

Extraction, preconcentration and spectrophotometric determination of trace levels of thiosulfate in environmental waters

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Abstract In the existing study, a new vortex-assisted cloud point extraction (VA-CPE) method was developed for determination of low levels of thiosulfate in environmental waters at 632 nm by spectrophotometry. The method is selectively based on charge-transfer-sensitive ion-pair complex formation of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, which is produced by the reaction of thiosulfate with excess Ag^+ ions with toluidine blue (3-amino-7-dimethylamino-2-methylphenazathionium chloride, TB^+) and then its extraction into micellar phase of polyethylene glycol 4-*tert*-octylphenyl ether (Triton X-45) in presence of Na_2SO_4 as salting-out agent at pH 7.0. All the factors affecting complex formation and VA-CPE efficiency were optimized in detail. Under the optimized conditions, the linear calibration curves for thiosulfate were in the range of 0.2–120 and 5–180 $\mu\text{g L}^{-1}$ with sensitivity improvement of 81-folds and 15-folds, respectively, as a result of efficient mass transfer obtained by CPE with and without vortex, while it changed in the range of 260–3600 $\mu\text{g L}^{-1}$ without preconcentration at 642 nm. The limits of detection and quantification of the method for VA-CPE were found to be 0.05 and 0.22 $\mu\text{g L}^{-1}$, respectively. The precision (expressed as the percent relative standard deviation) was in range of 2.5–4.8% (5, 10 and 25 $\mu\text{g L}^{-1}$, n : 5). The method accuracy was validated by comparing the results to those of an independent 5,5'-dithiobis(2-aminobenzoic acid) (DTNB) method as well as recovery studies from spiked samples. It has been observed that the results

are statistically in a good agreement with those obtained by DTNB method. Finally, the method developed was successfully applied to the preconcentration and determination of trace thiosulfate from environmental waters.

Keywords Thiosulfate · Water quality · Toluidine blue · Vortex-assisted cloud point extraction · Spectrophotometry

Abbreviations

VA-CPE	Vortex-assisted cloud point extraction
UA-CPE	Ultrasound-assisted cloud point extraction
CPT	Cloud point temperature
TB^+	Toluidine blue
Triton X-45	Polyethylene glycol 4- <i>tert</i> -octylphenyl ether
RSD	Relative standard deviation
DTNB	5,5'-Dithiobis(2-nitrobenzoic acid)
IC	Ion chromatography
CE	Capillary electrophoresis
CZE	Capillary zone electrophoresis
LLE	Liquid–liquid extraction
SPE	Solid-phase extraction
MECA	Molecular emission cavity analysis
GC with ECD	Gas chromatography with electron capture detector
MEKC	Micellar electrokinetic chromatography
GC–MS	Gas chromatography–mass spectrometry
HS-SDME	Headspace single-drop microextraction
FAAS	Flame atomic absorption spectrometry
HPLC	High-performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
5-HMF	5-Hydroxymethylfurfural
Tris	2-Amino-2-hydroxymethyl-propane-1,3diol

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TBAHS	Tetrabutylammoniumhydrogensulfate
TBAAc	Tetrabutylammoniumacetate
DPP	Differential pulse polarography
BTA	1,3,5-Benzenetricarboxylic acid
TPA	Tetrapropylammonium salt
CMC	Critical micelle concentration
RNA	Ribonucleic acid
LOD	Limit of detection
LOQ	Limit of quantification

Introduction

Thiosulfate is a common product of the inorganic oxidation of sulfide ions and iron sulfides, as well as the disproportionation of bisulfite and sulfite ions [1]. Thiosulfate as the reducing species is widely found in industrial wastewater and environmental waters. Determination of thiosulfate, one of the sulfur species, is very important in many environmental and industrial situations especially when monitoring anoxic waters and wastewaters from paper mills photographic laboratories [2–4]. The thiosulfate can be produced in anoxic conditions as a result of bacterial sulfate reduction, which is the most important source of sulfur compounds in waters. Thiosulfate entering the environment and natural waters from industrial pollution can influence the bioavailability of heavy metals due to the complexation, adsorption and precipitation and is the toxic at low concentrations [5]. It stimulates growth, detoxifies the dissolved free Ag^+ ions by forming a stable complex and also prevents the generation of toxic silver nanoparticles precipitates in tomato root cultures [6]. In marine water, thiosulfate $\text{S}_2\text{O}_3^{2-}$ exists only at the oxic/anoxic interface, generally in very low concentrations, mostly between >1 and $20 \mu\text{mol L}^{-1}$ [7, 8]. The extremely low concentration of $\text{S}_2\text{O}_3^{2-}$ is not due to its insignificance in the sulfur cycle, but rather to its versatility as a substrate for bacteria. Due to be reactive and unstable of thiosulfate including other sulfur anions, the accurate and reliable monitoring/determination in environmental waters, food and other materials is of great importance for environmental protection, food safety and quality control because of their potential toxicities.

The 5,5'-dithiobis (2-nitrobenzoic acid) (DTNB), which is also known Elman's reagent, is a versatile water-soluble reagent for a rapid determination of free sulfhydryl groups at neutral pH [9]. It is currently used for thiol quantification in biochemical samples such proteins, glutathione and thiamine, in which sulfite, thiosulfate, sulfide and cyanide generally are available as potential concomitants. Recently, its applications for sulfite determination in vegetal samples [10], dried fruit and vegetables [11] and simultaneous determination of sulfite and thiosulfate in environmental waters [12] after separation/preconcentration from matrix

with different sample pretreatment approaches such as headspace single-drop microextraction (HS-SDME), cloud point extraction (CPE) and in situ solid-phase extraction (in situ SPE) before spectrophotometric detection have been used by different author groups, respectively. In the first study, a sensitive method based on in situ SO_2 generation and HS-SDME combined with UV–Vis micro-spectrophotometry with detection limit of $0.06 \mu\text{g g}^{-1}$ was proposed for the determination of sulfite preservatives in fresh fruits and vegetables. In this study, an aqueous microdrop containing DTNB is used in order to provide a high enrichment factor to tackle difficulties related to the extraction and stability of sulfites [10]. In second study, due to the lack of a suitable certified reference material matching the sample matrix composition, standard DTNB method after modification with oxalic acid at pH 6.5 was used as a comparative method in preconcentration and determination of trace sulfite with detection limit of $1.5 \mu\text{g L}^{-1}$ in range of 2.5 – $350 \mu\text{g L}^{-1}$ in vegetables and dried fruits by combination of UA-CPE with spectrophotometry at pH 7.5 [11]. In third study, authors have developed a new spectrophotometric method after simultaneous preconcentration of sulfite and thiosulfate in fresh waters, brackish and sea water samples as well as by in situ SPE after retaining of DTNB derivatives of thiosulfate and sulfite on C18 cartridges [12].

Numerous reports on thiosulfate analysis have been published in the literature. In these studies, thiosulfate was separated from other species by ion chromatography (IC) [1], capillary electrophoresis (CE) [4], micellar electrokinetic chromatography (MEKC) [13] and capillary zone electrophoresis (CZE) [14]. A great disadvantage of IC with universal detection techniques such as conductivity and indirect UV is interference by the high concentrations of co-eluting matrix anions such as chloride and sulfate [15]. Furthermore, sulfide forms precipitates with heavy metal ions accumulated on the head of the column from metallic components of the IC system [16]. In the rapid, sensitive and selective CE determination of $\text{S}_2\text{O}_3^{2-}$, S^{2-} and SO_3^{2-} anions, a derivatization procedure should be used to improve poor peak shape and peak–peak resolution in separation/speciation analysis due to be a species of polarizable, lightly hydrated and has large deformable electron clouds of thiosulfate. However, conventional pre-capillary or on-capillary derivatization techniques are not suitable for this purpose because sulfur species are very similar in their chemical properties. In such case, the derivatization after separation of the analytes must be used [15]. Since CE is usually performed in free solution in a narrow capillary, a special section of the capillary can be reserved for derivatization reaction. To overcome this problem, an alternative way can be vortex-assisted cloud point extraction (VA-CPE) step based on a fast and efficient mass transfer at interface for separation and preconcentration

for thiosulfate from these samples. In this sense, a separation and preconcentration step is necessary especially for UV–Vis spectrophotometry with low sensitivity, in which the thiosulfate levels of samples are lower than detection limit of spectrophotometry as detection tool. In order to determine low contents of thiosulfate of real samples, the traditional separation and preconcentration procedures such as SPE [17], sweeping, which is based on in-line and online preconcentration of neutral and charge analytes in capillary and/or microchips or which is based on partition of the analytes between pseudo-stationary phase and the surrounding phase what promotes separation of analytes from matrix in MEKC [18, 19], solvent extraction [20], electrosorption before detection by cathodic stripping differential pulse voltammetry (CS-DPV) at pH 4.4 [21], electrochemical accumulation on a miniaturized modified mercury drop electrode before detection by cathodic stripping voltammetry (CSV) [22], electrochemical deposition before detection by linear sweeping voltammetry (LSV) in a study, which is based on anodic depolarization reaction between sulfur and the mercury electrode at pH 8.3 [23] as well as column-switching separation/preconcentration before analysis by suppressed IC [24] have been used. But these preconcentration procedures have generally limitations such as time-consuming and cumbersome to perform, utility of columns with a narrow internal diameter limiting the flow rates to a range of 1–10 mL min⁻¹, so as to large trace-enrichment time for large sample volumes, plugging the cartridge of samples with particulate matter, unsatisfactory enrichment factors, using toxic organic solvents, forming secondary waste for extraction. In cases of mercury electrodes (DME, MFE and HDME) and chemical modified electrodes (CMEs) used for electrochemical accumulation, there are frequently the limitations such as the formation of inter-metallic compounds with a co-existing metal ions at the electrode, which can cause serious error, toxicity of mercury and increase in cost of analysis, in some cases increase in the background current and resulting in a narrower potential windows in electrode modification with a suitable reagent, which is selective toward thiosulfate ions. VA-CPE is a versatile procedure with attractive characteristics such as simplicity, inexpensive, rapidity, selectivity with high sensitivity enhancement and preconcentration factors when especially compared with solvent extraction and SPE, which needs to use toxic organic solvents for the separation and preconcentration of metal ions. Moreover, the use of a vortex device provides a large surface area between two phases, fast extraction kinetics, less solvent usage, fast and efficient analyte transfer as well as being simple, inexpensive and easy to operate according to other CPE procedures [25]. Also, VA-CPE as a preconcentration way was successfully used in analysis of arsenic, acrylamide, phenolic antioxidants and fluoroquinolones in

different sample matrices by different detection techniques such as spectrophotometry, flame AAS, HPLC and spectrofluorometry, respectively [26–29].

Thiosulfate determination has been mostly performed using analytical techniques such as flame-containing molecular emission cavity analysis (MECA) [30], kinetic spectrophotometry [31], gas chromatography–mass spectrometry (GC–MS) [32], flame atomic absorption spectrometry (FAAS) [33], high-performance liquid chromatography (HPLC) [34], ion-pair chromatography with ultraviolet absorbance [35], ion chromatography (IC) based on isocratic elution with fluorescence detection [36] and inductively coupled plasma mass spectrometry (ICP–MS) [37]. Determination of thiosulfate via these methods is expensive, tedious and time-consuming as well as poor precision at low concentrations and requires expert user in her/his area. Thus, there is still a great need to develop a simple, sensitive, selective and inexpensive method for the determination of trace levels of thiosulfate in different waters requiring novel methods in terms of water quality and human health. In this sense, the UV–Vis spectrophotometry is still widely used in analytical chemistry and successfully can be able to couple to cloud point extraction (CPE) in order to enhance the detection limit and selectivity of the method in trace analysis. Also, it is well known that the use of vortex device in CPE procedure provides large surface area between two phases, fast extraction kinetics, less solvent usage, fast and efficient analyte transfer as well as being simple, inexpensive and easy to operate according to other CPE procedures in the literature [25], in which the CPE with and without ultrasonic induction successfully is applied to determination of essential and toxic species such as sulfite [38], 5-hydroxymethylfurfural (5-HMF) [39] and cyanide [40] in the monitoring of foods and beverages safety and environmental pollution by our research group.

In the present work, a VA-CPE method was developed for separation/preconcentration of low levels of thiosulfate from different water matrices prior to spectrophotometric detection. The method is based on the stable anionic complex formation of the thiosulfate with Ag⁺ ions, so as to give an ion-pairing complex with toluidine blue (3-amino-7-dimethylamino-2-methylphenazathionium chloride, TB⁺) in presence of Na₂SO₄ as salting-out agent, and the further extraction/preconcentration using the non-ionic surfactant, Triton X-45 (polyethylene glycol 4-*tert*-octylphenyl ether) at pH 7.0. The interest of the work is related to the possibility of using a simple, cheap and eco-friendly preconcentration method to determine thiosulfate in environmental waters such as wastewater, lake, river, tap and hot-/cold-spring waters. The majority of the works described in the literature for sulfur determination do not preconcentrate the species to enhance the sensitivity of the method. Thereby, the novelty of the work is the use of a

vortex-assisted preconcentration method as a prior step in spectrophotometric determination.

Experimental

Instrumentation

In the present study, the devices used in experimental are as follows: a Shimadzu model UV–visible 1601 PC spectrophotometer (Kyoto, Japan) equipped with a 1-cm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of ± 0.2 nm and a bandwidth of 2 nm in the wavelength range of 190–1100 nm. The absorbance measurements at 642 and 632 nm before and after preconcentration with VA-CPE, respectively, were made for determinations of trace thiosulfate in tap water, lake water, river water, hot-/cold-spring waters and wastewater samples. An ultrasonic bath (UCS-10 model, Jeio Tech, Co., Ltd., Seoul, Korea) was used to degas and extract the samples, also used to maintain the temperature in CPE experiments (300 W, 40 kHz). A vortex mixer (12 W, 60 Hz) was used for thorough mixing of solutions as well as efficiently removal of dissolved oxygen from reaction medium in presence of sodium azide solution (0.02 mol L^{-1}) (VM-96B model, Jeio Tech, Co., Ltd., Seoul, Korea). A centrifuge (Universal-320, Hettich Centrifuges, and England) was used to accelerate the phase separation process. The pH measurements were taken with a pH meter (pH-2005, JP Selecta, Spain). Eppendorf vary-pipettes (10–100 and 200–1000 μL) were used to deliver accurate volumes. A refrigerator at 4°C was used to keep the samples fresh and cool up to the analysis.

Reagents and standard solutions

Ultra-pure water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was prepared using a Labconco (Kansas City, USA) water purification system. All solutions were prepared with this ultra-pure water. All chemicals and reagents used were of analytical-reagent grade or higher purity. The thiosulfate 500 mg L^{-1} was prepared using dissolving an appropriate amount of sodium thiosulfate (Sigma, St. Louis, MO, USA) in water containing a small amount sodium carbonate (0.01%, w/v) as a stabilizer due to its instability especially in acidic solutions. The standard working solutions of thiosulfate (in 0.01%, w/v, Na_2CO_3) used for construction of calibration curves were prepared fresh daily by stepwise dilution of the stock solution with the water under vortex mixing. A stock solution of silver at a concentration of 1000 mg L^{-1} was prepared by dissolving 0.1574 g of AgNO_3 (Merck, Darmstadt, Germany) in the water containing 1 mL concentrated nitric acid, completing to the mark in a volumetric flask of

100 mL and stored in the dark. The working standard silver solutions used for optimization studies were prepared by stepwise dilution of the stock solution with the water. Stock solutions of $3.0 \times 10^{-3} \text{ mol L}^{-1}$ of toluidine blue (TB^+) (Sigma) solution were prepared fresh daily by dissolving the reagents in ethanol (Merck) and diluting with the water. All working solutions were prepared by a serial dilution of the stock solutions at suitable proportions. Solutions of 5.0% (v/v) of Triton X-45 (Sigma) were prepared by dissolving 5.0 mL of surfactant and 10 mL of ethanol in 90 mL of the water. The tris(2-amino-2-hydroxymethyl-propane-1,3-diol)/HCl buffer solution, 100 mL of 0.1 mol L^{-1} at pH 7.0, was prepared by using suitable amounts of Tris base (having a pK_a of 8.1) and 2.0 mol L^{-1} HCl solutions, and adjusting to pH 7.0 via pH meter when necessary. Stock solutions of $1000 \mu\text{g mL}^{-1}$ of interfering ions were prepared by dissolving appropriate amounts of suitable salts of each ion in the water, HNO_3 or NaOH. All the prepared stock solutions were stored in polyethylene bottles in a refrigerator at 4°C . The vessels and pipettes used for trace analysis were kept in 10% (w/v) HNO_3 for at least 24 h and subsequently washed five times with the water.

Preparation of water samples to analysis

Initially, all of the glassware and other mineralization containers used were acid-washed to avoid possible contamination. The cold-spring samples selected for analysis were supplied from water wells in Sivas, Turkey. Water samples of the dental clinic effluents, which are discharged to wastewater treatment unit of University (the Faculty of Dentistry of Cumhuriyet University, Sivas, Turkey), were collected during one working day and initially stabilized with 2 mL of 0.02 mol L^{-1} NaN_3 in a citrate medium (pH 5.5–6.0) for removal of dissolved oxygen. For tap water, the sample was collected after discharging tap water for about 30 min and mixed by vortex for 5 min to remove free chlorine. The hot thermal water was obtained from the thermal spa in Sivas. The wastewater samples were collected from the region industrial facilities in Sivas. Before preconcentration procedure, all the selected water samples were filtered by using a $0.45 \mu\text{m}$ membrane filter. All the water samples were safely stored at 4°C until analyzed.

Before separation and preconcentration with VA-CPE, to 100 mL of each fresh water sample, 5 mL of 0.1 mol L^{-1} $\text{Zn}(\text{CH}_3\text{COO})_2$ and 1.25 mL of 1.0 mol L^{-1} NaOH to remove sulfide ions from sample matrix were added. The mixture was thoroughly mixed by means of vortex, and then, the resulting precipitate ZnS or ZnS_x was filtered through $0.45 \mu\text{m}$ filter after centrifugation for 5 min at 3500 rpm. After that, the supernatant was passed through a capillary column containing 0.1 g of strongly

cation-exchange resin, Amberlite IR-120plus in order to prevent oxidation of sulfur species and possible interferences by metallic cations. After 2 min, a 1.0 (or 1.5) mL aliquot of the resulting supernatant was added to a flask of 50 mL containing 5 mL of $0.02 \text{ mol L}^{-1} \text{ NaN}_3$ to remove dissolved oxygen and 5 mL of 0.01 mol L^{-1} formaldehyde buffered to pH 6.0 (with a mixture of citric acid, 0.1 mol L^{-1} and Na_2HPO_4 , 0.2 mol L^{-1}) selectively to mask sulfite and tetrathionate in form of hydroxymethanesulfonates (HMS), and the resulting solution was degassed for 5 min at 40°C under ultrasonic power (250 W, 40 kHz). Three replicates were incubated and analyzed by both the developed method and independent DTNB method at each incubation time. Similarly, three replicate blank analyses were conducted to ensure the accuracy and reliability of results. Then, the preconcentrated water samples were submitted to VA-CPE procedure prior to spectrophotometric detection. Then, in order to determine free thiosulfate contents of water samples, the UV–Vis spectrophotometer was used at 632 nm. The accuracy of the method was statistically evaluated and validated by comparing the results obtained with those of standard DTNB method. Moreover, standard addition method at quantification limit for thiosulfate was adopted in order to calculate the recovery rates and to check the reliability of results and the matrix effect.

The VA-CPE procedure

For the VA-CPE, aliquots of the cold solution containing free $\text{S}_2\text{O}_3^{2-}$ in the range of $0.2\text{--}120 \text{ }\mu\text{g L}^{-1}$, $2.4 \text{ mg L}^{-1} \text{ Ag}^+$, 0.27 mmol L^{-1} of TB^+ , 1.0 mL of $0.2 \text{ mmol L}^{-1} \text{ Na}_2\text{SO}_4$ and 0.01% (v/v) Triton X-45, respectively, in a centrifugation tube of 50 mL, were adjusted to pH 7.0 using 4 mmol L^{-1} Tris/HCl buffer and kept for 5 min in the ultrasonic bath maintained at 40°C . To accelerate the extraction, the mixture was vigorously shaken using a vortex agitator for 3 min at 3000 rpm (maximum setting) leading to the formation of fine droplets. The resulting mixture was centrifuged for 5 min at 4000 rpm. Surfactant-rich phase was separated from bulk aqueous phase by a simple decantation. The surfactant-rich phase was dissolved and diluted to about 0.9 mL using a vortex mixer with 0.7 mL acetonitrile to decrease the viscosity. Finally, the amount of thiosulfate was determined by UV–Vis spectrophotometry after correction against analyte blank at 632 nm. Also, the contents of the thiosulfate in hot-/cold-spring waters, thermal water and wastewater were determined by using either the direct calibration curve or calibration curve based on spiked samples in order to control the possible matrix effect around the determination limit.

In order to control the accuracy of the method, the thiosulfate levels of samples similarly pretreated at pH 6.0 were measured and comparatively evaluated by the standard DTNB method. The analysis of the selected environmental waters by standard DTNB method [38, 41] was carried out as follows: A known amount of water samples was placed in a 50-mL volumetric tube and diluted to 40 mL with water. Then, 5 mL of DTNB solution was added, and the solution was diluted to the 50 mL with the water. The absorbance was measured at 412 nm against analyte blank after a reaction time of 15 min at 20°C .

Results and Discussion

The general aspects related to method development

The method is based on the selective charge-transfer-sensitive ion-association of anionic $\text{Ag}(\text{S}_2\text{O}_3)^-$ or $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complex, which is produced depending on concentration of thiosulfate in presence of excess Ag^+ ions with ion-pairing reagent, TB^+ as pH sensitive redox species at pH 7.0, and then extraction of ternary complex to micellar phase of Triton X-45 as extracting agent. The extracted surfactant-rich phase is diluted with acetonitrile, and its absorbance of ternary complex, which is linearly related to thiosulfate concentration, is spectrophotometrically measured at 632 nm. The absorption spectra of surfactant-rich phase as a function of absorption wavelength (nm) and thiosulfate concentration at levels of 10, 40 and $100 \text{ }\mu\text{g L}^{-1}$ under the optimized reagent conditions are given in Fig. 1. From the plot of the corrected absorbance values against thiosulfate concentration for analyte blank absorbance of 0.3856, a good linearity relationship (r^2 : 0.9998) was obtained, in which regression equation is $\text{Abs.} = 2.89 \times 10^{-3} [\text{S}_2\text{O}_3^{2-}, \text{ }\mu\text{g L}^{-1}] + 0.084$. Moreover, at lower concentrations than $10 \text{ }\mu\text{g L}^{-1}$, the calibration sensitivity was much higher because of the fast and efficient mass transfer provided by mixing with the vortex at the micellar interface. Thus, for further applications, the different analytical variables affecting CPE efficiency with and without vortex mixing was optimized in order to achieve the maximum sensitivity. TB^+ with pK_a values of approximately 3.5 and 7.2 [42] is a cationic phenothiazine group dye, which is nontoxic and has sharp absorption in the visible region. Also, it is a pH sensitive redox species, which can be aggregated by the electrostatic and π – π stacking interactions depending on concentration, pH and polarity of the environment in normal and reverse micellar media as follows, so as to give the oxidized and reduced forms of redox sensitive ion-pairing reagent, TB^+ [43–46].

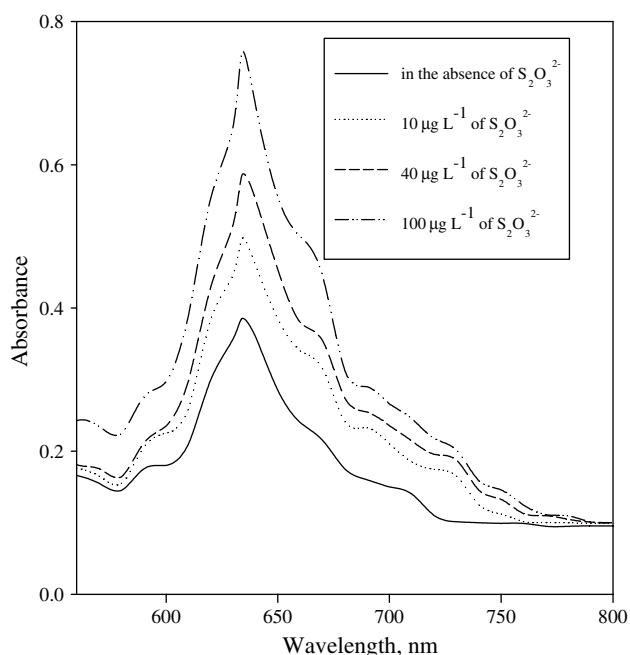
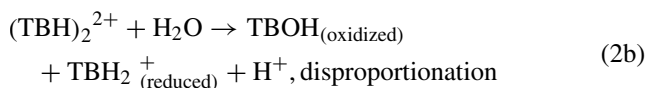
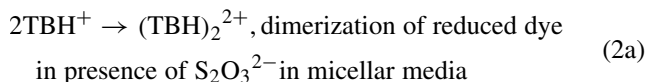
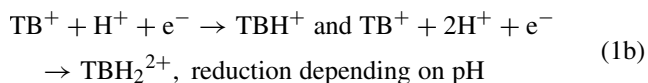
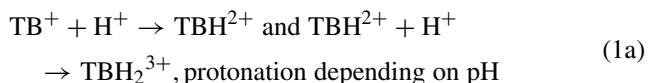


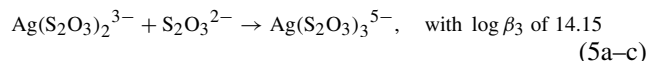
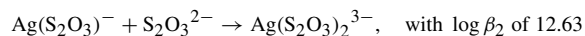
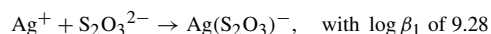
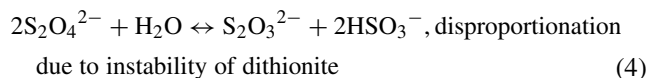
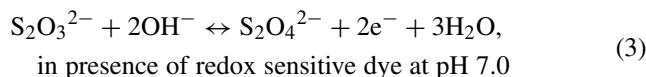
Fig. 1 The dependence of the maximum absorption peak to thiosulfate concentration at levels of 10, 40 and 100 $\mu\text{g L}^{-1}$ under the optimized reagent conditions. Conditions: 2.4 mg L^{-1} Ag(I) , 0.27 mmol L^{-1} TB^+ , 0.01% (v/v) Triton X-45, 0.2 mmol L^{-1} Na_2SO_4 , 4 mmol L^{-1} Tris buffer at pH 7.0 with sonication for 5 min at 40 $^\circ\text{C}$ and centrifugation of 5 min at 4000 rpm



It is a member of the phenothiazine group and is partially soluble in both water and alcohol. At lower pHs than 3.0 and in pH range of 3.5–6.5, it is predominantly present in tri- and di-cationic acidic forms of dye, TBH_2^{3+} , TBH^{2+} , respectively, while it is relatively in mono-cationic basic form, TB^+ at higher pHs than 8.0. From the literature information's, it is seen that the bisulfite- TBH_2^{3+}

combination at pH 1.0 is used as aldehyde reagent for the selective demonstration of ribonucleic acid (RNA) in tissues [47]. Also, the reduction of TB^+ or TBH^{2+} by ascorbic acid at 600 nm was used for the kinetic determination of ascorbic acid in fruits and vegetables in linear ranges of 3–35 and 5–50 mg L^{-1} by slope or fixed-time and variable time methods, respectively [48]. Similarly, it is seen that Cu^{2+} ion as soft metal ion selectively enhances the rate of reaction between TB^+ (or TBH^{2+}) and SO_3^{2-} at 633 nm by forming a ternary complex with a stability constant of $\log K_f$: 14.291 with standard deviation of 0.007 at pH 7.2 [49].

Due to all these properties, it is clear that the ion-pairing reagent TB^+ or TBH^{2+} tends to give charge-transfer-sensitive ion-association complex with anionic $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complex, formed in the presence of Ag^+ ions at pH 7.0. Because of its high solubility in aqueous micellar media, from prior studies, it was observed that the ion-association complex could efficiently be extracted into surfactant-rich phase above the critical micelle concentration (CMC) (0.265 mmol L^{-1}) of the nonionic surfactant, Triton X-45, with an optimum concentration of 0.8 mL of 2.5% (v/v) corresponding to a concentration of 0.804 mmol L^{-1} . To further improve the calibration sensitivity and selectivity of the method, the CPE has been explored using nonionic surfactant, Triton X-45 in presence of Na_2SO_4 as salting-out agent efficiently and rapidly to enhance the binding of hydrophobic complex to the surfactant-rich phase with and without vortex mixing. The CPE can efficiently be used when the target analytical species are hydrophobic in nature. Though the ion-association complex is water soluble, it can successfully be able to extract into surfactant-rich phase in the presence of ion-pairing reagent, TB^+ or TBH^{2+} at pH 7.0. The mechanism proposed for directly CPE and VA-CPE of trace thiosulfate (with pK_a values of 0.60 and 1.72) in aqueous micellar medium assisted by Triton X-45 micelles can be explained by Eqs. (3–7), in which the stability constants for $\text{Ag}(\text{S}_2\text{O}_3)_n^{1-2n}$ (n : 1,2,3) are given in the literature [50–52], as follows:



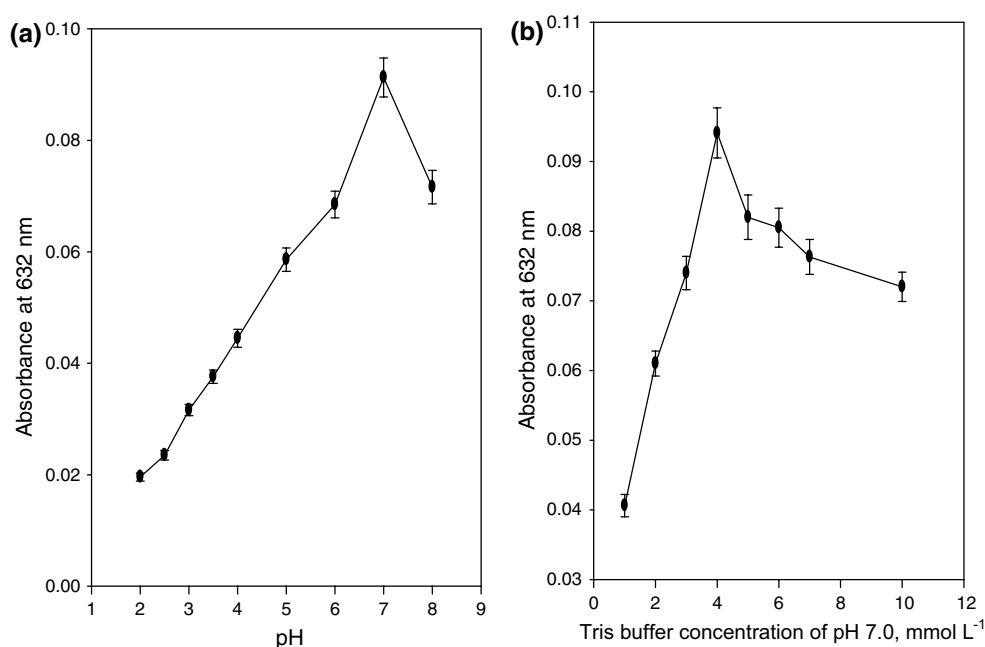
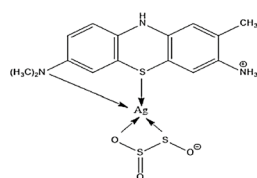
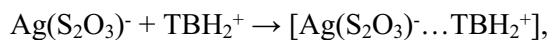


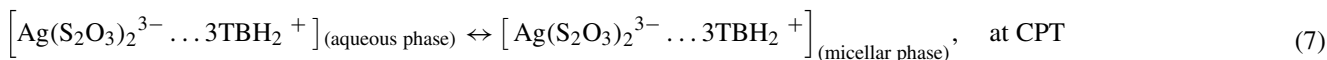
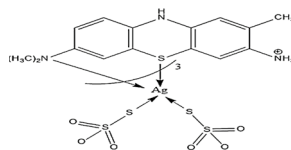
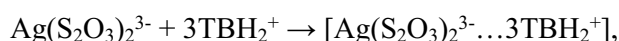
Fig. 2 Effects of **a** pH and **b** Tris buffer concentration of pH 7.0 on three replicate measurements of 10 $\mu\text{g L}^{-1}$ thiosulfate. Conditions: 2.4 mg L^{-1} Ag(I), 0.27 mmol L^{-1} TB⁺, 0.01% (v/v) Triton X-45,

0.2 mmol L^{-1} Na₂SO₄ with sonication for 5 min at 40 °C and centrifugation of 5 min at 4000 rpm



or

(6a–b)



Optimization studies

The various analytical variables were optimized by using model solutions in order to obtain the maximum extraction efficiency. So, parameters such as the effect of pH, concentrations of buffer, Ag⁺, ion-pairing reagent and surfactants, ionic strength, diluent agent for surfactant-rich phase and incubation conditions were studied in detail. All the other parameters were kept constant, while a parameter was optimizing. Each point in optimization were repeated three

times and indicated as error bars in terms of mean and their standard deviations in all figures.

Effects of pH and buffer concentration on the analytical signal

The preconcentration of S₂O₃²⁻ by VA-CPE method involves previous formation of a stable complex, which needs to present sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase. Thus, in

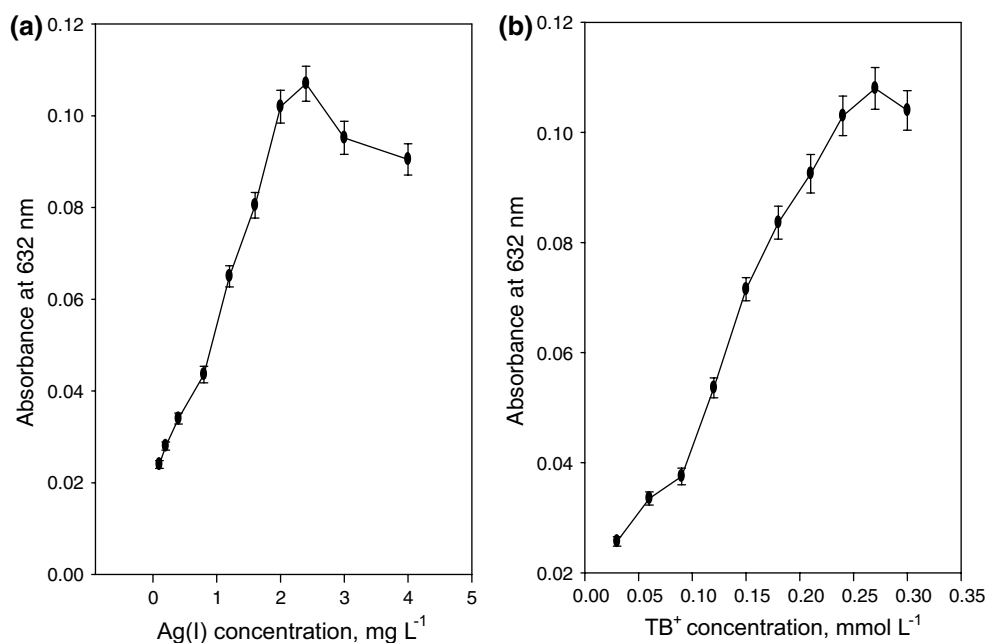


Fig. 3 Effects of **a** Ag(I) concentration and **b** TB⁺ concentration on three replicate measurements of 10 $\mu\text{g L}^{-1}$ thiosulfate. Conditions: 0.01% (v/v) Triton X-45, 0.2 mmol L^{-1} Na₂SO₄, 4 mmol L^{-1} Tris

buffer at pH 7.0 with sonication for 5 min at 40 °C and centrifugation of 5 min at 4000 rpm

this part of experiment, the effect of pH on the formation of selective ion-pairing complex in presence of Ag⁺, TB⁺ and/or TBH²⁺ was extensively investigated for the extraction and determination of 10 $\mu\text{g L}^{-1}$ thiosulfate in the surfactant-rich phase at 632 nm in the range pH 2.0–8.0. As can be seen from the absorbance change against pH, corrected for analyte blank absorbance of 0.595 in Fig. 2a, the maximum extraction efficiency was achieved by using Britton–Robinson buffer, a mixture consisting of citric acid, potassium dihydrogenphosphate and boric acid at isomolar concentrations of 0.0286 mol L^{-1} titrated with 0.2 mol L^{-1} NaOH at pH 7.0. Initially, the absorbance signal sharply increased with increasing pH up to 7.0 and then gradually decreased. Due to be instable of thiosulfate ion in acidic media, at the pHs lower than 4.0, signal difference was significantly low. The decrease in signal in higher pHs than 7.0 may be due to hydrolysis of Ag⁺ ions ($-\log K_s$: 7.71), so as to give AgOH and Ag(OH)₂⁻. Another cause may be pH dependent oxidation of thiosulfate to sulfite and sulfate in presence of dissolved oxygen, respectively. Therefore, a pH of 7.0 was selected as optimal pH for subsequent studies.

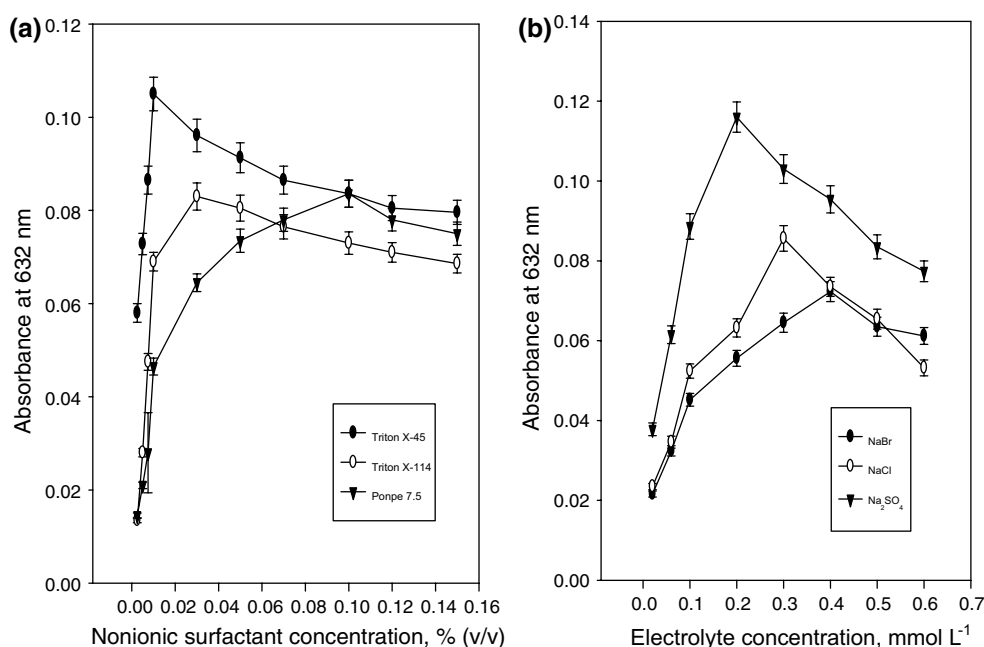
In order to obtain accurate, reproducible and stable signals in spectrophotometric detection of 10 $\mu\text{g L}^{-1}$ thiosulfate at pH 7.0, three different buffer systems such as Britton–Robinson, phosphate and Tris/HCl buffers were comparatively investigated. After 0.1 mol L^{-1} Tris/HCl solution was adopted as the best suitable buffer at pH 7.0,

due to give more stable and reproducible signals than other two buffers, the effect of Tris buffer concentration was also studied in range of 1–10 mmol L^{-1} in Fig. 2b, and from the absorbance change against buffer concentration, corrected for analyte blank absorbance of 0.5815, the best analytical signal was obtained by using a concentration of 4 mmol L^{-1} for this buffer system in the final volume of 50 mL. The cause of decreasing in signal at higher concentrations than 4 mmol L^{-1} may be increase in blank signal as a result of interaction among deprotonated neutral form of dye, TB, Ag⁺ and Tris as a neutral ligand in presence of Na₂SO₄ as salting-out agent.

Effects of Ag(I) and dye concentration on the analytical signal

In the present study, the effect of the Ag(I) concentration on the analytical signal in the presence of 10 $\mu\text{g L}^{-1}$ thiosulfate was studied in range of 0.1–4 mg L^{-1} , and the experimental results obtained from the absorbance change against Ag(I) concentration corrected for analyte blank absorbance of 0.5815 in Fig. 3a indicated that the analytical signal linearly increases with Ag(I) concentration up to 2.4 mg L^{-1} . The analytical signal gradually decreased with increasing slope at the higher concentrations than 2.4 mg L^{-1} . This decrease in signal may be due to complexation of Ag⁺ ions with both Tris (L) and TB in presence of sulfate ions, in form of Ag(OH)L(TB) or AgL₂(TB)SO₄ by acid–base

Fig. 4 Effects of **a** nonionic surfactant concentration and **b** electrolyte concentration on three replicate measurements of $10 \mu\text{g L}^{-1}$ thiosulfate. Conditions: 2.4 mg L^{-1} Ag(I) , 0.27 mmol L^{-1} TB^+ , 4 mmol L^{-1} Tris buffer at pH 7.0 with sonication for 5 min at 40°C and centrifugation of 5 min at 4000 rpm



or donor–acceptor interaction, so as to cause increase in blank signal. So, a Ag(I) concentration of 2.4 mg L^{-1} was selected as optimal value for further studies.

TB^+ or TBH^{2+} as ion-pairing agent were selected for determination of thiosulfate in presence of Ag^+ ions and Triton X-45 as extracting agent at pH 7.0. While all other variables were held constant in the presence of Triton X-45, the effect of basic thiazine group dye concentration TB^+ or TBH^{2+} on the analytical signal at pH 7.0 was examined in the range of $0.03\text{--}0.3 \text{ mmol L}^{-1}$, and the results were shown in Fig. 3b. As can be seen from the absorbance change against TB^+ concentration corrected for analyte blank absorbance of 0.5825 in Fig. 3b, the best analytical signal has been obtained when the dye concentration is 0.27 mmol L^{-1} , whereas the analytical signal is lower at the higher concentrations than 0.27 mmol L^{-1} . When the dye concentration is higher than 0.27 mmol L^{-1} , a significant analytical signal error has appeared and the repeatability has deteriorated due to aggregation of dye. Therefore, a dye concentration of 0.27 mmol L^{-1} was selected as optimal value for further studies.

Effects of concentration of nonionic surfactant and salting-out agent on the analytical signal

In VA-CPE, it is important to choose an appropriate surfactant, since the temperature corresponding to cloud point is correlated with the hydrophilic property of a surfactant. A successful CPE should maximize the extraction efficiency by minimizing the phase volume ratio, thus increasing its concentrating capability. In order to attract the resulting complex $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}\dots 3\text{TBH}_2^+$ to surfactant

phase, the effect of different types of nonionic surfactants such as Triton X-114 and Triton X-45, PONPE 7.5 was initially examined. The surfactants are the most frequently used surfactants in conventional CPE experiments. They have been extensively used to sensitize the reaction or to separate the analyte phase without using organic solvent as a medium. From prior studies conducted in range of $0.0025\text{--}0.15\%$ (v/v) for each nonionic surfactant, it has been observed that Triton X-45 is more suitable than other nonionic surfactants, and the maximum signal is obtained with 0.01% (v/v) Triton X-45 from the absorbance change against nonionic surfactant concentration corrected for analyte blank absorbance of 0.5840 in Fig. 4a. At lower concentrations than 0.01% (v/v), the analytical signal is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. Above this concentration, the analytical signal decreases because of the increment in the volumes and the viscosity of the surfactant phase. Therefore, a Triton X-45 concentration of 0.01% (v/v) was chosen for subsequent studies in order to achieve high analytical signal and good enrichment factors.

Studies on the effects of some additives, such as anionic and nonionic surfactants and organic/inorganic electrolytes, on the cloud point behavior of nonionic surfactants have been reported [53, 54]. It was observed that the presence of electrolytes decreased the cloud point (salting-out effect), resulting in a more efficient extraction. The lower cloud point is attributed to electrolytes promoting dehydration of the poly (oxyethylene) chains. According to Komaromy-Hiller et al. [55], the salting-out phenomenon is directly related to desorption of ions to the hydrophilic parts of the micelles, increasing inter-attraction between

micelles and consequently leading to the precipitation of surfactant molecules. Based on these discussions, NaCl, NaBr and Na₂SO₄ were investigated as salting-out agents in the concentrations ranging from 0.02 to 0.6 mmol L⁻¹ in Fig. 4b, and the highest analytical signal was obtained for 0.2 mmol L⁻¹ Na₂SO₄ from the absorbance change against electrolyte concentration corrected for analyte blank absorbance of 0.5805. The analytical signal decreased considerably for increasing Na₂SO₄ volumes in range of 0.2–0.6 mmol L⁻¹. This effect may be explained by the additional surface charge when the Na₂SO₄ concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that one blank solution containing all without analyte is also evaluated, and no significant signal is obtained. In this way, a Na₂SO₄ concentration of 0.2 mmol L⁻¹ was used in all further experiments.

Effects of equilibrium temperature and time on the analytical signal

Optimal equilibrium time and temperature are necessary to the completion of the complex formation and efficient phase separation as possible. They are desired to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency upon temperature and time of equilibrium was examined in the ranges of 25–65 °C and 2–15 min at water-bath at fixed ultrasonic power (300 W, 40 kHz), respectively. The results showed that 45 °C as temperature and 5 min as equilibrium time are appropriate and enough for VA-CPE experiments.

Effects of vortex time and velocity on the analytical signal

In this study, vortex has two main roles: One is to mix the solutions, reagents and chemicals for dissolution, and the other is to form homogeneous extractants and analytes, to ensure full contact between molecules so as to improve the extraction efficiency. To achieve these goals, the effect of vortex time and velocity on the analytical signal were examined in ranges of 2–10 min and 500–4000 rpm, respectively. The experimental procedures clearly show that after agitating the mixture for 3 min and 3500 rpm, the concentration of thiosulfate in the Triton X-45 extract reached to equilibrium. It appears that the fine droplets formed during the preconcentration procedure can be able to extract the target analyte toward equilibrium faster because of the shorter diffusion distance and larger specific surface area. Thus, a vortex extraction time and velocity of 3 min and 3500 rpm, respectively, were chosen as optimum values.

In addition, centrifugation time and rates are very necessary to preconcentrate trace amounts of thiosulfate with high CPE efficiency in a short time. Thus, under optimal conditions obtained, the effect of the centrifugation time and rate were studied in ranges of 2–10 min and 1000–4000 rpm, respectively. The results have showed that centrifugation for 5 min at 4000 rpm provides to the maximum absorbance and sensitivity for thiosulfate. The surfactant-rich phase obtained after phase separation is dissolved and diluted to about 0.9 mL by using 0.7 mL of acetonitrile prior to analysis by UV–Vis spectrophotometry.

Calibration curves, detection limit and precision

Analytical performance features of the proposed method for thiosulfate were as follows. A series of thiosulfate standard calibration solutions were sampled to measure absorbance according to the optimal experimental conditions. The results obtained with and without vortex induction showed that absorbance (Abs.) versus concentration of thiosulfate in the ranges of 0.2–120 and 5–180 µg L⁻¹ with calibration sensitivities of 9.7×10^{-3} and 1.8×10^{-3} obeyed a very wide linear relation. The calibration sensitivities obtained with and without vortex are described as the slopes of the calibration curves at the concentration of interest. Shortly, it can also be expressed as a change in analytical signal per unit change in analyte concentration, dA/dC. The following regression equation has been obtained in the range of 0.2–120 µg L⁻¹: Abs. = $(9.7 \pm 0.8) \times 10^{-3}$ [S₂O₃²⁻, µg L⁻¹] + $(1.10 \pm 0.02) \times 10^{-2}$ with vortex mixing (r^2 : 0.9978, n : 10), while it is obtained in the range of 5–180 µg L⁻¹: Abs. = $(1.8 \pm 0.1) \times 10^{-3}$ [S₂O₃²⁻, µg L⁻¹] + $(1.2 \pm 0.1) \times 10^{-2}$ without vortex mixing (r^2 : 0.9992, n : 7), in which coefficient of determination, r^2 is a number that indicates how well data fit a statistical model, sometimes, simply a line or a curve. It is simply the square of the sample correlation coefficient (r) between the outcomes and their predicted values. The precision of the proposed method was checked by the percent relative standard deviation (RSD %) of six independent measurements taken in solutions containing all ions. The precision after CPE with and without vortex induction were in range of 2.5–4.8 and 2.4–4.6% (5, 10 and 25 µg L⁻¹, n : 5). The recovery rates were in the range of 97–104 and 96–104% (5, 10 and 25 µg L⁻¹, respectively, n : 5). The limits of detection and quantification that is statistically based the calculation of LOD and LOQ: $3\sigma_{\text{blank}}/m$, $10\sigma_{\text{blank}}/m$ where the σ_{blank} is the standard deviation of ten replicate blank measurements, and m is the slopes of the calibration curves obtained after preconcentration with VA-CPE were found to be 0.05 and 0.22 µg L⁻¹, respectively, for

Table 1 Analytical performance properties of the VA-CPE method

Analytical properties	After preconcentration at 632 nm		Before preconcentration at 642 nm
	By VA-CPE	By CPE	
Linear working range ($\mu\text{g L}^{-1}$)	0.2–120	5–180	260–3600
Regression equation	$A = (9.7 \pm 0.8) \times 10^{-3} C_{\text{thiosulfate}, \mu\text{g L}^{-1}} + (1.10 \pm 0.02) \times 10^{-2}$	$A = (1.8 \pm 0.1) \times 10^{-3} C_{\text{thiosulfate}, \mu\text{g L}^{-1}} + (1.1 \pm 0.1) \times 10^{-2}$	$A = (1.2 \pm 0.1) \times 10^{-4} C_{\text{thiosulfate}, \mu\text{g L}^{-1}} + (4.1 \pm 0.3) \times 10^{-2}$
Correlation coefficient, r^2	0.9978	0.9992	0.9932
Precision, RSD % (n : 5; 5, 10 and 25 $\mu\text{g L}^{-1}$)	2.5–4.8	2.4–4.6	3.2–5.1
Recovery % (n : 5; 5, 10 and 25 $\mu\text{g L}^{-1}$)	97–104	96–104	96–103
Detection limit (LOD) (n : 10, $3\sigma_b/m$) ($\mu\text{g L}^{-1}$)	0.05	1.5	78
Quantification limit LOQ (n :10, $10\sigma_b/m$) ($\mu\text{g L}^{-1}$)	0.22	4.9	259
Preconcentration factor ^a	56	56	–
Sensitivity enhancement factor ^b	81	15	–

^a Preconcentration factor is defined as the ratio between the analyte concentration in the surfactant-rich phase (C_S) and the initial concentration of the analyte (C_0) in the aqueous sample

^b Sensitivity enhancement factor is calculated as the ratio of slope of calibration curves with and without preconcentration

thiosulfate along with sensitivity enhancement factor of 78, in which the sensitivity enhancement factor obtained after preconcentration with CPE without vortex mixing is 15 with limits of detection and quantification of 1.5 and $4.9 \mu\text{g L}^{-1}$ in linear range of $5\text{--}180 \mu\text{g L}^{-1}$. The preconcentration or enrichment factor (PF or $\text{EF} = C_S/C_0$) is defined as the ratio between the analyte concentration in the surfactant-rich phase (C_S) and the initial concentration of the analyte (C_0) in the aqueous sample [56]. The preconcentration factor for CPE with and without vortex mixing is approximately 56, in which the percent extraction efficiency is $\text{PF} \times (V_S/V_0) \times 100 = 56 \times (0.9/50 \text{ mL}) \times 100 = 100.8\% = 101\%$. The sensitivity enhancement factor is calculated as the ratio of slopes of the calibration curves obtained with and without preconcentration by VA-CPE. The analytical performance properties of method were indicated in Table 1.

Due to lack of a CRM, which is suitable to sample matrix, the proposed method was also validated by evaluating analytical curves, linearity, precision, recovery, selectivity, stability, limit of detection and quantitation. The linear relationship between analytical signal and thiosulfate concentration was demonstrated by using a seven-point matrix matched calibration curve in range of 1, 5, 15, 30, 60, 90 and $120 \mu\text{g L}^{-1}$ at 632 nm under the optimized reagent conditions after preconcentration with VA-CPE. We prepared two different sets of calibration samples by adding thiosulfate to mixture of lake water, cold- and hot-spring water (3:3:4, v/v) or mixture of two

wastewater sample (5:5, v/v). At each concentration level, three replicate measurements were taken. The calibration curve was highly linear with a slight change in calibration sensitivity in range of $1\text{--}120 \mu\text{g L}^{-1}$ for both sample matrices. The linear working range can be easily extended even up to a concentration of $175 \mu\text{g L}^{-1}$ by with a regression coefficient of 0.965 when required. The regression equations for the linear calibration curve were $\text{Abs.} = (9.5 \pm 0.6) \times 10^{-3} [\text{S}_2\text{O}_3^{2-}, \mu\text{g L}^{-1}] + (1.35 \pm 0.10) \times 10^{-2}$ for spring water matrix and $\text{Abs.} = (9.8 \pm 0.7) \times 10^{-3} [\text{S}_2\text{O}_3^{2-}, \mu\text{g L}^{-1}] + (1.50 \pm 0.10) \times 10^{-2}$ for wastewater matrix. The correlation coefficient for the calibration curves with LOD and LOQ of 0.32 and $1.10 \mu\text{g L}^{-1}$, respectively, was higher than 0.990 in both cases. The differences between calibration slopes in both sample matrices were not statistically significant. Thus, the matrix of calibration sample did not significantly affect quantification in terms of reliability. In order to judge the quality of the method, precision and recovery were determined. The intra- and inter-day precision and recovery studies were performed in matrix matched samples spiked with thiosulfate (5, 15 and $30 \mu\text{g L}^{-1}$) in three replicates. The inter-day precision and recovery were evaluated on three consecutive days in a week. From the results obtained, the intra-day and inter-day precision (as RSD %) were within 2.8–4.7 and 3.5–5.8% for spring water matrices, and within 1.6–5.2 and 3.5–6.3% for wastewater matrices, respectively. Recovery values were found to be in range of 93–106%.

Table 2 Interfering effect of matrix components on determination of $50 \mu\text{g L}^{-1} \text{S}_2\text{O}_3^{2-}$

Interfering species	Tolerance limit ^a
Na^+ , K^+ , NH_4^+ , F^- , NO_3^- , HCO_3^- , hydrazine, Sr^{2+} , and Mg^{2+}	>1000
Cl^- , Br^- , Ca^{2+} , Cr^{3+} , Zn^{2+} , thiourea, oxalate, HPO_4^{2-} , citrate, ascorbic acid, tartrate, Mn^{2+} , Cd^{2+} , and Co^{2+}	400–750
Fe^{2+} , Ag^+ , Pb^{2+} , V^{4+} (as VOSO_4), Sb^{3+} (as Sb_2O_3), As^{3+} (as As_2O_3), and Se^{4+} (as Na_2SeO_3)	250–350
Ni^{2+} , Mo^{6+} (as Na_2MoO_4), V^{5+} (as NH_4VO_3), CN^- , As^{5+} (as AsCl_5) and Sb^{5+} (as SbCl_5)	75–200
IO_3^- , SCN^- and S^{2-}	40–60
$(\text{S}_2\text{O}_4^{2-} \text{ and } \text{SO}_3^{2-})^b$	35 (500 ^b)
$(\text{Cu}^{2+} \text{ and } \text{Bi}^{3+})^c$ (Al^{3+} and $\text{Sn}^{4+})^d$	20–30 (150 ^c , 300 ^d)
$(\text{Fe}^{3+} \text{ and } \text{SiO}_3^{2-})^d$	5–15 (350 ^d)
$\text{Hg}^{2+,e}$	3 (200) ^e

^a Concentration ratios of interfering ions and thiosulfate at fixed concentration of $50 \mu\text{g L}^{-1}$

^b After pretreatment with $25 \mu\text{L}$ of 0.025% (w/v) formaldehyde solution

^c After pretreatment with $50 \mu\text{L}$ of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ascorbic acid solution

^d After pretreatment with 0.1 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ NaF for 15 min under sonication at 70°C

^e After pretreatment with $25 \mu\text{L}$ of 0.025% (w/v) hydrazine hydrochloride solution

Interference study

In view of reasonable selectivity provided by spectrophotometry due to give a stable anionic complex of analyte with Ag^+ ions and then its extractable ion-pairing complex with TB^+ or TBH^{2+} at pH 7.0, the only interference may be attributed to the separation and preconcentration step. Interferences studied are those related to the separation step, cations and anions that may react with the ion-pairing reagent, Ag^+ ions as well as thiosulfate and thus decrease the extraction efficiency. To perform this study, interference ions in different interference to analyte ratios were added to a model solution containing $50 \mu\text{g L}^{-1}$ of thiosulfate, and the mixtures were subjected to the recommended procedure. Table 2 shows the tolerance limits of the interference ions (error of $\pm 5.0\%$). The results demonstrate that the large amounts of possible interfering species commonly present in environmental waters have no significant effect on the VA-CPE of thiosulfate after pretreatment of water samples with suitable masking agents. Alternatively, for obtaining more accurate and reliable measurements in monitoring of environmental water quality, it has been observed that interferences arising from metal cations such as Hg(II) , Cu(II) , Fe(III) , Bi(III) will be able to suppress by passing through samples from strongly cation-exchange resin.

The accuracy and analytical applications of the proposed method

In order to ensure the accuracy and precision of the developed method, when a regression analysis (n : 6, independently) is conducted for a serial standard thiosulfate

solution in range of $0.2\text{--}3.5 \text{ mg L}^{-1}$ in the presence of oxalic acid at pH 6.5 phosphate buffer, according to standard DTNB method, a good improvement in regression data was obtained as follows:

$$\text{Abs} = 0.32 \pm 0.02 \left[\text{S}_2\text{O}_3^{2-}, \text{mg L}^{-1} \right] + (9.6 \pm 0.6) \times 10^{-3}, \quad r^2: 0.9980 \quad (1)$$

A good linear relationship was obtained in range of $0.02\text{--}3.0 \text{ mg L}^{-1}$ with limits of detection and quantification of 0.005 and 0.02 mg L^{-1} , respectively. Also, all the selected water samples were initially passed through a strongly cation-exchange resin in order to avoid from the interference of potential metal cations present in waters instead of using different masking agents. When necessary, in order to prevent possible nitrite interference in analysis of beverages, $150 \mu\text{L}$ of 0.01 mol L^{-1} sulfamic acid was added to the solution medium.

To confirm the analytical usefulness of the proposed method, the method was directly applied to the determination of thiosulfate in hot-/cold-spring waters, wastewaters and natural lake by means of UV–Vis spectrophotometry. The collected samples were prepared to analysis according to procedure mentioned in “Preparation of samples to analysis” Section. The analytical results were found by using directly standard calibration curve and standard addition methods around determination limit to reduce the matrix effect. The results and the recoveries for the spiked samples at concentration levels ranging from 5 to $25 \mu\text{g L}^{-1}$ depending on sample type are given in Table 3. It can be seen that the recoveries for the spiked samples are in the range of $97\text{--}104\%$ with RSDs of $1.1\text{--}3.3\%$ (n : 5) for the proposed method, whereas they are in the range of $98\text{--}102\%$ with RSDs of $0.9\text{--}3.0\%$ (n : 5) for standard

Table 3 Analysis results of free thiosulfate of some environmental water samples and the recovery rates of spiked samples ($n: 5$)

By using the proposed VA-CPE spectrophotometric method					By using standard DTNB method				The variance ratio, F test and Student' t test ^a
Samples	Added, $\mu\text{g L}^{-1}$ thio-sulfate	Found, $\mu\text{g L}^{-1}$ thio-sulfate	Recovery (%)	RSDs (%)	Added, $\mu\text{g L}^{-1}$ thio-sulfate	Found, $\mu\text{g L}^{-1}$ thio-sulfate	Recovery (%)	RSDs (%)	
<i>Lake and river waters</i>									
Imranlı dam water	–	8.8 ± 0.3	–	3.4	–	9.1 ± 0.3	–	3.3	1.5, 0.4
	5	13.4 ± 0.3	97	2.2	5	13.8 ± 0.3	98	2.2	–
	10	18.5 ± 0.3	98	–	10	18.8 ± 0.3	98	1.6	–
	25	33.9 ± 0.5	100	1.5	25	33.7 ± 0.5	99	1.5	–
Kızılırmak river water	–	12.7 ± 0.4	–	3.1	–	13.0 ± 0.4	–	3.1	1.5, 0.4
	5	17.4 ± 0.5	98	2.9	5	17.6 ± 0.5	98	2.8	–
	10	22.5 ± 0.5	99	2.2	10	22.7 ± 0.5	99	2.2	–
	25	37.5 ± 0.7	100	1.9	25	37.8 ± 0.7	100	1.8	–
Hafik lake water	–	9.8 ± 0.3	–	3.1	–	10.3 ± 0.3	–	2.9	1.8, 0.8
	5	15.1 ± 0.4	102	2.6	5	15.0 ± 0.4	98	2.7	–
	10	20.1 ± 0.5	101	2.5	10	20.0 ± 0.5	99	2.5	–
	25	34.5 ± 0.6	99	1.7	25	35.1 ± 0.6	99	1.7	–
<i>Hot- and cold-spring waters</i>									
Cold-spring water ¹	–	13.8 ± 0.4	–	2.9	–	14.1 ± 0.4	–	2.8	1.2, 0.6
	5	19.3 ± 0.5	103	2.6	5	19.8 ± 0.5	102	2.5	–
	10	24.2 ± 0.6	102	2.5	10	24.5 ± 0.6	102	2.4	–
	25	39.1 ± 0.7	101	1.8	25	38.8 ± 0.7	99	1.8	–
Cold-spring water ²	–	10.4 ± 0.3	–	2.9	–	11.1 ± 0.3	–	2.7	1.9, 1.1
	5	15.1 ± 0.4	98	2.6	5	15.6 ± 0.4	97	2.6	–
	10	20.2 ± 0.5	99	2.5	10	20.7 ± 0.5	98	2.4	–
	25	35.2 ± 0.6	99	1.7	25	35.7 ± 0.6	99	1.7	–
Hot-spring water ¹	–	18.7 ± 0.5	–	2.7	–	19.1 ± 0.5	–	2.6	1.9, 0.7
	5	24.1 ± 0.6	102	2.5	5	25.6 ± 0.6	98	2.3	–
	10	28.2 ± 0.6	98	2.1	10	28.6 ± 0.6	98	2.1	–
	25	43.4 ± 0.8	99	1.8	25	44.4 ± 0.8	101	1.8	–
Hot-spring water ²	–	21.4 ± 0.6	–	2.8	–	22.5 ± 0.6	–	2.7	1.2, 0.8
	5	26.3 ± 0.6	99	2.3	5	28.1 ± 0.7	104	2.5	–
	10	31.0 ± 0.7	99	2.2	10	33.2 ± 0.7	102	2.1	–
	25	45.9 ± 0.8	99	1.7	25	47.0 ± 0.8	99	1.7	–
<i>Tap water and wastewater</i>									
Tap water ¹	–	7.8 ± 0.2	–	2.6	–	7.9 ± 0.2	–	2.5	1.4, 0.2
	5	13.2 ± 0.3	104	2.3	5	12.8 ± 0.3	98	2.3	–
	10	17.4 ± 0.4	98	2.3	10	17.7 ± 0.4	99	2.3	–
	25	32.5 ± 0.6	99	1.8	25	32.7 ± 0.6	100	1.8	–
Tap water ²	–	9.3 ± 0.3	–	3.2	–	10.1 ± 0.3	–	3.0	1.9, 1.0
	5	14.2 ± 0.4	98	2.8	5	14.7 ± 0.4	98	2.7	–
	10	19.6 ± 0.5	101	2.6	10	19.7 ± 0.5	98	2.5	–
	25	34.5 ± 0.7	101	2.0	25	35.0 ± 0.7	100	2.0	–
Wastewater ^b	–	35.5 ± 1.0	–	2.8	–	36.4 ± 1.0	–	2.7	2.4, 0.6
	5	41.3 ± 1.0	10	2.4	5	42.5 ± 1.0	103	2.4	–
	10	44.8 ± 1.1	98	2.4	10	45.6 ± 1.1	98	2.4	–
	25	59.9 ± 1.2	99	2.0	25	60.8 ± 1.2	99	2.0	–

Table 3 continued

By using the proposed VA-CPE spectrophotometric method					By using standard DTNB method				The variance ratio, <i>F</i> test and Student's <i>t</i> test ^a
Samples	Added, $\mu\text{g L}^{-1}$ thio-sulfate	Found, $\mu\text{g L}^{-1}$ thio-sulfate	Recovery (%)	RSDs (%)	Added, $\mu\text{g L}^{-1}$ thio-sulfate	Found, $\mu\text{g L}^{-1}$ thio-sulfate	Recovery (%)	RSDs (%)	
Wastewater ^c	–	37.7 ± 1.1	–	2.9	–	37.9 ± 1.1	–	2.9	1.6, 1.0
	5	41.8 ± 1.1	98	2.6	5	43.7 ± 1.1	102	2.5	–
	10	47.0 ± 1.1	98	2.3	10	48.6 ± 1.1	101	2.3	–
	25	62.3 ± 1.2	99	1.9	25	63.2 ± 1.2	100	1.9	–

^a In order to compare two mean values for independent two sample *t*- and *F* tests with equal sample size the statistical *t*- and *F*-critical values at 95% confidence level and 8 degrees of freedom are 2.3 and 6.4, respectively

^b The waste water sample taken from the region industrial facilities, Sivas, Turkey

^c The waste water taken from the dental clinic effluents, Faculty of Dentistry of Cumhuriyet University, Sivas, Turkey

DTNB method. As can be seen from Table 2, the Student's *t* test and variance ratio *F* test for comparison of mean values demonstrated that there is statistically no significant difference between the mean values (and ratios of their variances) obtained by two detection methods at the significance level of 0.05, respectively. Because the experimental *t* values ranging from 0.2 to 1.1 and the experimental $F_{4,4}$ value ranging from 1.2 to 2.4 are lower than the tabulated *t* value and $F_{4,4}$ -value of 2.3 and 6.4, respectively. It is clear that the proposed method has good reproducibility as a measure of precision by variance analysis based on pooled standard deviation.

Comparison of the VA-CPE method with other methods

According to our knowledge's, the current preconcentration method is the first approach for preconcentration/determination of low levels of thiosulfate in presence of TB^+ or TBH^{2+} as ion-pairing reagent in environmental waters by combination of VA-CPE with UV–Vis spectrophotometry. When compared to the analytical performance properties of the current VA-CPE method with those of other detection methods in literature such as LODs, linear working range, precision, preconcentration and sensitivity enhancement factors [4, 5, 13, 14, 30, 32, 33], except for IC method based on catalytic effect of thiosulfate onto photometric reaction between I_3^- and N_3^- at pH 5.0 [1] in Table 4, it shows many advantages such as simplicity, minimum solvent consumption, reasonable repeatability/reproducibility, a linear working range of 600-fold, a low detection limit with comparatively little interference with a highly good calibration sensitivity. IC as detection tool has disadvantages such as long analysis time (>15 min), expensive analysis

equipment and chemicals, poor recovery due to peak tailing and/or peak overlapping especially at high concentrations, so as to lead to recalibration of instrument. Because IC analysis is based on charge separation, it is also subject to interferences from similarly charged particles. In this sense, thiosulfate is a polarizable anion such as thiocyanate and iodide. These anions have large deformable electron clouds and are lightly hydrated and therefore hydrophobic. Due to their hydrophobicity, these anions elute from previously existing anion-exchange stationary phases with poor peak shapes and poor peak efficiencies, which compromises the chromatographic and electrophoretic analysis. The addition of derivatization reagents, surfactants, organic modifiers and stabilizer to the eluent improves the peak shape and efficiencies but leads to increased eluent and waste disposal costs and reduces the sensitivity of detection. Moreover, in separation and speciation analysis of other sulfur species including thiosulfate by means of IC, CE, CZE and MEKC, the usage of these reagents will also lead to a deterioration of the precision. In addition, the method was successfully applied to the monitoring of trace amounts of thiosulfate in different water samples such as tap water, lake water, river water, dental wastewater, and hot-/cold-spring waters. Moreover, the rather low toxicity of the reagents used is very beneficial for human health and monitoring of environmental water quality. The environmental problems connected with accumulation and utilization of large amounts of hazardous organic solvents were reduced to the lowest ratios when possible. Thus, the application of the method to different water samples is analytically facilitated when comparing with sensitive, but poor precision especially at low concentrations, spectral and isobaric interferences, memory effect, expensive techniques such as GC with ECD and GC–MS [32], RP-HPLC [34] and ICP–MS [37] that require expert user in his/her area, a laborious and

Table 4 Comparison of the VA-CPE/Spectrophotometry with other detection methods

Sample matrix	Ion-pairing/derivatization reagents/EOF modifier	Detection tool	Linear range	Detection limit	Precision, RSD %	Conditions	One sample analysis time	References
Hot-spring waters	NaN_3 /excess I_2 or I_3^-	IC with photometric detection	0–0.5 $\mu\text{mol L}^{-1}$ (0–56.9 $\mu\text{g L}^{-1}$)	0.16 ng at 350 nm	1.5 (33.6 $\mu\text{g L}^{-1}$, n : 5), 3.6 (110 $\mu\text{g L}^{-1}$, n : 6 in real samples)	Acetate medium at 40 °C	15 min (retention time)	[1]
The spent fixing solutions during the electrolytic oxidation	Tetrabutylammonium acetate (TBAAc)	CE with UV detection	(0.01–1) $\times 10^{-3}$ mol L^{-1}	–	1.8	(NH_4) ₂ SO ₄ , KH_2PO_4 electrolyte at pH 5.0	4 min	[4]
Sulfidic waste effluent (produced water) generated during offshore oil production	Ellman's reagent (DTNB), 2,2'-dithiobis(5-nitropyridine)/tetrabutylammonium hydrogen-sulfate (TBAHS)	Sampled DC polarography, DPP, and HPLC with gradient elution at 320 nm	0–20 $\mu\text{mol L}^{-1}$	–	–	pH 6.0 acetate buffer for DPP/pH 3.5 for HPLC	–	[5]
Urine	2-Chloro-1-methylquinolinium tetrafluoroborate,	MEKC with UV detection	4–64 $\mu\text{mol L}^{-1}$	1.2 $\mu\text{mol L}^{-1}$ at 375 nm	1.2–4.8	pH 8.0, acetonitrile and SDS	45 min for capillary conditioning	[12, 13]
Commercial bleaching agents	Pyromellitic acid, tris, diethylenetriamine and formaldehyde	CZE with indirect UC detection	2–10 mg L^{-1}	0.6 mg L^{-1} at 214 nm	–	pH 7.0	9 min	[13, 14]
Wastewater	Al(III)/OH^- solutions for formation of SO_2 , in which a cool hydrogen flame is used to excite the analyte	MECA using catalytic properties of H^+	15–100 mg L^{-1}	0.11 mg L^{-1}	3.29	pH 8.0 at 40 °C	95 s $t_{90\%}$	[16, 30]
Urine and blood samples	Pentafluorobenzyl bromide	GC with ECD/GC-MS	0.005–2.0 $\mu\text{mol L}^{-1}$	0.003 $\mu\text{mol L}^{-1}$ (0.336 $\mu\text{g L}^{-1}$)	3.1 (0.5 $\mu\text{mol L}^{-1}$, n :5)	Ascorbic acid as stabilizer/NaCl as catalysts	t_R : 3.8 min internal standard, t_R : 6.4, derivatization product	[18, 32]
Table salt	1,5-Diphenylcarbazide/Cr(VI)	SPE/FAAS	0–2 mg L^{-1} for 50 mL	–	3.5 (10 mg L^{-1} , n : 5)	pH 1.0, H_2SO_4 in methanol as eluent	–	[19, 33]
Seawater, blood and coelomic fluid	A fluorescent reagent, monobromobimane	Reverse phase HPLC After derivatization at pH 8.0	0–150 $\mu\text{mol L}^{-1}$	0.03 $\mu\text{mol L}^{-1}$ (3.36 $\mu\text{g L}^{-1}$)	1.1 repeatability, 3.5 reproducibility (100 $\mu\text{mol L}^{-1}$, n : 5)	pH 4.5–5.0 for detection	t_R : 5.6 min, 40 min and 1 h for derivatization reaction	[34, 20]

Table 4 continued

Sample matrix	Ion-pairing/derivatization reagents/EOF modifier	Detection tool	Linear range	Detection limit	Precision, RSD %	Conditions	One sample analysis time	References
Hot-spring waters	Tetrapropylammonium salt (TPA)	IC with UV detection	–	30 nmol L ⁻¹ (or 3.36 µg L ⁻¹) for S/n:3 at 230 nm	–	pH 5.0, acetone-trile–water (20:80, v/v) solution	22 min to separate anions	[35, 21]
Water samples	1,3,5-benzenetricarboxylic acid (BTA)	IC with fluorescence detection	0–25 µmol L ⁻¹ (2.8 mg L ⁻¹)	37 µg L ⁻¹ at 256 and 354 nm	2.9	H ₂ SO ₄ medium/Ce(IV)	51.4 min (elution time)	[36, 22]
Saline waters	Separation on Dionex Ion-Pac® AS12A analytical column	IC/ICP-MS in presence of 10 µg L ⁻¹ Ce(IV)	0–100 mg L ⁻¹	270 µg L ⁻¹	–	Mobile phase, NH ₄ CO ₃ , Na ₂ CO ₃ and NaOH	<i>t_R</i> : 23.5 min for S ₂ O ₃ ²⁻ , ICP-MS signal at <i>m/z</i> = 48 ³² S ¹⁶ O ⁺ for the sulfur-containing anions	[37, 23]
Environmental waters	Toluidine blue/Ag ⁺	VA-CPE/spectrophotometry, 632 nm	0.2–120 µg L ⁻¹	0.05 µg L ⁻¹	2.5–4.8	pH 7.0, triton-45, EF: 81, PF 56	15 min	The present method

time-consuming separation/speciation procedures using gradient temperature program, gradient elution and internal standard for accurate and reliable measurements.

Conclusions

In this study, a new VA-CPE preconcentration procedure for an accurate and precise analysis of free thiosulfate in hot-/cold-spring waters, wastewaters, lake and river water using Triton X-45 as extracting agent and TB⁺ as ion-pairing agent was developed. The vortex-induced micellar extraction procedure has greener, economical, simple and fast, less reagent consumption, high preconcentration and sensitivity enhancement factors. In this method, the low levels of thiosulfate in the current samples were monitored using UV–Vis spectrophotometry at 632 nm. The advantages of using these device has adequate accuracy, economical, simplicity of usage and available in nearly every analytical research laboratory. Furthermore, for the samples available, a low detection limit (0.05 µg L⁻¹), preconcentration factor (56) and sensitivity enhancement factor (81) in a wide linear range (0.2–120 µg L⁻¹) after preconcentration with vortex mixing were easily obtained by this method using the optimized conditions. When considering all the mentioned results, the suggested VA-CPE/spectrometric method can be considered as an alternative tool to relatively comparable sensitive, but expensive, time-consuming, complex and experienced user-requiring analytical techniques such as GC with ECD, GC–MS, RP-HPLC, MEKC and IC/ICP–MS.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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