



Novel amide- and imide-co-polymers modified with sulfathiazole as efficient chelator for selective extraction, pre-concentration and determination of trace inorganic antimony (as Sb(III)) from edible vegetable oils by ultrasound assisted-cloud point extraction coupled to micro-volume UV-spectrophotometry

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ABSTRACT

The study described the synthesis, characterization, and application of newly prepared sulfathiazole-modified amide/imide co-polymers for the extraction of trace Sb(III) from edible vegetable oils. The method was based on the pH-dependent complexation between Sb(III) and chelators as a result of charge transfer via tautomerization in presence of the mixed ionic surfactants in 5%(v/v) 2-propanol, 1:1, v/v) at pH 2.0 and 8.0, respectively for amide and imide copolymers and then selectively ultrasound assisted-cloud point extraction of the Sb(III)-complexes into the micellar phase of extractant. The separated micellar phase by centrifugation was diluted to 0.4 mL with tetrahydrofuran, and detected at 269 nm by micro-volume UV-spectrophotometry. The parameters affecting extraction efficiency were optimized. The optimal extraction conditions were found to be: 0.6/0.8 mmol L⁻¹ of McIlvaine buffer, 30 μmol L⁻¹ of the mixed-ionic surfactant mixture, 120 μmol L⁻¹ KCl, 0.1/0.06% (v/v) of the nonionic surfactant and (0.4/0.2) × 10⁻³%(w/v) of sulfathiazole-modified amide/imide copolymers at pH 2.0 and 8.0 for 7 min at 40 °C in an ultrasonic bath (40 kHz, 300 W). From pre-concentration of 20-mL sample, the good linear relationships ($r^2 \geq 0.995$) between absorbance and Sb(III) concentration were obtained from calibration curves prepared in solvent in range of 1–40 and 1–62.5 μg L⁻¹ with the method detection limits of 0.30/0.47 and 0.51/0.51 μg L⁻¹ at 269 nm by spectrophotometer after 50-fold pre-concentration. The accuracy was statistically verified by analysis of a non-certified sample with and without spiking where the precision and relative recoveries are within 5–12% and 83–92%, respectively. Also, the matrix effect was evaluated by triplicate measurements of 25 μg L⁻¹ Sb(III) (n: 3) under optimal conditions. The method was successfully applied into the analysis of total iSb levels of edible vegetable oils. The results shown that the STZ-modified amide/imide co-polymers were efficient selective chelators even in presence of 50-fold excess Sb(V), and exhibited great potential as alternative binding chelators for the extraction of Sb(III) from edible vegetable oils.

1. Introduction

Antimony (Sb) is a toxic metalloid that is present in the diet at low concentrations (Arnich et al., 2012). The toxicity of Sb depends on its chemical form and oxidation state, and compounds of trivalent Sb (Sb(III), pK_a 11.8) are generally more toxic than pentavalent forms and their organic bound methylation compounds such as trimethylantimony oxide or hydroxide, (CH₃)₃SbO or (CH₃)₃Sb(OH)₂ (Sb(V), pK_a 2.7)

(Sánchez-Martínez et al., 2013). Oral exposure to Sb predominantly affects the gastrointestinal system (Sundar and Chakravarty, 2010). In addition, Sb (as Sb₂O₃), which is used as additive or catalyst in food contact materials and flame retardant in polymeric composites, is an important criterion for the quality of the edible vegetable oils (Westhoff et al., 2008). In fact, Sb in edible oils exists in extremely low concentrations (Cecchi et al., 2009), and due to its toxicity, a specific migration limit (SML) of 40 μg kg⁻¹ food or food simulant, was

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established by European Union (EU) (Commission Regulation EU, 2020). From migration tests performed to assess absorption of Sb from polyethylene terephthalate (PET) foils onto fatty food by Jung et al. (2006), Sb migration was established to be $15.6 \mu\text{g Sb kg}^{-1}$ food by atomic absorption spectrometry (AAS). Its toxicity is strongly dependent on its concentration, including its nature, oxidation step, pH, storage time, temperature in which Sb(III) is 10-fold more toxic than Sb(V). For this reason, monitoring and determination of trace or ultra-trace amounts of inorganic Sb (iSb: Sb(III) plus Sb(V)) in edible oils is important to protect the health of people and prevent environmental contamination.

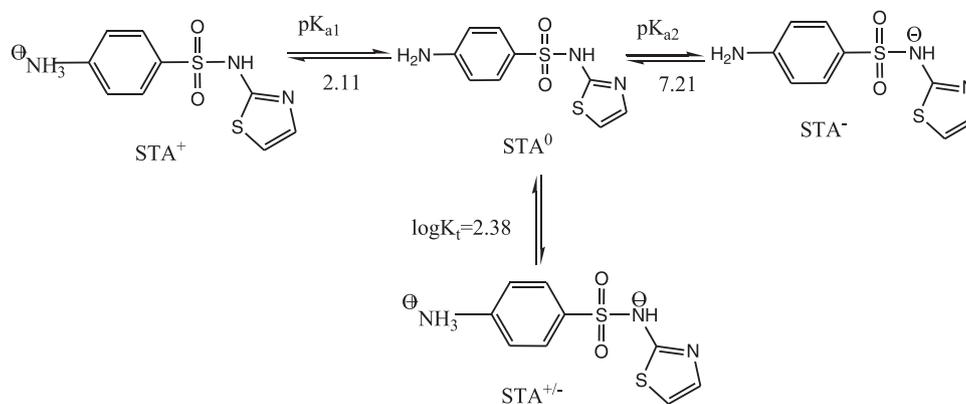
Until today, due to be available in very low concentrations in real samples as well as matrix effect, sensitive, selective but expensive, time-consuming and complex spectrometric techniques like inductively coupled plasma-optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS), online hydride generation- inductively coupled plasma-mass spectrometry (HG-ICP-MS), electro thermal-atomic absorption spectrometry (ETAAS), thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS), graphite furnace atomic absorption spectrometry (GFAAS), flow injection-electrothermal vaporization-inductively coupled plasma-atomic emission spectrometry (FI-ETV-ICP-AES), hydride generation-atomic absorption spectrometry (HG-AAS), hydride generation-atomic fluorescence spectrometry (HG-AFS), and total reflection-X ray fluorescence (TR-XRF) (Biata et al., 2017; Altunay et al., 2016; Altunay and Gürkan, 2015; Fornieles et al., 2013; Biata et al., 2019; Fan, 2005; Rivas et al., 2009; Eftekhari et al., 2015; Zeng et al., 2011; Huang et al., 2018; Yingjie et al., 2006; Gürkan and Eser, 2016; Altunay and Gürkan, 2016; Jiang et al., 2009; Marguí et al., 2013; Zhang et al., 2016; Altunay and Gürkan, 2015), including further detection techniques (HG-AFS, ICP-OES, and ICP-MS) hyphenated with liquid chromatography (LC) (de Gregori et al., 2007; Moreno-Andrade et al., 2020; Muller et al., 2009; Zheng et al., 2001) generally needing expert user in his or her area, have been used for the analysis of i-/o-Sb species in real sample matrices with and without 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. Moreover, detection techniques based molecular absorption and fluorescence may be more appropriate for food-sample analysis to avoid possible spectral or polyatomic interferences, which can appear in plasma techniques. Although the above-mentioned detection techniques 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 and metalloids are one of the most important issues of chemical analysis. Recently, UV-vis spectrophotometry in combination with off-line/on-line pre-concentration has been efficiently used for the determination of low levels iSb species (Samadi-Maybodi and Rezaei, 2012; Frizzarin et al., 2016), because it is an available and inexpensive versatile technique which can be found in most laboratories. However, due to low concentration of heavy metals (Pb, Cd, Hg, Cu, Ni) and metalloids (As, Bi, Sn, Se, including Sb) in different sample matrices, 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/preconcentration step prior to instrumental analysis is a pre-requisite (Anthemidis and Ioannou, 2009; Behbahani et al., 2013a,b,c plus 2015a, 2015b; Zarezaee et al., 2016; Sobhi et al., 2017). 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 ultrasound assisted-ionic liquid-dispersive liquid-liquid microextraction (UA-IL-DLLM) (Biata et al., 2017), flow injection-solid phase extraction (FI-SPE) (Fornieles et al., 2013), cloud point extraction (CPE) (Fan, 2005; Jiang et al., 2009), ultrasound assisted-cloud point extraction (UA-CPE) (Biata et al., 2019; Gürkan and Eser, 2016; Altunay and Gürkan, 2016), dispersive liquid-liquid microextraction (DLLME) (Rivas et al., 2009; Marguí et al., 2013), single drop microextraction (SDME) (Huang et al., 2018), vortex-assisted surfactant-enhanced emulsification microextraction based on solidification of floating organic drop (VASEME-SFOD) (Eftekhari et al., 2015), hollow fiber supported liquid membrane extraction (HF-SLLM) (Zeng et al., 2011), hollow fiber-liquid phase microextraction (HF-LPME) (Marguí et al., 2013), stir cake sorptive extraction (SCSE) (Zhang et al., 2016). Meanwhile, the concern for environmental pollution, food safety 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 (Gatuszka 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 amide-imidic acid, and sulfoamide-sulfoimidine (where the hydrogen atom on sulfonamide and/or heterocyclic thiazole ring 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 iSb species in different matrices. Also, it is implied in literature that the sensitivity, selectivity and adsorption efficiency are greatly improved by use of new polystyrene oleic acid imidazole polymer (Panhwar et al., 2018), nano-pore Sb imprinted polymer (Shakerian et al., 2014), chelating porous hollow-fiber membrane (Nishiyama et al., 2003), polyamide-graphene composite (Sari & Tüzen, 2017), and nano-modified chitosan (Xiong et al., 2020) for the determination and adsorptive removal of low levels Sb(III) and/or Sb(V) (Nishiyama et al., 2003; Sari & Tüzen, 2017; Xiong et al., 2020), including detection of trace Ag^+ ions in mushroom and vegetable samples after selective extraction using amine-functionalized nano-structured amide/imide copolymers (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 and Taheri, 2022). The 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 iSb (as Sb(III) in presence of excess Sb(V)) in especially edible oils.

On this occasion, the newly prepared and characterized sulfathiazole (STZ)-modified poly(styrene-co-maleic anhydride) copolymer matrix, (poly(SMANh)), as the Sb(III) chelating ligand was used in the selective



Scheme 1. The acid-base and tautomerization equilibria of antimicrobial STZ for selective coordination of Sb(III) in presence of 50-fold Sb(V) excessive via pH-dependent ICT.

extraction and pre-concentration of Sb(III) in presence of excess Sb(V) with and without pre-reduction from sample matrix. pH-dependent heterocyclic thiazole compounds, characterized by amine-imine and amide-imidic acid (or sulfamidine-sulfimidine) tautomerization ($-C(=O)-NH-/C(OH)=N-$) resulting from both solvation and intramolecular charge transfer (ICT) before and after modification, have been considered owing to their heterocyclic structure and metal binding properties via fast amine/imine tautomerization, $-SO_2-NH-$, $-SO_2-N=$ groups, and donor S, N-atoms in thiazole ring via pH-dependent protonation/deprotonation for efficient metal or metalloid chelation. It has been clearly implied in literature by authors (Richter et al., 2009) that displacement occurred up to pH 5.4, and exhibited high affinity to carboxylic and phenolic site groups of Leonardite humic acid in pH range of 3.0–8.0 with logK of 3.25 and 8.76 respectively, via donor-acceptor and cation- π interaction, at which < 1% of antimicrobial STZ (pK_{a1,2}: 2.11, 7.20, with tautomeric equilibrium constant of pK_t: 2.38 as ratio of neutral species and zwitterion) in solution was cationic. The pH-dependent tautomeric forms of STZ for possible coordination mechanism of iSb (as Sb(III)) with STZ-modified amide/imide copolymers is indicated in Scheme 1 as follows:

The main objective of the study is to prepare (i) amide and imide copolymers modified with STZ as efficient heterocyclic chelator for iSb (Sb(III) plus Sb(V)), (ii) to use an ultrasound energy as fast and eco-friendly tool in both sample preparation (UAE) and extractive pre-concentration steps (UA-CPE) against interconversion of iSb species with minimal loss, and (iii) to apply pH-dependent selective extraction of iSb (as Sb(III)) from edible oils prior to micro-volume UV-spectrophotometric detection. After optimization of the variables affecting intra-ligand CT sensitive complexation and extraction efficiency and determination of analytical features, the procedure was extended to the determination of trace/ultra-trace levels of iSb in edible oil samples. The method was validated by analysis of a non-certified and three quality control samples with and without spiking.

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) HNO₃ 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/imide copolymers formed by modification with STZ in THF. The Sb(III) stock aqueous solution at 100 mg L⁻¹ was prepared by dissolving a suitable amount of solid Sb₂O₃ with 2.0 mol L⁻¹ HCl and diluting with ultrapure water. The dilute working solutions of Sb(III) of 5 and 25 mg L⁻¹ were

diluted appropriately with 2% HNO₃ /20 mmol L⁻¹ tartaric acid as stabilizer before use. A solution of 5.0% (v/v) non-ionic surfactant, octyl phenol (ethylene glycol) n: 7 or 8 ether (Triton X-114), in water was used as the extractant. Methanol, ethanol, acetonitrile, acetone, THF, acidic methanol and ethanol (1.0 mol L⁻¹ HNO₃) were tested as the diluting agents. The dilute ionic surfactants mixture, cetyltrimethylammonium bromide-sodium dodecyl sulfate (CTAB-SDS) in 5% (v/v) 2-propanol (2 mmol L⁻¹, each one, 1:1, v/v) was prepared by sonication at 35 °C under ultrasonic power to prevent the precipitation via ion-pairing, and used with Triton X-114 to improve the sensitivity of the extraction process. The dilute KCl solution of 2.0 mmol L⁻¹ for salting-out effect was prepared by dissolving a suitable amount of solid KCl salt in water. The McIlvaine buffer solutions (in fact, it can be also used for stabilization of iSb 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⁻¹ Na₂HPO₄ and 98.0 mL of 0.1 mol L⁻¹ citric acid solutions for amide copolymer at pH 2.0 and (ii) 84.0 mL of 0.2 mol L⁻¹ Na₂HPO₄ and 16.0 mL of 0.1 mol L⁻¹ citric acid solutions for imide copolymer at pH 8.0 for 20 µg L⁻¹ Sb(III) in optimization step. A certified reference material (CRM): SRM1577b Bovine liver, 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 containing 2.0% (w/v) triethanolamine (TEA), 0.02 mol L⁻¹ oxalic acid and 1.0% (v/v) Triton X-114 as emulsifier (5:3:2, v/v), a mixture of 0.1 mmol L⁻¹ NH₄HCO₃, 0.02 mol L⁻¹ tartaric acid, and 1.0% (v/v) 2-propanol as emulsifier (2:3:5, v/v) and 1.5% (w/v) ascorbic acid as reductant for analysis of Sb (III) (as equivalents to iSb) were used in the dissolution/extraction of the CRM and edible oils under sonication conditions at 40/50 °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 Sb(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 (400 µL) where the analytical signals were obtained as the corrected absorbance of samples against analyte blank at 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). ¹H- and ¹³C-NMR spectra (in DMSO-d₆, 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 iSb 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 Lab-conco ultrapure water system (Kansas City, USA) was used to obtain ultrapure water to be used in experiments, resulting water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$.

2.3. Synthesis of STZ-modified copolymers

In this study, bulk copolymer of styrene and maleic anhydride monomers (with 1:1 molar mass ratio) with azobisisobutyronitrile (AIBN) initiator in benzene at $70\text{--}80^\circ\text{C}$ were obtained as a bulk copolymer. The obtained poly(SMAnh) copolymer was dried in air. Later, at 1:1 molar mass ratio, poly(SMAnh) copolymer and STZ 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 STZ-modified 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 imidation process based on ring closure was interacted with ethyl alcohol and then, precipitated. The obtained STZ-modified poly(SMIm) copolymer was left for drying after waiting in n-hexane.

2.4. Sampling, sample preparation

As iSb concentration in the samples, including CRM, is very low, even minor contamination at any stage of the sampling, sample storage, and handling or analysis, including interconversion of Sb(III) to Sb(V) or Sb(V) to Sb(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 non-certified sample, SRM1577b Bovine liver. The non-certified value is available for total iSb (Sb(III) plus Sb(V)) with informative value of $3.0 \mu\text{g kg}^{-1}$ for the assessment of the method's accuracy. The solid CRM 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 with slight modification according to those of author groups in literature (de Castro and Priego-Capote, 2007a, 2007b; Priego-Capote and de Castro, 2003) as follows:

Aliquot of (0.3 g) of the non-certified sample was transferred into the centrifuge tubes of 50-mL, and pre-treated by a mixture containing 2.0% (w/v) TEA, 0.02 mol L^{-1} 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 2.0 mL of 1.5%(w/v) ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions. To separate Sb from the matrix, facilitate sample homogenization and finally protect/stabilize against oxidation of Sb(III) to Sb(V) due to their reducing and chelating nature as proton acceptor and donor agents in presence of modifier, STZ and SbO(OH) or Sb(OH)₃ as an electron-donor (Karastogianni and Girousi, 2013; 2014; Li et al., 2017; Eynde et al., 2020; Gladys et al., 2003; Dorđević et al., 2021), the mixture was effectively vortexed for 5 min at 1200 rpm, finally so as to obtain a clear homogenous solution. Without dilution, for Sb(III) and total iSb level (Sb(III) plus Sb(V)), 10-mL of sample extracts buffered to pH 2.0 and 8.0 was analyzed by the method under the optimized reagent conditions with and without spiking.

Before analysis by the matrix-matched calibration curve, based on externally spiking of 1, 5 and $10 \mu\text{g L}^{-1}$ Sb(III) into sample extracts, 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 iSb species, edible oils were submitted to two different ultrasonic soft sample preparation procedures for analysis

of Sb(III) at pH 2.0 and 8.0, 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^{-1} oxalic acid and 1.0% (v/v) Triton X-114 as emulsifier (5:3:2, v/v) 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 (Method 1).
- (ii) 5.0 mL edible oils were pretreated and extracted using 10 mL of a mixture of 0.1 mol L^{-1} NH_4HCO_3 , 0.02 mol L^{-1} tartaric acid, and 1.0% (v/v) 2-propanol as emulsifier (2:3:5, v/v) for 20 min at 50°C in ultrasonic bath (300 W, 40 kHz). Herein, function of each reagent is to form a stable complex of Sb(III) and to maintain Sb(V) in form of Sb(OH)_6^- at pH 8.0 as both a stabilizer and disperser against interconversion with great stability difference, allowing leaching from the liquid oil matrix to the aqueous solution (Method 2).

Thus, the pretreated- and extracted-liquid oil samples were centrifuged for 5 min at 3500 rpm, reduced to Sb(III) using 2.0 mL of 1.5% (w/v) ascorbic acid, buffered to pH 2.0 and 8.0, and 2-fold diluted 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 Official methods of analysis, 2016), can also be used in place of standard addition method, was adopted in the range of $1\text{--}10 \mu\text{g L}^{-1}$ by spiking with known amounts of Sb(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 extracts with and without spiking after dilution of 2-fold, was submitted to pre-concentration by UA-CPE prior to detection by spectrophotometry at 269 nm, respectively.

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 Sb(III) ($20 \mu\text{g L}^{-1}$ in optimization step) in the ranges of $1\text{--}40$ and $1\text{--}62.5 \mu\text{g L}^{-1}$, $0.6/0.8 \text{ mmol L}^{-1}$ of the McIlvaine buffer solution (pH 2.0 and 8.0), $(0.4/0.2) \times 10^{-3}\%$ (w/v) of STZ-modified amide/imide copolymer solutions, $30 \mu\text{mol L}^{-1}$ of SDS-CTAB in 5%(v/v) 2-propanol, $120 \mu\text{mol L}^{-1}$ KCl, and 0.1/0.06% (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 3000 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 (~ 0.2 mL) 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 Sb(III)-complexes' absorbance measurement by micro-volume UV-spectrophotometry at 269 nm against an analyte blank prepared under similar conditions. The iSb levels of edible vegetable oils 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 matrix-matched calibration solutions.

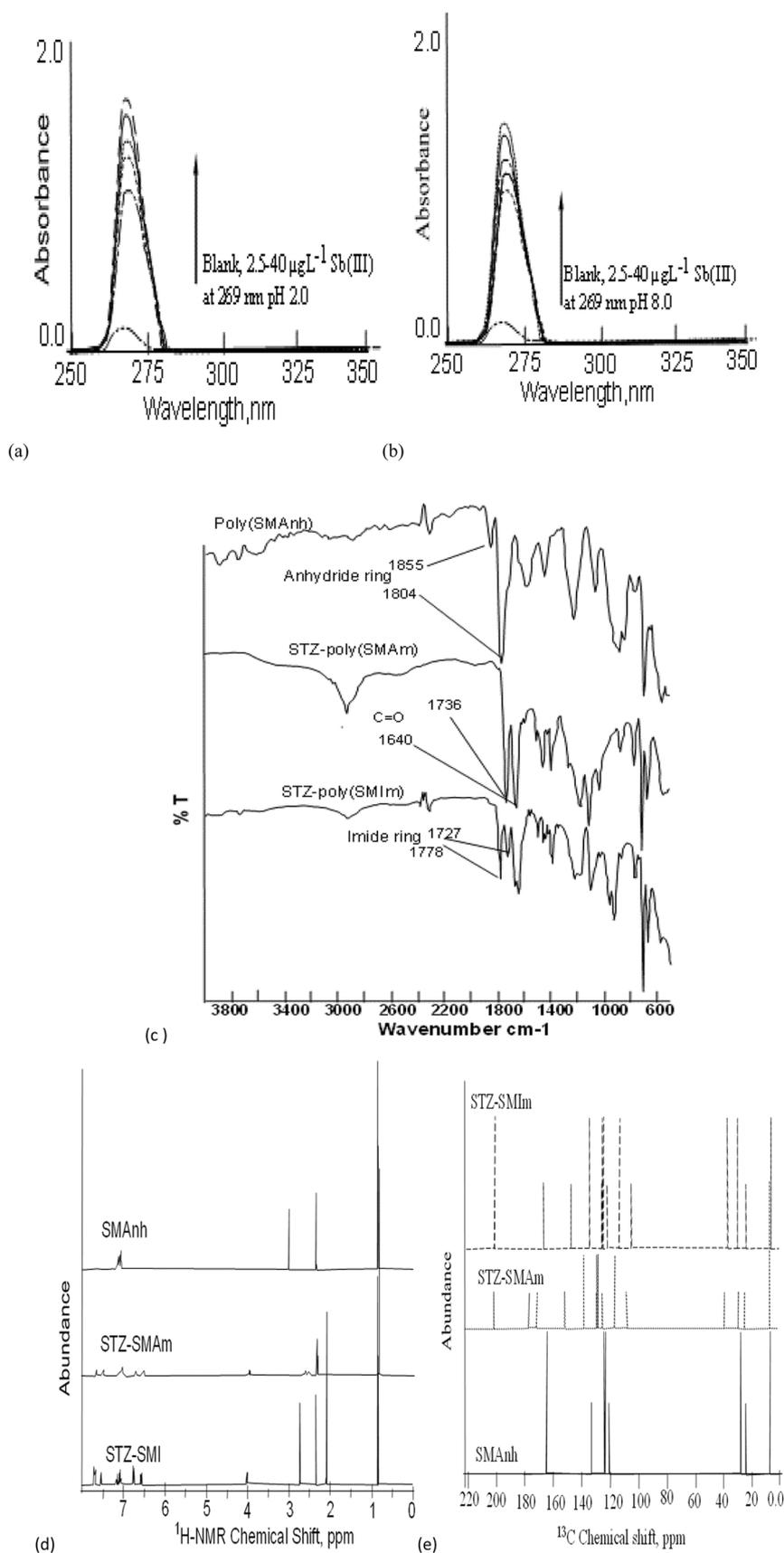


Fig. 1. The spectra of (a, b) UV as a function of increasing Sb(III) concentration in the range of 2.5–40 $\mu\text{g L}^{-1}$ against sample blank at 269 nm (c) ATR-FTIR spectra (d) $^1\text{H-NMR}$ and (e) $^{13}\text{C-NMR}$ of the amide and imide copolymers, poly(SMAm) and poly(SMIm) obtained by modification of poly(SMAnh) copolymer with STZ.

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

3.1. Characterization of the STZ modified amide/imide copolymers by UV, FT-IR, ^1H - and ^{13}C NMR spectra

The initial experiments showed that the stable chelate complex formed by the pH-dependent ICT among reagents and Sb(III) is extracted into the micellar phase of the mixed ionic/nonionic surfactants, CTAB-SDS/Triton X-114. Based on this observation, a UA-CPE procedure was developed for the determination of Sb(III). After complexation and extraction processes based on a pH-induced CT where the absorbance for amide and imide copolymer respectively is selectively a minimum as a result of tautomerization at pH 3.0, and either sharply or gradually increases at lower and higher pHs than 3.0; the absorption spectra of the micellar phase, diluted with THF, showed a maximum band at 269 nm including 238 nm without any blue or red shift in absorption wavelength and a significant change in sensitivity as well as pH difference in terms of selectivity of extraction, which was selected for further absorbance measurements. In fact, this is an indicator of stabilization of sulfoamidine and sulfoimidine formed with change in pH of the mixed micellar media, so as to improve coordination of Sb(III) with STZ. Similarly, it is implied in literature (Goyal et al., 1989) that 50 mmol L^{-1} STZ solution with pK_a values of 2.7 and 7.3 gives pH-dependent UV spectral data: a characteristic peak at 285 nm with a shoulder at 260 nm at $\text{pH} < 3.0$, a shoulder peak appeared at 260 nm in pH range of 3.0–7.5, and finally only one peak at 260 nm at $\text{pH} > 7.5$ –8.0. Also, two new peaks at 225 and 310 nm appeared as a result of CT depending on electrolysis time during electro-oxidation of 0.05 mmol L^{-1} STZ at pH 8.0.

The UV spectra for increasing Sb(III) concentration in range of 2.5–40 $\mu\text{g L}^{-1}$ at pH 2.0 and 8.0, respectively as a function of measurement wavelength under optimized reagent conditions were given in Fig. 1(a, b). As a result of all these observations, the effect of the different variables on extraction efficiency was independently optimized in order to achieve the maximum sensitivity for triplicate measurement of 20 $\mu\text{g L}^{-1}$ Sb(III).

From the IR spectra in Fig. 1(c), which are directly sampled at the ATR mode without the KBr pellet, it has been observed that SMAnh copolymer has the expected anhydride units at 1855 and 1804 cm^{-1} , which belong to symmetric and asymmetric $\text{C}=\text{O}$ stretching vibrations of maleic anhydride (MAnh), respectively. The $\text{C}-\text{O}-\text{C}$ stretching vibrations, from the MAnh ring, were observed at 1025 and 935 cm^{-1} . Instead of the MAnh units, new peaks emerged in the range of 1778–1640 cm^{-1} with characteristic peaks of 1640, 1736 cm^{-1} and 1727, 1778 cm^{-1} which probably corresponds to the maleamic acid and maleimide groups. The results indicate that the maleic anhydride rings in the SMAnh backbone are almost completely opened after modification with STZ in amidation process. It was observed that imide copolymer formed by ring closure as a result of further thermal pretreatment of amide copolymer at 150 $^\circ\text{C}$. The other IR spectral details of the copolymers before and after modification were as follows:

- (i) Without modification, wavenumber (cm^{-1}): 1853.5, 1779.2 (anhydride ring stretching); 1736.0 (carbonyl, $\text{C}=\text{O}$); 1636.7

($\text{C}=\text{C}$, non-aromatic); 1496.01, 1452.4 (ring stretching); 1224.4 ($\text{C}-\text{O}$ stretching); 1081.8, 954.5, 917.9 (phenyl ring stretching) 760.6, 703.4 ($\text{C}-\text{H}$ bending); 580.1, including 3437.6, 3032.5, 2926.8 ($\text{N}-\text{H}$, $\text{O}-\text{H}$ stretching)

- (ii) With modification, wavenumber (cm^{-1}): 3676.1, 3574.3, 3501.6 (sym/asym NH stretching); 1696, 1658 ($-\text{NH}$ or $-\text{N}$ stretching coupled to phenyl ring); 1616.2, 1658.1 (amide/imide $\text{C}(=\text{O})-\text{NH}/\text{C}(=\text{O})\text{N}=\text{stretching}$), 1571.5 (heterocyclic $\text{C}-\text{C}$, $\text{C}-\text{N}$, NH stretching), 1550.4 (in plane phenyl $\text{C}-\text{H}$ stretching), 1519.1 (heterocyclic amide, $\text{C}-\text{N}$ stretching), 1398.5 (in plane $\text{N}-\text{H}$ stretching), 1330, 1140 (sym and asym, $\text{S}=\text{O}$ stretching); 690 (sulfonamide $\text{S}-\text{N}$ stretching); 630 ($\text{C}-\text{S}$ stretching in thiazole ring), including 3437.6, 3032.5, 2926.8 ($\text{N}-\text{H}$, $\text{O}-\text{H}$ stretching)

Also, ^1H NMR and ^{13}C NMR spectra (in $\text{DMSO}-d_6$, single pulse at 400 MHz) in Fig. 1(d, e) confirmed and clearly supported the FT-IR results where new peaks appeared and significant changes and increase in positions of characteristic peaks and their peak intensities became due to increase in ring strain as a result of ring closure in imidation process. The spectral details of the amide, imide copolymers before and after modification were as follows:

- (a) ^1H NMR (relative to δ_{DMSO} : 2.49 ppm),

- (i) Without modification, poly(SMAnh), chemical shift (δ , ppm): 171.7 (C , carboxyl); 138.4, 129.1, 128.7 and 125.8 (CH , benzene); 28.4 (CH_2 , aliphatic); 24.3 (CH_3 , aliphatic); 21.8 (CH_2 , aliphatic, $-\text{C}(=\text{O})-\text{O}$), 6.6 (C , aliphatic)
- (ii) With modification, poly(SMAm), chemical shift (δ , ppm): 202.1 (CH , carbonyl); 177.3 ($\text{C}-\text{C}$, carbonyl); 171.7 (C , 2-thiazole); 151.6, (C , benzene); 138.4 (C , benzene; CH , 2-thiazole); 129.7 and 129.1 (C , CH , benzene); 128.7, 128.1, 125.8 (CH , benzene); 116.6, 108.0 (CH , benzene and 2-thiazole); 38.7 (CH_2 , aliphatic); 28.8 (CH_2 , aliphatic); 24.3 (CH_3 , aliphatic); and 6.6 (CH_3 , aliphatic).
- (iii) With modification, poly(SMIm), chemical shift (δ , ppm): 207.7 (C , carbonyl); 171.7 (C , 2-thiazole); 151.6, (C , benzene); 138.4 (C , benzene; CH , 2-thiazole); 129.7 and 129.1 (C , CH , benzene); 128.7, 128.1, 125.8 (CH , benzene); 116.6, 108.0 (CH , benzene and 2-thiazole); 37.8 (CH_2 , aliphatic); 30.6 (CH_3 , aliphatic); 24.3 (CH_3 , aliphatic); and 6.6 (CH_3 , aliphatic).

- (a) ^{13}C NMR (relative to δ_{DMSO} : 39.5 ppm),

- (i) Without modification, poly(SMAnh), chemical shift (δ , ppm): 171.7 (C , carboxyl); 138.4, 129.1, 128.7 and 125.8 (CH , benzene); 28.4 (CH_2 , aliphatic); 24.3 (CH_3 , aliphatic); 21.8 (CH_2 , aliphatic, $-\text{C}(=\text{O})-\text{O}$), 6.6 (C , aliphatic)
- (ii) With modification, poly(SMAm), chemical shift (δ , ppm): 202.1 (CH , carbonyl); 177.3 ($\text{C}-\text{C}$, carbonyl); 171.7 (C , 2-thiazole); 151.6, (C , benzene); 138.4 (C , benzene; CH , 2-thiazole); 129.7 and 129.1 (C , CH , benzene); 128.7, 128.1, 125.8 (CH , benzene); 116.6, 108.0 (CH , benzene and 2-thiazole); 38.7 (CH_2 , aliphatic); 28.8 (CH_2 , aliphatic); 24.3 (CH_3 , aliphatic); and 6.6 (CH_3 , aliphatic).
- (iii) With modification, poly(SMIm), chemical shift (δ , ppm): 207.7 (C , carbonyl); 171.7 (C , 2-thiazole); 151.6, (C , benzene); 138.4 (C , benzene; CH , 2-thiazole); 129.7 and 129.1 (C , CH , benzene); 128.7, 128.1, 125.8 (CH , benzene); 116.6, 108.0 (CH , benzene and 2-thiazole); 37.8 (CH_2 , aliphatic); 30.6 (CH_3 , aliphatic); 24.3 (CH_3 , aliphatic); and 6.6 (CH_3 , aliphatic).

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-

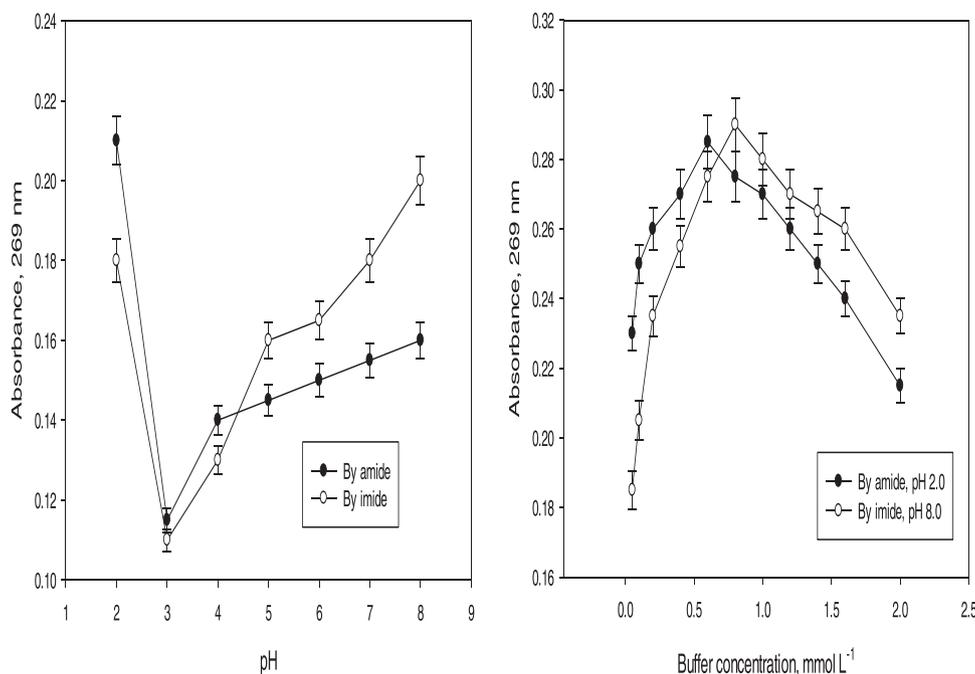


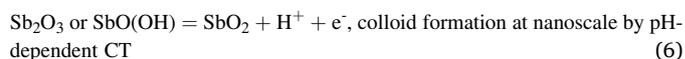
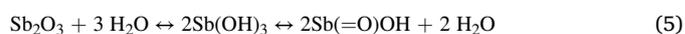
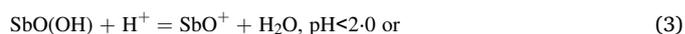
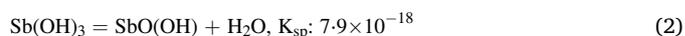
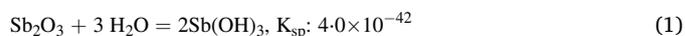
Fig. 2. Effect of (a) pH and (b) buffer concentration on absorbance at 269 nm as a measure of the sensitivity for measurement of 20 µg L⁻¹ Sb(III) for amide/imide copolymer, respectively.

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 Sb(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 iSb from sample matrix for the formation of a stable complex. In order to achieve the maximum sensitivity for quantitative extraction of 20 µg L⁻¹ Sb(III) by amide and imide copolymer, the effect of pH on the sensitivity was studied in Fig. 2(a). The effect of pH on the complex formation was studied in a range of 2.0–8.0 suitable for pH dependent condensation based coordination with the chelator, due to be uncharged neutral weak Lewis acid-base molecule with a pair of unpaired electrons (:Sb(OH)₃) where Sb(V) is predominantly in form of ionized Sb(OH)₆ in this pH range in terms of chelation. For both STZ modified-amide and imide copolymer matrix, in pH 3.0, the sensitivity was minimal at pH 3.0, with absorption increasing sharply or gradually at lower and higher pHs at 269 nm. This may be a proof that two pH-dependent tautomeric forms of the ligand exist in equilibrium. In fact, it is implied in literature (Richter et al., 2009; Goyal et al., 1989) that free STZ can exist in cationic, neutral and anionic forms depending on pH, and even shows a micro-scale tautomerization equilibrium in the zwitterion structure. It is clear that this minimal/maximal change in sensitivity may be due to tautomerization of STZ-modified chelating matrix by pH-dependent ICT among reagents and Sb(III) in micellar environment. At lower or higher pHs (<3.0 or >3.0), according to hard-soft acid-base principle, Sb(III) being a toxic borderline metalloid in form of Sb(OH) or Sb(OH)₃ with pK_a value of 11.8 can be available in ionic forms of SbO⁺ or Sb(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 Sb(III) for binding sites on the amide or imide carbonyl (C=O), ionizable sulfonamide or sulfonimide (-SO₂-NH- or -SO₂-N=) and heterocyclic thiazole donor N- and S-atoms (as hard and soft Lewis bases) on the surface of the copolymer matrix. Once these groups were protonated, for both copolymer, the strong ion-dipole interaction increased contacting Sb(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 Sb(OH)₃ into SbOOH (around pH 2.0), so as to facilitate or accelerate CT sensitive complexation. At lower or higher pHs (<3.0 or >3.0), the surface of copolymer matrix can both positively and negatively be charged due to its protonation or deprotonation of sulfonamide moiety as well as thiazole moiety where sulfonamide H-atom is intramolecularly exchanged. Also, when considered the very small amount of Sb(III) (~1 µmol L⁻¹) in equilibrium and the low solubility of Sb₂O₃ (3.3 mg L⁻¹) and solubility product constants (K_{sp}) values of 7.9 × 10⁻¹⁸ for SbO(OH) and 4.0 × 10⁻⁴² for Sb(OH)₃ when complexing with STZ (Rahman et al., 2021), it can be concluded as a support that theoretical pH of 2.90 approximately equals to experimental pH corresponding to the tautomerization point in this study.



For nanoscale detection of trace Sb(III), complex formation based on pH-dependent CT is also overlapped and supported by findings of two author groups (Chin et al., 2011; Ye et al., 2006) that Sb₂O₃ NPs with particle size ranges 2–12 nm and spherical in shape particles with UV-spectral details in wavelength range of 280–310 nm (with characteristic peaks of 280–285 nm with a sharp shoulder peak around 240 nm, including 260 nm) are obtained depending on [N₂H₅OH]/[Sb³⁺] and [NaOH]/[Sb³⁺] ratio in presence of hydrazine and CTAB as reductant and stabilizer or micellar enhancer around its CMC, so as to form ion-pair, [CTA⁺][Sb(OH)₄] in different geometric structures with charge neutralization at pH ≥ 5.0, respectively while the Sb₂O₃ NPs with a characteristic wavelength of 260 nm in presence of PVA as stabilizer is successfully synthesized and combined with polyaniline (PANI)/acid functionalized single-walled carbon nanotubes

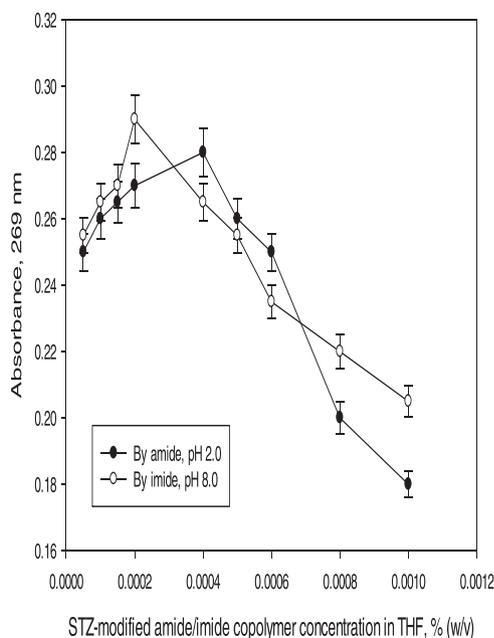


Fig. 3. Effect of STZ-modified amide/imide copolymer concentration, % (w/v) in THF on absorbance at 269 nm as a measure of the sensitivity for measurement of $20 \mu\text{g L}^{-1}$ Sb(III) at pH 2.0 and 8.0, respectively.

(SWCNTs) used as a nanoscale catalyst in detection of organochlorine pesticide, lindane (Masibi et al., 2018).

Clearly, it can be seen in Fig. 2(a) that amide copolymer gives maximum sensitive at acidic pHs, <pH 3.0 while imide copolymer gives maximum sensitivity at pH 8.0. Therefore, a pH of 2.0 and 8.0 for Sb(III) was selected as optimal for the further studies. In the selected pHs, it is thought that Sb(III) has effectively participated in coordination via ionizable sulfonamide/sulfonimide and thiazole donor S- and N-atom groups in presence of the mixed SDS-CTABr as both sensitivity enhancer and charge compensator for ionizable end groups that cannot participate

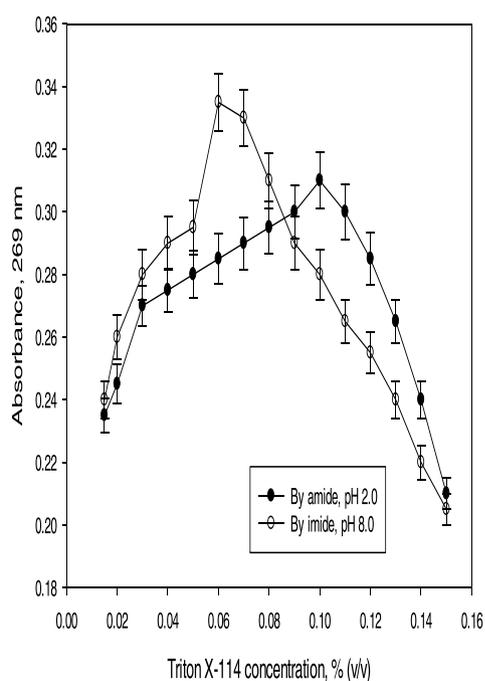
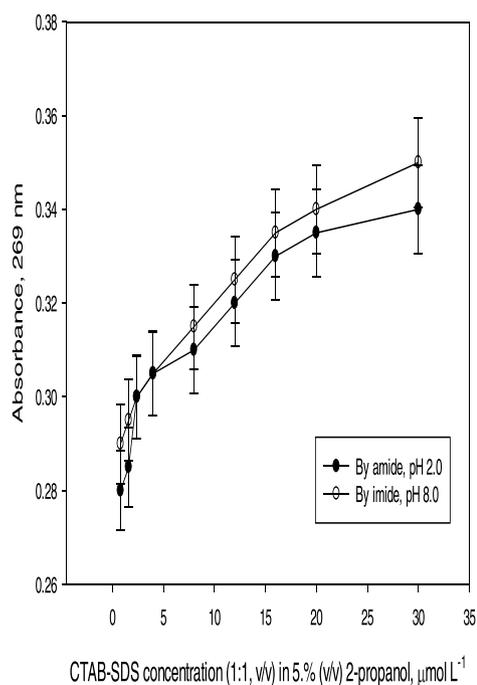


Fig. 4. Effect of (a) CTAB-SDS concentration, $\mu\text{mol L}^{-1}$ in 5.0% (v/v) 2-propanol (1:1, v/v) (b) 5.0% (v/v) Triton X-114 concentration on absorbance at 269 nm as a measure of the sensitivity for measurement of $20 \mu\text{g L}^{-1}$ Sb(III) for amide/imide copolymer at pH 2.0 and 8.0, respectively.

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 donor N- and S-containing ligand of lower basicity (pK_a 2.5, thiazole moiety as functional group) and citrate ($\text{pK}_{a1,2,3}$: 3.13, 4.76 and 6.40) with a $\log\beta$ of 4.6 for $\text{Sb}(\text{OH})_2(\text{HCitr})^{2-}$ as stabilizer in micellar environment can also protect Sb(III) against oxidation via complexation by chelation (Hu and He, 2017). In order to control the pH during the analytical procedure, it was adjusted to 2.0 and 8.0 for Sb(III) with a McIlvaine buffer solution.

Also, the effect of buffer concentration on the sensitivity was studied in range of $0.05\text{--}2 \text{ mmol L}^{-1}$. From the results in Fig. 2(b), it can be seen that the best sensitivity was observed in a buffer concentration of 0.6/0.8 mmol L^{-1} for Sb(III) at pH 2.0 and 8.0, respectively. At lower and higher buffer concentrations, the sensitivity was gradually decreased. Therefore, buffer concentrations of 0.6/0.8 mmol L^{-1} were concluded to enough as optimal for further studies.

3.2.2. Effect of STZ-modified amide/imide copolymers

In fact, STZ as modifier for chelation of Sb(III) is a poor ligand due to the withdrawal of the electron density from N-atom onto the electronegative O-atoms; i.e., sulfonamide N-atom tends a dissociable hydrogen atom, which increases its acidity (deprotonation) and efficacy as donor ligands. In this respect, it is clear that Sb(III) will act as a base by cation- π interaction at low pHs and chelation at high pHs for a pH-dependent chelation. The effect of the quantity of STZ-modified amide/imide copolymers on the sensitivity was studied in Fig. 3. To study this effect, the concentration of the copolymer matrix as effective chelator was tested in range of $(0.05\text{--}1) \times 10^{-3}\%$ (w/v). In range of $0.05\text{--}0.4/0.2) \times 10^{-3}\%$ (w/v), the sensitivity was reached to a maximum with concentration of $(0.4/0.2) \times 10^{-3}\%$ (w/v) for $20 \mu\text{g L}^{-1}$ Sb(III) at pH 2.0 and 8.0, respectively. At lower and higher concentrations, the sensitivity was gradually decreased. Thus, for further studies, $(0.4/0.2) \times 10^{-3}\%$ (w/v) of amide and imide polymeric chelator were adopted as optimal.

3.2.3. Effect of ionic and nonionic surfactants

In UA-CPE, choosing an appropriate surfactant is important, since the temperature corresponding to cloud point is correlated with the

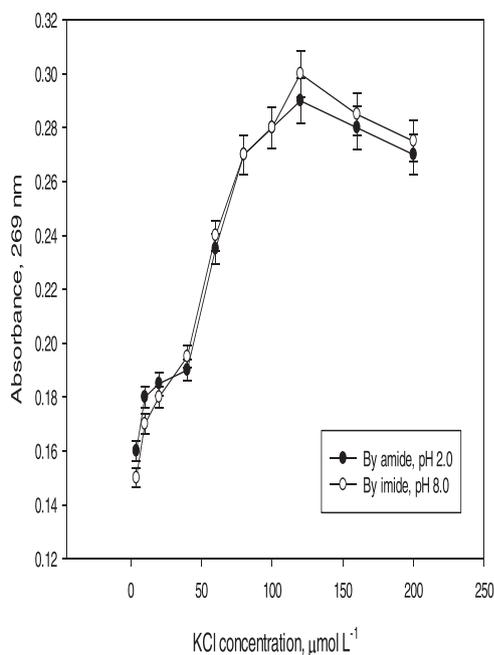


Fig. 5. Effect of KCl concentration, $\mu\text{mol L}^{-1}$ on absorbance at 269 nm as a measure of the sensitivity for measurement of $20 \mu\text{g L}^{-1}$ Sb(III) for amide/imide copolymer at pH 2.0 and 8.0, respectively.

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 CTAB-SDS concentration in 5% (v/v) 2-propanol on the sensitivity was studied in range of $0.8\text{--}30 \mu\text{mol L}^{-1}$ in Fig. 4(a). The sensitivity for both amide and imide copolymer linearly increased with difference in slope in range of $0.8\text{--}30 \mu\text{mol L}^{-1}$, and then reached almost a maximum in range of $20\text{--}30 \mu\text{mol L}^{-1}$. It is thought that this difference in slope as a measure of sensitivity resulted from either pH-dependent solubilization and charge neutralization capability or pH-controlled size/shape of each surfactant around their critical

micelle concentration (CMC) in micellar and/or premicellar region when considered ionizable --COOH group not participating into the chelation on surface sites of amide copolymer (Patel et al., 2014). This difference can be also due to pH-dependent zwitter-ionic structure of STZ (pK_a: 2.38) used as modifier for selective extraction of Sb(III) as a consequence of CT-sensitive sulfoamidine-sulfoimidine tautomerization. For all these reasons, in this study, instead of only SDS or CTAB for charge neutralization and micellar enhancement as counter-ion, their mixtures at low concentrations were preferably used to provide improvement in extraction efficiency (Tah et al., 2011; Kumar and Shyamala, 2019). This clearly 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 $30 \mu\text{mol L}^{-1}$ for Sb(III) 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. 4(b), UA-CPE of Sb(III) at pH 2.0 and 8.0 was carried out in range of 0.015–0.15% (v/v) Triton X-114. The sensitivity for amide copolymer increased with increasing concentration from 0.015% to 0.1% (v/v), and reached a maximum at a concentration of 0.1% (v/v) while it increased with increasing volume from 0.015% to 0.06% (v/v) for imide copolymer, and reached a maximum at a concentration of 0.06% (v/v). However, at higher concentrations than 0.06 or 0.1% (v/v), the sensitivity was gradually decreased with slope difference. This indicates that the quantity of Triton X-114 is enough for the chelates extracted absolutely to ensure completeness of the extraction and improve the sensitivity. Thus, a Triton X-114 concentrations of 0.1% and 0.06% (v/v) were 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 and 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.

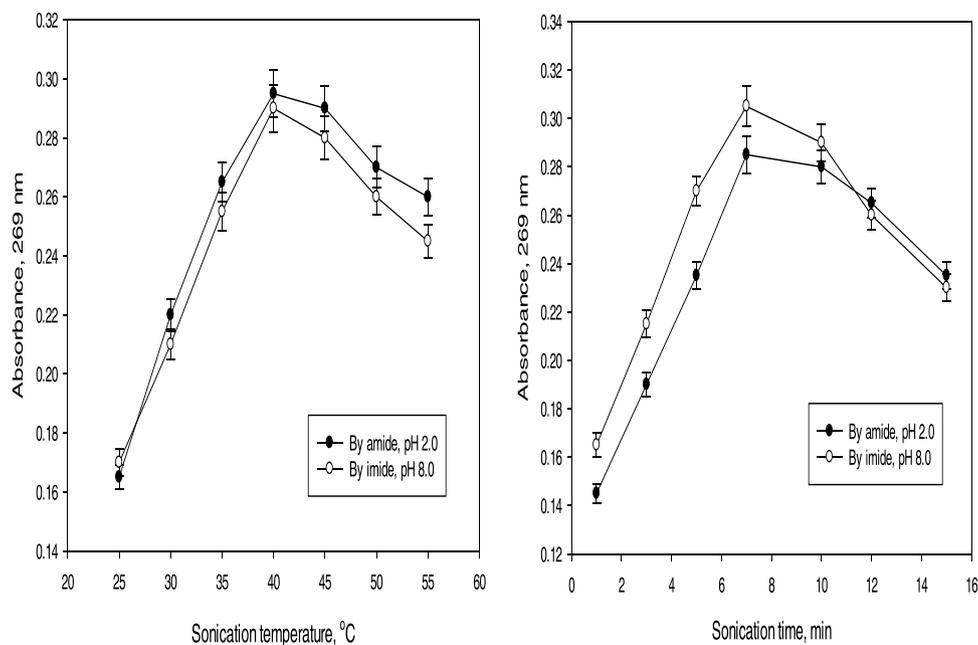


Fig. 6. Effect of (a) sonication temperature, °C and (b) sonication time, min on absorbance at 269 nm as a measure of the sensitivity for measurement of $20 \mu\text{g L}^{-1}$ Sb(III) for amide/imide copolymer at pH 2.0 and 8.0, respectively.

Table 1

Analytical figures of merit of the method for CT-sensitive detection of trace Sb(III) by UV-spectrophotometry at pH 2.0 and 8.0 respectively, due to tautomerisation of amide/imide copolymers under optimal reagent conditions.

Analyte	Calibration type	From regression analysis by UV-spectrophotometry at 269 nm				^a MDLs, $\mu\text{g L}^{-1}$	^a MQLs, $\mu\text{g L}^{-1}$	Precision		Accuracy
		Linear range, $\mu\text{g L}^{-1}$	Slope \pm SD	Intercept \pm SD	Determination coefficient, r^2			Repeatability (as RSD, % for same day, 5, 15 and 30 $\mu\text{g L}^{-1}$, n: 5)	Intermediate precision (as RSD _R % for three consecutive days, 5, 15 and 30 $\mu\text{g L}^{-1}$, n: 5)	
For Sb(III) with STZ modified amide and imide copolymers at pH 2.0	By the calibration curve in solvent	1–40	(8.88 \pm 0.60) $\times 10^{-3}$	(1.83 \pm 0.09) $\times 10^{-2}$	0.9956	0.30	1.01	3.0–4.3	4.7–6.0	92.0–95.5
		1–40	(7.61 \pm 0.60) $\times 10^{-3}$	(2.13 \pm 0.12) $\times 10^{-2}$	0.9951	0.47	1.58	3.2–4.5	5.0–6.5	91.0–94.0
	*By the matrix-matched calibration curve prepared from blank sample extracts	1–50	(7.70 \pm 0.5) $\times 10^{-3}$	(1.90 \pm 0.10) $\times 10^{-2}$	0.9950	0.39	1.30	3.5–4.7	4.6–6.6	91.0–95.0
For Sb(III) with STZ modified amide and imide copolymer at pH 8.0	By the calibration curve in solvent	1–62.5	(5.33 \pm 0.30) $\times 10^{-3}$	(1.60 \pm 0.09) $\times 10^{-2}$	0.9970	0.51	1.69	3.7–4.5	4.5–6.0	92.5–96.5
		1–62.5	(4.68 \pm 0.25) $\times 10^{-3}$	(1.43 \pm 0.08) $\times 10^{-2}$	0.9961	0.51	1.71	3.5–4.5	4.2–5.8	92.0–95.3
	*By the matrix-matched calibration curve prepared from blank sample extracts	1–62.5	(5.10 \pm 0.25) $\times 10^{-3}$	(1.56 \pm 0.09) $\times 10^{-2}$	0.9954	0.53	1.76	3.2–4.5	4.2–6.1	92.5–95.0
^b Matrix effect, %		-13.3, + 1.18% at pH 2.0; - 4.32, + 8.97% at pH 8.0								
^c Sensitivity enhancement factor (EF)		27.8, 24.1 at pH 2.0; 16.7, 14.6 at pH 8.0								
^d Preconcentration factor (PF)		50								

*Based on externally spiking into the blank sample extracts at concentration levels of 1.0, 5.0, 15, 25, 50, 75 and 100 $\mu\text{g L}^{-1}$ of Sb(III) before analysis

^a Method detection and quantification limits (MDLs, MQLs) for Sb(III) were determined according to the expressions at $3.0 \times s_{\text{blank}}/m$ and $10 \times s_{\text{blank}}/m$, respectively (where s_{blank} is the standard deviation of twelve 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, $\text{ME}\% = (m_{\text{matrix-matched}} - m_{\text{solvent}} / m_{\text{solvent}}) \times 100$

^c Ratio of slopes of the calibration curves established with and without preconcentration where the regression equation for Sb(III) is $A: 3.20 \times 10^{-4} C (\mu\text{g L}^{-1}) + 0.0118$, $r^2: 0.998$ with limits of detection and quantification of 4.78, 15.9 $\mu\text{g L}^{-1}$ in linear range of 15–300 $\mu\text{g L}^{-1}$

^d Ratio of the bulk aqueous sample solution volume (20 mL) to that of the diluted surfactant-rich phase (0.4 mL)

Based on this discussion, the salting-out effect was studied in the range of 4–200 mmol L^{-1} KCl at 40 °C in Fig. 5. It was found that KCl resulted in the maximum sensitivity, and the extraction efficiency increased with increasing KCl volume until reach a maximum at 120 $\mu\text{mol L}^{-1}$. This effect may be due to the enhanced hydrophobic interactions among the surfactant aggregates and chelate complexes of Sb(III) as well as the decrease in the cloud point temperature of Triton X-114 in the presence of KCl. At higher volumes than 300 μL , the sensitivity 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 120 $\mu\text{mol L}^{-1}$ was concluded to be enough for extraction of Sb(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. 6(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 8.0 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. 6(b) were studied at 40 °C, according to the method. As a function of sonication time, the maximum sensitivity was accomplished in a duration of 7 min for both amide and imide copolymer. 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 3000 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 Sb- chelating polymer matrices 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 ($1.0 \text{ mol L}^{-1} \text{ HCl}$) 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 Sb(III) at pH 2.0 and 8.0. 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 ($(\text{CH}_2\text{CH}_2\text{O})_{n:7 \text{ or } 8}$) of extractant, Triton X-144 by hydrogen bonding, even including $\text{SbO}(\text{OH})$ or $\text{Sb}(\text{OH})_3$ as well as sufficient electrostatic attraction to extract the hydrophilic STZ-modified co-polymeric Sb(III)-chelate complex into the mixed micelle rich phase (Temel and Gürkan, 2018). Therefore, to obtain the maximum sensitivity, a serial standard solution containing $0.2 \mu\text{g Sb(III)}$ in range of 5–35 mL was submitted to analysis by UA-CPE/micro-volume UV-spectrophotometry, the dense micellar phase ($\sim 0.2 \text{ mL}$) separated by centrifugation 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 in a quartz cell with micro-capacity ($400 \mu\text{L}$) at 269 nm . By pre-concentration of 20-mL sample, a pre-concentration of 50-fold ($= 20/0.4$) was obtained.

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, 1–62.5 $\mu\text{g L}^{-1}$ Sb(III) for amide/imide copolymer at pH 2.0/8.0, 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 1–62.5 $\mu\text{g L}^{-1}$ with an suppression or enhancement in signal of $-13.3, +1.18\%$; $-4.32, +8.97\%$ for amide/imide copolymer at pH 2.0 and 8.0 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 that the calibration curves in solvent will be reliably able to use in analysis of iSb-contents of edible oils instead of standard addition method for possible matrix effect. The regression equations were $A = (8.88 \pm 0.60) \times 10^{-3} C + (1.83 \pm 0.09) \times 10^{-2}$ and $A = (7.61 \pm 0.60) \times 10^{-3} C + (2.13 \pm 0.12) \times 10^{-2}$ in range of 1–40 $\mu\text{g L}^{-1}$ Sb(III) for amide/imide copolymer at pH 2.0, while they were $A = (5.33 \pm 0.30) \times 10^{-3} C + (1.60 \pm 0.09) \times 10^{-2}$ and $A = (4.68 \pm 0.25) \times 10^{-3} C + (1.43 \pm 0.08) \times 10^{-2}$ in range of 1–62.5 $\mu\text{g L}^{-1}$ Sb(III) at pH 8.0 (where Abs is the absorbance and C is Sb(III) concentration in $\mu\text{g L}^{-1}$), with a determination coefficient (r^2), > 0.995 , which indicates good linearity in the mentioned concentration ranges. The method detection and quantification limits (MDLs, MQLs), based on the ratio of 3 and 10 times the standard deviation of twelve replicates of the sample blank to slope of calibration curves prepared in solvent and sample extracts (as $3.0 \times s_{\text{blank}}/m$ and $10 \times s_{\text{blank}}/m$ for Sb(III), respectively) (Long and Winefordner, 1983) were 0.39, 0.47/0.51 and 1.30, 1.58/1.69, $1.71 \mu\text{g L}^{-1}$. The precision (as RSDs) and accuracy (as the relative recoveries) of the method, determined by analyzing the standard solutions at 5, 15 and $30 \mu\text{g L}^{-1}$ of Sb(III) five times in same day and three consecutive days from calibration curves prepared in solvent, were 3.0–4.7/4.2–6.6% and 91.0–96.5%. When compared with the threshold values (with a $\text{RSD}_r / \text{RSD}_R$ of 22–45, 15–30% and recovery rates of 60–115, 80–110%) recommended by the AOAC Official methods of analysis (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

Table 2a

The matrix effect of potential interfering species on the extraction efficiency of $25 \mu\text{g L}^{-1}$ Sb(III) (n: 3).

Co-existing ions	Tolerance ratio (Interfering / Sb (III))	Recovery \pm SD ^a (%) at pH 2.0	Recovery \pm SD ^a (%) at pH 8.0
NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+}	1500	98.5 ± 2.0	97.5 ± 2.5
CH_3COO^- , HCO_3^- , PO_4^{3-} , NO_3^- , Cl^- , I^- , Br^-	1250	96.0 ± 2.0	97.0 ± 2.0
Fe^{2+} , Zn^{2+}	1000	98.0 ± 3.0	97.0 ± 2.0
Ni^{2+} , Mn^{2+} , Sn^{2+}	750	98.0 ± 2.0	97.1 ± 3.0
V^{4+} , Ag^+	600	95.5 ± 2.5	94.5 ± 2.0
Benzaldehyde	500	96.0 ± 2.5	96.5 ± 2.0
V^{5+} , Fe^{3+} , Cr^{3+} , Pb^{2+}	500	102.5 ± 2.0	101.5 ± 3.0
Phenol	350	93.5 ± 2.0	92.5 ± 2.0
Cd^{2+} , Co^{2+}	250	103.7 ± 2.5	100.5 ± 2.5
CH_3Hg^+ , Hg^{2+}	200, 150	102.1 ± 3.0	98.5 ± 3.0
NO_2	100 (>1000) ^b	91.5 ± 2.0	94.5 ± 2.0
Formaldehyde, acetaldehyde	75 (>500) ^c	92.5 ± 2.0	93.5 ± 3.0
Sb^{5+}	1–50	$(92.5–95.5) \pm 2.5$	$(90.5–92.0) \pm 3.0$

^a The percent recovery rates and their standard deviations obtained from three replicate measurements of $25 \mu\text{g L}^{-1}$ Sb(III) in medium adjusted to pH 2.0 and 8.0 for amide and imide copolymers, respectively by McIlvaine buffer by UV-spectrophotometry

^b Tolerance ratio after removal with dilute sulfamic acid (1.0 mL of 0.02 mol L^{-1}) in acidic media before extraction

^c Tolerance ratio after signal suppression with dilute metabisulfite solution (2.0 mL of 0.02 mol L^{-1}) so as to give to stable anionic bisulfite adduct around pH 5.0 before extraction

27.8, 24.1 at pH 2.0; 16.7, 14.6 at pH 8.0 for Sb(III). From pre-concentration of 20-mL sample, a pre-concentration factor of 50-fold 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 interferences, speciation analysis of iSb (Sb(III) plus Sb(V))

The effects of potential interfering species in Table 2a were tested in tolerance ratio ranging from 1:5–1:1500 by the high selectivity for Sb(III)-ligand complex formation at pH 2.0 and 8.0 by using solutions containing $25 \mu\text{g L}^{-1}$ Sb(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 less than 5.0%. Table 2a 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 Sb(III) in tolerance range of 150–1500-fold, $\text{Cd}^{2+}/\text{Co}^{2+}$ did not interfere at more than a 250-fold excess, $\text{CH}_3\text{Hg}^+/\text{Hg}^{2+}$ did not interfere at more than a 200, 150-fold excess, NO_2 did not interfere up to 100-fold excess, the formaldehyde and acetaldehyde did not disturb determination up to 75-fold excess, and finally Sb^{5+} did not interfere in a range of (1–50)-fold excess, where the recovery rate is in range of 91.5–103.7 and 90.5–101.5% with a precision, $\leq 3.0\%$ from triplicate measurements for extraction of $25 \mu\text{g L}^{-1}$ Sb(III) at pH 2.0 and 8.0, respectively. 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 500- and 1000-fold in tolerance ratio by the use of 1.0 or 2.0 mL of sulfamic acid and metabisulfite solutions (each one, 0.02 mol L^{-1}) as suitable masking agents in acidic medium and citrate medium adjusted to pH 5.0 before pre-concentration by UA-CPE.

The performance and reliability of the method for the applicability to

Table 2b

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

Added, $\mu\text{g L}^{-1}$		^a Found, $\mu\text{g L}^{-1}$			Accuracy/precision of speciation analysis					
Sb (III)	Sb (V)	^b Sb (III)	^c Sb (V)	^d Total iSb	RSD%			Recovery%		
					Sb (III)	Sb (V)	Total iSb	Sb (III)	Sb (V)	Total iSb
0	40	–	36.5 ± 1.5	36.5 ± 1.5	–	4.1	4.1	–	91	91
5	35	4.3 ± 0.2	32.2 ± 1.2	36.5 ± 1.6	4.7	3.7	4.4	86	92	91
10	30	9.0 ± 0.4	28.0 ± 1.0	37.0 ± 1.6	4.4	3.6	4.3	90	93	93
20	20	18.2 ± 0.7	18.8 ± 0.7	37.0 ± 1.6	3.8	3.7	4.3	91	94	93
30	10	27.5 ± 1.0	9.5 ± 0.4	37.0 ± 1.5	3.6	4.2	4.0	92	95	93
35	5	32.5 ± 1.2	4.5 ± 0.2	37.0 ± 1.5	3.7	4.4	4.0	93	90	93
40	0	37.5 ± 1.5	–	38.3 ± 1.7	4.0	–	4.4	94	–	96

^a The mean and standard deviations of five replicate measurements under optimal reagents' conditions

^b The Sb(III) levels found by using 10 mL of a mixture containing 2.0% (w/v) TEA^a, 0.02 mol L⁻¹ 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 Sb losses via interconversion of iSb species around pH 5.0–5.5

^c The Sb(V) levels calculated from difference between Sb(III) and total iSb levels.

^d The total iSb levels (as Sb(III) plus Sb(V)) found by using 10 mL of a mixture containing 2.0% (w/v) TEA^a, 0.02 mol L⁻¹ 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

Table 3a

The intra-day and inter-day accuracy/precision of replicate measurements of Sb(III) in two edible oil samples plus non-certified sample selected for quality control purposes by the developed method under the optimal conditions (n: 3 or 5).

Samples	Spiking level $\mu\text{g L}^{-1}$	Measurement accuracy and precision					
		Intra-day precision (repeatability)			Inter-day precision (reproducibility)		
		Found	Relative recoveries (%)	RSD _r (%)	Found	Relative recoveries (%)	RSD _R (%)
^a Grape vinegar	–	0.70 ± 0.05 *	–	7.1	0.71 ± 0.05	–	7.0
	2.5	2.8 ± 0.2	84.0	7.1	2.8 ± 0.2	84.0	7.1
	5	5.1 ± 0.3	88.0	5.9	5.0 ± 0.3	86.0	6.0
	10	9.7 ± 0.5	90.0	5.2	9.7 ± 0.5	90.0	5.2
Fish oil	–	1.8 ± 0.1	–	5.6	2.1 ± 0.1	–	4.8
	5	6.3 ± 0.3	90.0	4.8	6.6 ± 0.3	90.0	4.5
	15	15.8 ± 0.7	93.0	4.4	15.8 ± 0.7	91.3	4.4
	30	30.4 ± 1.2	95.3	3.9	30.4 ± 1.2	94.3	3.9
Edible salad oil	–	2.1 ± 0.1	–	4.8	2.3 ± 0.1	–	4.7
	5	6.6 ± 0.3	90.0	4.5	6.8 ± 0.3	90.0	4.4
	15	15.7 ± 0.7	91.0	4.4	16.0 ± 0.7	91.0	4.4
	30	30.4 ± 1.2	94.0	3.9	30.5 ± 1.2	94.0	3.9
SRM1577b Bovine liver	–	0.80 ± 0.05 * (2.6 ± 0.2 **)	– (87.0)	6.2 (7.7)	0.76 ± 0.05 * (2.5 ± 0.3 **)	– (83.0)	6.6 (12.0)
	2.5	3.0 ± 0.2 (4.8 ± 0.3)	88.0 (88.0)	6.7 (6.3)	2.9 ± 0.2 (4.7 ± 0.3)	86.0 (88.0)	6.9 (6.4)
	5	5.3 ± 0.3 (7.1 ± 0.4)	90.0 (90.0)	5.7 (5.6)	5.2 ± 0.3 (7.0 ± 0.4)	89.0 (90.0)	5.8 (5.7)
	10	10.0 ± 0.5 (11.8 ± 0.6)	92.0 (92.0)	5.0 (5.1)	9.8 ± 0.5 (11.6 ± 0.6)	90.0 (91.0)	5.1 (5.2)

*The values found by the present method for five replicate measurements (n: 5) without 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⁻¹ 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 2.0 mL of 1.5% (w/v) ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions where the non-certified value for iSb (as Sb(III) and Sb(V) equivalent to total Sb) is 3.0 $\mu\text{g kg}^{-1}$, respectively

* The values found by the present method in parentheses for five replicate measurements (n: 5) without 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⁻¹ 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 2.0 mL of 1.5% (w/v) ascorbic acid as reductant under ultrasound power (300 W, 40 kHz) under optimal reagents' conditions where the non-certified value for iSb (as Sb(III) plus Sb(V) equivalent to total Sb) is 3.0 $\mu\text{g kg}^{-1}$.

^a Where it may be accepted as a food simulant, it is grape vinegar with an acidity of 4.5% and a shelf life of 6 months, containing E-223 (bisulfite) as a food additive against microbial degradation.

analysis of real samples were checked by speciation analysis of Sb(III), Sb(V), and total iSb contents in binary mixtures. In order to determine Sb(III), Sb(V) and total iSb using a mixture containing 2.0% (w/v) TEA, 0.02 mol L⁻¹ 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 Sb losses via interconversion of iSb species around pH 5.0–5.5 before and after pre-reduction using 2.0 mL of 1.5% (w/v) ascorbic acid (n: 5), model solutions that contain different amounts of Sb(III) and Sb(V) with ratios of 1:1, 1:3 and 1:7 (or 1:1, 3:1 and 7:1) as equivalent to total iSb level of 40 $\mu\text{g L}^{-1}$ were prepared. Then, the Sb(III), Sb(V) and total iSb levels

with and without reduction in the test solutions was performed by the procedure explained. The results show that the proposed method with RSDs of 3.6–4.7, 3.6–4.4, 4.0–4.4% and recovery rates of 86–94, 90–95, 91–96% for Sb(III), Sb(V) and total iSb, respectively could be successfully applied to the speciation analysis of iSb in [Table 2b](#).

3.5. Application of the method to edible vegetable oils

At initial, the method was validated by analysis of a non-certified sample (SRM1577b Bovine liver) for free Sb(III) and total Sb content and three quality control samples, including a food simulant, in terms of iSb (Sb(III) and Sb(V)) contents in [Table 3a](#). It was observed that there is

Table 3b

The replicate analysis results of trace Sb(III) (as equivalents to total Sb) in edible vegetable oils by the matrix-matched calibration curves after pre-reduction and preconcentration by UA-CPE (n: 5).

Sample matrix	Added, $\mu\text{g L}^{-1}$	By the matrix-matched calibration curve based on externally spiking of 1, 5 and 10 $\mu\text{g L}^{-1}$ Sb (III) into sample extracts before analysis						^a The two-sample t-test	^b The variance ratio test
		Method 1 ^c			Method 2				
		^d Found, $\mu\text{g L}^{-1}$	RSD _r , %	Relative recoveries%	^d Found, $\mu\text{g L}^{-1}$	RSD _r , %	Relative recoveries%		
Peanut oil	-	3.7 ± 0.2	5.3, 5.5	-	3.9 ± 0.2	5.8, 6.1	-	0.30	1.21
	5	8.2 ± 0.4	4.9, 5.2	90	8.5 ± 0.4	4.7, 5.0	92		
Soybean oil	-	3.5 ± 0.2	5.7, 6.0	-	3.7 ± 0.2	5.4, 5.7	-	0.45	1.00
	5	8.0 ± 0.4	5.0, 5.1	90	8.3 ± 0.4	4.8, 5.0	92		
Sunflower oil	-	7.1 ± 0.4	5.6, 5.8	-	7.4 ± 0.4	5.4, 6.0	-	1.58	1.00
	5	11.7 ± 0.5	4.3, 4.7	92	12.0 ± 0.5	4.2, 4.7	92		
Fish oil	-	1.8 ± 0.1	5.6, 6.1	-	2.0 ± 0.1	5.0, 5.5	-	1.86	1.00
	5	6.5 ± 0.3	4.7, 5.2	94	6.7 ± 0.3	4.5, 5.1	94		
Mixed frying oils	-	2.2 ± 0.1	4.5, 4.8	-	2.5 ± 0.1	4.0, 5.1	-	0.79	1.00
	5	6.8 ± 0.3	4.4, 4.7	92	7.1 ± 0.3	4.2, 5.3	92		
Sesame oil	-	3.5 ± 0.2	5.7, 6.1	-	3.7 ± 0.2	5.4, 6.0	-	1.43	1.56
	5	8.2 ± 0.4	4.9, 5.3	94	8.5 ± 0.4	4.7, 5.3	96		
Edible salad oil	-	2.3 ± 0.1	4.3, 4.8	-	2.5 ± 0.1	4.4, 5.1	-	1.58	1.00
	5	7.0 ± 0.3	4.3, 4.5	94	7.3 ± 0.3	4.1, 4.6	96		
Riviera olive oil	-	5.7 ± 0.3	5.3, 5.6	-	5.8 ± 0.8	5.1, 5.8	-	0.21	1.31
	5	10.1 ± 0.5	5.0, 5.3	88	10.3 ± 0.5	4.8, 5.5	90		
Virgin olive oil	-	5.1 ± 0.3	5.9, 6.2	-	5.3 ± 0.3	5.7, 6.1	-	0.49	1.36
	5	9.6 ± 0.5	5.2, 5.5	90	10.0 ± 0.5	5.0, 5.5	94		

^a 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

^b 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 ($F_{4,4} = s_1^2/s_2^2$).

^c Herein, due to its property to act as an emulsifier or co-surfactant, TEA was primarily used to neutralize fatty acids, and facilitate hydrolysis and dissolution of oils and other ingredients such as phenolics that are not completely soluble in water, thus accelerating their removal from the matrix as well as adjusting the pH in presence of oxalic acid

^d The means plus standard deviations of five replicate measurements by the present method after 2-fold dilution of the pretreated-, extracted- and reduced-edible oil samples using 2.0 mL of 1.5%(w/v) ascorbic acid

not statistically a significant difference between the iSb results found by the present method and the non-certified value without dilution after sample preparation step, pre-reduction with ascorbic acid, extraction and analysis using a mixture containing 2.0% (w/v) TEA, 0.02 mol L⁻¹ Oxalic acid and 1.0% (v/v) Triton X-114 as emulsifier (5:3:2, v/v) for 12 min at 40 °C where the recovery rate is 87% and 83% with an intra-day and inter-day precision of 7.7% and 12% (as RSD_r, %). Also, after spiking with 2.5, 5 and 10 $\mu\text{g L}^{-1}$ for Sb(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 Official methods of analysis (2016), the method in terms of accuracy and precision was reliable, and it was observed that the results obtained for control of the possible matrix effect could quantitatively be accepted with the RSDs of 5.0–7.7% and 5.1–12%, and the relative recoveries of 87–92% and 83–91% in terms of free Sb(III) and total iSb contents (Sb(III) plus Sb(V)). 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 Sb(III) to Sb(V) or Sb(V) to Sb(III), in terms of total iSb contents of no-certified sample (in fact, with and without pre-reduction). It can be seen that the major species is predominantly Sb(V) when it is considered the difference between free Sb(III) and total iSb contents of non-certified sample.

After the method validation, the analysis of edible oil samples was performed in Table 3b. To control the matrix effect, the matrix-matched calibration curve based on externally spiking of 1, 5 and 10 $\mu\text{g L}^{-1}$ Sb (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⁻¹ 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 effect (300 W, 40 kHz) (Method 1) and (ii) with 10 mL of a mixture of 0.1 mol L⁻¹ NH₄HCO₃, 0.02 mol L⁻¹ tartaric acid, and 1.0%

(v/v) 2-propanol as emulsifier (2:3:5, v/v) for 20 min at 50 °C under ultrasonic power (300 W, 40 kHz) (Method 2) was adopted, reduced to Sb(III) using 2.0 mL of 1.5%(w/v) ascorbic acid and applied to the analysis of samples after dilution of 2-fold. Also, the spiking at levels of 5 $\mu\text{g L}^{-1}$ was made into each sample matrix, and their relative recoveries were established for five replicate measurements before and after pre-reduction and preconcentration by UA-CPE. The two-sample t-test was used to evaluate the changes/differences in relative recoveries between two sample preparation procedures, performing edible oils analysis where the recovery must be in range of 70–120% for accepted range. In terms of accuracy and precision of total Sb-contents of samples via matrix-matched calibration after reducing with ascorbic acid, 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 with lower experimental t- and F-values (0.21–1.86 and 1.00–1.56 respectively) than the critical t- and F-values of 2.31 and 6.39 for degree of freedom of 8 and 4 at 95% confidence level, according to the two paired Student's t-test and variance ratio test. The relative recoveries for analysis of the spiked real samples were in the acceptable range of 88–96% with lower intra-day and inter-day precisions than 5.7% and 6.2% (as RSD_r, %). When a safe limit of 6 or 5 $\mu\text{g L}^{-1}$ for drinking water and/or a specific migration limit (SML) of 40 $\mu\text{g kg}^{-1}$ for plastic materials intended to come into contact with food established by European Commission (EC) (European Commission, 2003, 2005) is considered, it is clear that the results comparably found by two sample preparation methods (Method 1 and Method 2) will not pose to a serious risk on human health, except for sunflower oil sample, where the iSb contents of edible oils after 2-fold dilution are in range of 1.8–7.1 and 2.0–7.4 $\mu\text{g L}^{-1}$, respectively. 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 (<5 or 6 μL^{-1}) exposure levels in the short and long run. In fact, when considered aliquots (5.0, 5.0 mL) of sample

Table 4
Comparison of the method with other reported methods on selective extraction, preconcentration and determination of Sb in different sample matrices.

Analyte	Sample matrix	*Chelating agent	**Detection technique	**Pre-concentration procedure	Linear range, $\mu\text{g L}^{-1}$	MDLs, $\mu\text{g L}^{-1}$	MQLs, $\mu\text{g L}^{-1}$	PF (or EF)	RDs%	Recovery%	References
Sb(III)	Beverages	Aliquat 336/butylacetate in ligandless medium	ICP-OES	UA-IL-DLLM/ optimization with CCD	0.0025–250	0.0012	0.0025	250	2.1–2.5	99–100.4	Biata et al., 2017
Sb(III)	Food/beverages	Morin/CTAB	FAAS	UA-CPE/	0.1–140	0.03	0.1	114.5	2.3–5.2	98–104	Altunay et al., 2016
Sb(III)	Beverage and milk products	Azomethin-H/CPC	FAAS	CPE	0.5–180	0.15	0.51	40 (85)	2.1–3.8	98–103	Altunay and Gürkan, 2015
Sb(III)	Certified natural waters, seawater	Silica gel functionalized with 1,5-bis (di-2-pyridyl) methylene thiocarbonohydrazide	Online HG-ICP-MS	FI-SPE	0.5–1.5	0.011	0.037	7	1.4	97–107.5	Fornieles et al., 2013
Sb(III)	Tap water, bottled mineral water, vegetables samples	1-(2-pyridylazo)– 2-naphthol (PAN)/SDS	ICP-OES	UA-CPE/ optimization with RSM	0.027–650	0.008	0.027	150 (77.3)	1.8–4.1,3.4–5.5	99.3–101	Biata et al., 2019
Sb(III)	Artificial seawater, wastewater	BPHA/Triton X-114	FAAS	CPE	–	1.82	6.1	-(45)	2.6	95.3–106	Fan, 2005
Sb(III)	Waters	APDC/ CCl_4	ETAAS	DLLM ^a	0.05–5	0.05		115	2.9–4.5	–	Rivas et al., 2009
Sb(III), Sb(V)	Different water samples	Dithizone/1-undecanol	ETAAS	VASEME-SFOD	0.4–8	0.09	0.3	53	5.4	94.6–107.5	Eftekhari et al., 2015
Sb(III), Sb(V)	Environmental and biological samples	DDTC/1-octanol	TS-FF-AAS	HF-SLME	5–200	0.8	2.7	160	7.8	–	Zeng et al., 2011
Sb(III)	Water samples	BPHA/[C ₄ mim][PF ₆]	GFAAS	SDME	0.02–50	0.01	0.03	112	4.2	98–104	Huang et al., 2018
Sb(III)	Environmental and urine samples	APDC/Triton X-114	FI-ETV-ICP-AES	On line CPE ^a	–	0.09	0.3	827	4.3	95.4–105	Yingjie et al., 2006
Sb(III)	Beverages, milk based products	TAR, TAC/SDS	FAAS	UA-CPE	0.5–180, 1–180	0.13, 0.28	0.43, 0.93	45, 40 (80,85)	<3.9	95–98	Gürkan and Eser, 2016
Sb(III)	Different sample matrices	Pyrogallol/Neutral red/CTAB	HG-AAS	UA-CPE	0.012–0.25	0.0036	0.012	120	<5.3	> 96	Altunay and Gürkan, 2016
Sb(III)	Food packaging materials	APDC	ET-AAS	CPE	0.1–3	0.02	0.07	30	7.8	91–118	Jiang et al., 2009
Sb(III), Sb(V)	Seawater, bottled-mineral water and river water	DDTC/1-octanol, APDC/ CCl_4	TR-XRF	HF-LPME, DLLM	5–50, 0.2–100	1.1, 0.09	3.7, 0.3		17, 5	84–108	Marguí et al., 2013
Sb(III)	Mineral water, tap water, well water	Polymeric IL- 3-(1-ethyl imidazolium-3-yl) propyl-methacrylamido bromide and ethylene dimethacrylate	HG-AFS	SCSE	0.2–100	0.084	0.28		<10	80.4–107	Zhang et al., 2016
Sb(III), Sb(V)	Milk and beverage samples in PET containers	Pyronine B/SDS	FAAS	UA-CPE	5–400, 15–500	1.68, 4.28	5.6,14.3	62.5 (117.6,83.4)	1.9, 5.3	95–99.1	Altunay and Gürkan, 2015
Sb(III)	Edible oils	STZ-modified poly(SMAm/SMIm) copolymers/CTAB, SDS	UV-spectrophotometry	UA-CPE	1–40, 1–62.5	0.30–0.51	1.01–1.69	50 (14.6–27.8)	4.2–6.6	91.0–96.5	This study

*APDC: Ammonium pyrrolidine dithiocarbamate; Dithizone: 1,5-diphenylthiocarbazone; DDTC: Diethyldithiocarbamate.; BPHA: N-Benzoyl-N-phenylhydroxylamine; [C₄mim][PF₆]:1-Butyl-3-methylimidazolium hexafluorophosphate; TAR: 4-(2-Thiazolylazo)resorcinol; TAC: 2-(2-Thiazolylazo)-p-cresol; STZ: Sulfathiazole; SDS: Sodium dodecyl sulfate; CTAB: Cetyltrimethylammonium bromide; Aliquat 336: Tri-octylmethylammonium chloride; Morin: 2',3,4',5,7-pentahydroxyflavone; Pyronin B: 3,6-Bis(diethylamino)xanthylium chloride

**UA-IL-DLLME: Ultrasound-assisted ionic liquid dispersive liquid-liquid phase microextraction; CPE: Cloud point extraction; UA-CPE: Ultrasound assisted-cloud point extraction; FI-SPE: Flow injection-solid-phase extraction; SDME: Single drop microextraction; DLLME: Dispersive liquid liquid-liquid microextraction, HF-SLME: Hollow fiber supported liquid membrane extraction; VASEME-SFOD: Vortex-assisted surfactant-enhanced emulsification microextraction based on solidification of floating organic drop; HF-LPME: Hollow fiber-liquid phase microextraction; SCSE: Stir cake sorptive extraction

***HG-AFS: Hydride generation-atomic fluorescence spectrometry; TR-XRF: Total reflection-x ray fluorescence; FAAS: Flame atomic absorption spectrometry; HG-ICP-MS: Hydride generation-inductive coupled plasma mass spectrometry, ICP-OE: Inductive coupled plasma-optical emission spectrometry; GFAAS: Graphite furnace atomic absorption spectrometry; TS-FF-AAS: Thermospray-furnace flame atomic absorption spectrometry; ETAAS: Electrothermal atomic absorption spectrometry; FI-ETV-ICP-AES: Flow injection-electrothermal vaporization-inductive coupled plasma-atomic emission spectrometry

amount and sample extracts and 2-fold dilution where the average density of edible oils is approximately 0.92 g mL^{-1} in range of $0.9143\text{--}0.9211 \text{ g mL}^{-1}$, these results were within $3.91\text{--}15.43$ and $4.35\text{--}16.1 \mu\text{g kg}^{-1}$, respectively for UAE of trace iSb by two separate reagent groups in sample preparation step. A similar result, with a value of $15.6 \mu\text{g kg}^{-1}$ for olive oil in PET by AAS, was established by Jung et al. (2006). All the results indicated that the newly developed analytical method could be satisfactorily used for monitoring and determination of the iSb levels in the selected edible oils in terms of quality control.

3.6. Comparison of the method with other methods

It has been demonstrated that the STZ-modified amide/imide copolymers provide a new, efficient, eco-friendly and fast route for separation/pre-concentration and speciation analysis of Sb(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 o-/i-Sb 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 Sb(III) in 50-fold excess of Sb(V) from selected edible oils without matrix effect. Table 4 shows a comparison of the method performance with that of other methods using atomic spectrometry reported in literature (Biata et al., 2017; Altunay et al., 2016; Altunay and Gürkan, 2015; Fornieles et al., 2013; Biata et al., 2019; Fan, 2005; Rivas et al., 2009; Eftekhari et al., 2015; Zeng et al., 2011; Huang et al., 2018; Yingjie et al., 2006; Gürkan and Eser, 2016; Altunay and Gürkan, 2016; Jiang et al., 2009; Marguí et al., 2013; Zhang et al., 2016; Altunay and Gürkan, 2015), due to absence of any molecular spectrophotometric method for the detection of iSb in edible oils. It could be seen that some values obtained by the proposed method such as RSD_r or $\text{R}\%$, relative recoveries, preconcentration or enhancement factor, linear range, and MDLs and MQLs are either comparable or better than some of the previously reported-sensitive, selective but complex, costly, time-consuming detection methods such as HGAAS, HG-AFS, FAAS, TS-FF-AAS, ICP-OES, FI-ETV-ICP-AES, ETAAS, GFAAS, TR-XRF, and online HG-ICP-MS requiring expert user in his or her area, with and with FI, according to reductant type and pre-treatment step of sample matrix. Furthermore, CT-based micro-volume UV-spectrophotometry in combination with UA-CPE can be reliably used for food-sample analysis to avoid possible spectral or polyatomic interferences, which can appear in plasma techniques such as ICP-OES and ICP-MS. GC-MS methods are not capable of directly analyzing compounds that are nonvolatile, polar, or thermally labile. Before detection, derivatization requires to increase their volatility and thermal stability. GFAAS and ETAAS require slow furnace program, and have narrow working range and poor precision especially at ppb levels. The main benefits of the method are simplicity, low cost, versatile and selectivity (due to formation of pH-dependent CT complex in pre-concentration step), fast complexation/phase separation, and accessible in almost every analytical research laboratory.

4. Conclusions

A novel method based on selective extraction and preconcentration by mixed micellar UA-CPE prior to micro-volume UV-spectrophotometric analysis was successfully developed to detect and quantify total Sb (as Sb(III)) in edible oils. As a result of pH-dependent tautomerization, the CT-sensitive amide/imide copolymers modified with heterocyclic STZ as selectively Sb(III) binding chelator in presence of excess Sb (V) at pH 2.0 and 8.0 respectively, due to contain ionizable sulfonamide and thiazole moiety, were used in the optimization of variables affecting extraction efficiency to quantitatively detect Sb(III) in edible oils. Under ultrasonic power, the results obtained by two sample preparation methods were statistically in agreement with each other. As an eco-

friendly extraction approach, UA-CPE was successful in recovering the relevant Sb species with an acceptable extraction efficiency and minimal transformation as well as eliminating the matrix effect related to Sb(III) studied. With the ultrasound energy, accuracy and extraction efficiency were greatly improved by reducing the need of time-consuming sample pretreatment. Finally, via calibration curves prepared in solvent, the determination coefficient of R^2 was better than 0.995 for correlation between absorbance and Sb(III) concentration in the linear range of $1\text{--}40$ and $1\text{--}62.5 \mu\text{g L}^{-1}$ with MDLs of 0.30, 0.47/0.51 $\mu\text{g L}^{-1}$ at pH 2.0 and 8.0 for amide and imide copolymers, indicating that the method was efficient in the detection of iSb (Sb(III) and Sb(V)) in edible oils, and could be applied to monitor/check safety issues (related to total Sb) in other edible oils of interest. Verified by analysis of a non-certified sample, the effectiveness of the existing method has proven to be satisfactorily accurate and precision. In addition, the use of cells with micro-capacity in detection step results in low consumption of samples and reagents, and so negligible generation of wastes. As a result, the developed method could be reliably used for detection of iSb species in other oily matrices.

CRedit authorship contribution statement

H.B. Zengin: Conceptualization, Investigation, Formal analysis, Conduction of experimental studies, Data collection, Interpretation of IR spectral data. **R. Gürkan:** Supervision, Method development, Methodology, Validation, Writing – original draft, Writing – review & editing.

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

The authors are unable or have chosen not to specify which data has been used.

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

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Abstract The study described the synthesis, characterization, and application of newly prepared sulfathiazole-modified amide/imide co-polymers for the extraction of trace Sb(III) from edible vegetable oils. The method was based on the pH-dependent complexation between Sb(III) and chelators as a result of charge transfer via tautomerization in

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presence of the mixed ionic surfactants in 5%(v/v) 2-propanol, 1:1, v/v) at pH 2.0 and 8.0, respectively for amide and imide copolymers and then selectively ultrasound assisted-cloud point extraction of the Sb(III)-complexes into the micellar phase of extractant. The separated micellar phase by centrifugation was diluted to 0.4 mL with tetrahydrofuran, and detected at 269 nm by micro-volume UV-spectrophotometry. The parameters affecting extraction efficiency were optimized. The optimal extraction conditions were found to be: 0.6/0.8 mmol L⁻¹ of McIlvaine buffer, 30 μ mol L⁻¹ of the mixed-ionic surfactant mixture, 120 μ mol L⁻¹ KCl, 0.1/0.06% (v/v) of the nonionic surfactant and (0.4/0.2) x 10⁻³%(w/v) of sulfathiazole-modified amide/imide copolymers at pH 2.0 and 8.0 for 7 min at 40 degrees C in an ultrasonic bath (40 kHz, 300 W). From preconcentration of 20-mL sample, the good linear relationships ($r^2 \geq 0.995$) between absorbance and Sb(III) concentration were obtained from calibration curves prepared in solvent in range of 1-40 and 1-62.5 μ g L⁻¹ with the method detection limits of 0.30/0.47 and 0.51/0.51 μ g L⁻¹ at 269 nm by spectrophotometer after 50-fold preconcentration. The accuracy was statistically verified by analysis of a non-certified sample with and without spiking where the precision and relative recoveries are within 5-12% and 83-92%, respectively. Also, the matrix effect was evaluated by triplicate measurements of 25 μ g L⁻¹ Sb(III) (n: 3) under optimal conditions. The method was successfully applied into the analysis of total iSb levels of edible vegetable oils. The results shown that the STZ-modified amide/imide co-polymers were efficient selective chelators even in presence of 50-fold excess Sb(V), and exhibited great potential as alternative binding chelators for the extraction of Sb(III) from edible vegetable oils.

Keywords

Author Keywords: Sb(III); Poly(styrene-co-maleic anhydride); Sulfathiazole; Sodium dodecyl sulfate; Cetyltrimethylammonium bromide; Edible vegetable oils; Pre-concentration; Ultrasound assisted-cloud point extraction; Micro-volume UV spectrophotometry

Keywords Plus: SOLID-PHASE EXTRACTION; ATOMIC-ABSORPTION-SPECTROMETRY; LIQUID-LIQUID-EXTRACTION; SPECIATION ANALYSIS; IMPRINTED POLYMER; PET



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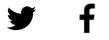
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