



# Temperature controlled ionic liquid-dispersive liquid phase microextraction for determination of trace lead level in blood samples prior to analysis by flame atomic absorption spectrometry with multivariate optimization

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## ABSTRACT

This paper described a new approach for the pre-concentration of lead ( $Pb^{2+}$ ) by temperature controlled ionic liquid-dispersive liquid phase microextraction (TIL-DLME) prior to analyzing by flame atomic absorption spectrometry (FAAS). An ionic liquid (IL) 1-Butyl-3-methylimidazolium hexafluorophosphate [ $C_4MIM$ ][ $PF_6$ ] was used as an extractant solvent. The  $Pb^{2+}$  was complexed with ammonium pyrrolidinedithiocarbamate (APDC) and then entered into the infinite IL drops at high temperature ( $>70^\circ C$ ). Important variables affecting the microextraction efficiency such as pH, ligand concentration, amount of IL, temperature and incubation time were investigated. The results showed that the coexistent ions had no obvious negative effect on the determination of  $Pb^{2+}$ . In the optimum experimental conditions, the limit of detection (LOD) and the enhancement factor (EF) were  $0.13 \mu g L^{-1}$  and 93, respectively. The relative standard deviation (RSD) of  $10 \mu g L^{-1}$   $Pb^{2+}$  was 4.3%. The developed method was validated by determining  $Pb^{2+}$  in certified reference material (CRM) and the results showed that the determined values of  $Pb^{2+}$  were in good agreement with the certified value. The proposed method was applied satisfactorily for the pre-concentration of  $Pb^{2+}$  in acid digested blood samples of children with different respiratory disorders.

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## 1. Introduction

Lead ( $Pb^{2+}$ ) and other toxic metals are released into the environment by several processes including waste and coal burning, industrial processes, volcanic emissions, metal mining and smelting [1,2]. Epidemiologic studies have found higher blood and body burdens of toxic metals in subjects living near waste incinerators [3]. The fetus, infant, and young child are considered among the most susceptible to pollutants in the air. In children, ambient (outdoor) air pollution has been associated with respiratory problems, development of asthma, preterm birth, infant mortality, and deficits in lung growth [4]. One percent of global childhood deaths from acute respiratory disease are attributed to air pollution [5]. In recent years, heavy metals associated with suspended particulate matter (SPM) present in the urban environment, have received much attention due to their diverse toxic effects on human health by their inhalation. Among different anthropogenic sources

vehicular emission contributes significantly to the SPM and gaseous species load in an urban environment. Singh et al., has reported negative association between  $Pb^{2+}$  and the lung functioning [6].  $Pb^{2+}$  has the potential to interfere with many biochemical actions present in cells throughout the body and it can produce a number of consequences [7–9].

Being a toxicant, determination of trace and ultra trace  $Pb^{2+}$  level in blood samples have become of increasing significance [10].  $Pb^{2+}$  determination in blood samples is particularly not easy because of complex matrix and generally its low concentration in blood, which requires sensitive instrumental techniques and frequently a pre-concentration step. In this regard, a variety of techniques have been proposed for the trace and ultra-trace determination of  $Pb^{2+}$ , such as liquid-liquid extraction (LLE) [11], coprecipitation [12], ion exchange [13], cloud point extraction (CPE) [14] and solid phase extraction [15]. The LLE has been used for decades, but this technique is usually time-consuming and requires quite bulk amount of high purity solvents. Furthermore the disposal of these solvents used, may also create a severe environmental problem. In this sense, substantial interest has been manifested on the usage of RTILs as the green solvent to replace the conventional organic solvents in a broad range of application, especially in LLE of heavy metal ions and other pollutants [16,17]. RTILs are organic salts which are present in liquid state at room temperature [18]. This particular behavior can be ascribed to

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the poor coordination of their constituent ions, since at least one of them has a delocalized charge preventing the formation of a stable crystal lattice [19]. RTILs consists of large organic cations like quaternary ammonium, imidazolium or pyridinium ions combined with anions of smaller size and more symmetrical shape such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{AlCl}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{ROSO}_3^-$ , trifluoromethanesulfonate and others. The possible applications of RTILs for LLE of metal ions from various matrices are mainly based on combination with some chelating compounds that are capable of metal binding and extraction at the final step in the extraction procedure that is referred as the partition between the two phases [20]. These properties are mainly due to their lack of vapor pressure, high conductivity, high stability, and low viscosity, polarity as well as solvent solubility and miscibility [21–24]. A number of research papers have been recently focused on the successful applications of RTILs for extraction of metal ions. Several methods of IL-based microextraction have been developed for the determination of  $\text{Pb}^{2+}$  [25–27].

However, ILs have not been often used in dispersive liquid-phase microextraction. The aim of the present work was to combine the temperature controlled ionic liquid-dispersive liquid phase microextraction (TIL-DLME) with FAAS for the determination of  $\text{Pb}^{2+}$  in blood samples of children with respiratory disorders. For comparison purposes the blood samples of healthy children of same age group were also collected. The effect of different variables such as the volume of  $[\text{C}_4\text{MIM}][\text{PF}_6]$ , sample pH, concentration of complexing reagent, extraction time and salt effect were investigated and discussed in detail.

## 2. Experimental

### 2.1. Reagents and standard solutions

Ultrapure water obtained from ELGA labwater system (Bucks, UK), was used throughout the work. 1-Butyl-3-methylimidazolium hexafluorophosphate  $[\text{C}_4\text{MIM}][\text{PF}_6]$  was purchased from Sigma-Aldrich (Germany), and used as obtained. Standard solutions of  $\text{Pb}^{2+}$  were prepared by dilution of certified standard solution ( $1000 \text{ mg L}^{-1}$ ) Fluka Kamica (Bush, Switzerland). Dilute working standard solutions were prepared by stepwise dilution of the stock standard solution with 0.2 M  $\text{HNO}_3$ . A stock buffer solution was prepared by dissolving appropriate amounts of acetic acid and its sodium salt in ultrapure water, and solutions were prepared with  $0.1 \text{ mol L}^{-1}$   $\text{HNO}_3/\text{NaOH}$ . For the accuracy of method, certified reference material (CRM), Clincheck control-lyophilized human whole blood (Recipe, Munich, Germany), was used.

### 2.2. Apparatus

A PEL domestic microwave oven (Osaka, Japan), programmable for time and microwave power from 100 to 900 W, was used for digestion of blood samples. A pH meter (Ecoscan Ion 6, Malaysia) was employed for pH adjustments. Centrifugation was carried out using a WIROWKA Laboratoryjna type WE-1, nr-6933 centrifuge (speed range 0–6000 rpm, timer 0–60 min, 220/50 Hz, Mechanika Pheczyjna, Poland). A Perkin Elmer Model A Analyst 700 (Norwalk, CT) flame atomic absorption spectrophotometer was used. A single element hollow cathode lamp was operated at 7.5 mA at spectral bandwidth of 0.7 nm. The analytical wavelength was set at 283.3 nm.

### 2.3. Selection of subjects

We carried out a cross-sectional study to evaluate the association of blood  $\text{Pb}^{2+}$  level (BLL) with respiratory disorders in children. The blood samples of 39 children aged 1–5 years with different respiratory disorders, attending the OPD (outpatient department) of pediatric ward of civil hospital, Karachi, were collected. For comparative purposes the

healthy children of same age group (referent children) were selected. Among 56 referents, 25 belonged to industrial (exposed) area, while 31 referent children were from non-industrial (non-exposed) area. The blood samples were collected from children with the help of paramedical staff of hospital. Subjects did not report any accidental exposure to  $\text{Pb}^{2+}$ , and therefore, the main sources of the detected  $\text{Pb}^{2+}$  were expected to be environmental exposure.

### 2.4. Temperature controlled ionic liquid-dispersive liquid phase procedure

10 mL of standard solution containing  $10 \mu\text{g L}^{-1}$  of  $\text{Pb}^{2+}$  was placed in a screw cap glass conical tube and 1 mL of 0.2% (m/v) APDC solution was added. pH was adjusted in the range (1–4) by the addition of  $0.1 \text{ mol L}^{-1}$   $\text{HCl}/\text{NaOH}$  solution in acetate buffer. After adding  $45 \mu\text{L}$  of  $[\text{C}_4\text{MIM}][\text{PF}_6]$ , the mixed solution was heated on ultrasonic water-bath at  $75^\circ\text{C}$ . A cloudy solution formed and the test tube was dipped in ice water for 10 min. During this stage, the hydrophobic chelate of  $\text{Pb}^{2+}$  was extracted into the fine droplets of  $[\text{C}_4\text{MIM}][\text{PF}_6]$ . Then the mixture was centrifuged at 3500 rpm for 10 min to achieve phase separation. After this step IL phase was sedimented at the conical bottom of the test tube. 0.5 mL of acidic methanol was added to the viscous IL phase prior to its analysis by FAAS.

## 3. Experimental design

### 3.1. Plackett–Burman design

A Plackett–Burman design as screening approach was carried out by using Minitab (release 13 of MINITAB) Version 5.1 [28,29]. To estimate the optimum levels of factors for the proposed procedure at two levels Plackett–Burman design with only 16 experiments were described instead of the  $2^5=32$  required for full factorial designs. Table 1 shows low (–) and high (+) levels, while optimization by Plackett–Burman matrix is shown in Table 2. These results can be visualized by standardized ( $P=95.0\%$ ) Pareto chart of main effects shown in Fig. 1. The application of this experimental design reduced the development time of the methods and provided less ambiguous extraction conditions, hence facilitating data interpretation.

### 3.2. Central $2^3+star$ orthogonal composite design

After screening out the variables with insignificant effect on the recovery of analyte, remaining three factors were optimized to provide the maximum metal recovery. A central  $2^3+star$ , orthogonal composite design with six degree of freedom and involving 16 new experiments was performed to optimize the variables, i.e., ionic liquid (IL), pH (P) and heating temperature (T) for % recovery of  $\text{Pb}^{2+}$  (Table 3). Less significant factors (after PBD) were fixed at convenient values as incubation time of 10 min and ligand concentration of 0.2%.

## 4. Results and discussion

### 4.1. Optimization of experimental variables

Five factors were selected to be examined. The factors and their levels, low (–) and high (+), are described in Table 1. The sample

**Table 1**  
Variable and levels used for the Plackett–Burman designs in the factorial design.

Variables	Symbol	Low (–)	High (+)
Ionic liquid ( $\mu\text{L}$ )	IL	20	60
Complexing agent (% APDC)	C	0.05	0.35
pH	P	1	4
Incubation time (min)	I	5	20
Temperature ( $^\circ\text{C}$ )	T	50	100

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