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RESEARCH ARTICLE



Assessment of toxic metal ions in tea samples using new microextraction technique based on the solidified deep eutectic solvent followed by GFAAS

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ABSTRACT

In this research, an environmental friendly extraction method based on vortex-assisted liquid-phase microextraction and the solidified deep eutectic solvent (VALPME-SDES) has been developed for the determination of Pb, Cd, Cu, As, and Hg in tea prior to their analysis by graphite furnace atomic absorption spectrometry (GFAAS). A new deep eutectic solvent consisting of 1-decyl-3-methylimidazolium chloride and *n*-butanoic acid was used as an extraction solvent, yielding the advantages of material stability, low density, and a suitable freezing point near room temperature. The accuracy of the proposed procedure was also assessed by determining the concentration of the studied metal ions in a certified reference material for Green Tea (GBW 10052).

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Liquid-phase microextraction; solidified deep eutectic solvent; extraction solvent lighter than water; toxic metal ions; black tea

Introduction

Heavy metals accumulation and contamination in agricultural soils have aroused widespread attention due to their toxicity, persistence, and non-biodegradability (Ran *et al.* 2016, Wen *et al.* 2018). The heavy metals in contaminated soils enter the human body by food chain and it creates significant risks to human health (Chen *et al.* 2015). Tea is the second most common consumed beverage in the globe because of its taste and nutritional value, since it is a major dietary source of Al element (De Oliveira *et al.* 2018). The global production of tea in the past decade has grown at 1.81% per year, and global tea consumption has grown at a rate of 2.5% (Protano *et al.* 2014). Also per capita consumption of tea in Iran is about 1.5 kg per year (Duodu *et al.* 2016). According to the fact that in Iran in the process of leaf production of green tea no pesticides was used, Iranian tea is considered as the purest and most healthy tea in the world (Karimzadeh *et al.* 2013). Most of the imported teas are coming from Sri Lanka, India, Bangladesh, China, and Pakistan illegally, so official regulatory agencies are not able to assure quality of the products. The good taste and relatively cheap price of this imported product has gained popularity among the Iranian people. During growth and

production, tea can be contaminated to heavy metals via soil and water. These trace elements can enter to the human body through food chain and causes accumulation in different tissues. The high reception of these elements is harmful for human body and can cause several complications such as renal function disorders, liver cirrhosis, brain complications, cardio-vascular problems, and informing RBC disorders (Habibiyan *et al.* 2017; Habibollahi *et al.* 2018).

Typically, heavy metals are determined by graphite furnace atomic absorption spectrometry (GFAAS) (Pirsaheb and Fattahi 2015, Ataee *et al.* 2016, Zounr *et al.* 2017), flame atomic absorption spectrometry (FAAS) (Flores *et al.* 2009; Xu *et al.* 2013; Acar *et al.* 2016), inductively coupled plasma-mass spectrometry (ICP-MS) (Batista *et al.* 2008, Lin and Jiang 2013, Malassa *et al.* 2014, Chen *et al.* 2015) and inductively coupled plasma-optical emission spectrometry (ICP-OES) (Feist and Mikula 2014, Froes *et al.* 2014, Pirsaheb *et al.* 2016). However, it is possible to detect small amounts of heavy metals using recent powerful analytical devices, but it is difficult to determine these metals at very low concentrations due to matrix interference. Therefore, in order to enhance the sensitivity of this method, there is often a need for a preliminary and

phase separation of the pre-concentration. In addition, complex samples like tea are also required to be converted into a form compatible with these devices.

Many sample pretreatment methods have been developed based on sample traits for the measurement of heavy metals in trace levels, namely coprecipitation (Saracoglu *et al.* 2003), liquid-liquid extraction (LLE) (Oliva *et al.* 2002), cloud point extraction (CPE) (Rahnama and Najafi 2016), solid-phase extraction (SPE) (Tuzen and Soylak 2009, Ghaedi *et al.* 2013), solid-phase microextraction (Kaur *et al.* 2007), dispersive liquid-liquid microextraction (DLLME) (Shamsipur *et al.* 2014, Allothman *et al.* 2015; Sharafi *et al.* 2015; Eftekhari *et al.* 2016) and dispersive liquid-liquid microextraction based on solidification of a floating organic drop (DLLME-SFO) (Chamsaz *et al.* 2014, Ezoddin *et al.* 2015).

Currently, cheap, affordable, and green extractants, called deep eutectic solvents (DESs), are being used as an alternative to ionic liquids and conventional organic solvents to extract trace amounts of organic and inorganic analytes (Bajkacz and Adamek 2018, Liu *et al.* 2018, Malaeke *et al.* 2018). DESs consist of two or three components that offer several environmental and economic advantages. These components form eutectic mixture having lowest melting point than each individual components and have the maximum capability to bound them self through hydrogen bonding (Rykowska *et al.* 2018). DESs are formed mostly with the complexation of choline chloride with an inexpensive and non-toxic hydrogen bond donor or metal salts, such as urea, glycerol, carboxylic acid, sugar, etc. DESs not only have the advantages of low volatility, low vapor pressure, high thermal stability, and high ability to extract organic and inorganic compounds, but also have low cost and easy preparation of nontoxic compounds. Choline based DESs also overcome the health and safety challenges toward human and eco-toxicity issues.

The main goal of this work was to focus on the miniaturization, simplification, and improvement of the extraction of metal ions from black tea samples. We developed a very simple, rapid, sensitive, and small-scale extraction method that was named vortex-assisted liquid-phase microextraction based on the solidified deep eutectic solvent (VALPME-SDES). Low hydrophilic DES, consisting of imidazolium ionic liquid as HBA and *n*-butanoic acid as HBD in a certain proportion, is prepared. To our knowledge, the application of VALPME-SDES for the determination of heavy metals in black tea samples has not been reported until now.

Experimental

Reagents and solutions

Stock standard solutions for Pb(II) and Cu(II) with a concentration of 1000 mg L^{-1} were prepared from analytical reagent grade $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) by separately dissolving them in double-deionized water. Stock standard solutions of As(III) (1000 mg L^{-1}) was obtained by dissolving appropriate amounts of As_2O_3 (Merck, Darmstadt, Germany). An Hg(II) standard stock solution (1000 mg L^{-1} in 1% nitric acid, 250 mL) was purchased from Fluka, Buchs, Switzerland. The cadmium stock solution (1000 mg L^{-1} for atomic spectroscopy standard) was purchased from Merck (Darmstadt, Germany). Standard solutions were prepared by appropriate dilution of the stock solutions daily. The chelating agent, diethyldithiophosphoric acid (DDTP) with the density of 1.17 kg L^{-1} and H_2O_2 were supplied from Merck (Darmstadt, Germany). The *n*-butanoic acid as HBD, 1-decyl-2,3-dimethylimidazolium chloride [DDMIM]Cl, 1-octyl-2,3-dimethylimidazolium chloride [ODMIM]Cl, 1-octyl-3-methylimidazolium chloride [OMIM]Cl, 1-dodecyl-3-methylimidazolium chloride [C_{12}MIM]Cl and 1-decyl-3-methylimidazolium chloride [DMIM]Cl, were purchased from Sigma (St. Louis, MO, USA). A mixture of 1000 mg L^{-1} $\text{Pd}(\text{NO}_3)_2$ and 300 mg L^{-1} $\text{Mg}(\text{NO}_3)_2$ solutions, both from Merck (Darmstadt, Germany), were used as chemical modifiers. Ultra-pure water (distilled six times and also double-deionized, with $18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) purchased from Shahid Ghazi Pharmaceutical Co. (Tabriz, Iran).

Instrumentation

The experiments were performed using a Model nov AA 400 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), equipped with deuterium background correction, a transversely heated graphite tube atomizer and a MPE 60 auto-sampler. The optimized temperature programs for GFAAS are recommended in Table 1. Pyrolytic graphite coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.026) were used. Argon (99.999%) was purchased from Air Products (UK) as a purge and protective gas at a flow rate of 500 mL min^{-1} during all stages, except during atomization, when the flow was stopped. A Hettich Zentrifugen (EBA20, Tuttlingen, Germany) was used for centrifugation. The pH values were measured with a Metrohm pH meter (Model: 692, Herisau, Switzerland) supplied with a glass-combined electrode.

Table 1. Instrumental parameters for the metal ions determination using GFAAS.

Spectrometer parameters	Cd	Pb	Cu	Hg	As
Wavelength (nm)	228.8	283.3	324.8	253.7	193.7
Slit width (nm)	0.7	0.7	0.6	0.2	0.8
Lamp current (mA)	8	10	7	5	5

Step	Temperature (°C)					Time (s)		Gas flow (mL min ⁻¹)
	Cd	Pb	Cu	Hg	As	Ramp	Hold	
Pre-warming	50	50	50	50	50	1	2	500
Inject modifier	80	80	80	80	80	5	20	500
Inject sample								
Drying I	90	120	150	90	100	10	15	500
Drying II	110	250	300	110	220	5	20	500
Ashing	300	600	1000	200	750	10	10	500
Gas stop step	300	600	1000	200	750	0	1	0
Atomization	2100	1800	2000	1200	2100	0	3	0
Cleaning	2400	2200	2500	1600	2300	0	2	1000

Sampling and sample preparation

The studied samples in this research are tea imported from the border crossing at western Iran in contraband and then tea were offered in the Javanroud border market and were distributed to all parts of the country. Ten different brands with the highest supply and demand (more than 90%) were selected, and from each brands a sample was randomly selected. A total of 10 samples representing 10 marks of black tea (Green hammer, Sa'dal-Din 444, Sa'dal-Din 222, Butterfly, Elephant, Mobile, Ghazal pair, Perfume world, Golden hammer, and Hammer two fans) were collected in the Javanroud, which originate from six countries (Silan, Sri Lanka, India, China, Pakistan, and Bangladesh). The contents of Pb(II), Cd(II), Cu(II), Hg(II), and As(III) were determined in total concentrations.

Aliquots of 0.50 g of dried black tea powder were weighed and added into the digestion vessel with 6.0 mL of concentrated nitric acid and 1.0 mL of H₂O₂. Subsequently, the samples were digested using a temperature program. First, the temperature was linearly increased to 180 °C over 10 min. In the following, the temperature was maintained at 180 °C for 30 min. The solution was cooled, filtered off through filter paper (Whatman No. 42), and transferred to 50-mL volumetric flask. The volume was made up to the mark with distilled water and finally, 10.0 mL of this sample solution was subjected to the VALPME-SDES procedure.

Preparation of hydrophobic DESs

The synthesis of different DESs were carried out separately by mixing five imidazolium chloride ionic liquids as HBA with *n*-butanoic acid as HBD in different molar ratios i.e. 1:1, 1:2, 1:3, 2:5, 3:7 in a 20-mL polypropylene tube. The tubes were placed into a water bath thermostated at 80 °C. After 5 min, they were vortexed for 5 min and then returned back into

the water bath. The heating/vortexing cycle was repeated two more times and finally, homogeneous liquids (DESs) were obtained.

VALPME-SDES procedure

An aliquot of 10.0 mL of ultra-pure water (or sample solution) containing 0.50 µg L⁻¹ of Hg(II) and As(III), and 0.10 µg L⁻¹ of Pb(II), Cd(II), and Cu(II) was placed in a 20-mL screw cap glass test tube. Then, a mixture of 20.0 µL DDTP (chelating agent) and 60.0 µL of DES (ChCl:*n*-butanoic acid) as the extraction solvent was rapidly injected into the sample solution with a 100-µL syringe (gastight, Hamilton, Reno, NV, USA). The tube was then sealed and maintained at 50 °C in a water bath. The mixture was shaken using a vortex agitator for 4 min to ensure full contact of the extractant and target compounds from the sample solution. In this stage, the complexed metal ions were extracted into the fine droplets of DES. The mixture was then centrifuged for 5 min at 5000 rpm in order to separate the mixture to phases. After centrifugation, the fine droplets of DES float at the top of the test tube. The test tube was transferred into an ice bath and the DES was solidified after 3 min. The obtained solidified DES was transferred into a conical vial where it was melted immediately and dissolved in 15 µL acetonitrile. Finally, 20.0 mL of the extract using an auto-sampler was injected into the GFAAS and was subjected to the temperature program, shown in Table 1.

Results and discussion

Study of DES type

Some characteristics such as low solubility in water, high extraction efficiency for the analytes, density lower than water, melting point close to room temperature, and low toxicity, provided extra limitations

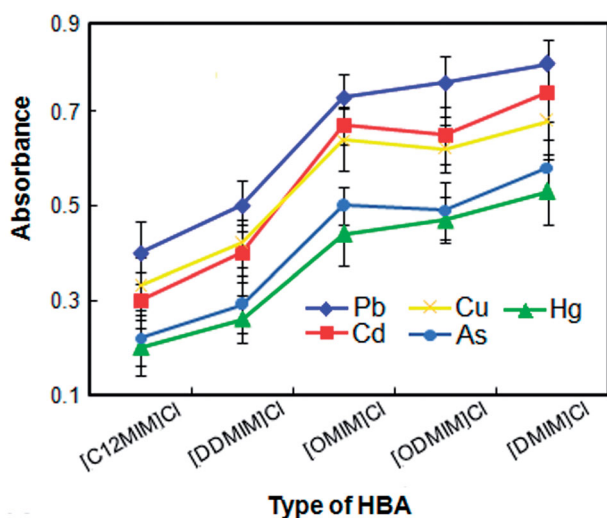


Figure 1. Effect of the different types of hydrogen bond acceptors on the absorbance of the metal ions. Extraction conditions: volume of the sample solution, 10.0 mL; volume of the extraction solvent, 60.0 μ L; extraction temperature, 50 $^{\circ}$ C; DDTP volume, 20.0 μ L; vortex time, 4 min; centrifugation time, 5 min; centrifuge speed, 5000 rpm.

on the selection of DES in the VALPME-SDES method. In the present study, different ionic liquids of imidazolium chloride ([DDMIM]Cl, [ODMIM]Cl, [OMIM]Cl, [C₁₂MIM]Cl, and [DMIM]Cl) were mixed with *n*-butanoic acid in a mole ratio of 1 to 2. As it can be seen from Figure 1, the DES produced from [DMIM]Cl:*n*-butanoic acid provides rather higher absorbance for all analytes compared to the other DESs used. The other DESs absorbance for the analytes is not suitable, because the dispersion of these DESs is not very strong in the absence of a disperser solvent and they do not disperse well. Therefore, [DMIM]Cl:*n*-butanoic acid was selected as the extraction solvent for the further studies.

Study of molar ratio of HBA to HBD

In this research, the most suitable mole ratio for [DMIM]Cl to *n*-butanoic acid was obtained to achieve high analytical signal. For this purpose, the DES was selected by using [DMIM]Cl and *n*-butanoic acid with different ratios of 1:1 (DES11), 1:2 (DES12), 1:3 (DES13), 2:5 (DES25), and 3:7 (DES37). The results in Figure 2 show that all DESs except DES11 have a positive effect on the extraction of the metal ions. The DES11 is gelatinous at room temperature and cannot be completely dispersed in the aqueous solution. The results revealed that DES12 has the highest absorbance in comparison with the other tested DESs. Thus, the optimal ratio of [DMIM]Cl to *n*-butanoic acid was chosen to be 1:2.

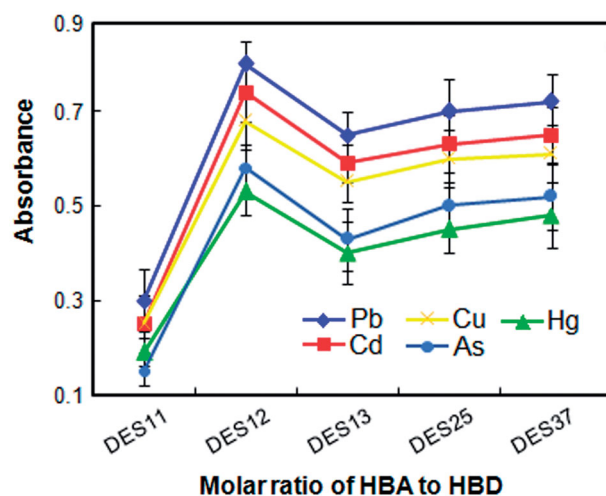


Figure 2. Effect of the molar ratio of HBA to HBD on the absorbance of the metal ions. Extraction conditions: as in Figure 1.

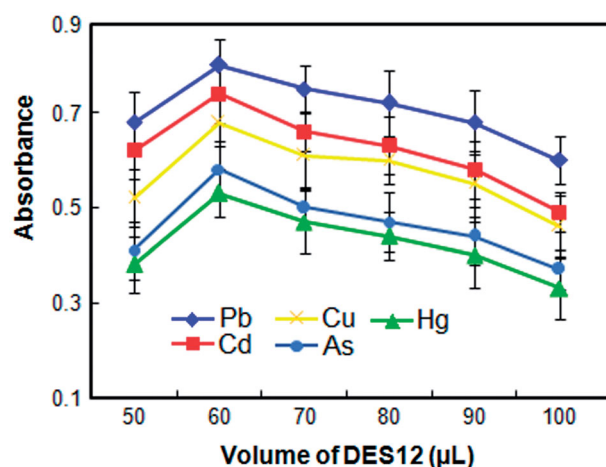


Figure 3. Effect of the volume of DES12 on the absorbance of the metal ions. Extraction conditions: as in Figure 1.

Study of DES volume

The volume of DES12 is important parameter which can directly influence the extraction efficiency of the analytes and subsequently the quantification and detection limit of the method. The influence of the volume of DES12 as the extraction solvent on the absorbance of metal ions was studied. For this purpose, different volumes of DES12 (50, 60, 70, 80, 90, and 100 μ L) were used with the same VALPME-SDES procedure. As shown in Figure 3, by increasing the volume of DES12 from 50 to 60 μ L, the absorbance of metal ions increases and by further increasing the DES12 volume, the absorbance slightly decreases because of dilution effect. A volume of less than 50 μ L of DES12 resulted in a final volume less 20.0 μ L, which was insufficient for determination by the GFAAS, and, as a result, a systematic error would be generated.

Thus, in the subsequent studies, 60 μL of DES12 was used as the optimal volume of the DES.

Study of sample solution pH

The pH of the solution plays a unique role in metal-chelate formation and subsequent extraction. DDTP was selected as chelating agent due to its great ability to form stable complexes with several metals even in acidic media. In the present research, DDTP was totally transformed to the DDTP ammonium salt with NH_3 and the effect of pH upon the complex formation of metal ions was studied within the pH range of 0.2–7, using hydrochloric acid and sodium acetate. Figure 4 shows the influence of the sample solution pH on the analytical signal intensity. As it is demonstrated, the absorbance of complexed ions is nearly constant and shows a maximum in the pH range of 0.2–3, followed by a reduction at higher pH values. On the other hand, due to the acidic nature of DDTP in aqueous solutions ($\text{pH} \approx 2$ in 10.0 mL aqueous solutions), in this study, the use of an acidic solution for the pH adjustment, being the contamination sources, was not necessary.

Study of salt addition

Salt addition is frequently used to adjust the ionic strength, improve the extraction efficiency, and reduce the detection limit. To study the effect of salt addition on the analytical signal of the metal ions, the concentration of NaCl was changed in the range of 0–10% (w/v). Other experimental conditions were kept constant at their optimized values. According to the obtained results (data not shown), in the case of all metal ions, the analytical signal will remain more or less constant

upon increasing ionic strength of solution. The solubility of DES in aqueous phase is expected to decrease by increasing the ionic strength, which in turn results in an increase in the volume of collected phase. On the other hand, the solubility of analytes in aqueous phase will also decrease and, consequently, their extraction in DES is expected to increase with increasing ionic strength of solution. Such a compensation behavior occurred in the extraction system will result in some constancy of the analytical signals with change in ionic strength of solution. Thus, the subsequent experiments were conducted in the absence of sodium chloride.

Study of vortex time

In the VALPME-SDES procedure, the main role of vortex time is the complete dispersion of DES12 in the aqueous phase to enhance the extraction process. Therefore, the influence of vortex time on the extraction efficiency was studied in the range of 0–10 min at 2 min intervals. It was found that the analytical signal of the analytes increased with increasing vortex time from 0 to 4 min and, with increasing vortex time, analytical signal is constant. Before the mixture is centrifuged for the separation of the cloud system, the demulsification process is more important than the complete equilibrium of the analyte phase in an unmixable two-phase mixture. This method requires a sufficient vortex time to complete the demulsification process. Thus, 4 min was selected as the optimum vortex time.

Study of temperature

The suitable temperature can accelerate the mass transfer and increase the contact surface of the DES12 and the aqueous phase. In order to examine this impact, extraction procedure was done in different temperatures such as 20, 30, 40, 50, 60, and 70 $^{\circ}\text{C}$. The results obtained from these tests show that, by increasing the bath temperature from 20 to 50 $^{\circ}\text{C}$, the absorbance of heavy metals increased and the best performance was obtained at 50 $^{\circ}\text{C}$. At the solution temperature of more than 50 $^{\circ}\text{C}$, the analytical signal of the analytes decreased as the solubility of the desired analytes and DES12 increased in aqueous phase. As a result, 50 $^{\circ}\text{C}$ was chosen as the optimum extraction temperature.

Study of DDTP concentration

DDTP was a good chelating agent for heavy metals extraction and enough DDTP was needed to assure that

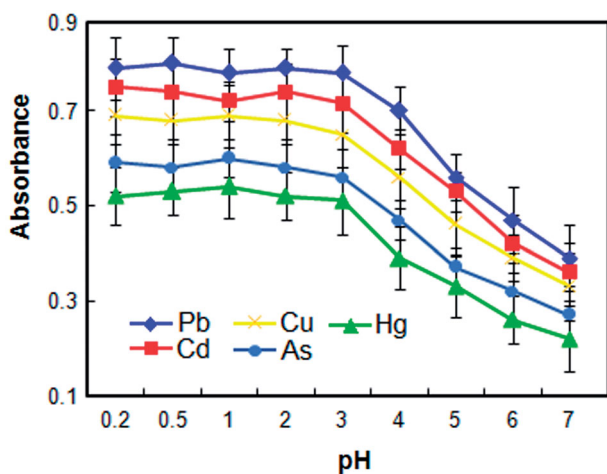


Figure 4. Effect of the pH on the absorbance of the metal ions. Extraction conditions: as in Figure 1.

metal ions would be extracted completely. Therefore, the DDTP concentration was investigated over the range of 0.02–0.50% (v/v). It was found (results not shown) that the analytical signal was increased with the increasing concentration of DDTP from 0.02 to 0.20% (v/v). At higher concentration of DDTP the background absorbance increases. Therefore, the concentration of 0.20% (v/v) DDTP was selected as the best choice to prevent any interference.

Study of interference

The potential interferences of some ions on the extraction and determination of target metal ions were examined. Interferences studied were those related to the separation step, cations that may react with the chelating agent and decrease the extraction efficiency. To perform this study, interference ions in different interference-to-analyte ratios were added to aqueous solution containing $0.50 \mu\text{g L}^{-1}$ of Hg(II) and As(III), and $0.10 \mu\text{g L}^{-1}$ of Pb(II), Cd(II), and Cu(II), and were subjected to the recommended procedure. Table 2 shows the tolerance limits of the interference ions (error $\pm$

Table 2. Tolerance limits of diverse ions in the determination of the metal ions.

Interference	Interference-to-metal ions ratio ^a	Recovery (%)				
		Pb(II)	Cd(II)	Cu(II)	As(III)	Hg(II)
Na ⁺	10,000	93	97	91	104	92
K ⁺	2000	101	102	99	100	104
Ca ²⁺	1000	98	103	93	99	91
Zn ²⁺	1000	103	94	99	90	90
Zn ²⁺	500	94	91	95	95	93
Mn ²⁺	1000	95	97	105	97	86
Mn ²⁺	100	92	99	101	94	94
Fe ²⁺	500	106	103	100	88	94
Al ³⁺	500	91	96	101	99	104
Co ²⁺	500	90	95	96	94	107
Fe ³⁺	200	95	94	94	99	95
Cr ³⁺	200	105	104	91	90	97
Sn ²⁺	100	100	99	99	97	88
Ni ²⁺	100	90	90	103	101	99
Ni ²⁺	50	99	95	96	93	101
Cl ⁻	10,000	96	97	95	98	96
NO ₃ ⁻	10,000	104	101	96	94	101
SO ₄ ²⁻	10,000	99	93	99	91	95
SCN ⁻	10,000	105	98	90	106	94

^aConcentration of Pb(II), Cd(II) and Cu(II) are $0.10 \mu\text{g L}^{-1}$ and, Hg(II) and As(III) are $0.50 \mu\text{g L}^{-1}$.

5%). The results demonstrate that the presences of large amounts of species commonly present in tea samples have no significant effect on the VALPME-SDES of target metal ions.

Analytical validation of proposed method

The optimized VALPME-SDES procedure was validated with respect to linear ranges, detection limits, repeatability (intra-day), reproducibility (inter-day) and enrichment factor (Table 3). By and large, repeatability and reproducibility of a method is calculated based on seven replicate measurements. Thus, the repeatability and reproducibility of the VALPME-SDES coupled with GFAAS for $0.50 \mu\text{g L}^{-1}$ of Hg(II) and As(III), and $0.10 \mu\text{g L}^{-1}$ of Pb(II), Cd(II), and Cu(II) were determined to be 2.2–3.5 and 3.6–6.0%, respectively. The detection limits were calculated to be in the range of 0.005 – $0.1 \mu\text{g kg}^{-1}$ for different metal ions, using the definition $C_L = 3S_b/m$, where C_L , S_b , and m are the detection limit, blank standard deviation and slope of the calibration curve, respectively. Linear ranges (LRs) were obtained as follows: 0.01 – $10 \mu\text{g kg}^{-1}$ for Cd(II), 0.3 – $50 \mu\text{g kg}^{-1}$ for Hg(II) and As(III), and 0.1 – $100 \mu\text{g kg}^{-1}$ for Pb(II) and Cu(II) with correlation coefficient better than 0.992. Finally, the high enrichment factors (164–235) were obtained for heavy metals only for small volume of aqueous solution (10 mL).

Analysis of tea samples

The efficiency of the VALPME-SDES method was validated with the monitoring of the different metal ions including Pb(II), Cd(II), Cu(II), Hg(II), and As(III) in black tea samples. Table 4 summarizes the metal ions concentrations in black tea samples. The concentrations of Pb(II), Cd(II), Cu(II), Hg(II), and As(III) in tea samples ranged from 0.22 to 1.41, 0.03 to 0.13, 6.8 to 25, 0.008 to 0.11, and 0 to 0.12 mg kg^{-1} with a mean value of 0.757, 0.082, 14.51, 0.058, and 0.047 mg kg^{-1} , respectively. The amount of toxic metal ions in tea can be considered as a quality indicator. Lower concentrations

Table 3. Figures of merit of the proposed method.

Analyte	Enrichment factor	Extraction recovery%	Detection limit ($\mu\text{g kg}^{-1}$) ^a	RSD% ^b (intra-day, $n = 7$)	RSD%(inter-day, $n = 7$)	Linear range ($\mu\text{g kg}^{-1}$)	r^2
Pb	226	66	0.03	2.8	4.1	0.1–100	0.996
Cd	235	71	0.005	2.2	3.6	0.01–10	0.998
Cu	210	63	0.03	3.1	4.2	0.1–100	0.996
As	188	57	0.1	3.2	5.1	0.3–50	0.995
Hg	164	50	0.1	3.5	6.0	0.3–50	0.993

^aDetection limits were calculated based on $3S_b/m$.

^bPercent relative standard deviation for seven replicate measurements of the elements with the concentration of $0.5 \mu\text{g L}^{-1}$ for Hg(II) and As(III), and $0.1 \mu\text{g L}^{-1}$ for Pb(II), Cd(II), and Cu(II).

Table 4. Metal ions concentrations in the black tea samples^a.

Sample name	Origin country	Analyte	Added (mg kg ⁻¹)	Found (mg kg ⁻¹) ± SD (n = 3)	Relative recovery (%)
Green hammer	Silan	Pb	–	0.5 ± 0.04	–
			0.1	0.59 ± 0.03	90
		Cd	–	0.06 ± 0.004	–
			0.05	0.11 ± 0.02	100
		Cu	–	8.2 ± 0.6	–
			5	13.4 ± 0.8	104
		As	–	0.05 ± 0.004	–
			0.1	0.14 ± 0.009	90
		Hg	–	0.11 ± 0.006	–
			0.2	0.30 ± 0.02	95
Sa'dal-Din 444	Sri Lanka	Pb	–	0.7 ± 0.06	–
			0.2	0.89 ± 0.05	95
		Cd	–	0.09 ± 0.006	–
			0.2	0.30 ± 0.03	105
		Cu	–	12.4 ± 0.7	–
			10	23.2 ± 1.3	108
		As	–	0.04 ± 0.003	–
			0.2	0.25 ± 0.01	105
		Hg	–	0.06 ± 0.005	–
			0.4	0.44 ± 0.03	95
Sa'dal-Din 222	Sri Lanka	Pb	–	0.22 ± 0.01	–
			0.3	0.55 ± 0.04	110
		Cd	–	0.11 ± 0.01	–
			0.3	0.39 ± 0.04	93
		Cu	–	6.8 ± 0.5	–
			15	22.2 ± 1.3	103
		As	–	0.008 ± 0.001	–
			0.3	0.31 ± 0.01	101
		Hg	–	0.08 ± 0.01	–
			0.6	0.71 ± 0.05	105
Butterfly	India	Pb	–	0.35 ± 0.06	–
			0.4	0.74 ± 0.05	98
		Cd	–	0.08 ± 0.006	–
			0.4	0.51 ± 0.03	107
		Cu	–	19.3 ± 1.4	–
			20	40.2 ± 3.3	104
		As	–	0.05 ± 0.006	–
			0.4	0.46 ± 0.04	102
		Hg	–	N.D. ^b	–
			0.8	0.77 ± 0.04	96
Elephant	China	Pb	–	1.1 ± 0.08	–
			0.5	1.56 ± 0.06	92
		Cd	–	0.13 ± 0.007	–
			0.5	0.64 ± 0.05	102
		Cu	–	24.1 ± 2.0	–
			25	47.4 ± 3.6	93
		As	–	0.08 ± 0.005	–
			0.5	0.52 ± 0.04	88
		Hg	–	0.12 ± 0.01	–
			1	1.14 ± 0.06	102
Mobile	Bangladesh	Pb	–	0.42 ± 0.03	–
		Cd	–	0.08 ± 0.004	–
		Cu	–	18.2 ± 1.1	–
		As	–	0.07 ± 0.002	–
		Hg	–	0.008 ± 0.001	–
Ghazal pair	Bangladesh	Pb	–	0.65 ± 0.08	–
		Cd	–	0.03 ± 0.004	–
		Cu	–	10.6 ± 0.7	–
		As	–	0.09 ± 0.002	–
		Hg	–	0.03 ± 0.005	–
Perfume world	Pakistan	Pb	–	1.41 ± 0.05	–
		Cd	–	0.10 ± 0.009	–
		Cu	–	25.0 ± 2.3	–
		As	–	0.11 ± 0.007	–
		Hg	–	N.D.	–
Golden hammer	Silan	Pb	–	0.92 ± 0.06	–
		Cd	–	0.08 ± 0.006	–
		Cu	–	9.3 ± 0.6	–
		As	–	0.02 ± 0.001	–
		Hg	–	N.D.	–

(continued)

Table 4. Continued.

Sample name	Origin country	Analyte	Added (mg kg ⁻¹)	Found (mg kg ⁻¹) ± SD (n = 3)	Relative recovery (%)
Hammer two fans	Silan	Pb	–	1.3 ± 0.07	–
		Cd	–	0.06 ± 0.005	–
		Cu	–	11.2 ± 1.0	–
		As	–	0.06 ± 0.005	–
		Hg	–	0.06 ± 0.002	–
CRM- Green Tea (GBW 10052)		Pb	1.6 ± 0.2 ^c	1.62 ± 0.12	101
		Cd	0.076 ± 0.004 ^c	0.075 ± 0.004	99
		Cu	24 ± 1 ^c	23.4 ± 1.5	97

^aThese data are based on the diluted volumes of aqueous samples and dilution effect was considered for calculation of them.

^bNot detected.

^cCertified values (mg kg⁻¹).

Table 5. Comparison of VALPME-SDES with other extraction methods for determination of metal ions in different samples.

Methods	LOD ^a (µg kg ⁻¹)	LR ^b (µg kg ⁻¹)	RSD ^c %	Extractant volume (µL)	Sample amount (gr)	Metal ions	Samples	Reference
WD-ICP-OES ^d	–	–	1.16–5.53	4500	0.1	Zn, Ni, Mn, Cr, Pb, Cu	Tea and soil	Wen <i>et al.</i> (2018)
WD- ICP-MS ^e	0.19–1.33	–	<9	5000	0.5	Al, As, Cd, Cr, Pb	Tea	De Oliveira <i>et al.</i> (2018)
DLLME- SDES-GFAAS ^f	0.01–0.03	0.02–200	2.3–4.1	50	1–2	Pb, Cd, Hg	Soil and vegetables	Habibollahi <i>et al.</i> (2018)
DLLME- SFO-GFAAS ^g	0.04–0.1	0.1–100	3.5–6.2	40	0.5	Pb, Cd, Hg	Trout fish	Pirsaheb and Fattahi (2015)
CPE-FAAS ^h	0.6	2.0–200	2.3	10 + 1 mL	0.5–6	Ni	Food and water samples	Rahnama and Najafi (2016)
SPE-FAAS ⁱ	1.0–2.6	3.0–300	2.4–3.4	6000	1	Pb, Fe, Ni, Cu, Zn	Food samples	Ghaedi <i>et al.</i> (2013)
PSCME-GFAAS ^j	0.01–0.05	0.03–200	3.1–4.2	40	0.5	Pb, Cd, Hg	Fish samples	Safari <i>et al.</i> (2018)
CSDF-ME-GFAAS ^k	0.002	0.005–0.05	3.2	37	0.5	Cd	Cosmetics	Ahmadi-Jouibari <i>et al.</i> (2017)
VALPME-SDES	0.005–0.10	0.01–100	2.2–3.5	60	0.5	Pb, Cd, Cu, Hg, As	Tea	This work

^aLOD, limit of detection.

^bLR, linear range.

^cRSD, relative standard deviation.

^dWet digestion and inductivity coupled plasma-optical emission spectroscopy.

^eWet digestion and inductivity coupled plasma-mass spectrometry.

^fDispersive liquid-liquid microextraction and the solidification of deep eutectic solvent-graphite furnace atomic absorption spectrometry.

^gDispersive liquid-liquid microextraction based on the solidification of floating organic drop and graphite furnace atomic absorption spectrometry.

^hCloud point extraction and flame atomic absorption spectroscopy.

ⁱSolid-phase extraction and flame atomic absorption spectroscopy.

^jPersistent sample circulation microextraction and graphite furnace atomic absorption spectrometry.

^kContinuous sample drop flow-based microextraction and graphite furnace atomic absorption spectrometry.

of toxic metal ions indicate higher quality of tea. The results in Table 4 show that lead concentration in tea produced in India, Ceylon and Bangladesh is lower than in other countries. The amount of cadmium in tea produced in Sri Lanka, China, and Pakistan is higher. Arsenic and mercury levels are higher in tea produced in Pakistan and China, respectively. The accuracy of the proposed method was tested by calculating the relative recovery of the metal ions from five spiked tea samples. As shown in Table 4, the relative recoveries of the spiked tea samples were in the range of 88–110%. The accuracy of the proposed procedure was also assessed by determining the concentration of the Pb(II), Cd(II), and Cu(II) in a certified reference material for Green Tea (GBW 10052). The results are given in the Table 4. As can be seen, the determined values are in satisfactory agreement with the certified values. These results demonstrated that the matrices of the analyzed tea samples possess negligible effect

on the proposed VALPME-SDES followed by GFAAS determination of the metal ions.

Comparison of VALPME-SDES with previously reported methods

Determination of metal ions in black tea samples by VALPME-SDES procedure was compared with those of the previously reported methods to extract metal ions from different samples in Table 5. As it can be seen, the EFs of the selected analytes obtained in the proposed method are high. In addition, the LODs and linear range of the proposed method are comparable or less than those of the reported methods. The repeatability of the method is good and the relative standard deviations (RSDs) of the proposed method are comparable or better than other methods, except for conventional DLLME. In contrast to conventional DLLME, there is no need for disperser solvent, so less

organic solvent is used. These results show that the proposed method has more advantages over the other methods such as less hazardous for the environment, low-costing, reliable, and efficient.

Conclusions

In the present study, a VALPME-SDES method has been developed for the microextraction and pre-concentration of metal ions from black tea samples prior to their GFAAS analysis. This coupling enables the VALPME-SDES approach to benefit both VALPME and SDES method advantages. In this method, a few microliters of a DES were used as the extractant instead of toxic organic solvents that are commonly used in microextraction methods. The new DES consists of two 1-decyl-3-methylimidazolium chloride and *n*-butanoic acid parts with a molar ratio of 1 to 2. The evaluation of the target compounds yielded satisfactory precision, recovery, enrichment factor, linearity, and detection limit, making the developed method suitable for the determination of metal ions in tea samples. In addition, the application of VALPME-SDES is quite simple, fast, sensitive, and cheap because there is no need of expensive and special laboratory equipment. The data presented in this research provides useful information about toxic metal ions concentration in tea samples. The VALPME-SDES method does not require an organic solvent as disperser, in comparison with other DLLME techniques, and the organic solvent consumption is very low.

Disclosure statement

No potential conflict of interest was reported by the authors.

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