



Determination of As, Cr, Mo, Sb, Se and V in agricultural soil samples by inductively coupled plasma optical emission spectrometry after simple and rapid solvent extraction using choline chloride–oxalic acid deep eutectic solvent

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ABSTRACT

A rapid, simple and green ultrasound-assisted extraction method using deep eutectic solvents (DES) for extraction of As, Cr, Mo, Sb, Se and V in soil samples, has been developed. Choline chloride–oxalic acid based DES was used as a solvent. The target analytes were subsequently quantified using inductively coupled plasma optical emission spectrometer (ICP OES). The parameters that affect the extraction of the target analytes was optimized using standard reference material of San Joaquin soil (SRM 2709a). In the optimization step, a two-level full factorial experimental design was used. The factors under investigation include extraction time, sample mass and acid concentration. Under optimized conditions, limits of detection (LOD) and limits of quantification (LOQ) ranged from 0.009 to 0.1 and 0.03–0.3 $\mu\text{g g}^{-1}$, respectively. The repeatability ($n=20$) estimated in terms of relative standard deviation (%RSD) ranged from 0.9% to 3.7%. The accuracy of the proposed method was carried out using SRM 2709a. The obtained and certified/ indicative values were statistically in good agreement at 95% confidence level. The proposed method applied for quantification of As, Cr, Mo, Sb, Se and V in real soil samples. For comparison, the analytes of interest were also determined using a conventional acid digestion method. According to the paired *t*-test, the analytical results were not significant differences at 95% confidence level. The method was found to be accurate, precise and environmentally friendly.

1. Introduction

Soil pollution by trace metals attracts great attention because of its possible threat to food safety and security as well as harmful effects on the ecosystem (Lee et al., 2013; Lu et al., 2012). The source of trace elements in soils may be due to the natural occurrence or anthropogenic activity. However, the natural contents of trace elements in soils depend mostly on the geological composition of the parent materials (Lu et al., 2012). Anthropogenic activities (such as industrial development, mining, transportation consuming, fossil fuel combustion and agricultural practices) on the other hand, significantly contribute to the increase of trace metal content in the environmental matrices, particularly soils (Khan et al., 2013; Lu et al., 2012). In addition, it has been reported that the elevated concentration of trace elements in agricultural soils is due to the excessive use of metal containing fertilizers and pesticides, wastewater irrigation and sewage sludge application (Khan et al., 2013; Lu et al., 2012). Therefore, the determination of trace metals in different samples has a significant part in the environmental

safety and agricultural science (Ghaedi et al., 2009; Korn et al., 2008).

The determination of trace metals in complex matrices frequently involves extensive sample preparation processes prior to quantification using analytical techniques (ALothman et al., 2012; Mketto et al., 2014; Nomngongo and Ngila, 2015; Yimaz and Soylyak, 2015). For this reason, several sample preparation and extraction methods both traditional and modern have been developed to extract target analytes from complex matrices such as soil, coal, and food, among others. These methods include wet/or dry ashing digestion (Akinyele et al., 2015; Pereira et al., 2016; Ramanathan et al., 2015), microwave-assisted acid digestion (Bakircioglu et al., 2011; Krishna et al., 2015; Patole et al., 2016; Zhao et al., 2015), ultrasound-assisted extraction (Peronico et al., 2016; Schneider et al., 2016) and direct slurry introduction (Borges et al., 2014; Guo et al., 2015; Zmozinski et al., 2015), among others. However, some of these methodologies utilize toxic chemicals such as sulphuric acid, hydrochloric acid and nitric acids and oxidizing agents such as fluorine, chlorine, bromine, and iodine. Therefore, the main drawback of using the aforementioned

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analytical methodologies, especially in the routine analysis is that they involve serious health risks for analysts, as well as damage in the environment (Habibi et al., 2013). Therefore, there is a need to develop green sample preparation methods that use less toxic reagents (Habibi et al., 2013).

In view of the above, ionic liquids (ILs) are qualified as green solvents because of their low vapour pressure and high boiling points (Martín-Calero et al., 2011) and they have been used for extraction of trace elements in different matrices such as fuel (Nomngongo et al., 2014), water (Ranjbar et al., 2012), food (Jalbani et al., 2015) and biological samples (Stanisz et al., 2013). Although, ionic liquids have been extensively used as a solvent in different microextraction procedures, some ILs has drawbacks. For instance, pyridinium or imidazolium-based ionic liquids are not completely “green” because their toxicity is the same or more than that of traditional organic solvents (Xu et al., 2015). Therefore, deep eutectic solvents (DESs), which have similar physicochemical properties as ILs, have emerged (Abbott et al., 2006; Bi et al., 2013; Habibi et al., 2013). The preparation, properties and analytical use of deep eutectic solvents are well recorded in literature (Abbott et al., 2006; Smith et al., 2014; Zhang et al., 2012).

Deep eutectic solvents are normally obtained by utilizing of a mixture of ammonium salts (such as choline chloride) and hydrogen bond donors (HBD, urea, carboxylic acids) (Abbott et al., 2006; Choi et al., 2011; Zhang et al., 2012). Due to the attractive properties of DES, they have been applied as solvents in different chemistry fields (Durand et al., 2013; Lindberg et al., 2010; Zhao et al., 2013). Ghanemi et al. (2014) developed an ultra-fast microwave-assisted digestion in choline chloride–oxalic acid deep eutectic solvent for determining Cu, Fe, Ni and Zn in marine biological samples. Karimi et al. (2016), on the other hand, reported the use of deep eutectic liquid organic salt as a new modifier of magnetic nanoparticles for micro-solid phase extraction. The new solvent was used for ligandless extraction and preconcentration of lead and cadmium in edible oils. Deep eutectic solvents have been also used for extraction of trace elements in food (Yilmaz and Soyak, 2015), environmental (Karimi et al., 2016) and biological samples (Habibi et al., 2013; Yilmaz and Soyak, 2015), among others.

In agricultural environments, the concentration of some trace elements can be increased by input by different activities such as the addition of fertilizers, biosolids, metal-containing pesticides and occasionally wastewater (Takeda et al., 2005). For instance, processed phosphate fertilizers are believed to be the main sources of trace elements such as As, Cr, Se, Mo, and V, among others in agricultural soils (McBride and Spiers, 2001). This is because the phosphates blended in these fertilizers are processed from rock phosphate deposits. These rocks have been identified as the predominant source of most of the trace metals than their average content in earth's crust or soils. Therefore, significant concentrations of these elements remain in the phosphate fertilizer (Soyak and Türkoglu, 1999; McBride and Spiers, 2001; Jiao et al., 2012). In view on of the above, this study seeks to develop ultrasound assisted DES extraction method combined with heating for extraction of As, Cr, Mo, Sb, Se and V in agricultural soil samples. Choline chloride/oxalic acid mixture was selected as a deep eutectic solvent to extract the target analytes from soil samples. Choline chloride/oxalic acid DES was chosen because of its high ability for dissolving metal oxide as compared to other DESs, such as ChCl–urea and ChCl–ethylene glycol (Abbott et al., 2006; Ghanemi et al., 2014). A two-level full factorial design (FFD) was used as a multivariate approach for optimization of factors of affecting the extraction of selected trace elements. Parameters influencing the developed extraction method include extraction time, sample mass and nitric acid concentration. The effect of DES composition was investigated separately. To the best of our knowledge, there is no report on the application of DES for extraction of As, Cr, Mo, Sb, Se and V in agricultural soil samples.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade unless otherwise stated and were employed without additional purification. Double-distilled deionized water prepared by Millipore-Q-plus purification system (Bedford, USA) was used throughout the experiments. Choline chloride ($C_5H_{14}NClO$, > 99%), ultra-pure nitric acid (HNO_3 , 65%), ultrapure hydrochloric acid (HCl, 37%) and oxalic acid (purified grade, 99.999% trace metals basis) were purchased from Sigma (St. Louis, MO, USA). The standard working solutions applied for calibration were prepared by diluting 1000 mg L^{-1} multi-element standard solutions (Spectrascan) with 1% HNO_3 . A standard reference material of San Joaquin soil (SRM 2709a, Gaithersburg, MD, USA) was used for the development and validation of the developed method. To reduce the possibility of metal contamination, the plastic ware was soaked in 5% HNO_3 for 24 h, washed with deionized water and rinsed double distilled deionized water.

2.2. Instrumentation

The quantification of the analytes (As, Cr, Mo, Sb, Se and V) was performed using an inductively coupled plasma optical emission spectrometer (iCAP 6500 Duo, Thermo Scientific) equipped with a charge injection device (CID) detector. The samples were introduced with a concentric nebulizer and a cyclonic spray chamber. The operating parameters of the instruments are presented in Table 1.

2.3. Sampling and sample pre-treatment

Soil samples were collected from three different vegetable plots (tomato, cabbage and unplanted) near Glen Agricultural College (Bloemfontein, Free state province, South Africa) and the samples were stored in a polyethylene bags. The soil in the selected site is classified as clay-loamy soil. The composition of the soil was found to be 31–43% silt, 29–35% clay and 29–37% sand. To evaluate whether the developed method is applicable to other soil types, two additional soil samples, silt loam, and loamy sand were collected from Westrand and Eastrand regions (Johannesburg, Gauteng Province), respectively. The composition of these silt loam soil sample was 15–41% sand, 51–71% silt, and 5–13% clay, while the composition of the loamy sand was 73–81% sand, 5–25% silt and 3–10% clay. The samples of each soil were taken to the laboratory then placed on trays in laminar flow cabinet and allowed to dry at room temperature for a week. The dried

Table 1
Operating parameter of an inductively coupled plasma optical emission spectrometer (ICP-OES).

ICP-OES parameters	
RF generator power (W)	1150
Frequency of RF generator (MHz)	40
Coolant gas flow rate ($L\text{ min}^{-1}$)	12
Carrier gas flow rate ($L\text{ min}^{-1}$)	0.7
Auxiliary gas ($L\text{ min}^{-1}$)	1.0
Max integration times (s)	15
Pump rate (rpm)	50
Viewing configuration (Touch mode)	Axial
Replicate	3
Flush time (s)	30
Spectral lines	$^{189.0}\text{As}$, $^{283.5}\text{Cr}$, $^{202.0}\text{Mo}$, $^{206.0}\text{Sb}$, $^{196.0}\text{Se}$ and $^{309.3}\text{V}$

Branson 5800 ultrasonic Cleaner (Danbury, CT, USA) and Eppendorf 5702 Centrifuge (Eppendorf Ag, Hamburg Germany), respectively, were used for ultrasound-assisted extraction and centrifugation, respectively. An aqua-regia digestion method was performed using digestion block (DigiBlock Digester ED36S, Labtech, Wilmington, MA).

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