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# Development of a new green non-dispersive ionic liquid microextraction method in a narrow glass column for determination of cadmium prior to couple with graphite furnace atomic absorption spectrometry

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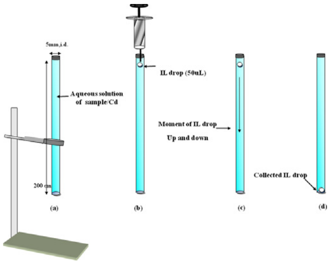
## HIGHLIGHTS

- A novel and rapid non-dispersive ionic liquid based microextractions.
- We used a long narrow glass column to provide more contact area between two media (aqueous and extractive).
- APDC using as complexing agent and analyzed by GFAAS.
- Introduced a novel approach that reduced solvent consumption, effort, time.
- It was applied for determination of understudy analytes in real water sample.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Easy and innovative non-dispersive ionic liquid based microextraction (NDILME) has been developed for preconcentration of trace level of cadmium (Cd) in aqueous real surface water samples prior to couple with graphite furnace atomic absorption spectrometry (GFAAS). A 200 cm long narrow glass column containing aqueous solution of standard/sample was used to increase phase transfer ratio by providing more contact area between two medium (aqueous and extractive), which drastically improve the recoveries of labile hydrophobic chelate of Cd ammonium pyrrolidinedithiocarbamate (APDC), into ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [$C_4$mim][$PF_6$]. Different aspect of the desire method have been investigated and optimized. Under the optimized key experimental variables, limit of detection (LOD) and enhancement factor (EF) were achieved to be 0.5 ng $L^{-1}$ and 150, respectively. Reliability of the model method was checked by relative standard deviation (%RSD), which was found to be < 5%. Validity and accuracy of the developed method was checked by analysis of certified reference water samples (SLRS-4 Riverine water) using standard addition method.

Application of the model method was productively performed by analysis of Cd in real surface water samples (tap and sea).

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## 1. Introduction

Monitoring trace level of toxic metals in diverse environmental condition is an extremely important job to assess occupational and environmental exposure. Cd is one of the most accumulative toxic metal in different parts of the human body with a biological half-life of 10–30 years [1]. Cd is considered as important part of the modren industry which increases the risk of environmental contamination [2–4]. The contaminating content of cadmium in natural sea and fresh water is in the range of 70–110 ng $L^{-1}$, 2–960 ng $L^{-1}$, respectively [5]. The maximum contaminant level allowed by Environmental Protection Agency (EPA) in standard drinking water is 5 $\mu g\,L^{-1}$ [6]. Different analytical techniques have been used for determination of Cd in different environmental samples [7–14]. Development of reliable and sensitive methodologies have become an important demand in spite of major advances in the analytical instrumentation [15]. Prior to assess low concentration in complex matrix, separation and preconcentration techniques are compulsory to eliminate or minimize matrix effects which lower the detection limit and enhancing sensitivity of detection techniques towards metals [16]. Recently new innovation in separation techniques has been built but most of them are tedious and leading cause of environmental contamination [17–19].

Liquid–liquid microextraction is one of the most reliable and convenient separation tools for best dealing with samples. Miniaturizing the liquid–liquid extraction (LLE) procedure by greatly reducing the solvent to aqueous phase ratio, leads to the development of single drop microextraction (SDME) [20]. The basic principle of SDME is the distribution effect of the analytes between a microdrop of extraction solvent at the tip of a microsyringe needle and aqueous sample solution. After extracting for a prescribed period of time, the microdrop is retracted back into the microsyringe and transferred to the instrumentation for further analysis [21]. A great deal of care and highly concise practical handling are required to design SDME. As prolonged extraction time may result in drop dissolution and have a high incidence of drop loss, thus poor accuracy and precision [22,23]. The use of a large organic drop results in an increase of the analytical response of the instrument. However, larger drop is difficult to manipulate and less reliable [24]. Practical considerations are also important issue by ensuring reproducible and stable positioning of the sample vial and syringe needle, with the help of stands and clamps [25].

New modifications in microextraction technique based on dispersive liquid–liquid microextraction (DLLME) have been carried out. Dispersing of extraction medium physically or chemically, are usually decreases the partition coefficient of the analyte into the extracting solvent, it might be due to loose or dissolve which probably decrease extraction efficiency of the developed methods [26–32]. Room temperature ionic liquids (RTILs) have attracted considerable attention in recent years, due to their unique chemical and thermal properties [33]. RTILs are highly viscous and water immiscible than common organic solvent and are considered potential alternatives to conventional organic solvents which can significantly contribute to environmental contamination with volatile organic compounds [34–36].

To overcome all of the above problems, we introduced a new method, non-dispersive ionic liquid based liquid–liquid microextraction (NDILME). In this research approach, we used a long 200 cm narrow glass column containing aqueous sample solution to provide more contact area between two media (aqueous and extractive) which drastically improve recoveries of analytes and it also improve the volume ratio of sample to extraction solvent by using high sample size, which lead to high enrichment factors (EFs). The extraction time of the present method relative to the other methods is very short due to the large surface area for contact between the ionic extraction solvent and aqueous sample. The propose method have not required centrifugation and dispersing. The aim of this work was to introduce a novel and simple microextraction approach for the trace determination of Cd in water samples of different ecosystem and open a horizon for their application in different environmental samples.

## 2. Experimental

### 2.1. Chemicals and reagents

The chemicals used were of analytical grade and all solutions were prepared with ultrapure water. A certified stock standard solution of 1000 $\mu g\,mL^{-1}$ Cd was obtained Fluka Kamica (Bush, Switzerland). Working standard solutions were obtained by appropriate dilution of the stock standard solutions before analysis. 1-Butyl-3-methylimidazolium hexafluorophosphate [C4MIM][PF6] was purchased from Sigma-Aldrich (Germany) and used as obtained. The 0.1 mol $L^{-1}$ acetate buffer was used to control the pH of the solutions. Working standard solution was obtained by appropriate dilution of the stock standard solutions before analysis. The pH of the samples was adjusted to the desire pH by the addition of (0.1 mol $L^{-1}$ $HNO_3$/NaOH) solution in the buffer.

### 2.2. Instrumentation

A Perkin Elmer Model 700 (Norwalk, CT, USA) atomic absorption spectrometer equipped with a deuterium background correction system and electrothermal atomizer, HGA-800. Cd was measured at 228.8 nm with a hollow cathode lamp and a slit width of 0.7 nm. pH by pH meter (720-pH meter, Metrohm). The operating conditions of the spectrometer and the graphite furnace for Cd determination were followed in previously reported methods [37].

### 2.3. Procedure

The proposed NDILME set up was quite simple, required a long narrow-column glass tube (200 cm × 5 mm i.d.) as an extraction unit. Initially inner wall of the narrow-glass tube was cleaned with 4 mol $L^{-1}$ sodium hydroxide solution and rinsed thoroughly with de-ionized water. Later it was washed with 0.1% of Triton X-114 as a antisticking agent to prevents adhering of ionic liquid in inner wall of tube during extraction. 25 mL of each standard and real sample containing analytes (20–150 ng $L^{-1}$), chelating reagent APDC (0.05–0.5%) (m/v) and ionic liquid [C6MIM][PF6] (30–80 $\mu$L) were gradually added to extraction unit to obtain the desired working values. A very fine droplet of extraction solvent were formed and started to go down along the tube. During this step, Cd–APDC complex was gradually extracted from aqueous medium into the fine droplets of ionic liquid, which flow down along the tube. In less than 1 min, all fine droplets reached bottom of the tube and formed a single drop which was adhere on the surface of tube due to its higher density. The aqueous phase was removed carefully. Finally, drop of the ionic liquid enrich phase containing the target analyte was treated with 200 $\mu$L of 0.1 mol $L^{-1}$ $HNO_3$ in ethanol (1:1, v/v) in order to reduce its viscosity, facilitated sample handling and easily injected into the GFAAS for analysis. After each extraction, septum was removed and the narrow-bore tube was cleaned by passing distilled water, 0.01% Triton X-114 and distilled water for next assay. Blank solution was submitted to same procedure and measured in parallel to the standards and real samples.