TÜBİTAK

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2016) 40: 1019 – 1033

doi:10.3906/kim-1512-37

Ionic liquid based microextraction combined with derivatization for efficient enrichment/determination of asulam and sulfide

Habibollah ESKANDARI*, Mahnaz SHAHBAZI-RAZ
Department of Chemistry, Faculty of Basic Sciences, University of Mohaghegh Ardabili, Ardabil, Iran

Received: 08.12.2015 • **Accepted/Published Online:** 09.04.2016 • **Final Version:** 22.12.2016

Abstract: This study reports 2 new simple derivatization-based dispersive liquid–liquid microextraction (DLLME) methods for spectrophotometric ultratrace determination of asulam and sulfide. 1-Naphthol (in the presence of nitrite) and N,N-diethyl-p-phenylenediamine (in the presence of Fe(III)) were used to derivatize asulam and sulfide, respectively. In the enrichment methods, the formed derivatives were preconcentrated into microdroplets of the in situ formed water insoluble ionic liquid (IL), 1-hexyl-3-methylimidazolium hexafluorophosphate. Monitoring was performed at 526 nm for asulam and at 664 nm for sulfide, after dissolution of the IL-rich phases into the basic ethanolic solution and ethanol for asulam and sulfide, respectively. Beer's law was obeyed in the ranges of 1.0–80.0 and 0.1–5.0 ng mL^{-1} for asulam and sulfide, respectively. Limits of detection for asulam and sulfide determination by the DLLME methods were 0.18 and 0.019 ng mL^{-1}, respectively. Various foreign cations, anions, organics, and pesticides were tested to evaluate the selectivity of the DLLME methods. The methods were successfully applied to the determination of asulam and sulfide in various environmental, wastewater, and urine samples.

Key words: Asulam, sulfide, ionic liquid, dispersive liquid–liquid microextraction

1. Introduction

One of the most commonly used carbamate pesticides is asulam, methyl-4-aminobenzenesulfonyl carbamate, which has a broad spectrum of applications in agricultural activities as an insecticide, herbicide, and fungicide. Asulam stops cell division and growth of plant tissues. It also acts as a postemergence herbicide for controlling deciduous and perennial grasses. The carbamate pesticide is accumulated in soil and remains for more than one season. Due to its high water solubility and stability, it exhibits high mobility; therefore, it acts as a potential pollutant for both ground and underground water resources and soils. This justifies asulam control in the environment in an accurate, sensitive, and selective manner.[1]

Various analytical methods have been introduced for asulam determination in different samples. Some of the methods are chemiluminometric methods based on enhancing or inhibiting effects of asulam on the luminol/peroxidase system[2,3] and UV photoreaction-oxidation system,[1] electrocatalytic detection using nickel(II) phthalocyanine-multiwall carbon nanotubes (MWCNTs)[4] and cobalt(II) phthalocyanine modified MWCNTs,[5] an immunoassay method using a specific reactive antibody,[6] micellar electrokinetic capillary chromatography by UV and electrochemical detection,[7] capillary electrophoresis by UV and electrochemical detection,[8] ultra-HPLC–tandem MS[9] and spectrofluorimetry after derivatization with fluorescamine.[10] Because of asulam's high

*Correspondence: heskandari@uma.ac.ir

polarity, development of an efficient asulam enrichment method is both difficult and important. Some justifiable microextraction-based methods have been reported for determination of carbamate-based pesticides. One of them is an in-capillary microextraction method. That method uses monolithic-based poly(butyl methacrylate) and polydivinylbenzene adsorbents trying to develop an enrichment/determination procedure for asulam and other carbamate pesticides.[11] The analytical signals obtained versus the amount of the analytes preconcentrated depends on their polarity. The more polar analytes, such as asulam, were not preconcentrated and therefore were not detected. Another report used a dispersive liquid–liquid microextraction method by using chloroform as the extractant for analysis of N-methylcarbamates pesticides.[12] However, asulam was detected with lower sensitivity than some of the other analytes tested.

Most microorganisms produce sulfide from amino acids. Some sulfate-reducing microorganisms also convert sulfate to sulfide. In addition, effluents of some industries contain sulfide. The sources of sulfide pollute water resources. Therefore, determination of sulfide in water resources is important biologically and industrially.

Sulfide reacts with appropriate aromatic amines in the presence of Fe(III) to produce their related phenothiazines. Spectrophotometric determination of sulfide as phenothiazine derivatives has been reported in the literature. Some of the nonextractive reported methods are flow injection or sequential injection based methods with detection of methylene blue or thionine[13–16] products. Enrichment/spectrophotometric sulfide determination methods are more favorable for achieving more sensitivity and selectivity. Different solid phase extractants have been used for enrichment/spectrophotometric determination of sulfide. The adsorbents are Sep-Pak C_{18} cartridge,[17] CN containing cartridge[18], and C_{18} bonded silica.[19] A well-established cloud point extraction method has also been reported.[20]

Over the past 2 decades, comprehensive information about analytical enrichment techniques has been produced. Some of the techniques that are low cost and easy to operate, and have sufficient reliability for precise analytical determinations are solid phase microextraction,[21] magnetic solid phase extraction,[22] cloud point extraction,[23] single drop microextraction,[24] stir-bar sorptive extraction,[25] solidified floating organic drop,[26] hollow fiber liquid microextraction,[27] and dispersive liquid–liquid microextraction (DLLME).[28,29] DLLME is one of the most interesting ones, due in particular to its efficiency, application, and enrichment factor in the analysis of environmentally important species.[30,31] DLLME can be considered a miniaturized version of conventional LLE and requires only microliter volumes of solvents. In DLLME, extraction solvent and time, disperser, and electrolyte added are the basic parameters that determine the efficiency of extraction. Various alternatives have made DLLME as a greener method for analysis. One way to establish a greener DLLME method is cancellation of dispersive solvent in the extraction process. Irradiation by ultrasonic waves is another efficient method to establish a disperser-less homogeneous extraction procedure. Another modification that makes DLLME safer is applying green water-immiscible extractants such as ionic liquids (ILs). The disperser-less DLLME using the fine droplets of ILs is performed by cold-induced process, sonication, and in situ IL formation. Among the techniques, in situ formation of an immiscible IL is simpler and easier to achieve. Generally, in situ formation of an immiscible IL is performed via an ion exchange process by mixing the solutions containing appropriate electrolytes prior to (or during) a DLLME experiment.[28]

UV-Vis spectrophotometry is a cheap, common, simple, and easy to operate determination technique that is applicable for a wide range of analytes in many laboratories. Compared with chromatography, spectrophotometry has less selectivity. A suitable enrichment-separation step prior to spectrophotometry enhances both selectivity and sensitivity. In order to attain the purpose, a low volume of an extractant in conjunction with a microvolume cuvette is necessary. In this work, 2 derivatization reactions were used to develop 2 ef-

ficient spectrophotometric methods for trace determination of asulam and sulfide. This work aimed to show when derivatization reactions are coupled with an IL-based DLLME enrichment method powerful methods for spectrophotometric determination of different types of analytes (sulfide as an inorganic and asulam as an organic) are created. The established DLLME methods have provided appropriate sensitivity and selectivity. The highly extractable dyes formed (the asulam based azo dye and the sulfide based ethylene blue) with high molar absorptivities were enriched into in situ formed 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF_6]). The established methods were satisfactorily applied to the determination of asulam and sulfide in various samples.

2. Results and discussion

The triangular phase diagrams of some 1-alkyl-3-methylimidazolium hexafluorophosphates (the alkyl group is butyl, hexyl, or octyl) in ethanol–water mixtures at ambient condition show that the ionic liquids have different ethanol solubility behaviors. [Bmim][PF_6] has limited solubility in ethanol but [Hmim][PF_6] and [Omim][PF_6] are completely soluble in ethanol. [Bmim][PF_6] is dissolved in water more than [Hmim][PF_6] and [Omim][PF_6]. Moreover, small amounts of water are dissolved in the ethanolic solutions of these ILs but large amounts of water are dissolved in these IL-ethanol solutions containing large amounts of ethanol.[32,33] To prepare a clear IL phase for spectrophotometry, some amounts of ethanol must be added to the IL-rich phase after extraction.

2.1. Optimization of the DLLME method for asulam

Optimization is necessary for obtaining the best condition. The absorbance difference between the sample and blank at 526 nm was considered the analytical signal. A step-by-step optimization procedure was evaluated for optimizing the parameters. The steps that must be optimized are diazotization, excess nitrite decomposition, azo-coupling, extraction process, and handling of the IL-rich phase prior to spectrophotometry. The derivatization reaction for asulam determination is shown in Figure 1. Figure 2 shows the absorbance spectra for an asulam-containing sample and the related blank.

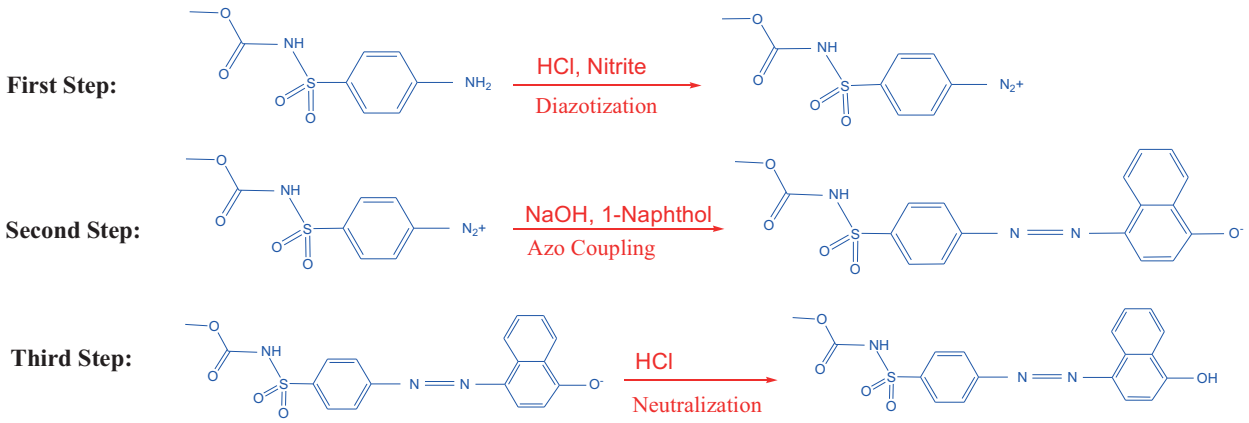

Figure 1. The asulam derivatization pathway.

In the first step, nitrite was used to diazotize asulam. The effective parameters are nitrite and hydrochloric concentrations, and diazotization time. The sensitivity of the method was investigated in the range of 0.5–45 mmol L^{-1} hydrochloric acid. The results are given in Figure 3. The experimental results reveal that the

sensitivity is independent of hydrochloric acid in this range. For further experiments, hydrochloric acid as 10 mmol L^{-1} was selected.

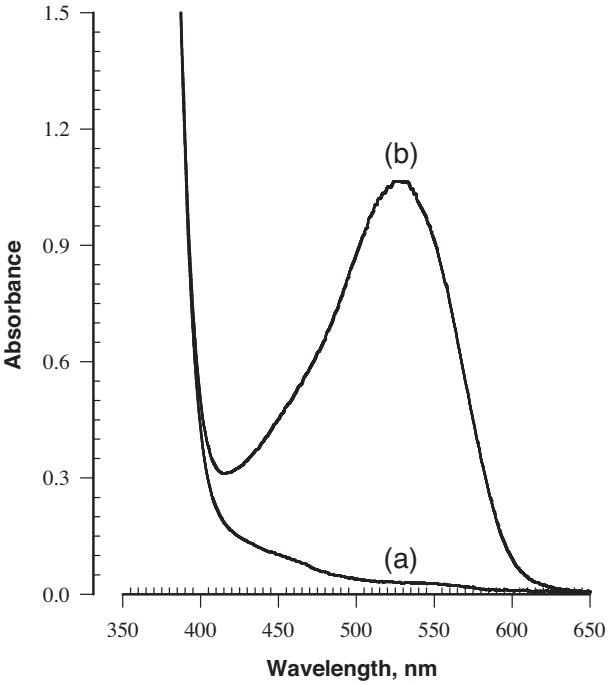

Figure 2. Absorption spectra of extract for: a) blank and b) sample, against ethanol for the proposed asulam determination method. Condition for: a) diazotization: 10.0 mL of aqueous solution (without or with asulam 50 ng mL^{-1}) containing hydrochloric acid 10 mmol L^{-1}, nitrite 0.8 mmol L^{-1}, and diazotization time 5 min; b) excess nitrite removal reaction: sulfamic acid 10 mmol L^{-1} and reaction 3 min; c) coupling: sodium hydroxide 40 mmol L^{-1}, 1-naphthol 0.2 mmol L^{-1} and coupling time 1 min; d) extraction: hydrochloric acid 110 mmol L^{-1}, [Hmim][Cl] 50 mmol L^{-1}, KPF_6 50 mmol L^{-1} and extraction time 3 min; and centrifuging for 2 min at 1000 rpm. For spectrophotometric determination 40 μL of a basic ethanolic solution (sodium hydroxide 30 mmol L^{-1}) was added to the IL phase.

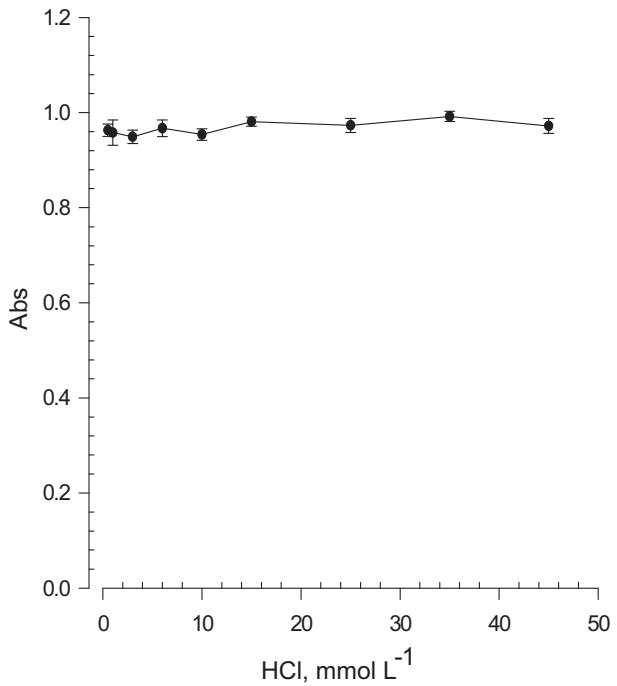

Figure 3. Effect of hydrochloric acid on the asulam diazotization reaction. Condition for: a) diazotization: 10.0 mL of aqueous solution (without or with asulam 50 ng mL^{-1}) containing nitrite 0.6 mmol L^{-1} and diazotization time 4 min; b) excess nitrite removal reaction: sulfamic acid 8 mmol L^{-1} and reaction 5 min; c) coupling: sodium hydroxide 140 mmol L^{-1}, 1-naphthol 0.3 mmol L^{-1} and coupling time 3 min; d) extraction: hydrochloric acid 200 mmol L^{-1}, [Hmim][Cl] 50 mmol L^{-1}, KPF_6 50 mmol L^{-1}, and extraction time 5 min; and centrifuging for 7 min at 1000 rpm. Sodium chloride 0.2 mol L^{-1} was used to adjust ionic strength. For spectrophotometric determination 40 μL of a basic ethanolic solution (sodium hydroxide 40 mmol L^{-1}) was added to the IL phase.

To evaluate the effect of nitrite concentration on the sensitivity of the proposed method, nitrite in the range of 0.1–2.0 mmol L^{-1} was varied and the procedure was followed. According to the obtained results, it appeared that the sensitivity of the method was independent of nitrite concentration in this range. Therefore, 0.8 mmol L^{-1} nitrite was used for the subsequent experiments.

The effect of the diazotization reaction time was investigated in the range of 1–10 min at room temperature. The results are displayed in Figure 4. The diazotization rate of asulam was relatively fast and the reaction was completed after 5 min. Therefore, a reaction time 5 min was chosen for further experiments.

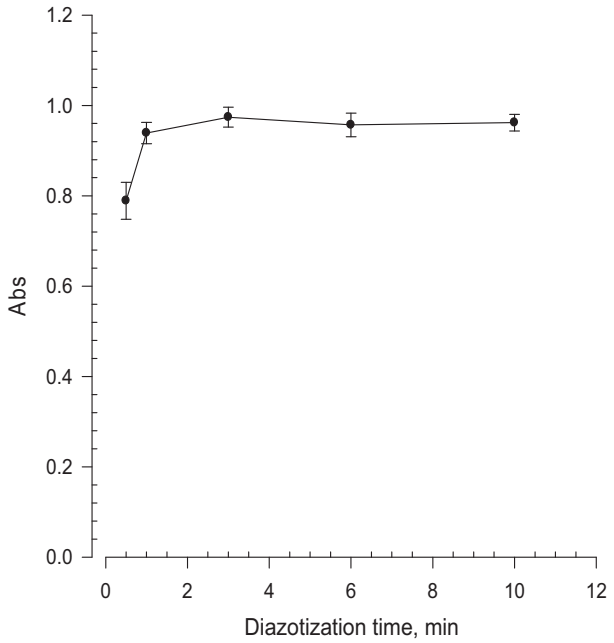

Figure 4. Influence of diazotization time on the sensitivity of the asulam determination. Condition for: a) diazotization: 10.0 mL of aqueous solution (without or with asulam 50 ng mL^{-1}) containing hydrochloric acid 10 mmol L^{-1} and nitrite 0.8 mmol L^{-1}; b) excess nitrite removal reaction: sulfamic acid 8 mmol L^{-1} and reaction 5 min; c) coupling: sodium hydroxide 140 mmol L^{-1}, 1-naphthol 0.3 mmol L^{-1} and coupling time 3 min; d) extraction: hydrochloric acid 200 mmol L^{-1}, [Hmim][Cl] 50 mmol L^{-1}, KPF_6 50 mmol L^{-1} and extraction time 5 min; and centrifuging for 7 min at 1000 rpm. Sodium chloride 0.2 mol L^{-1} was used to adjust ionic strength. For spectrophotometric determination 40 μL of a basic ethanolic solution (sodium hydroxide 40 mmol L^{-1}) was added to the IL phase.

The effect of the sulfamic acid concentration in the range of 1–15 mmol L^{-1} was tested. Sulfamic acid is reacted with nitrite to destroy the excess nitrite.[34] Nitrite is reacted with 1-naphthol and makes a terrible blank. The results of the experiments showed that sulfamic acid in the tested range removes the excess nitrite and has no unfavorable effects on the extraction. For further experiments, 10 mmol L^{-1} sulfamic acid was chosen. The duration of the excess nitrite removal reaction was investigated in the range of 1–7 min. The reaction was completed after 3 min.

For achieving the best condition for coupling of the asulam-based diazonium cation with 1-naphthol, sodium hydroxide concentration in the range of 5–150 mmol L^{-1} was tested. The obtained results showed that sodium hydroxide equal to or greater than 40 mmol L^{-1} gives the best sensitivity. Sodium hydroxide as 40 mmol L^{-1} was used for the subsequent studies. For optimization of 1-naphthol, its concentration was varied in the range of 0.06–0.60 mmol L^{-1}. The obtained results showed that 1-naphthol concentrations equal to or higher than 0.2 mmol L^{-1} provide the best sensitivity. Therefore, 1-naphthol as 0.2 mmol L^{-1} was selected for the next experiments. Moreover, the sensitivity of the method on the coupling reaction time was investigated in the range of 1–7 min. The sensitivity was constant in this range. Therefore, 1 min coupling duration was selected for the subsequent experiments.

Some experiments were conducted to extract the basic form of the produced azo dye. The results of the experiments showed that the basic form of the azo product (a negative ion) is not extractable in the ionic liquid phase. Therefore, in this stage, hydrochloric acid in the range of 15–200 mmol L^{-1} was added to produce the

acidic form of the azo dye (the chargeless azo dye). The obtained results showed that hydrochloric acid equal or larger than 110 mmol L^{-1} produces the best sensitivity. For the subsequent studies, hydrochloric acid as 110 mmol L^{-1} was selected. Moreover, conversion of the basic form of the produced azo dye to its acid form (violet to yellow) is instantaneous. One minute was waited after the addition of hydrochloric acid.

[Hmim][Cl] and KPF_6 solutions were added to the extraction medium for in situ production of the extractant, [Hmim][PF_6]. Various concentrations of [Hmim][Cl] were added to the working solution and the extraction process was followed. The results are given in Figure 5. The extraction efficiency is increased by increasing [Hmim][Cl], because of increasing the volume of [Hmim][PF_6]. On the other hand, the volume of the extract is increased; therefore, the formed azo dye is diluted. Based on the results, [Hmim][Cl] as 50 mmol L^{-1} was selected for the subsequent extraction experiments. Furthermore, KPF_6 solutions of different concentrations were tested. Based on the results in Figure 6, KPF_6 as 50 mmol L^{-1} was chosen for the subsequent investigations. The effects of extraction time and centrifugation time were also studied. Extraction

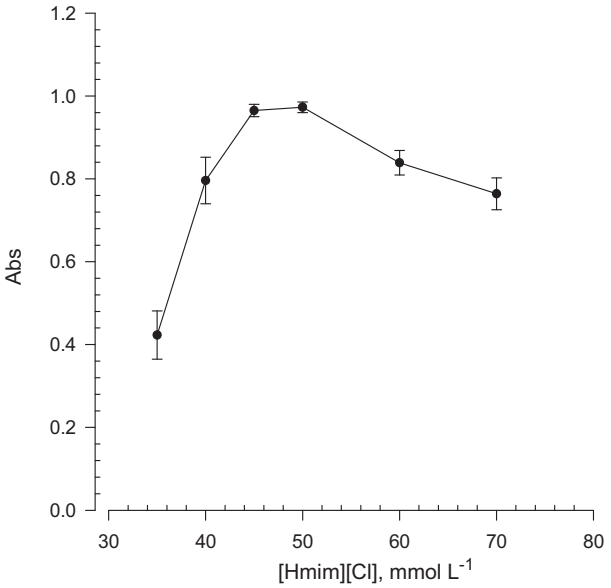

Figure 5. Influence of [Hmim][Cl] on the extraction of asulam. Condition for: a) diazotization: 10.0 mL of aqueous solution (without or with asulam 100 ng mL^{-1}) containing hydrochloric acid 10 mmol L^{-1}, nitrite 0.8 mmol L^{-1}, and diazotization time 5 min; b) excess nitrite removal reaction: sulfamic acid 10 mmol L^{-1} and reaction 3 min; c) coupling: sodium hydroxide 40 mmol L^{-1}, 1-naphthol 0.2 mmol L^{-1} and coupling time 1 min; d) extraction: hydrochloric acid 110 mmol L^{-1}, KPF_6 50 mmol L^{-1} and extraction time 3 min; and centrifuging for 2 min at 1000 rpm. Sodium chloride 0.2 mol L^{-1} was used to adjust ionic strength. For spectrophotometric determination 40 μL of a basic ethanolic solution (sodium hydroxide 40 mmol L^{-1}) was added to the IL phase.

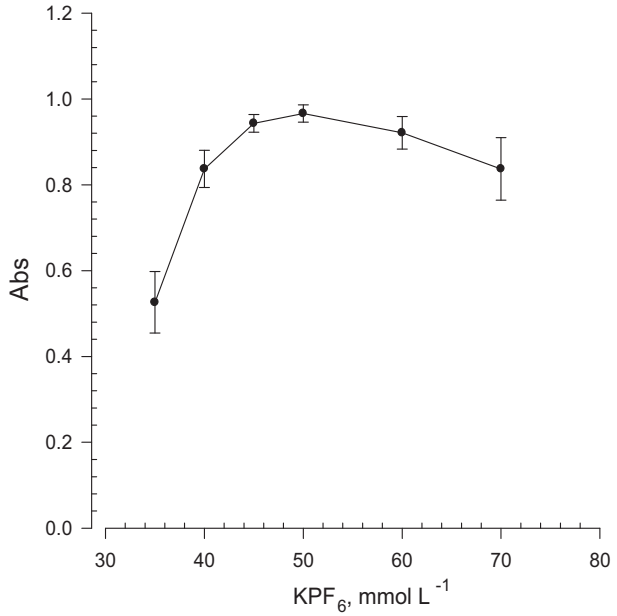

Figure 6. Influence of KPF_6 on the extraction of asulam. Condition for: a) diazotization: 10.0 mL of aqueous solution (without or with asulam 100 ng mL^{-1}) containing hydrochloric acid 10 mmol L^{-1}, nitrite 0.8 mmol L^{-1} and diazotization time 5 min; b) excess nitrite removal reaction: sulfamic acid 10 mmol L^{-1} and reaction 3 min; c) coupling: sodium hydroxide 40 mmol L^{-1}, 1-naphthol 0.2 mmol L^{-1} and coupling time 1 min; d) extraction: hydrochloric acid 110 mmol L^{-1}, [Hmim][Cl] 50 mmol L^{-1} and extraction time 3 min; and centrifuging for 2 min at 1000 rpm. Sodium chloride 0.2 mol L^{-1} was used to adjust ionic strength. For spectrophotometric determination 40 μL of a basic ethanolic solution (sodium hydroxide 40 mmol L^{-1}) was added to the IL phase.

time and centrifugation time (with 1000 rpm) were varied in the ranges of 1–9 and 2–15 min. Extraction duration in the range of 3–9 min produced constant and maximum sensitivity, while 2 min centrifugation was sufficient for isolation of the IL-rich phase from the aqueous solution. Therefore, 3 min extraction time and 2 min centrifugation time were selected for the subsequent experiments.

After extraction, the aqueous phase was discarded and the IL-rich phase was dissolved in ethanolic solutions for spectrophotometry. Complementary experiments showed that the acidic and basic forms of the produced azo dye had absorbance maximums at 460 and 526 nm, respectively. The molar absorptivity of the basic form of the dye was higher than that of the acidic form. Therefore, an ethanolic solution containing sodium hydroxide was used to dissolve the IL-rich phase. The volume of the ethanolic solution and its hydroxide concentration must be optimized. Ethanol (40 μL) containing sodium hydroxide concentration in the range of 8–60 mmol L^{-1} was used to dissolve the IL-rich phase prior to spectrophotometric detection at 526 nm. The sensitivity was constant in the tested sodium hydroxide concentration range. Then different volumes of ethanol in the range of 10–150 μL (containing 30 mmol L^{-1} sodium hydroxide) were used and the experiments were followed. The volumes lower than 40 μL did not dissolve the IL-rich phase completely. Therefore, spectrophotometric detection was not possible for the volumes lower than 40 μL. On the other hand, more diluting of the IL phase decreased the sensitivity of the determination. Therefore, addition of the lowest possible volume of the ethanolic solution is preferred. For achieving the best sensitivity, 40 μL of ethanolic solution containing 30 mmol L^{-1} sodium hydroxide was selected.

The behavior of ionic strength may be complex. Salting-out or salting-in effects may be observed in the extraction experiments. On the other hand, solubility of ILs is increased in aqueous solutions containing high ionic strength.[35,36] The effect of ionic strength on the sensitivity of the proposed method was investigated by the addition of sodium chloride in the range of 0.0–0.8 mol L^{-1}. The obtained results showed that the electrolyte had no considerable effects on the sensitivity of the method.

2.2. Optimization of the DLLME method for sulfide

Figure 7 shows the absorbance spectra for a sulfide-containing sample and the related blank. The absorbance difference between the sample and blank at 664 nm was considered the analytical signal for the sulfide method and a comprehensive study was performed for the optimization of the affecting parameters. The affecting parameters were Fe(III), DPD, total sulfuric acid, 1-hexyl-3-methylimidazolium chloride, potassium hexafluorophosphate concentrations, reaction time, extraction time, centrifugation time, and ethanol volume for diluting the IL-rich phase. Step-by-step optimization was performed. Table 1 indicates the parameter variation ranges and the selected values.

Table 1. Effective parameters, tested ranges and selected values for sulfide determination after optimization.

Step	Parameter	Tested range	Selected value
Reaction	Fe(III)	0.0–10.0 mmol L^{-1}	0.5 mmol L^{-1}
	DPD	0.0–1.0 mmol L^{-1}	0.5 mmol L^{-1}
	Sulfuric acid	4–64 mmol L^{-1}	34 mmol L^{-1}
	Time	0–15 min	5 min
Extraction	[Hmim][Cl]	70 mmol L^{-1}	34 mmol L^{-1}
	KPF_6	70 mmol L^{-1}	34 mmol L^{-1}
	Time	1–12 min	3 min
Centrifugation	Time	1–10 min	3 min
Detection	Ethanol	15–40 μL	25 μL

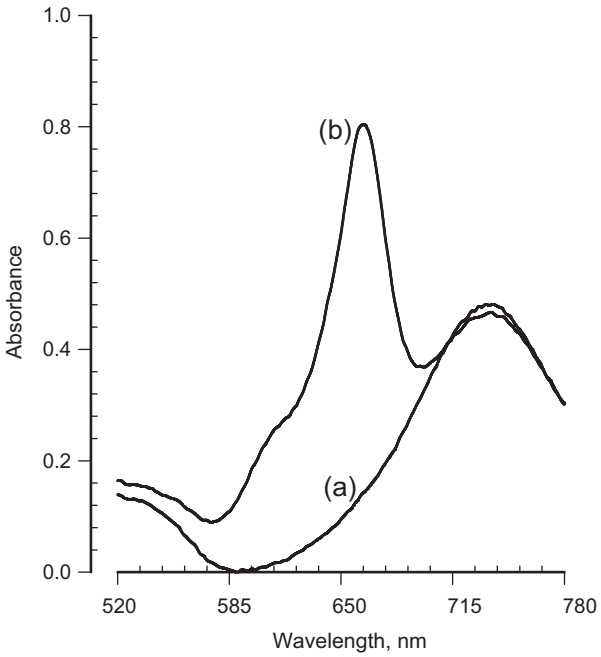

Figure 7. Absorption spectra of extract for: a) blank and b) sample, against ethanol for the proposed sulfide determination method. Condition: 10.0 mL of aqueous solution containing Fe(III) 0.5 mmol L^{-1}, DPD 0.5 mmol L^{-1}, sulfuric acid 34 mmol L^{-1}, reaction time 5 min, extraction time 3 min, centrifugation time 3 min at 1000 rpm, [Hmim][Cl] 34 mmol L^{-1}, KPF_6 34 mmol L^{-1}. For spectrophotometric determination 25 μL of ethanol was added to the IL phase.

Ionic strength was varied by using sodium chloride and sodium nitrate up to 0.7 mol L^{-1}. The results showed that variation of the salts has no considerable effect on the sensitivity of the sulfide determination method.

2.3. Analytical figures of merit

The optimal conditions for the established DLLME methods were applied and calibration graphs were obtained.

The dependency of absorbance at 526 nm on the asulam concentration was evaluated. One linear range was observed. The calibration equation was Abs = 1.97×10^{-2} C_{Asulam} – 0.005 ($R^2 = 0.9991$) in the range of 1.0–80.0 ng mL^{-1}.

The accuracy and precision of the asulam determination method were investigated. Asulam concentrations as 3.0 and 60.0 ng mL^{-1} were analyzed by the method (n = 8), and the absorbances were evaluated by the obtained linear calibration curve. The recoveries and relative standard deviations as percentages for 3.0 and 60.0 ng mL^{-1} asulam were 106 and 5.0, and 99 and 1.4, respectively. Moreover, the obtained limit of detection (LOD) was calculated by using the equation $3S_b/m$ (S_b is standard deviation of blank absorbance for 10 times analysis of blank and m is the slope of the calibration curve). LOD was 0.18 ng mL^{-1}. Limit of quantification for the asulam enrichment/determination method was 0.60 ng mL^{-1}.

In addition, in the sulfide determination method, selected values of the parameters in Table 1 were considered and absorbance was measured at 664 nm for different concentrations of sulfide. The linear calibration range was 0.1–5.0 ng mL^{-1}. The calibration equation was Abs = 3.50×10^{-1} $C_{Sulfide}$ – 0.004 ($R^2 = 0.9981$).

Sulfide concentrations as 0.4 and 3.0 ng mL^{-1} were analyzed (n = 8) by the DLLME method and the recoveries and relative standard deviations as percentages were obtained. The values were 100 and 3.5 for 0.4 ng mL^{-1}, and 101 and 2.7 for 3.0 ng mL^{-1}, respectively. LOD was 0.019 ng mL^{-1} sulfide. Limit of quantification for the sulfide DLLME determination method was 0.063 ng mL^{-1}.

2.4. Effect of foreign species

An interference study was carried out using various foreign cations, anions, organics, and pesticides. The study presents the selectivity of the DLLME methods. Known concentrations of the species were added, individually, to a solution containing 20 ng mL^{-1} asulam or 1.0 ng mL^{-1} sulfide. The tolerance limit was defined as the concentration of the species when it caused an error in the range of $\pm 5\%$ for asulam or $\pm 7\%$ for sulfide.

Foreign ions such as ClO_4^-, Br^-, Cl^-, HPO_4^{2-}, SCN^-, NO_3^-, HCO_3^-, SO_4^{2-}, NO_2^-, Na(I), Ca(II), Al(III), Ba(II), Sr(II), Mg(II), Cd(II), Ni(II), Cr(III), Co(II), Bi(III), Mn(II), V(V), Mo(VI), Pb(II), Zn(II), Au(III), Ag(I), Hg(II), F^-, Cu(II), and Fe(III) did not interfere in the determination of asulam at 500-fold (wt/wt) concentration, and species such as parathion, methyl-parathion, fenitrothion, diazinon, metribuzin, carbendazim, benomyl, sodium tartrate, and sodium citrate showed interference at 300-fold level. Sulfanilamide showed interference at 0.2-fold level.

The selectivity of the sulfide determination method also was investigated. Foreign ions such as ClO_4^-, Br^-, Cl^-, $C_2O_4^{2-}$, HPO_4^{2-}, SCN^-, NO_3^-, HCO_3^-, SO_4^{2-}, SO_3^{2-}, CrO_4^{2-}, NH_4^+, NO_2^-, Na(I), K(I), Ca(II), Al(III), Mg(II), Cd(II), Ni(II), Cr(III), Co(II), Mn(II), V(V), Zn(II), F^-, and I^- did not interfere in sulfide at 500-fold (wt/wt) concentration, and $S_2O_3^{2-}$ and Pb(II) showed interference at 200-fold and 20-fold levels, respectively.

2.5. Real sample analysis

Various water, soil, and urine samples were analyzed to investigate the validity of the asulam determination method. The results are given in Tables 2 and 3.

Table 2. Determination of asulam in water samples.

Sample	Concentration of asulam, ng mL^{-1}		Recovery %
	Added	Found (n = 5)	
Tap water	-	ND[a]	-
	10.0	9.7 ± 0.2	97
	20.0	19.6 ± 0.3	98
Mineral water	-	ND	-
	10.0	10.4 ± 0.2	104
	20.0	19.8 ± 0.3	99
River water	-	ND	-
	10.0	10.3 ± 0.3	103
	20.0	19.2 ± 0.3	96
Lake water	-	ND	-
	10.0	9.5 ± 0.3	95
	20.0	20.8 ± 0.3	104
Well water	-	ND	-
	10.0	10.5 ± 0.2	105
	20.0	20.6 ± 0.4	103

[a] ND means nondetectable. ±amounts are standard deviation.

Table 3. Determination of asulam in soil and urine samples by the DLLME method.

Sample	Asulam[a]		Recovery %
	Added	Found (n = 4)	
Soil[b]	-	98 ± 2	-
	113	204 ± 4	94
	245	333 ± 8	96
Soil[c]	-	ND[e]	-
	116	112 ± 3	97
	255	247 ± 6	97
Soil[d]	-	ND	-
	145	140 ± 3	97
	275	269 ± 7	98
Urine 1	-	ND	-
	11.8	12.2 ± 0.3	103
	23.6	23.3 ± 0.4	99
Urine 2	-	ND	-
	15.5	16.1 ± 0.4	104
	31.0	31.8 ± 0.5	103

[a] For soil samples as ng g^{-1} and for urine samples as ng mL^{-1}. [b] The agricultural soil was analyzed 2 days after asulam spraying. [c] The soil was an urban soil. [d] The soil was an ornamental soil. [e] ND means nondetectable. ± amounts are standard deviation.

In addition, to validate the presented method for asulam determination, 1.0 mL of standard 100 μg mL^{-1} asulam (AccuStandard Company, P-276S) in methanol was purchased and then was analyzed. The obtained asulam in the 1.0 mL of solution was 100.9 ± 0.7 (±0.7 is standard deviation of the determination).

The validity of the sulfide determination method for water and wastewater analysis was investigated. The results of the experiments are given in Table 4.

The obtained precisions and recoveries show that the presented methods were successful in the determination of asulam and sulfide.

2.6. Comparison with the other methods

Some distinct analytical features of the proposed methods were compared with those of a variety of previously reported asulam and sulfide determination methods in Tables 5 and 6, respectively. Compared with the presented asulam determination method, the methods in Table 5 show some disadvantages in the limit of detection,[1,4,5,7,8,12,37] linear dynamic range[3–5,10], and the range of the sample analyzed.[1–10,12,37]

Moreover, the analytical characteristics of the presented sulfide determination method were compared with the others as shown in Table 6. Compared with the presented sulfide enrichment/determination method, the others show some limitations in the limit of detection,[19,20,38–44] linear dynamic range,[20,42] and the range of the sample analyzed.[19,20,38,40,41,43,44]

2.7. Conclusions

As can be seen, the developed DLLME methods were studied comprehensively, and were evaluated for trace determination of asulam in water, soil, and urine samples as well as sulfide in water and wastewater samples. The enrichment-microcuvette spectrophotometric determination methods used some microliters of the in situ formed

Table 4. Determination of sulfide in water and wastewater samples.

Sample	Concentration of sulfide, ng mL^{-1}		Recovery %
	Added	Found (n = 5)	
Tap water	-	ND[a]	-
	1.00	0.98 ± 0.03	98
	2.00	2.02 ± 0.08	101
Mineral water	-	ND	-
	1.00	0.99 ± 0.01	99
	2.00	1.97 ± 0.02	99
Lake water	-	ND	-
	1.00	0.98 ± 0.02	98
	2.00	1.98 ± 0.02	99
Wastewater[b]	-	12.63 ± 0.11	-
	10.00	22.89 ± 0.15	103
	20.00	32.23 ± 0.13	98
Wastewater[c]	-	2.07 ± 0.06	-
	3.00	5.00 ± 0.06	98
	5.00	6.94 ± 0.09	97
Wastewater[d]	-	4.55 ± 0.08	-
	5.00	9.37 ± 0.09	96
	8.00	12.71 ± 0.14	102

[a] ND means nondetectable. ± amounts are standard deviation. [b, c, d] The wastewater samples were gathered from different streets in Ardabil city.

Table 5. Comparison of the established asulam DLLME determination method with some of the other methods.

Detection method	Enrichment method	LDR[a]	LOD[b]	Samples analyzed	Ref.
Chemiluminescence	-	Up to 5000	40	Water	1
Chemiluminescence	-	0.36–35	0.12	Water	2
Chemiluminescence	SPE	0.0012–0.014	0.00035	Water	3
Voltammetry	-	20748–93936	65	Water	4
Voltammetry	-	1026–4560	262	Water	5
Immunoassay	-	-	0.1	Water	6
MECC	SPE	-	1.0	Water	7
MECC	-	Up to 25,000	400	Water	7
CE	-	7524–114,000	10900	Water	8
CE	-	684–57,000	900	Water	8
HPLC-MS/MS	-	-	0.2[c]	Vegetable oil	9
Fluorescence	-	43–214	-	Peach	10
SMEC	DLLME	16–1000	5.0	Juice	12
Fluorescence	-	5–15,000	5.0	Water	37
Spectrophotometry	DLLME	1.0–80	0.18	Water, soil, and urine	This work

MECC: Micellar electrokinetic capillary chromatography; SPE: Solid phase extraction; CE: Capillary electrophoresis; HPLC: High performance liquid chromatography; MS: Mass spectrometry; SMEKC: Sweeping-micellar electrokinetic chromatography; DLLME: Dispersive liquid–liquid microextraction. [a] LDR means linear dynamic range (ng mL^{-1}). [b] LOD means limit of detection (ng mL^{-1}). [c] LOD means limit of detection (ng g^{-1}).

green extractant; an organic solvent was not used as extractant. Asulam was derivatized by a diazotization-coupling reaction to prepare an extractable azo dye with high molar absorptivity. Sulfide was derivatized as the extractable ethylene blue with high molar absorptivity. The obtained limits of quantification made the methods suitable for accurate and precise analysis of asulam and sulfide in various samples.

Table 6. Comparison of the developed sulfide DLLME determination method with some sulfide determination methods.

Detection method	Enrichment method	LDR[a]	LOD[b]	Samples analyzed	Ref.
Turbidity	HSDM	5–100	0.5	Water	38
Reflectometry	SPE	20–200	2.9	Water	20
ICP/MS	Vapor generation	2–500	2	Water and sediment	39
SC	-	5–400	0.5	Water	40
Spectrophotometry	-	16–320	2.56	Water	41
Spectrophotometry	-	0.64–3.84	0.32	Water and wastewater	42
Colorimetry	-	Up to 4640	3.2	Water	43
ICP/AES	HG	-	5	Water	44
Spectrophotometry	SPE	1–100	0.2	Water	19
GC-PID	Vapor generation	-	0.004	Water and sediments	45
AFS	HG-SPE	0.1–2.5	0.05	Water and wastewater	46
Spectrophotometry	DLLME	0.1–5	0.019	Water and wastewater	This Work

HSDM: Headspace single-drop microextraction; SPE: Solid phase extraction; ICP/MS: Inductively coupled plasma/mass spectrometry; SC: Stripping chronopotentiometry; AFS: Atomic fluorescence spectrometry; HG: Hydride generation; GC-PID: Gas chromatography-photoionization detection; ICP/AES: Inductively coupled plasma/atomic emission spectrometry; DLLME: Dispersive liquid–liquid microextraction. [a] LDR means linear dynamic range (ng mL^{-1}). [b] LOD means limit of detection (ng mL^{-1}).

3. Experimental

3.1. Reagents and apparatus

Sodium nitrite, sodium chloride, sodium hydroxide, hydrochloric acid, 1-naphthol, $FeCl_3.6H_2O$, and sulfamic acid were purchased from Merck. KPF_6 was purchased from Ionic Liquid Technology (Germany) and 1-hexyl-3-methylimidazolium chloride [Hmim][Cl] was prepared in our laboratory according to the method described previously.[47] N,N-diethyl-p-phenylenediamine (DPD) was purchased from Loba-Chemie (India). Sodium sulfide.xH_2O was prepared from Riedel-Dehaen and was used to prepare a solution of sulfide as 500 μg mL^{-1} after standardization.[48] KPF_6 and [Hmim][Cl] solutions were prepared in deionized water. The stock solution of asulam (Fluka) and 1-naphthol were prepared in ethanol.

All UV-Vis spectra and absorbance measurements were performed using a double beam spectrophotometer, Shimadzu (Tokyo, Japan) model UV-1650 PC, equipped with a 20-μL quartz cell with 10.0-mm path length (Hellma, Germany). A pH meter (Metrohm model 744, Switzerland), a centrifuge model CE. 144 (Shimifan company, Iran), and an ultrasonic bath (Bandelin model DT 255 H, Germany) were also used. A 50-μL syringe (Hamilton, Switzerland) and a micropipette (Treff, Switzerland) were used to handle the IL-containing phases.

3.2. Procedure for asulam determination

First, 6.0 mL of asulam sample, 0.3 mL of 0.33 mol L^{-1} hydrochloric acid, and 0.2 mL of 0.04 mol L^{-1} sodium nitrite were added to a 12-mL screw-cap conical-bottom plastic centrifuge tube. After 5 min, 0.2 mL of 0.5

mol L^{-1} sulfamic acid was added and, after 3 min, 0.4 mL of 1.0 mol L^{-1} sodium hydroxide solution and 0.2 mL of 0.01 mol L^{-1} 1-naphthol (in ethanol) were transferred to the tube. After 1 min, 0.4 mL of 2.75 mol L^{-1} hydrochloric acid, 0.5 mL of 1.0 mol L^{-1} [Hmim][Cl], and 2.0 mL of 0.25 mol L^{-1} KPF_6 were added and the solution was shaken for 3 min. The mixture was centrifuged at 1000 rpm for 2 min. Spectrophotometric determination of asulam was performed after diluting the IL-rich phase (43 $\pm$ 1 μL) with 40 μL of 0.03 mol L^{-1} sodium hydroxide in ethanol. The absorption spectrum of the resulting solution was recorded against the same manner prepared blank in the range of 350–750 nm. Absorbance at 526 nm was used as analytical signal.

The water samples were filtered, and were analyzed according to the presented DLLME procedure.

The soil samples were sieved and their water contents were determined. Then equivalent to 5.0 g of the dry soil samples and 20 mL of a basic ethanolic solution (1 mL of aqueous solution of sodium hydroxide 0.2 mol L^{-1} plus 19 mL of ethanol) were transferred to a 100-mL round bottom flask and the mixture was sonicated in a water bath for 15 min. The extract was filtered and was equilibrated with another 20 mL of the basic ethanolic solution under the sonication condition. Both fractions were placed in another 100-mL round bottom flask, were neutralized with hydrochloric acid, and then were evaporated to about 2–3 mL. Then the residue was transferred to a 50-mL volumetric flask prior to dilution with deionized water. Five milliliters of the final solution was analyzed according to the DLLME procedure.

In addition, 2 urine samples were analyzed according to the presented DLLME procedure by analyzing 3.0 mL of the sample solutions.

The standard addition method was applied to all of the samples in order to verify the validity of the DLLME determination method.

3.3. Procedure for sulfide determination

First, 7.8 mL of sulfide sample, 0.2 mL of 0.025 mol L^{-1} Fe(III) in sulfuric acid 1.0 mol L^{-1}, and 0.2 mL of N,N-diethyl-p-phenylenediamine 0.025 mol L^{-1} in sulfuric acid 0.2 mol L^{-1} were added to a 12-mL screw-cap conical-bottom plastic centrifuge tube. After 12 min, 0.4 mL of 0.85 mol L^{-1} [Hmim][Cl] and 1.4 mL of 0.243 mol L^{-1} KPF_6 were added and the mixture was shaken for 3 min. The mixture was centrifuged at 1000 rpm for 3 min. Spectrophotometric determination of sulfide was performed after diluting the IL-rich phase (24 $\pm$ 1 μL) with 25 μL of ethanol. The absorption spectrum of the resulting solution was recorded against the blank in the range of 500–800 nm. Absorbance at 664 nm was used as analytical signal.

For the analysis of water samples, 5.0-mL samples were analyzed. Wastewater samples were treated with the depicted gas-phase separation/sorption apparatus.[49] Ten milliliters of a concentrated sulfuric acid (18.5 mol L^{-1}) was added to the reaction tube containing 30 mL of the wastewater samples, and the procedure was followed. The standard solutions of sulfide were also added to all of the original samples in order to evaluate the validity of the DLLME determination method.

Acknowledgments

The authors wish to thank the Research Council of the University of Mohaghegh Ardabili for the financial support of this work.

References

1. Chivulescu, A.; Catalá-Icardo, M.; Mateo, J. V. G.; Calatayud, J. M. *Anal. Chim. Acta* **2004**, *519*, 113-120.
2. Sánchez, F. G.; Díaz, A. N.; Bracho, V.; Aguilar, A.; Algarra, M. *Luminescence* **2009**, *24*, 448-452.

3. Sánchez, F. G.; Díaz, A. N.; Téllez, C. D.; Algarra, M. *Talanta* **2008**, *77*, 294-297.
4. Siswana, M. P.; Ozoemena, K. I.; Geraldo, D. A.; Nyokong, T. *J. Solid State Electrochem.* **2010**, *14*, 1351-58.
5. Siswana, M. P.; Ozoemena, K. I.; Geraldo, D. A.; Nyokong, T. *Electrochim. Acta* **2006**, *52*, 114-122.
6. Spoors, J. A.; Winger, L. A.; Siew, L. K.; Dessi, J. L.; Jennens, L.; Self, C. H. *J. Environ. Monit.* **2002**, *4*, 917-921.
7. Chicharro, M.; Zapardiel, A.; Bermejo, E.; Sánchez, A. *Anal. Chim. Acta* **2002**, *469*, 243-252.
8. Chicharro, M.; Zapardiel, A.; Bermejo, E.; Sanchez, A.; Gonzalez, R. *Electroanal* **2004**, *16*, 311-318.
9. Moreno-González, D.; Huertas-Pérez, J. F.; García-Campaña, A. M.; Gámiz-Gracia, L. *Talanta* **2014**, *128*, 299-304.
10. Sanchez, F. G.; Gallardo, A. A.; Blanco, C. C. *Talanta* **1992**, *39*, 1195-1198.
11. Rodriguez-Gonzalo, E.; Ruano-Miguel, L.; Carabias-Martinez, R. *Electrophoresis* **2009**, *30*, 1913-1922.
12. Moreno-Gonzalez, D.; Gamiz-Gracia, L.; Garcia-Campana, A. M.; Bosque-Sendra, J. M. *Anal. Bioanal. Chem.* **2011**, *400*, 1329-1338.
13. Santos, J. C. C.; Santos, E. B. G. N.; Korn, M. *Microchem. J.* **2008**, *90*, 1-7.
14. Silva, M. S. P.; Galhardo, C. X.; Masini, J. C. *Talanta* **2003**, *60*, 45-52.
15. Silva, M. S. P.; da Silva, I. S.; Abate, G.; Masini, J. C. *Talanta* **2001**, *53*, 843-850.
16. Leggett, D. J.; Chen, N. H.; Mahadevappa, D. S. *Anal. Chim. Acta* **1981**, *128*, 163-168.
17. Okumura, M.; Yano, N.; Fujinaga, K.; Seike, Y.; Atsuo, S. *Anal. Sci.* **1999**, *15*, 427-431.
18. Singh, V.; Gosain, S.; Mishra, S.; Jain, A.; Verma, K. *Analyst* **2000**, *125*, 1185-1188.
19. Ferrer, L.; de Armas, G.; Miro, M.; Estela, J. M.; Cerda, V. *Analyst* **2005**, *130*, 644-651.
20. Afkhami, A.; Norooz-Asl, R. *Sep. Sci. Technol.* **2009**, *44*, 983-994.
21. Bessonneau, V.; Boyaci, E.; Maciazek-Jurczyk, M.; Pawliszyn, J. *Anal. Chim. Acta* **2015**, *856*, 35-45.
22. Eskandari, H.; Naderi-Darehshori, A. *Anal. Chim. Acta* **2012**, *743*, 137-144.
23. Zeng, C.; Ji, L.; Zhou, C.; Zhang, F.; Liu, M.; Xie, Q. *Microchem. J.* **2015**, *119*, 1-5.
24. Ruiz-Palomero, C.; Soriano, M. L.; Valcarcel, M. *Talanta* **2014**, *125*, 72-77.
25. Xu, X.; Yang, Z.; Liu, Z. *J. Chromatogr. A* **2014**, *1358*, 52-59.
26. Pelit, F. O.; Yengin, C. *J. Chromatogr. B* **2014**, *949-950*, 109-114.
27. Ge, D.; Lee, H. K. *Talanta* **2015**, *132*, 132-136.
28. Eskandari, H. *Turk. J. Chem.* **2012**, *36*, 631-643.
29. Wen, X.; Yang, S.; Zhang, H.; Zhao, X.; Guo, J. *Int. J. Environ. Anal. Chem.* **2014**, *94*, 1243-1253.
30. Niazi, A.; Khorshidi, N.; Ghaemmaghami, P. *Spectrochim. Acta A* **2015**, *135*, 69-75.
31. Pourreza, N.; Rastegarzadeh, S.; Larki, A. *Talanta* **2015**, *134*, 24-29.
32. Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2002**, *4*, 81-87.
33. Li, Y.; Wang, L. S.; Cai, S. F. *J. Chem. Eng. Data* **2010**, *55*, 5289-5293.
34. Agrawal, B. B. L.; Margoliash, E. *Anal. Biochem.* **1970**, *34*, 505-516.
35. Molaakbari, E.; Mostafavi, A.; Afzali, D. J. *J. Hazard. Mater.* **2011**, *185*, 647-652.
36. Baghdadi, M.; Shemirani, F. *Anal. Chim. Acta* **2009**, *634*, 186-191.
37. Subova, I.; Assandas, A. K.; Icardo, M. C.; Calatayud, J. M. *Anal. Sci.* **2006**, *22*, 21-24.
38. Lavilla, I.; Pena-Pereira, F.; Gil, S.; Costas, M.; Bendicho, C. *Anal. Chim. Acta* **2009**, *647*, 112-116.
39. Colon, M.; Iglesias, M.; Hidalgo, M. *Spectrochim. Acta B* **2007**, *62*, 470-475.
40. Manova, A.; Strelec, M.; Cacho, F.; Lehotay, J.; Beinrohr, E. *Anal. Chim. Acta* **2007**, *588*, 16-19.

41. Deng, H. H.; Weng, S. H.; Huang, S. L.; Zhang, L. N.; Liu, A. L.; Lin, X. H.; Chen, W. *Anal. Chim. Acta* **2014**, *852*, 218-222.

42. Pandya, A.; Joshi, K. V.; Modi, N. R.; Menon, S. K. *Sens. Actuators B* **2012**, *168*, 54-61.

43. Ariza-Avidad, M.; Agudo-Acemel, M.; Salinas-Castillo, A.; Capitan-Vallvey, L. F. *Anal. Chim. Acta* **2015**, *872*, 55-62.

44. Colon, M.; Todoli, J. L.; Hidalgo, M.; Iglesias, M. *Anal. Chim. Acta* **2008**, *609*, 160-168.

45. Cutter, G. A.; Oatts, T. J. *Anal. Chem.* **1987**, *59*, 717-721.

46. Jin, Y.; Wu, H.; Tian, Y.; Chen, L.; Cheng, J.; Bi, S. *Anal. Chem.* **2007**, *79*, 7176-7181.

47. Liu, J. F.; Chi, Y. G.; Jiang, G. B.; Tai, C.; Peng J. F.; Hu, J. T. *J. Chromatogr. A* **2004**, *1026*, 143-147.

48. Williams, W. J. *Handbook of Anion Determination*; Butterworths: London, UK, 1984.

49. Afkhami, A.; Khalafi, L. *Microchim. Acta* **2005**, *150*, 43-46.