considered to be toxic only after metabolic conversion to the trivalent form of As. Exposure to iAs is primarily of concern because of its cancer-causing properties. When considered a safe limit is 0.1 and/or 0.2 mg kg^{-1} for infants and young children (Shibata et al., 2016; Cubadda et al., 2017), according to the WHO, especially iAs is among the most toxic substances impacting human wellbeing and is highly toxic in its inorganic form. Long-term exposure increases the risk of cancer, skin lesions, pigmentation, cardiovascular disease, and diabetes (IARC, 2012). Due to its high toxicity of iAs, there is importance of knowing iAs (As(III) and As(V))

concentration in edible vegetable oils. Hence, monitoring and determination of trace iAs in edible oils is of great importance for quality control.

So far, due to be available in very low concentrations in real samples as well as matrix effect, sensitive, selective but expensive, time-consuming and complex atomic spectrometric detection techniques such as atomic absorption/emission spectrometry, atomic fluorescence spectrometry, inductively coupled plasma-mass spectrometry with hydride generation and electrothermal volatilization (HG-AAS, HG-AFS, HG-ICP-MS, ETV-ICP-MS), electrothermal atomic absorption spectrometry (ET-AAS) and finally, inductively coupled plasma-mass spectrometry coupled to ion chromatography (IC-ICP-MS) generally needing expert user in his or her area (Elik et al., 2021; Ni et al., 2017; Ni et al., 2015; López-García et al., 2015; Hsu et al., 2013; dos Santos Costa & Coelho, 2020; Altunay et al., 2019; Zounr et al., 2017), have been used for the analysis of i-/o-As species in liquid/solid food matrices, including edible vegetable oils after separation/pre-concentration. However, in addition to volatilization, reduction, derivatization and conversion of analyte into a stable volatile hydride with a suitable reagent in the

sample clean up step before detection, these detection techniques require to use internal standard, a suitable chemical modifier and dynamic reaction cell in order to minimize signal fluctuation, improve signal stability and control the memory effect at low concentration levels in detection step. All these processes increase the cost of the method even more. There is only one study for separation and speciation analysis of possible all As species in the used and fresh soybean oils and determination of their total As contents by combination of IC with ICP-MS as element selective detector in dynamic reaction mode at pH 8.5 after microwave-assisted extraction (MAE) using 0.5 % HNO_3 in methanol at 80 °C for 120 min without pre-concentration (Chu & Jiang, 2011). Moreover, in this study, to control and greatly improve reliability of the method, standard addition method and 2 µg/L Ge as internal standard were used in analysis of As species in linear range of 0.1–10 µg/L with detection limit of < 0.15 µg/L. Although the above-mentioned detection methods are very fast, sensitive and have low detection/quantification limits, they have generally poor precision, low recovery rates, require the expert user in his or her area, and are not available in almost every analytical research laboratory due to be expensive and complex.

Trace determination of heavy metals is one of the most important issues of chemical analysis. Recently, UV–vis spectrophotometry has been widely used for the determination of low levels iAs species (Altunay et al., 2016; Gurkan et al., 2015), because it is an available and inexpensive technique which can be found in most laboratories. However, due to low concentration of heavy metals, insufficient sensitivity of the instrument and matrix effect, there are some difficulties for determination of trace amounts of such analytes using this technique. Therefore, developing and application of a sample preparation/pre-concentration step prior to instrumental analysis is a pre-requisite (Anthemidis & Ioannou, 2009). A sample preparation step must be fast, economical, eco-friendly, easy to perform, and useful for broad spectrum of analytes in various matrices. Recently, miniaturization of sample preparation has become an important factor for new sample preparation techniques. Some of these techniques include solid phase microextraction (SPME) (Elik et al., 2021), cloud point extraction (CPE), solid phase extraction (SPE) (dos Santos Costa & Coelho, 2020), microwave assisted extraction (MAE) (Chu & Jiang, 2011), vortex assisted extraction (VAE) (López-García et al., 2015), dispersive liquid–liquid microextraction (DLLME) (Hsu et al., 2013), carrier mediated-single drop microextraction (CM-SDME) (dos Santos Costa & Coelho, 2020), deep eutectic solvent-vortex assisted-microextraction (DES-VAME) (Altunay et al., 2019), deep eutectic liquid-ultrasound assisted-liquid phase microextraction (DES-UA-LPME) (Zounr et al., 2017). Meanwhile, the concern for environmental pollution and human health has led to the development of green analytical methods. Green chemistry focus on eliminating or reducing the consumption of organic solvents, and/or replacing the organic solvent with non-toxic and eco-friendly solvents (Gałuszka et al., 2013). One of favorite approach in green chemistry is replacing organic solvent with non-toxic and non-flammable solvents such as ionic liquids (ILs) (Li et al., 2007); however, it must be noted that they are expensive solvents, many of them are not commercialized and they can also decompose in contact with moisture, giving harmful volatiles (Swatloski et al., 2003).

In comparison with the above-mentioned sensitive, but expensive and complex methods, spectrophotometric methods are among the relatively low-cost, simple, easy to use, highly sensitive and selective methods in especially presence of suitable chromophores and/or fluorophores with pH-dependent charge transfer (CT) transition due to their tautomeric forms such as amine-imine, amide-imidic acid, and hydrazine-hydrazone (where the hydrogen atom on heterocyclic structure is intramolecular exchanged under the influence of temperature, pH, solvent polarity, even an external stimulus such as ultrasound energy) as well as good accuracy and precision, and therefore are very popular. This simple and cost-effective analytical technique is preferably used in underdeveloped analytical research labs for the determination of

low levels of iAs species in different matrices. Also, it is implied in literature that the sensitivity is greatly improved by use of new chelating polymers and nanoscale graphene oxide and magnetic chitosan modified or functionalized with polyethyleneimine (PEI) for the determination of trace/ultra-trace levels iAs (Ociński & Kociolek-Balawejder, 2011; Ahmad et al., 2018; Alsaiari et al., 2021), including detection of trace Ag^+ ions in mushroom and vegetable samples (Zengin 2019). Ultrasound has become an important aspect of sample preparation in food analysis. In fact, it allows samples to be processed rapidly, cheaply and accurately. Tedious procedures can be speeded up with ultrasound - samples are very homogeneous and provide reproducible results (Mahmoodnezhad & Taheri, 2022). The CPE, assisted by ultrasound (UA-CPE), is a technique in which extraction of organic/inorganic compounds from sample matrices, using eco-friendly extractants like non-ionic surfactants is done which tend to separate out from the bulk solution forming clouds, when heated to critical temperature or above the temperature (Arya et al., 2019). It is thought in this study that the combination of UA-CPE with spectrophotometry can overcome the difficulties encountered in the separation, pre-concentration and speciation analysis of trace iAs (as As(III)) in especially edible oils.

On this occasion, newly prepared and characterized 2-hydrazinobenzothiazole (2-HBT) modified poly(styrene-*alt*-maleic anhydride) copolymer matrix, (poly(SMAnh)), as the As(III) chelating ligand was used in the selective extraction and pre-concentration of As(III) in presence of excess As(V) with and without pre-reduction from sample matrix. pH-dependent heterocyclic benzothiazole compounds, characterized by hydrazine-hydrazone and amide-imidic acid (or amide–iminol) tautomerization (–C(=O)–NH–/–C(OH) = N-) resulting both from solvation and intramolecular hydrogen bonding before and after modification, have been considered owing to their heterocyclic structure and metal binding properties via fast hydrazine/hydrazine tautomerization, C=N, =N-C=N groups, and donor S, *N*-atoms in benzothiazole ring for efficient metal chelation. Recently, it has also been reported by two author groups, including our research group (Wright 1983; Gvozdjakova & Ivanovičová, 1986; Zengin & Gürkan, 2019) that 2-HBT ligand as a good chromophore in UV–vis region is successfully applied to the selective extraction and speciation analysis of trace Hg^{2+} and CH_3Hg^+ in seafood samples in presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB) as sensitivity enhancer at pH 4.5 by combination of UA-CPE with spectrophotometry, via 2-HBT modified amide and imide copolymers. In the mentioned study, from pre-concentration of 35-mL sample, a pre-concentration of 70-fold and good detection limits of 1.40 and 1.58 µg/L in linear working ranges of 5–125 and 5–150 µg/L for Hg(II) at 325 nm using amide and imide copolymers.

In the present study, UA-CPE using ultrasound in sample preparation/pre-concentration steps, based a newly prepared- and 2-HBT modified-amide/imide chelating agents, poly(SMAm) and poly(SMIm) from poly(SMAnh), was adopted in determination of toxic iAs (as As(III)) in edible oils. The main variables affecting CT sensitive pH-controlled selective complexation/extraction efficiency were evaluated and optimized in detail. The method has been extended to include the selective extraction of As(III) in presence of 35-fold excess As(V) from edible oils in the presence of matrix components before spectrophotometric analysis.

2. Experimental

2.1. Standards and reagents

In the present study, all the chemicals used were at least of analytical purity; they were purchased from Sigma (St. Louis, MO, USA) and Merck (E. Merck, Darmstadt, Germany). Before beginning the experiments, all the containers were kept in 10 % (v/v) HNO_3 for at least 24 h and subsequently washed five times with ultrapure water. Their stock solutions, 0.1 % (w/v) were prepared by dissolving 0.1 g of the amide and imide copolymers formed by modification with 2-HBT in

tetrahydrofuran (THF). The As(III) stock aqueous solution at 100 mg L^{-1} was prepared by dissolving a suitable amounts of solid As$_2$O$_3$ with 2.0 mol L^{-1} HCl and diluting with ultrapure water. The working solutions of As(III) were diluted appropriately with dilute HNO$_3$ before use. A solution of 5.0 % (v/v) non-ionic surfactant, Triton X-114, in water was used as the extractant. Methanol, ethanol, acetonitrile, acetone, THF, acidic methanol and ethanol (1.0 mol/L HNO$_3$) were tested as the diluting agents. The dilute ionic surfactant mixture, CTAB-SDS in 5 %(v/ v) 2-propanol (2.0 mmol/L, each one, 1:1, v/v) was prepared by sonication at 35 °C under ultrasonic power, and used with Triton X-114 to improve the sensitivity of the extraction process. The dilute KCl solution of 2.0 mmol/L for salting-out effect was prepared by dissolving a suitable of solid KCl salt in water. The McIlvaine buffer solutions (in fact, it can be also used for stabilization of iAs species in range of pH 2.0–8.0, 100 mL in volume), providing an improvement in selectivity, were prepared by mixing (i) 2.0 mL of 0.2 mol/L Na$_2$HPO$_4$ and 98.0 mL of 0.1 mol/L citric acid solutions for amide copolymer at pH 2.0 and (ii) 63.0 mL of 0.2 mol/L Na$_2$HPO$_4$ and 37.0 mL of 0.1 mol/L citric acid solutions for imide copolymer at pH 6.0 for 20 μg/L As(III) in optimization step. A certified sample: SRM 1568b Rice flour, supplied from NIST (Gaithersburg, Canada), were used to validate the method, due to the absence of a certified sample compatible with the sample matrix. Also, for comparison of the results, a mixture of 1.0 mol/L H$_3$PO$_4$, 0.1 mmol/L EDTA and 0.1 % (v/v) Triton X-114 as extractant (5:3:2, v/v) for 20 min at 55 °C and a mixture of 2.0 % (w/v) TEA, 0.02 mol/L oxalic acid and 1.0 % (v/ v) Triton X-114 as emulsifier (5:3:2, v/v) for analysis of As(III) (as equivalents to iAs) were used in the dissolution/extraction of the SRM and edible oils under sonication conditions at 40/55 °C for 12/20 min in ultrasonic bath.

2.2. Instrumentation

A UV–visible spectrophotometer PC (UV-1800 Shimadzu model, Kyoto, Japan) was used for measurements of As(III) in the samples by placing a 0.4 mL of the mixed micellar phase diluted with THF into a quartz cell of 1.0-cm optical path with micro-capacity where the analytical signals were obtained as the corrected absorbance of samples against analyte blank at 266 and 269 nm. FT-IR spectra were taken using a Bruker (Tensor II model, Billerica, MA, USA) spectrometer (with direct sampling at ATR mode without KBr pellet). ^{1}H NMR spectra (in DMSO-d_6, 400 MHz, single pulse) were recorded on a JEOL JNM-ECZ400S/L1 spectrometer (JEOL ltd., Akishima, Tokyo, Japan) operating at 298 K with tetramethylsilane (TMS) as an internal standard. An ultrasonic bath (UCS-10 model, Seoul, Korea) operating at 40 kHz and 300 W was used for the extraction/pre-concentration step of Hg from the sample matrix by UA-CPE. A vortex (VM96-B model, Seoul, Korea) operating at 50 Hz and 12 W was used for the homogenization of the samples. A centrifuge (Universal 320 Hettich model, London, England) was used to separate the sample extract from the aqueous phase. The pH measurements were performed using a pH meter with a combined glass electrode (Selecta 2001 Sartorius docu-model, North America). A Labconco ultrapure water system (Kansas City, USA) was used to obtain ultrapure water to be used in experiments, resulting water with a resistivity of 18.2 MΩ cm^{-1}.

2.3. Synthesis of 2-HBT-modified amide/imide copolymers

In this study, bulk copolymer of styrene and maleic anhydride monomers (with 1:1 M mass ratio) with azobisisobutyronitrile (AIBN) initiator in benzene at 70–80 °C were obtained as a bulk copolymer. The obtained poly(SMAnh) copolymer was dried in air. Later, at 1:1 M mass ratio, poly(SMAnh) copolymer and 2-HBT was continuously mixed in THF at 55 °C for 4 h. The produced yellow-colored solution was precipitated from ethyl alcohol, and the precipitate was filtered, kept waiting in *n*-hexane for 20 min, and then, filtered for once again and left for drying. Aliquot (5 g) of the obtained 2-HBT-modified poly (styrene-

co-maleamidic acid), 2-HBT-poly(SMAm) copolymer was weighed and was solved in DMF. This solute was continuously mixed in a constant temperature of 150 °C for 5 h, and the red-colored solute produced by ring closure was interacted with ethyl alcohol and then, precipitated. The obtained 2-HBT modified poly (styrene-*co*-maleimide), 2-HBT-poly (SMIm) copolymer was left for drying after waiting in *n*-hexane.

2.4. Sampling, sample preparation

As the iAs concentration in the samples, including SRM, is very low, even minor contamination at any stage of the sampling, sample storage, and handling or analysis, including interconversion of As(III) to As(V) or As(V) to As(III) under the ultrasonic effect during the preparation of the samples, has the potential to affect the accuracy of the results. The accuracy of the method was tested using a certified sample, SRM1568b Rice flour. The certified value is available for iAs and total As with values of 0.092 and 0.284 mg kg^{-1} for the assessment of the method's accuracy. The solid SRM was used as stored, without further grinding and sieving. The commercial edible oils were generally purchased from the local markets in Sivas, Turkey. The edible oils were in either glass bottles, or in PET bottles. All the samples were ultrasonically extracted as follows:

Aliquot of (0.3 g) of the certified sample was transferred into the centrifuge tubes of 50-mL, and pre-treated by a mixture containing 2.0 % (w/v) TEA[a], 0.02 mol/L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C in absence and presence of ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions. To separate iAs from the matrix, and facilitate sample homogenization, the mixture was effectively vortexed for 5 min at 1200 rpm, finally so as to obtain a clear homogenous solution. After 10-fold dilution, for iAs level, 10-mL of sample solution was analyzed by the proposed method under the optimized reagent conditions with and without spiking, based on adding directly to the sample aliquot before the extraction.

Before analysis by the five point matrix-matched calibration curve, based on directly adding of 5, 10, 15, 20 and 30 μg/L As(III) into sample aliquot before extraction and analysis, in order to facilitate the mass transfer between two phase and to ensure the repeatability/stability of the results against possible matrix effect, and to minimize interconversion of iAs species (As(III) and As(V)), edible oils were submitted to two different ultrasonic soft sample preparation procedures for analysis of As (III) at pH 2.0 and 6.0, respectively, under the optimized reagent conditions as follows:

(i) 5.0 mL edible oils were pretreated and extracted using 10 mL of a mixture of 2.0 % (w/v) TEA, 0.02 mol/L oxalic acid and 1.0 % (v/ v) Triton X-114 as emulsifier (5:3:2, v/v) buffered to pH 5.0–5.5 for 12 min at 40 °C in ultrasound bath (300 W, 40 kHz). Herein, function of each reagent is to form stable complexes at pH 5.0–5.5 as both a stabilizer and disperser against interconversion with great stability difference, allowing leaching from the liquid oil matrix to the aqueous solution.

(ii) 5.0 mL edible oils were pretreated and extracted using 10 mL of a mixture of 1.0 mol/L H$_3$PO$_4$, 0.1 mmol/L EDTA and 0.1 % (w/v) Triton X-114 as extractant (5:3:2, v/v) buffered to pH 3.0–3.5 for 20 min at 55 °C in ultrasonic bath (300 W, 40 kHz). Herein, function of each reagent is to form stable complexes at pH 3.0–3.5 as both a stabilizer and disperser against interconversion with great stability difference, allowing leaching from the liquid oil matrix to the aqueous solution.

Thus, the pretreated- and extracted-liquid oil samples were diluted at ratios of 1:2 with 2.0 % (v/v) HNO$_3$ and HCl solutions at equal volumes to overcome the possible matrix effect.

To check the matrix effect in terms of reliability of the method, the matrix-matched calibration curves with five calibration point according

to AOAC recommendations for validation of the method performance criteria (AOAC, 2016), can also be used in place of standard addition method, was adopted in the range of 5–30 µg L^{-1} by spiking with known amounts of As(III) around the quantification limit of the method. For all the pre-treatment processes, a blank control was carried out in the same way. Then, an aliquot (5.0 mL) of the final clear extract or pre-treated sample solutions with and without spiking after dilution of 2-fold, was submitted to pre-concentration by UA-CPE prior to analysis by spectrophotometry at 266 nm, due to be more sensitive of As(III) to amide copolymer at pH 2.0 than imide copolymer at pH 6.0. The iAs contents of the samples were determined using the matrix-matched calibration curves.

2.5. UA-CPE procedure

Aliquots of 5.0 mL of the pre-treated sample solutions (20 mL for determination of pre-concentration factor in range of 5–35 mL) or a standard solution containing As(III) (20 µg/L in optimization step) in the ranges of 1–40 and 3–75 µg L^{-1}, 0.4 mmol/L of the McIlvaine buffer solution (pH 2.0 and 6.0), $1.5 \times 10^{-4}/4.0 \times 10^{-4}$ %(w/v) of 2-HBT-modified amide/imide copolymer solutions, 30 µmol/L of SDS-CTAB in 5 % (v/v) 2-propanol, 100 µmol/L KCl, and 0.08/0.1 % (v/v) of Triton X-114 were mixed in a centrifuge tube of 50-mL and diluted to mark with water, and sonicated for phase separation in an ultrasonic bath (40 kHz, 300 W) for 7 min at 40 °C. Separation of the phases was accelerated by centrifuging at 3500 rpm for 5 min. Without cooling, the surfactant-rich phases became viscous. Then, the aqueous phase could be separated by using a syringe. Subsequently, the surfactant-rich phase was diluted to a volume of 0.4 mL with THF in order to decrease its viscosity and make the final volume feasible to transfer into the optical cell of 1.0 cm for the As(III)-amide/imide complexes' absorbance measurement at pH 2.0 and 6.0 respectively by spectrophotometry at 266 and 269 nm against an analyte blank prepared under similar conditions. The iAs levels of the samples were determined by using the matrix-matched calibration curve to suppress the matrix effect. To determine the signal contributions resulting from the used reagents, a blank control solution subjected to the same procedure was measured in parallel with the samples or standard calibration solutions.

2.6. Statistical analysis

For optimization studies, the standard deviations of the absorbance measurements were calculated (n: 3) and represented as error bars. According to AOAC International (2016), the repeatability was expressed as the RSDs for five replicate measurements at three different concentration levels. The average plus standard deviation of the analyte concentrations (n: 3) were calculated for each sample. The results were statistically evaluated by employing the Student's *t* test, and the calculated *t*-values were compared with the tabulated value for two degrees of freedom at the 95 % confidence level.

3. Results and discussion

The initial experiments showed that the extractable stable chelate complex formed by the pH-dependent CT among reagents and As(III) is extracted into the micellar phase of the mixed ionic/nonionic surfactants, CTAB-SDS/Triton X-114. As a result of this observation, an UA-CPE was developed for the determination of As(III). After complexation and extraction processes based on a pH-induced charge transfer (CT) where the absorbance for amide and imide copolymer, respectively, is selectively minimum and maximum as a result of tautomerization at pH 6.0, the absorption spectra of the micellar phase diluted with THF showed a maximum band at 266 and 269 nm for As(III) detection by amide and imide copolymer at pH 2.0 and 6.0 with a blue or red shift of 3-nm in absorption wavelength and a noticeable change in sensitivity as well as pH difference in terms of selectivity of extraction,

which was selected for further absorbance measurements. The UV spectra for increasing As(III) concentration in range of 2.5–40 µg/L at pH 2.0 and 6.0 respectively as a function of measurement wavelength under optimized reagent conditions were given in Figs. S1(a, b). The effect of the different variables was independently optimized in order to achieve the maximum sensitivity for the fixed concentrations of 20 µg/L As(III).

3.1. Characterization of the amide/imide copolymers by instrumental tools

From the FT-IR spectra, which are directly sampled at the ATR mode without the KBr pellet in Fig. S2 (a), it has been observed that SMAnh copolymer has the expected anhydride units at 1855 and 1804 cm^{-1}, which belong to symmetric and asymmetric C=O stretching vibrations of maleic anhydride (MAnh), respectively. The C—O—C stretching vibrations, resulting from the MAnh ring, were observed at 1025 and 935 cm^{-1}. Instead of the MAnh units, new peaks appeared in the range of 1778–1727 cm^{-1}, which probably corresponds to the maleamidic acid and maleimide groups. The results indicate that the maleic anhydride rings in the SMAnh backbone are almost completely opened after modification with 2-HBT.

Also, ^{1}H NMR spectra (in DMSO, D$_6$, single pulse at 400 MHz) in Fig. S2(b) confirmed and supported the FT-IR results. In the SMAnh copolymer, chemical shifts, resulted from two methane –CH– protons on the furan unit at 6.3 ppm and aromatic hydrogen of the benzene ring of styrene at 6.7–7.4 ppm, were observed. The chemical shifts between 7.2 and 7.4 ppm belong to the aromatic ring hydrogen of styrene, indicating a proton signal of the styrene residue. These aromatic hydrogen peaks indicate that SMAnh copolymer is partially modified with 2-HBT. The characteristic peaks observed in the ^{1}H NMR spectra of the SMAnh are as follows: (i) a chemical shift of two protons on the MAnh groups at 3–4 ppm (overlapped with the water signal) and (ii) distinct spectral features of the SMAnh copolymer with two methane –CH– protons on the furan unit at 3.3 ppm, methylene –CH$_2$– protons at 2 ppm close to that of DMSO, D6 solvent, and a –CH peak at 1 ppm. The characteristic aromatic ring protons on 2-HBT moieties formed a broad peak at 2–4 ppm. Amide –NH (–CONH–) protons were observed at 8.4 ppm, confirming that 2-HBT was bound to the SMAnh by an amidation reaction.

Thermal properties of poly(SMAnh), and its amide and imide copolymers modified with 2-HBT were also established by thermal analysis techniques such as TGA/DrTGA and DSC (by heating from room temperature to 600 °C at heating rate of 10 °C/min and N$_2$ flow of 25 cm^3/min) in Fig. S2(c). From TGA/DrTGA and DSC results, it has been observed that the thermal stability of the poly(SMAnh) is greatly enhanced through the incorporation of 2-HBT in the copolymers. The glass transition temperatures (T$_g$) of each copolymer with and without modification were determined separately in the first transformation intervals of the DSC curves using the tangential slope method. From the results, it was observed that the thermal stability of the imide structure is higher than those of others, with increasing T$_g$ of 115, 131 and 146 °C in order of poly(SMAnh) < 2-HBT/poly(SMAm) < 2-HBT/poly(SMIm).

3.2. Optimization of the UA-CPE system variables

Due to its simplicity and ease to use, the variables affecting the UA-CPE efficiency was optimized by univariate optimization, based on one-factor-at-a-time. In this approach, we observe the effect of one factor at a time on the analytical signal. Shortly, the main variables affecting the complexation and extraction efficiency for analysis of 20 µg L^{-1} As(III) were optimized step by step.

3.2.1. Effect of pH

The pH of the aqueous phase is one of the most important factors in extraction of iAs from various media for the formation of a stable complex. In order to obtain the maximum extraction efficiency of 20 µg/

L As(III) by amide and imide copolymer, the effect of pH on the absorbance as a measure of sensitivity was studied in Fig. 1(a). The effect of pH on the complex formation was studied in a range of 2.0–8.0. For 2-HBT modified-amide copolymer matrix, in range of pH 2.0–8.0, the absorbance at 266 nm decreases linearly, reaching a minimal value of 6.0 for As(III) as soft Lewis acid, and then gradually increases increasing pH in the pH range of 6.0–8.0 while it gradually increases in range of pH 2.0–6.0, reaching a maximum value of 6.0, and then gradually decreases in in range of pH 6.0–8.0 for imide copolymer matrix at 269 nm. This minimal/maximal change in absorbance may be due to tautomerization of chelating matrix by pH-dependent CT among reagents and As(III). At lower or higher pHs (<6.0 or < 6.0), As(III) in form of:AsO(OH) or:As(OH)$_3$ with pK$_a$ value of 9.2 can be available in ionic forms of AsO$^+$ or As(OH)$_4^-$ by protonation and deprotonation, leading to a change in coordination ability via acid-base interaction or donor–acceptor mechanism, and the H$^+$ ions may have also competed with As(III) for binding sites on the amide or imide carbonyl (C=O), hydrazinic (–NH-NH- or = N-NH-) and heterocyclic benzothiazole donor N- and especially S-atoms (as soft Lewis base) on the surface of the copolymer matrix. Once these groups were protonated, for amide copolymer, the strong ion–dipole interaction increased contacting As(III) with the surface of the copolymer matrix, resulting in higher metalloid binding capacities at lower pHs, which can be attributed to the conversion of As(OH)$_3$ into As(=O)OH (around pH 2.0), so as to accelerate CT sensitive complexation.

At lower or higher pHs (<6.0 or > 6.0), the surface of copolymer matrix can positively or negatively be charged due to protonation or deprotonation of hydrazinic moiety as well as benzothiazole moiety. A similar case was also observed in pH-dependent electrochemical behavior of phenylhydrazine (with pK$_a$ of 5.1 or 5.3), structurally similar to 2-HBT where the peak potential was linearly changed with increasing pH in pH 2.0–10.0 (Bax et al., 2017; Goyal & Srivastava, 1995). In the mentioned-study, implying a CT process, it has been observed that the peak potential decreases with increasing pH over a wide pH range, and exhibits a linear intersecting behavior, passing through the minimum around pH 5.0 by both cyclic voltammetry and UV-spectral analysis. Consequently, the absorbance was maximum at pH values of 2.0 and 6.0, respectively for complexation of As(III) with amide and imide copolymer. The cause of sharply increase in absorbance may be signal enhancement effect of HSO$_4^-$ (and/or H$_2$SO$_4$) ions and dodecanol produced by hydrolysis of SDS, so as to lead pH-dependent change of its CMC at below pH 4.0. By the way, both the chelate formation and the mass transfer of the chelate into the micellar phase in presence of dodecanol acting as a stabilizing co-surfactant will greatly fasten and facilitate as a result of conversion of As(OH)$_3$ to AsO(OH) with increasing acidity as well as improvement in nanoscale detection capability (Rahman & Brown, 1983). Therefore, a pH of 2.0 and 6.0 for As(III) detection by amide and imide copolymer, respectively, was selected as optimal for the further studies. In the selected pHs, it is thought that As(III) has effectively participated in complexation by coordination via hydrazinic N, N-, carbonyl (C=O) and benzohiazole donor S- and sp^2 N-atom groups in presence of SDS and CTAB mixture as both sensitivity enhancer and charge compensator for ionizable end groups that cannot participate in coordination on the polymer matrix surface, and citrate as stabilizer against oxidation, so as to form a complex in a tetrahedral geometry as a function of pH. The N- and S-containing ligands of lower basicity (pK$_a$ < 5.2, like pyridine or benzothiazole moiety) and citrate (pK$_{a1,2,3}$: 3.1, 4.7 and 6.4) with logβ of 1.39, 7.22, 11.78 as AsL, AsLH, AsLH$_2$) as stabilizer can also protect As(III) against oxidation via complexation (Chillé et al., 2022; Alispahic et al., 2021). Due to high affinity to both graphene oxide and inorganic/organic Hg, Se and As species, 2-thiosalicylic acid (pK$_a$: 3.5) as a similar modifier to 2-HBT was also used in column separation of As species in presence of cationic surfactant, benzylhexadecyldimethylammonium (BHDMA) and phenylalanine as additives in range of pH 1.5–4.5 (Cheng et al., 2018). In order to control the pH during the analytical procedure, it was adjusted to 2.0 and 6.0 for As(III) with a McIlvaine buffer solution.

In fact, for nanoscale detection of trace As(III), complexation based on pH-dependent CT represented by equations (1–5), is also overlapped and supported by findings of two author groups in terms of UV spectral data. In their studies, the first author group efficiently synthesized the dextran-As$_2$O$_3$ nanocomposite with a particle size ranging from 135 to 500 nm with a characteristic wavelength of 283 nm, and then used it for potential antitumor drug material, depending on pH, dextran and As(III) concentration in pH range of 2.5–5.5, so as to form a chelate by acid catalyzed-condensation in presence of H$_2$SO$_4$ where particle size gradually decreased from 260 to 135 nm with decrease in pH (Lan et al., 2021) while the As-NPs with a characteristic wavelength of 300 nm and average particle size of 45 nm without stabilizer is synthesized in pH range of 7.0–9.0 after reduction with NaBH$_4$ by the second author groups (Pal et al., 2012) where As-NPs specifically absorbed in the range
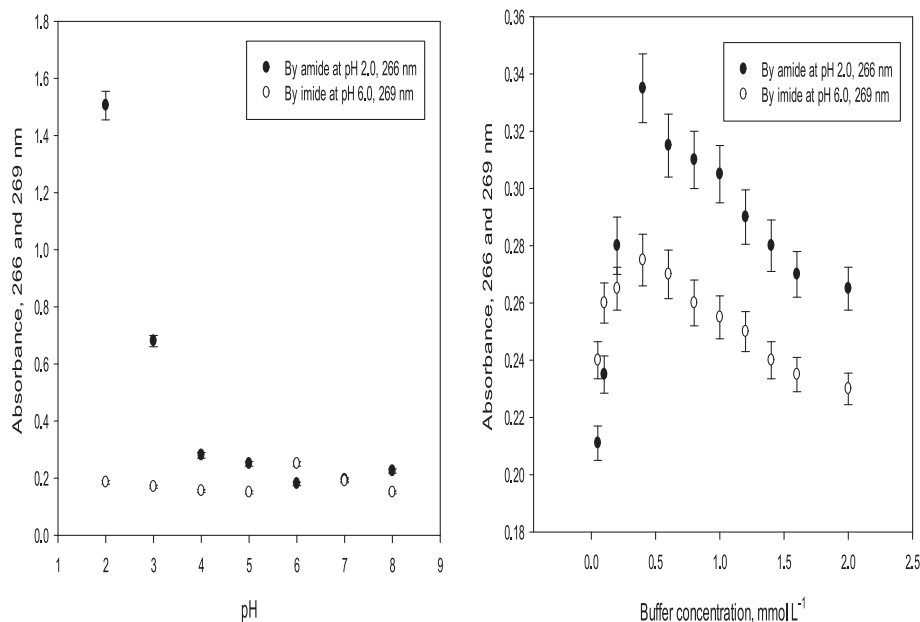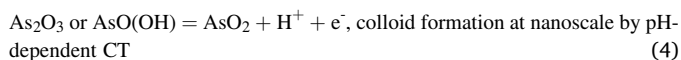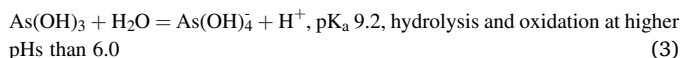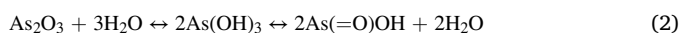

Fig. 1. Effect of (a) pH and (b) buffer concentration on the sensitivity of As(III) (20 μg/L) for 2-HBT modified amide/imide copolymer at pH 2.0 and 6.0, respectively.

of 250–350 nm.

$$As(OH)_2(HCitr)^{2-} + H^+ = As(OH)(HCitr)^- + H_2O, pH < 6.0 \quad (1)$$

$$As_2O_3 + 3H_2O \leftrightarrow 2As(OH)_3 \leftrightarrow 2As(=O)OH + 2H_2O \quad (2)$$

$$As(OH)_3 + H_2O = As(OH)_4^- + H^+, pK_a\ 9.2,\ \text{hydrolysis and oxidation at higher pHs than 6.0} \quad (3)$$

$$As_2O_3\ \text{or}\ AsO(OH) = AsO_2 + H^+ + e^-,\ \text{colloid formation at nanoscale by pH-dependent CT} \quad (4)$$

Also, the effect of buffer concentration on the sensitivity was studied in range of 0.05–2.0 mmol/L. From the results in Fig. 1(b), it can be seen that the best sensitivity was observed in a buffer concentration of 0.4 mmol/L for As(III) at pH 2.0 and 6.0, respectively. At lower and higher buffer concentrations, the absorbance was either gradually decreased or fluctuated. Therefore, a buffer concentration of 0.4 mmol/L was considered as optimal for further studies.

3.2.2. Effect of 2-HBT modified amide/imide copolymers

The effect of the quantity of 2-HBTmodified amide/imide co-polymers on the absorbance was studied in Fig. 2. To study this effect, the volume of the copolymer matrix as effective chelator was tested in range of 5.0×10^{-5}-1.0×10^{-3} % (w/v). In range of 5.0×10^{-5}-1.0×10^{-3} % (w/v), the absorbance was reached to a maximum with concentration of 1.5×10^{-4} and 4.0×10^{-4} % (w/v) for 20 μg/L As(III) at pH 2.0 and 6.0, respectively. At lower and higher concentrations, the sensitivity was gradually decreased. Thus, for further studies, 1.5×10^{-4} and 4.0×10^{-4} % (w/v) of amide and imide polymeric chelator was adopted as optimal.

3.2.3. Effect of ionic and nonionic surfactants

In UA-CPE, choosing an appropriate surfactant is important, since

Fig. 2. Effect of 2-HBT modified amide/imide copolymer concentration in THF on the sensitivity of As(III) (20 μg/L) at pH 2.0 and 6.0, respectively.

the temperature corresponding to cloud point is correlated with the hydrophilic property of a surfactant. A successful UA-CPE should maximize the extraction efficiency by minimizing the phase volume, thus increasing its concentrating capability. In the separation/pre-concentration process, the effect of the mixed CTAB-SDS (1:1, v/v) concentration in 5 % (v/v) 2-propanol on the absorbance was studied in range of 0.8–30 μmol/L in Fig. 3(a). The absorbance for both amide and imide copolymer linearly increased with difference in slope in range of 0.8–8 μmol/L, and then reached almost a maximum in range of 20–30 μmol/L. It is thought that this difference in slope as a measure of sensitivity resulted from pH dependent charge neutralization capability of each surfactant. This indicates that the quantity of CTAB-SDS mixture at equal molar concentrations is quantitatively enough to obtain the best sensitivity. Thus, a mixed ionic surfactant concentration of 30 μmol/L for As(IIII) extraction by amide/imide copolymer was adopted as optimal for further studies.

Triton X-114 as extractant is one of the non-ionic surfactants extensively used in UA-CPE. Due to its beneficial properties such as commercial availability with high purity, low toxicity and cost; high density of the surfactant-rich phase can promote the phase separation by centrifugation, and relatively low cloud point temperature. As can be seen in Fig. 3(b), UA-CPE of As(III) at pH 2.0 and 6.0 was carried out in range of 0.015–0.15 % (v/v) Triton X-114. The absorbance for amide copolymer increased with increasing concentration from 0.015 to 0.08 % (v/v), and reached a maximum at a concentration of 0.08 % (v/v) while it increased with increasing volume from 0.015 to 0.15 % (v/v) for imide copolymer, and reached a maximum at a concentration of 0.1 % (v/v). However, at higher concentrations for both copolymers, the absorbance was gradually decreased, including a fluctuation in amide copolymer. This indicates that the quantity of TritonX-114 is enough for the chelates extracted absolutely to ensure completeness of the extraction and improve the sensitivity. Thus, a Triton X-114 concentration of 0.08 % (v/v) and 0.1 % (v/v) was adopted as optimal for further studies.

3.2.4. The salting-out effect

The presence of inorganic electrolytes decreases the cloud point temperature due to dehydration of the poly(oxyethylene) chains (Ojeda & Rojas, 2009). Additionally, inorganic salts enhance the hydrophobic interactions among the surfactant aggregates and the analytes, thus favoring their extraction from the aqueous to the micellar phase.

Based on this discussion, the salting-out effect was studied in the presence of different concentrations of KCl (4–200 μmol/L for amide/imide copolymer) at 40 °C in Fig. 4. It was found that KCl resulted in increase in the absorbance with increasing KCl concentration until reach a maximum at 100 μmol/L. This effect may be due to the enhanced hydrophobic interactions among the surfactant aggregates and chelate complexes of As(III) as well as the decrease in the cloud point temperature of Triton X-114 in the presence of KCl. At higher concentrations than 100 μmol/L, the absorbance decreased gradually. High salt concentration can increase the density of water drops accompanied by the surfactant-rich phase, and hence disturb the phase separation. Hence, a concentration of 100 μmol/L was concluded to be enough for effective extraction of As(III).

3.2.5. Effect of sonication temperature and time

The temperature in UA-CPE procedure is an important factor affecting the formation of a stable chelate complex. In this study, the temperature was evaluated from 25 to 55 °C in Fig. 5(a). From the results, it was observed that the sensitivity increased by increasing the temperature to 40 °C, in which it is linearly related to extraction efficiency. Accordingly, a temperature of 40 °C for both amide and imide copolymer at pH 2.0 and 6.0 was adopted as optimal for further studies.

Sonication time is a reflection of extraction efficiency, which determines the time required for quantitative extraction. Different sonication times in the range of 1–15 min in the ultrasonic bath (40 kHz, 300 W) in Fig. 5(b) were studied at optimal 40 °C, according to the method.
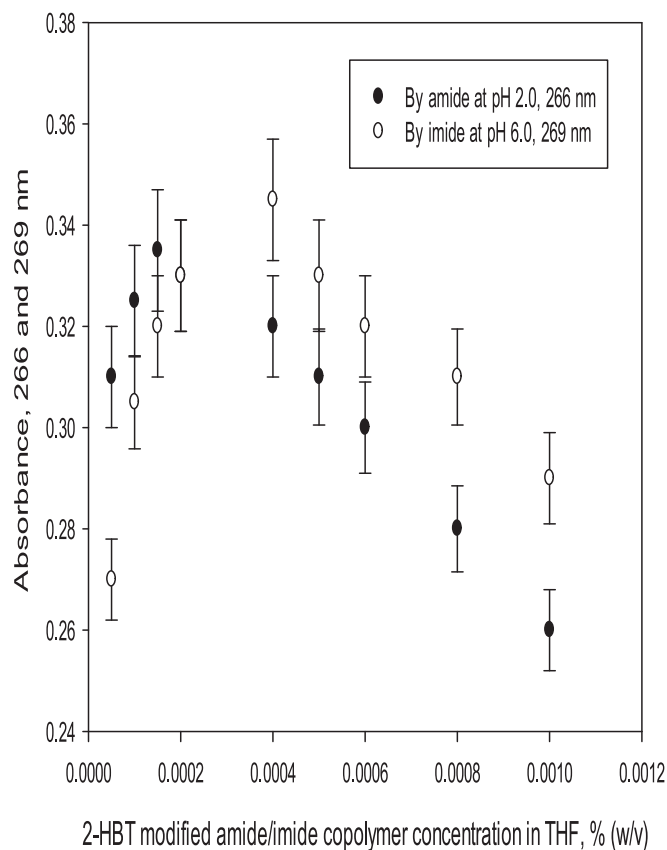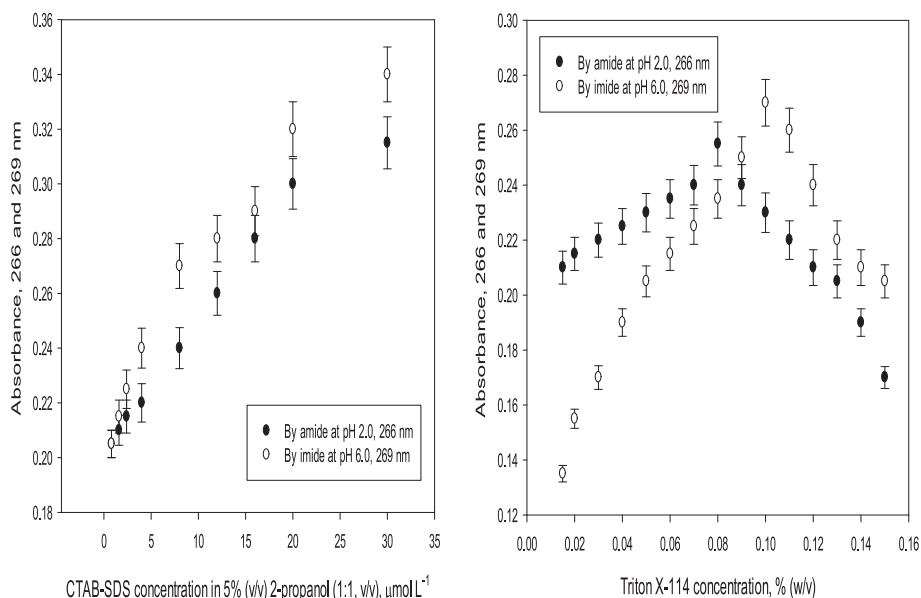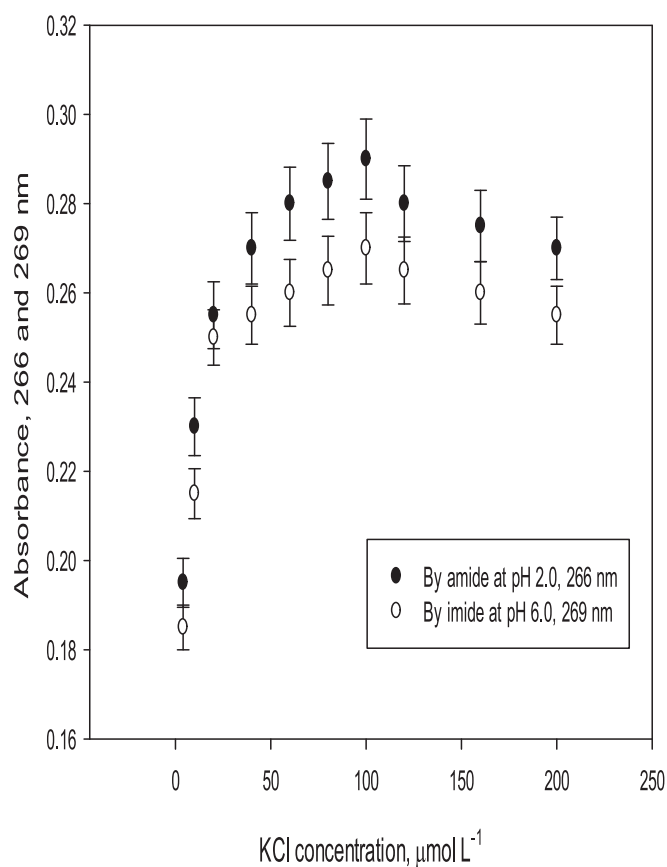
Fig. 3. Effect of (a) CTAB-SDS concentration in 2.0 % propanol (1:1, v/v) (b) Triton X-114 concentration, % (v/v) on the sensitivity of As(III) (20 μg/L) for 2-HBT modified amide/imide copolymer at pH 2.0 and 6.0, respectively.

Fig. 4. Effect of KCl concentration on the sensitivity of As(III) (20 μg/L) for 2-HBT modified amide/imide copolymer at pH 2.0 and 6.0, respectively.

As a function of sonication time, the maximum absorbance was accomplished in a duration of 7 min for both amide and imide copolymer at pH 2.0 and 6.9, respectively. Thus, a duration of 7 min was adopted as optimal for further studies.

3.2.6. Effect of centrifugation rate and time

At initial, the effects of centrifugation rate (1000–4000 rpm) and time (1–15 min) on the sensitivity of each ion were independently studied. It was also found that when the solution was centrifuged at 3500 rpm for 5 min, the sensitivity (or extraction efficiency) linearly increased and reached rapidly to a maximum. Hence, a centrifugation time of 5 min was adopted as optimal.

3.2.7. Effect of suitable solvent for dilution of micellar phase

It should be noted that after UA-CPE, the surfactant-rich phase obtained becomes very viscous owing to the Triton X-114 that it contains. In order to facilitate its transfer into spectrophotometric cell, it is necessary to decrease the viscosity of the surfactant-rich phase to improve the solubilization of As-pre-concentration chelating polymer matrix and detection sensitivity. So, it is usually necessary for the addition of a diluting solution in the surfactant-rich phase to obtain a clear and homogenous solution of low viscosity compatible and miscible with the aqueous micellar solution. Diluents such as methanol, ethanol, acetonitrile, acetone, THF, acidic methanol and ethanol (1.0 mol/L HCl) was in triplicate added to the surfactant-rich phase after UA-CPE. From the results obtained, it was found that THF gave the maximum sensitivity and good signal reproducibility and stability for As(III) at pH 2.0 and 6.0. In fact, THF is a relatively nontoxic polar solvent, and can dissolve a wide range of nonpolar and polar chemical compounds. It is a water-miscible Lewis base that bonds to a Lewis acid such as phenols and polar ethoxyl groups of extractant, Triton X-144 by hydrogen bonding. Therefore, for a pre-concentration of 20-mL sample optimized from analysis of a serial standard solution containing 0.2 μg As(III) in range of 5–35 mL, the surfactant-rich phase was diluted to a volume of 0.4 mL with THF to have an appropriate amount of sample for transferring and measuring the sample absorbance.

3.3. Analytical figures of merit

The validation study for assessing standard method performance requirements was performed according to AOAC recommendations (2016), and the achieved analytical parameters were evaluated as follows: Under the selected optimal conditions, the calibration curves in solvent were observed to be highly linear in the concentration range of 1–40, 3–75 μg/L As(III) for amide/imide copolymer at pH 2.0/6.0,
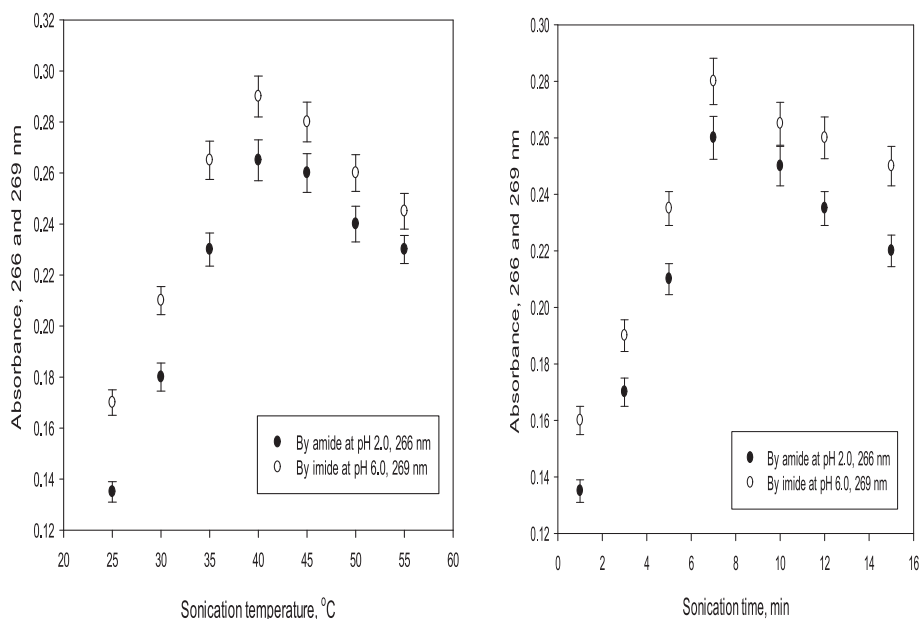
Fig. 5. Effect of (a) sonication temperature, °C and (b) sonication time, min on the sensitivity of As(III) (20 μg/L) for 2-HBT modified amide/imide copolymer at pH 2.0 and 6.0, respectively.

respectively while the five point matrix-matched calibration curves based on adding directly to the sample aliquot before extraction were linear in concentration ranges of 1–50 and 3–75 μg/L with an enhancement in signal of 4.90 % and 5.13 % where the Student's *t*-test is applied to compare slope of the calibration curves when using 20-mL of the sample solution. Without a serious matrix effect, it can be concluded

Table 1
Analytical features of the method for detection of trace As(III) by UV spectrophotometry at pH 2.0 and 6.0 under optimized reagent conditions.

Analyte	Calibration type	From regression analysis by UV spectrophotometry				[a] LOD, μg L^{-1}	[a]LOQ, μg L^{-1}	Precision		Accuracy
		Linear range, μg L^{-1}	Slope ± SD	Intercept ± SD	Determination coefficient, r^2			Repeatability (as RSD% for same day, 5, 15 and 30 μg/L, n: 5)	Intermediate precision (as RSD% for three consecutive days, 5, 15 and 30 μg/L, n: 5)	Recovery %
For As(III) with 2-HBT modified amide copolymer at pH 2.0, 266 nm	By the calibration curve in solvent	1–40	(7.55 ± 0.60) × 10^{-3}	(1.16 ± 0.08) × 10^{-2}	0.9956	0.32	1.06	3.0–4.2	4.7–6.1	92.0–94.5
	*By the matrix-matched calibration curve prepared from blank sample extracts	1–50	(7.92 ± 0.5) × 10^{-3}	(1.04 ± 0.12) × 10^{-2}	0.9950	0.45	1.52	3.5–4.7	4.6–6.6	91.5–94.0
For As(III) with 2-HBT modified imide copolymer at pH 6.0, 269 nm	By the calibration curve in solvent	3–75	(3.90 ± 0.23) × 10^{-3}	(3.92 ± 0.13) × 10^{-2}	0.9965	1.00	3.30	3.1–4.5	4.3–5.7	93.0–95.5
	*By the matrix-matched calibration curve prepared from blank sample extracts	3–75	(4.10 ± 0.25) × 10^{-3}	(4.15 ± 0.15) × 10^{-2}	0.9951	1.10	3.66	3.2–4.5	4.2–6.1	92.5–95.0
[b] Matrix effect, %	+4.90, +5.13 %									
[c] Sensitivity enhancement factor (EF)	24.4, 12.6									
[d] Pre-concentration factor (PF)	50									

*Based on externally spiking into the blank sample extracts at concentration levels of 1.0, 5.0, 15, 25, 50 and 75 μg/L of As(III) before analysis.

[a] Limits of detection and quantification ((LODs, LOQs) for TCS were determined according to the expressions at $3.0 \times s_{blank}/m$ and $10 \times s_{blank}/m$, respectively (where s_{blank} is the standard deviation of ten consecutive blanks (n: 12), and m is the slope of the calibration curves prepared in solvent and from sample extracts, respectively).

[b] Based on comparison of slopes of two calibration curves established in solvent and sample extracts by using formula, $ME\% = (m_{matrix-matched} - m_{solvent} / m_{olvent}) \times 100$.

[c] Ratio of slopes of the calibration curves established with and without pre-concentration where the regression equation for As(III) is Abs.: $3.10 \times 10^{-4}C$ (μg/L) + 0.0104, r^2: 0.997 with limits of detection and quantification of 4.16, 13.9 μg/L in linear range of 15–300 μg/L.

[d] Ratio of the bulk aqueous sample solution volume to that of the surfactant-rich phase.

that the calibration curves in solvent will be reliably able to use in analysis of iAs contents of edible oils instead of standard addition method for possible matrix effect. The regression equations were Abs= $(7.55 \pm 0.60) \times 10^{-3}$C + $(1.16 \pm 0.08) \times 10^{-2}$ for As(III) at pH 2.0, and Abs = $(3.90 \pm 0.23) \times 10^{-3}$C+ $(3.92 \pm 0.13) \times 10^{-2}$ for As(III) at pH 6.0 (where A is the absorbance and C is mercury concentration in $\mu g L^{-1}$), with a determination coefficient (r^2) of 0.9956 and 0.9965, which indicates good linearity in the mentioned concentration ranges. From the calibration curves in solvent, the limits of detection and quantification (LODs, LOQs), based on a signal-to- noise ratio (S/N) of 3 and 10, were 0.32/1.06 and 1.00/3.30 μg/L. The precision (as RSDs) and accuracy (as the percent recovery rate) of the method, determined by analyzing the standard solutions at 5, 15 and 30 μg/L of As(III) five times in same day and three consecutive days, were in ranges of 3.0–4.7 %/4.2–6.6 % and 90.2–96.0 % when compared with the threshold values (with a RSD_r / RSD_R of 22–45, 15–30 % and recovery rates of 60–115, 80–110 %) recommended by the AOAC (2016) in the used concentration range, it can be concluded that the results are quantitatively acceptable. It has been found that the sensitivity enhancement factors, defined as the slope ratio of two calibration curves for each ion with and without pre-concentration, were 24.4, 12.6 for As(III). From pre-concentration of 20-mL, a pre-concentration factor of 50 was obtained for each ion in optimal conditions. The other analytical figures of merit achieved were given in detail in Table 1.

3.4. The matrix effect

The effects of potential interfering species in Table 2(a) were tested in tolerance ratio ranging from 1:5 to 1:1500 by the high selectivity for As(III)-ligand complex formation at pH 2.0 and 6.0 by using solutions containing 25 μg/L As(III) and adding various concentrations of potentially interfering ions. The tolerance limits of the co-existing ions, defined as the largest amount decreasing the recovery of each ion to <5.0 %. Table 2 shows the tolerance limits of the interfering neutral, anionic and cationic species' concentrations. Most of the studied neutral and ionic interfering species including phenol did not interfere with the determination of As(III) in tolerance range of 150–1500-fold, Cd^{2+}/ Sn^{2+} did not interfere at more than a 250-fold excess, Hg^{2+} did not interfere at more than a 150-fold excess, NO_2^- did not interfere up to 100-

Table 2a
The matrix effect of potential interfering species on the extraction efficiency of 25 μg/L As(III) (n: 3).

Co-existing ions	Tolerance ratio(Interfering/ As(III))	Recovery $\pm SD^a$ (%)
NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}	1500	97.5 ± 2.5
Fe^{2+}, Zn^{2+}	1250	98.0 ± 3.0
CH_3COO^-, HCO_3^-, PO_4^{3-}, NO_3^-, I^-, Br^-	1000	96.0 ± 2.0
Ni^{2+}, Co^{2+}	750	97.4 ± 3.0
V^{4+}, Pb^{2+}, Ag^+	600	95.5 ± 2.5
Benzaldehyde	500	96.1 ± 2.5
V^{5+}, Fe^{3+}, Cr^{3+}, Mn^{2+}	500	102.5 ± 3.0
Phenol	350	95.4 ± 2.0
Cd^{2+}, Sn^{2+}	250	103.7 ± 2.5
Hg^{2+}	150	96.2 ± 3.0
NO_2^-	100 (>1000)[b]	104.5 ± 2.0
Formaldehyde, acetaldehyde	50 (>250)[c]	95.5 ± 3.0
As^{5+}	5–35	(90.5–95.5) ± 3.5

[a] The percent recovery rates and their standard deviations obtained from three replicate measurements of 25 μg/L As(III) by UV spectrophotometry.
[b] Tolerance ratio after removal with dilute sulfamic acid (1.0 mL of 0.02 mol/ L) in acidic media before extraction.
[c] Tolerance ratio after signal suppression with dilute metabisulfite solution (2.0 mL of 0.02 mol/L) so as to give to stable anionic bisulfite adduct around pH 5.0 before extraction.

fold excess, the formaldehyde and acetaldehyde did not disturb determination up to 50-fold excess, and finally As^{5+} did not interfere in a range of (5–35)-fold excess, where the recovery rate is in range of 90.5–104.5 % with a precision ranging from 2.0 % to 3.5 % from triplicate measurements. According to the obtained data, most foreign cations and major cations in the samples have no obvious influence on determination of each ion under the selected conditions, so as to imply the selectivity of the method. Moreover, in the case of serious interference of nitrite, formaldehyde and acetaldehyde, the interference effect of these species can be controlled, and greatly suppressed with improvement of 250- and 1000-fold in tolerance ratio by the use of 1.0 or 2.0 mL of sulfamic acid and metabilsulfite solutions (each one, 0.02 mol/L) as suitable masking agents in acidic medium and around pH 5.0 before pre-concentration by UA-CPE.

3.5. Speciation analysis

The performance and reliability of the method for the applicability to analysis of real samples were checked by determination of As(III), As(V), and total iAs content in binary mixtures. In order to determine As(III), As (V) and total iAs using a mixture containing 2.0 % (w/v) TEA, 0.02 mol/ L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions to ensure the repeatability and stability of the results, and especially to prevent possible As losses via interconversion of iAs species around pH 5.0–5.5 before and after pre-reduction with ascorbic acid (n: 5), model solutions that contain different amounts of As (III) and As(V) with ratios of 1:1, 1:3 and 1:7 (or 1:1, 3:1 and 7:1) as equivalent to total iAs level of 40 μg/L were prepared. Then, the As(III), As(V) and total iAs levels with and without reduction in the test solutions was performed by the procedure explained. The results show that the proposed method with a RSD of 2.5–4.4 % a recovery rate of 90–96 % could be successfully applied to the speciation analysis of iAs in Table 2(b).

3.6. Application of the method to edible vegetable oils

At initial, the method was validated by analysis of a certified sample plus two quality control sample in terms of iAs (As(III) and As(V)) contents in Table 3(a). It was observed that there is not statistically a significant difference between the results found by the present method and the certified value after 10-fold dilution, via use of the one-paired t-test. Also, after spiking with 5, 15 and 30 μg/L for As(III) in absence and presence of ascorbic acid as reductant under the optimized reagent conditions, based on the threshold values of 21 % and 60–115 % recommended by the AOAC (2016), the method in terms of accuracy and precision was reliable, and it was observed that the results obtained could quantitatively be accepted with RSDs of 3.7–5.3 % and 3.7–6.3 %, and recovery rates of 88–94 % and 87–94 %. The results achieved after pre-reduction with ascorbic acid refer to a comparison between observed and reported values given in parentheses against possible interconversion of As(III) to As(V) or As(V) to As(III), in terms of total iAs contents of CRM (in fact, with and without pre-reduction).

After the method validation, the analysis of edible oil samples was performed in Table 3(b). To control the matrix effect, the matrix-matched calibration curve based on externally spiking of 5, 15 and 30 μg/L As(III) into sample extracts before analysis after two soft sample preparation procedures based on using (i) 5.0 mL edible oil with 10 mL of a mixture containing 2.0 % (w/v) TEA, 0.02 mol/L oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C in ultrasonic bath and (ii) 5.0 mL edible oil with 10 mL of a mixture of 1.0 mol/L H_3PO_4, 0.1 mmol/L EDTA and 0.1 % (v/v) Triton X-114 as extractant (5:3:2, v/v) for 20 min at 55 °C in ultrasonic bath was adopted and applied to the analysis of samples after dilution of 2-fold. Also, the spiking at levels of 10 μg/L was made into each sample matrix, and their recoveries were established for five replicate

Table 2b
The speciation analysis results of binary mixtures, As(III), As(V) and total iAs at known concentration ratios with and without pre-reduction using 1.5%(w/v) ascorbic acid (n: 5).

Added, µg L⁻¹		*Found, µg L⁻¹			Accuracy/precision of speciation analysis					
					RSD%			Recovery%		
As(III)	As(V)	**As(III)	****As(V)	***Total iAs	As(III)	As(V)	Total As	As(III)	As(V)	Total As
0	40	–	37.1	37.1 ± 1.2	–	–	3.2	–	93	93
5	35	4.5 ± 0.2	33.0	37.5 ± 1.2	4.4	–	3.2	90.0	94	94
10	30	9.4 ± 0.4	28.9	38.3 ± 1.2	4.2	–	3.1	94.0	96	96
20	20	18.6 ± 0.6	19.8	38.4 ± 1.2	3.2	–	3.1	90.7	99	96
30	10	28.3 ± 0.7	9.8	38.1 ± 1.3	2.5	–	3.4	91.5	98	95
35	5	33.5 ± 1.0	4.6	38.1 ± 1.3	2.8	–	3.4	94.0	92	95
40	0	38.1 ± 1.3	–	38.3 ± 1.3	3.4	–	3.4	93.7	–	96

*The mean and standard deviations of five replicate measurements under optimal reagents' conditions.

**The As(III) levels found by using 10 mL of a mixture containing 2.0 % (w/v) TEA[a], 0.02 mol/L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C in absence of ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions to ensure the repeatability and stability of the results, and especially to prevent possible As losses via interconversion of iAs species around pH 5.0–5.5.

***The total As levels found by using 10 mL of a mixture containing 2.0 % (w/v) TEA[a], 0.02 mol/L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) in presence of 1.5 %(w/v) ascorbic acid for 12 min at 40 °C under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions.

**** The As(V) levels calculated from difference between As(III) and total iAs levels.

Table 3a
The intra-day and inter-day accuracy/precision of triplicate measurements of iAs (as As(III)) in a certified and two edible oil samples selected for quality control purposes by the present method under the optimal conditions (n: 3 or 5 in same day and three consecutive days).

Samples	Spiking level µg L⁻¹	Measurement accuracy and precision					
		Intra-day precision (repeatability)			Inter-day precision (reproducibility)		
		Found	Recovery (%)	RSD (%)	Found	Recovery (%)	RSD (%)
Fish oil	–	3.8 ± 0.2	–	5.3	4.1 ± 0.2	–	4.9
	5	8.4 ± 0.4	92.0	4.8	8.6 ± 0.4	90.0	4.7
	15	17.6 ± 0.8	92.0	4.5	17.8 ± 0.8	91.3	4.5
	30	32.0 ± 1.2	94.0	3.8	32.2 ± 1.2	93.7	3.7
Edible salad oil	–	4.1 ± 0.2	–	4.9	4.3 ± 0.2	–	4.7
	5	8.6 ± 0.4	90.0	4.7	8.8 ± 0.4	90.0	4.5
	15	17.7 ± 0.8	91.0	4.5	18.2 ± 0.8	93.0	4.4
	30	32.4 ± 1.2	94.0	3.7	32.5 ± 1.2	94.0	3.7
SRM1568b Rice flour	–	8.1 ± 0.4* (8.3 ± 0.4**)	88.0 (90.0)	4.9 (4.8)	8.0 ± 0.5* (8.3 ± 0.5**)	87.0 (90.0)	6.3 (6.0)
	5	12.6 ± 0.6 (12.8 ± 0.6)	90.0 (90.0)	4.8 (4.7)	12.4 ± 0.7 (12.8 ± 0.7)	88.0 (90.0)	5.6 (5.5)
	15	21.7 ± 1.0 (22.0 ± 1.0)	91.0 (91.0)	4.6 (4.5)	21.5 ± 1.1 (22.0 ± 1.1)	90.0 (91.0)	5.1 (5.0)
	30	36.0 ± 1.5 (36.5 ± 1.5)	93.0 (94.0)	4.2 (4.1)	35.5 ± 1.5 (35.8 ± 1.5)	92.0 (91.7)	4.2 (4.2)

*The values found by the present method for five replicate measurements (n: 5) after 1:10 dilution of the sample extract with and without spiking before extraction and analysis using a mixture containing 2.0 % (w/v) TEA[a], 0.02 mol/L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C in absence of ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions where the certified value for iAs (as As(III) and As(V)) and total As is 0.092 and 0.284 mg kg-1, respectively.

**The values found by the present method in parentheses for five replicate measurements (n: 5) after 1:10 dilution of the sample extract with and without spiking before extraction and analysis using a mixture containing 2.0 % (w/v) TEA[a], 0.02 mol/L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C in presence of ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions where the certified value for iAs (as As (III) and As(V)) and total As is 0.092 and 0.284 mg kg-1, respectively.

measurements before and after pre-reduction and pre-concentration by UA-CPE. In terms of accuracy and precision of iAs contents of samples, it was observed that there is statistically not a significant difference between the results found by the present method after two soft sample preparation procedures, according to the two paired Student's *t*-test and variance ratio test. The recoveries for the spiked samples were in the acceptable range of 90–95 % with lower RSD than 7.5 %. When a safe limit of 15 µg/L for iAs in foods established by Joint Expert Committee on Food Additives (JECFA) (JECFA, 2003) is considered, it is clear that the results found by for two soft sample pretreatment procedures will not pose to a serious risk on human health, except for peanut sample, where the iAs contents of edible oils are in range of 3.7–18.7 and 4.0–18.9 µg/L, respectively. The results were higher than iAs levels found by Lorentz-Martinez et al. (Llorent-Martínez et al., 2011a, Llorent-Martínez et al., 2011b), but it is consistent with those found by other author groups and falls within the same range (Zhu et al., 2011). As a result, it is clear that if used consistently and repeatedly, it will become a threat for especially infants and children even at low (<10 µ L⁻¹)

exposure levels in the short and long run (Kapaj et al., 2006). All the results indicated that the newly developed analytical method could be satisfactorily used for monitoring and determination of the iAs levels in the selected liquid samples in terms of quality control.

3.7. Comparison of the method with other methods

It has been demonstrated that the 2-HBT modified amide/imide co-polymers provide a new, efficient, eco-friendly and fast route for separation/pre-concentration and speciation analysis of As(III). The method is certainly simpler, faster and more convenient than other complex methods that have been proposed for either single or multiple analysis after separation and pre-concentration of i-/o-As species. Micellar separation and pre-concentration by UA-CPE, based on pH-controlled CT sensitive complexation with modified copolymer matrices, greatly shortened the analysis time of the method. These chelating matrices were successfully applied to efficient enrichment of trace As(III) in 35-fold excess of As(V) from selected edible oils without

Table 3b

The replicate analysis results of trace iAs (as As(III)) in edible vegetable oils by the five point matrix-matched calibration curves before extraction, pre-concentration and analysis by UA-CPE/spectrophotometry (n: 5).

Sample matrix	Added, $\mu g \, L^{-1}$	By the matrix-matched calibration curve based on directly adding of 5, 10, 15, 20 and 30 μg/L As(III) into sample aliquot before extraction/analysis						[c]The paired t-test	[d]The variance ratio test
		After extraction of 5.0 mL edible oil with 10 mL of a mixture containing 2.0 % (w/v) TEA[a], 0.02 mol/L Oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C under ultrasound power (300 W, 40 kHz)			After extraction of 5.0 mL edible oil with 10 mL of a mixture of 1.0 mol/L H_3PO_4, 0.1 mmol/L EDTA[e] and 0.1 % (w/v) Triton X-114 as extractant (5:3:2, v/v) for 20 min at 55 °C under ultrasonic power (300 W, 40 kHz)				
		[b]Found, $\mu g \, L^{-1}$	RSD%	Recovery%	[b]Found, $\mu g \, L^{-1}$	RSD%	Recovery%		
Peanut oil		18.7 ± 1.0	5.3	–	18.9 ± 1.1	5.8	–	0.30	1.21
	10	28.0 ± 1.2	4.3	93	28.2 ± 1.2	4.2	93		
Soybean oil		13.5 ± 0.7	5.2	–	13.7 ± 0.7	5.1	–	0.45	1.00
	10	22.5 ± 1.0	4.4	90	22.8 ± 1.0	4.4	91		
Sunflower oil		7.1 ± 0.3	4.2	–	7.4 ± 0.3	4.0	–	1.58	1.00
	10	16.3 ± 0.6	3.7	92	16.8 ± 0.7	4.2	94		
Fish oil		3.7 ± 0.2	5.4	–	4.0 ± 0.3	7.5	–	1.86	1.00
	10	12.8 ± 0.6	4.7	91	13.5 ± 0.7	5.2	94		
Mixed frying oils		12.2 ± 0.6	4.7	–	12.5 ± 0.6	4.8	–	0.79	1.00
	10	21.2 ± 0.8	3.8	90	21.8 ± 0.9	4.1	93		
Sesame oil		8.5 ± 0.4	4.7	–	8.7 ± 0.5	5.7	–	1.43	1.56
	10	17.7 ± 0.7	4.0	92	18.0 ± 0.7	4.2	93		
Edible salad oil		4.3 ± 0.2	4.7	–	4.5 ± 0.2	4.4	–	1.58	1.00
	10	13.5 ± 0.5	3.7	92	13.8 ± 0.5	3.6	93		
Riviera olive oil		15.7 ± 0.7	4.4	–	15.8 ± 0.8	5.1	–	0.21	1.31
	10	25.1 ± 1.0	4.0	94	25.0 ± 1.0	4.0	92		
Virgin olive oil		15.1 ± 0.6	4.0		15.3 ± 0.7	4.6	–	0.49	1.36
	10	24.6 ± 1.0	4.1	95	24.8 ± 1.0	4.0	95		

[a] Herein, due to its property to act as an emulsifier or co-surfactant, triethanolamine (TEA) was primarily used to neutralize fatty acids and solubilize oils and other ingredients that are not completely soluble in water as well as adjusting the pH in presence of oxalic acid as stabilizer.

[b] The means plus standard deviations of five replicate measurements by the present method after 2-fold dilution of the pretreated and extracted edible oil samples.

[c] Based on statistical comparison of the mean values obtained by two calibration curves, in which the critical t-value is 2.31 for degree of freedom of 8 at 95% confidence level.

[d] Based on statistical comparison of the variance of two calibration approaches, in which the critical F-value is 6.39 for degree of freedom of 4 at 95 % confidence level.($F_{4,4} = s_1^2/s_2^2$).

[e] Herein, for stabilization of As species, EDTA was used as both extractant and preservative against precipitation/co-precipitation with trace amounts $Fe^{2+,3+}$, $Mn^{2+,3+,4+}$, $Cu^{+,2+}$ and Al^{3+} ions present in oily matrices.

matrix effect. Table 4 shows a comparison of the method performance with that of other detection methods reported in literature (Elik et al., 2021; Ni et al., 2017; Ni et al., 2015; López-García et al., 2015; Hsu et al., 2013; dos Santos Costa & Coelho, 2020; Altunay et al., 2019; Zounr et al., 2017). It could be seen that some values obtained by the proposed method such as RSD%, recovery rate, pre-concentration or enhancement factor, and linear working range, except for LODs and LOQs are comparable and better with those of the previously reported-sensitive, selective but complex, costly, time-consuming detection methods such as HG-AAS with and without FI, HG-AFS, ETAAS, ETV-ICP-MS, and IC-ICP-MS, requiring expert user in his or her area, according to reductant type and pre-treatment step of sample matrix. Furthermore, it avoids the time-consuming sample pretreatment (suitable elution mode in IC-ICP-MS), derivatization and/or reduction of analyte to a volatile species, slow furnace program in ETAAS, and no further sample processing and clean-up steps were required. The main benefits of the method are simplicity, good precision, high recovery rate, selectivity (due to formation of pH-dependent CT complex in pre-concentration step), pre-concentration factor, fast complexation/phase separation, low cost, and available/accessible in almost every analytical research laboratory.

4. Conclusions

In this study, the poly(SMAnh) co-polymers functionalized with 2-HBT acting as a soft chelator due its heterocyclic donor S- and N-atoms were prepared and applied to highly selective pH-dependent separation/pre-concentration of As(III) from aqueous solution in UA-CPE procedure before nanoscale detection by UV-spectrophotometry. Main variables affecting selective extraction of 20 μg/LAs(III) in presence of 35-fold excess As(V) were optimized. The optimal pHs for the extraction of As(III) was found to be 2.0 and 6.0 for amide and imide copolymer. Subsequently, the CT-based fast complexation equilibrium and phase separation in mixed micellar interface was achieved for As (III) with sonication time of 7 min at 40 °C and a centrifugation time of 5 min at 3500 rpm. In addition, the effects of matrix components potentially available in selected liquid samples were tolerable by the present method.

The findings indicate that the 2-HBT-modified amide/imide co-polymers can be used as an inexpensive, efficient, fast (due to complexation by pH-dependent CT) and environmentally safe As(III) binding chelator in separation/pre-concentration step. With the proposed method, good LODs, precisions, accuracy and sensitivity and a RSD of 3.0–6.6 % at even low concentration levels were achieved. Moreover, due to be use a mixture of 2.0 % (w/v) TEA, 0.02 mol/L oxalic acid and 1.0 % (v/v) Triton X-114 as emulsifier (5:3:2, v/v) against interconversion of As(III) to As(V) or As(V) to As(III) in ultrasound assisted-sample preparation step, a unique green approach was introduced as an alternative to toxic organic solvents. Trace/ultra-trace As (III) in edible oils, in terms of detection capability of iAs by a simple UV spectrophotometer, could be reliably detected with good precision and recoveries after spiking.

CRediT authorship contribution statement

R. Gürkan: Methodology, Validation, Writing – review & editing, Writing – original draft, Supervision. **H.B. Zengin:** Conceptualization, Investigation, Writing – review & editing, Formal analysis, Data curation.

Table 4
Comparison of the method with other reported methods on selective extraction, pre-concentration and determination of trace As in different sample matrices.

Analyte	Sample matrix	Chelating agent	Detection technique	Pre-concentration procedure	Linear range, μg L-1	LOD, μg L-1	LOQ, μg L-1	PF (or EF)	RSDs%	Recovery%	References
As(III)	Foods and waters	PMAEMA	HG-AAS	SPME	0.01–0.5	0.0033	0.011	100	4.3	91.5–98.6	Elik et al., 2021
As(III), total As	Vegetable oils	Dilute HNO$_3$ (1.0 %, v/v) for 15 min	HG-AFS	VAE	1–20	0.3	1.0	–	0.8–4.7	84.4–105	Ni et al., 2017
As(III), total As	Camellia oils	Dilute HNO$_3$ (10 %, v/v) for 20 min	HG-ICP-MS	VAE	0.2–20	0.03	0.1	–	<7.0	84.3–102.3	Ni et al., 2015
As(III), As(V), MMA, DMA,AsB	Edible oils	300 μL mixture of isopropanol-3.0 % (v/v) HNO$_3$ (3:1, v/v) for 3 min 80 °C under ultrasonic power (200 W, amplitude of 20 %) or 20 μL of a solution containing 35 % TMAH, 3.5 % starch and 20 % conc. NH$_4$OH	HG-AFS, ETAAS	DLLME	0.1–2, 0.1–1.5	0.03, 0.03	0.1, 0.1	–	0.17–11.1	94–105	López-García et al., 2015
As(III), As(V), MMA, DMA, AsB, AsC	Fresh and used soybean oils	0.5 % v/v HNO$_3$ in 80 % methanol at 80 °C for 120 min	IC-IC-MS	MAE	0.1–10	0.024, 0.013, 0.010, 0.008, 0.010, 0.015	<0.15	–	<7.0	90–105	Chu & Jiang, 2011
As(III), total As	Vegetable oils	5 %(w/v) edible oils/1.5 %(v/v) Triton X-100/50 ppm ascorbic acid/500 ng Pd NPs as modifier for 5 min ultrasonic bath	ETV-ICP-MS using DRC, 1 μg/L Rh as internal standard	Emulsion breaking procedure	0–20	0.02 (or 0.5 μg kg-1)	0.07 (0r 1.7 μg kg-1)	–	<10	90	Hsu et al., 2013
As(III), total As	Rice	APDC/(TBA)ClO$_4$	FI-HGAAS	In situ μ-sorbent formation SPE	0.12–10	0.04	0.12	-(17)	5.5	92.3	dos Santos Costa & Coelho, 2020
As(III), Sb(III)	Environmental water, honey and rice	Dithizone/DES	HGAAS	DES-VAME	0.015–0.35	0.008	0.026	104	2.1	>92	Altunay et al., 2019
As(III), total As	Edible mushroom, fish, tea, cigarette, sediment, oil and environmental waters	DEDTC	ETAAS	DES-UA-LPME	–	0.01	0.033	25	4.3	96.4–99.2	Zounr et al., 2017
As(III), total As	Edible oils	2-HBT modified poly(SMAm/SMIm) copolymers/CTAB, SDS/Triton X-114	pH-sensitive CT controlled UV-spectrophotometry	UA-CPE	1–40, 3–75	0.32, 1.00	1.06, 3.30	50 (24.2, 12.6)	3.0–6.6	91.5–95.5	This study

* APDC: Ammonium pyrolydinedithiocarbamate; DEDTC: Diethyldithiocarbamate; Dithizone: 1,5-diphenylthiocarbazone; PMAEMA: Poly(methyl methacrylate-co-2-aminoethyl methacrylate amphiphilic copolymer; TMAH: Tetramethylammonium hydroxide; 2-HBT: 2-hydrazinobenzothaizole; CTAB: Cetyltrimethylammonium bromide; SDS: Sodium dodecyl sulfate.

** UA-CPE: Ultrasound assisted-cloud point extraction; μSPE: Micro solid phase extraction; SPME: Solid phase microextraction; DLLME: Dispersive liquid–liquid microextraction; VAE: Vortex assisted extraction; MAS: Microwave assisted extraction; DES-UA-LPME: Deep eutectic liquid-ultrasound assisted-liquid phase microextraction.

***HG-AFS: Hydride generation-atomic fluorescence spectrometry; HG-AAS: Hydride generation-atomic absorption spectrometry; FI-HG-AAS: Flow injection-hydride generation-atomic absorption spectrometry; HG-ICP-MS: Hydride generation-inductive coupled plasma mass spectrometry, ETAAS: Electrothermal atomic absorption spectrometry; ETV-ICP-MS: Electrothermal vaporization-inductively coupled plasma-mass spectrometry; IC-ICP-MS: Ion chromatography- inductively coupled plasma-mass spectrometry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.135335.

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A new pre-concentration procedure based on poly(styrene-co-maleamide and imide) copolymers modified with 2-hydrazinobenzothiazole prior to spectrophotometric monitoring of inorganic as (as As(III)) in edible vegetable oils

By   Gürkan, R (Gurkan, R.) [1] ; Zengin, HB (Zengin, H. B.) [1]

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Abstract   This study describes the development of 2-hydrazinobenzothiazole modified-amide/imide co-polymers for the extraction/pre-concentration of trace As(III), from edible vegetable oils. Their characterization was realized by help of instrumental techniques. The method is based on pH-dependent complexation between As(III) and co-polymeric chelators in presence of 35-fold excess As(V), their selective extraction into the mixed micellar phase, and detected at pH 2.0 and 6.0 by UV-vis

spectrophotometer. The variables affecting extraction efficiency were optimized. From pre-concentration of 20-mL sample, the good linear relationships were obtained in range of 1-40 and 3-75 mu g/L with DLs of 0.32 and 1.00 mu g/L. The accuracy was verified by analysis of a certified sample without and with spiking. The method was applied into the analysis of iAs levels of samples. The results show that the functional co-polymers are efficient chelators, and exhibit great potential for the selective extraction of As(III) from edible vegetable oils.

Keywords	**Author Keywords:** As(III); 2-HBT; poly(MAnh); CTAB; SDS; Edible vegetable oils; Pre - concentration; UV -vis spectrophotometry
	Keywords Plus: CLOUD-POINT EXTRACTION; ARSENIC COMPOUNDS; SOLVENT; METALS; GREEN; WATER; MICROEXTRACTION; SPECTROMETRY; SEPARATION; SPECIATION

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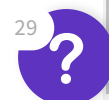**Journal Citation Indicator ™**

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