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Flow injection wetting-film extraction system for flame atomic absorption spectrometric determination of cadmium in environmental waters

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ABSTRACT

A newly simple flow injection wetting-film extraction system coupled to flame atomic absorption spectrometry (FAAS) has been developed for trace amount of cadmium determination. The sample was mixed on-line with sodium diethyl dithiocarbamate and the produced non-charged Cd(II)–diethyl dithiocarbamate (DDTC) chelate complex was extracted on the thin film of diisobutyl ketone (DIBK) on the inner wall of the PTFE extraction coil. The wetting-film with the extracted analyte was then eluted by a segment of the cover solvent, and transported directly to the FAAS for evaluation. All the important chemical and flow parameters were optimized. Under the optimized conditions an enhancement factor of 35, a sample frequency of 22 h^{-1} and a detection limit of $c_L = 0.7\ \mu g\ l^{-1}$ Cd(II) were obtained for 60 s preconcentration time. The calibration curve was linear over the concentration range 1.5–45.0 $\mu g\ l^{-1}$ Cd(II) and the relative standard deviation, R.S.D. ($n = 10$) was 3.9%, at 10.0 $\mu g\ l^{-1}$ concentration level. The developed method was successfully applied to cadmium determination in a variety of environmental water samples as well as waste-water sample.

1. Introduction

The environment is continuously contaminated with large amount of toxic elements as consequence of human activities. Exposure to these toxic pollutants imposes not only risks to human health, but also potentially unacceptable ecological risks to plants, animals and microorganisms [1]. As the result, years of effort have been devoted to the development of more effective, fast, precise and accurate approaches for the determination of different elements like cadmium, in various environmental matrices using numerous analytical methods. The adverse effects of cadmium are the result not only of its high toxicity even at trace concentrations, but also of its bioaccumulation processes along the food chain and into vital human organs like kidney.

Flame atomic absorption spectrometry (FAAS) is among the most widely used techniques for determination of heavy metals, however, its sensitivity is usually insufficient for monitoring the low level concentrations of these metals in environmental samples. In addition, the interfering effect of the matrix components of complicated samples like sea-water, many times is a serious problem in the determinations by atomic spectrometry (AS). Consequently, a preconcentration and/or separation process is usually required prior the measurement. Although, liquid–liquid extraction (LLE) has proven to be a reliable and efficient separation and/or preconcentration technique for metal determination, it is time and reagent consuming, as well as tedious and laborious procedure and hence, potentially prone to contamination of sample and environment, when it is performed in batch (off-line) mode. However, the marriage of LLE with flow injection (FI) [2,3] offers a great ease to the analysis eliminating to a great extent, many of the drawbacks encountered in the batch mode.

In classical FI–LLE systems, the on-line extraction process is accomplished by three major operations: (i) segmentation, (ii) extraction and (iii) separation [4]. The extraction efficiency into the narrow tube of the extraction coil is usually high and it is completed in a few seconds. These parameters are attributed to the formation of a very thin film of one phase on the inner wall of the extraction coil, surrounding the segments of the other phase. The material of the coil (hydrophobic or hydrophilic) defines which phase will form the wetting-film according to the polarity of the solvent [5].

However, FI–LLE has not been widely accepted for routine analysis, due to the critical instrumentations, segmentor and phase separator, which affect significantly the reproducibility, stability and robustness of the method. Their design construction and operation performance have been studied in detail [6–8]. On the other hand, several efforts have been made to eliminate the need for segmentation and phase separation.

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A new concept called wetting-film extraction (WFE) has been proposed for sequential injection (SI) systems, without the need of segmentor and phase separator [9]. Wetting-film extraction is based on the formation of a thin film coating on the inner wall of the extraction coil, with major aim on sample preconcentration and separation. When an organic solvent is passed through a hydrophobic tube such as PTFE, a stationary thin film of the solvent is formed on the inner wall of the tube. When an aqueous solution with extractable analyte complex is aspirated into the tube extraction/preconcentration takes place at the interface of the organic thin film with the aqueous phase. After that, the preconcentrated analyte can be eluted, with a small plug of suitable solvent or back-extraction solution. The theoretical aspects and fundamentals of the WFE technique have been well presented by Miró et al. in a recent comprehensive review [10]. Christian and coworkers, developed a SI-WFE system for speciation of Cr(VI)/Cr(III) [11] and V(IV)/V(V) [12] and also for trace Mo(VI) determination in natural water samples [13]. In this case the consumption of the organic solvent was reduced tenth time than in the conventional automated FI-LLE. Paterson et al. [14] demonstrated that WFE is also suitable for sample preparation prior to high-pressure liquid chromatography (HPLC). Miró et al. [15] presented a flow-reversal SI-WFE set-up for radionuclide ^{90}Sr (b-emitter) determination in environmental samples and daily products. van Staden and Taljaard [16] determined seven heavy metals as dithizone complexes in environmental and biological samples. Cai et al. [17] established a microflow WFE for determination butyl rhodamine B and Chen et al. [18] coupled WFE in a FI system for copper determination by FAAS.

Diethyl dithiocarbamate (DDTC) form strong and mostly neutral complexes with a large number of heavy metals such as Cd(II), Cu(II), Pb(II), Ni(II), Zn(II) and Fe(III) [19–21], which can be separated from large excess of alkali and alkaline earth elements. In addition the complex formation is sufficiently rapid. These attributes makes the above chelating reagent ideal for the on-line preconcentration procedures of heavy metals in natural waters sample as well as in sea-water samples.

In the present work wetting-film extraction is exploited as versatile automatic approach for the implementation of liquid–liquid extraction in a simple low cost manifold for on-line metal preconcentration and determination by flame atomic absorption spectrometry. To the best of our knowledge, there is only one paper in the literature, dealing with WFE and FAAS [18], which presents copper determination and suffers from the complexity of the manifold and the procedure. The proposed method was evaluated for determination of Cd in natural water, using diisobutyl ketone (DIBK) as coating solvent and sodium diethyl dithiocarbamate as chelating reagent.

2. Experimental

2.1. Apparatus

A PerkinElmer, Norwalk, Connecticut, U.S.A. (http://las.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer with deuterium arc background corrector was exploited as detection system. Cadmium electrodeless discharge lamp (EDL) was used as light sources operated at 5 W. The wavelength was set at 228.8 nm resonance line, while the slit was fixed at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. The flame conditions were slightly leaner than those recommended by the manufacturer, in order to compensate the effect of DIBK, which serves as additional fuel during the measuring step. The air and acetylene flow rate was set at 10.0 and 0.9 l min^{-1}, respectively.

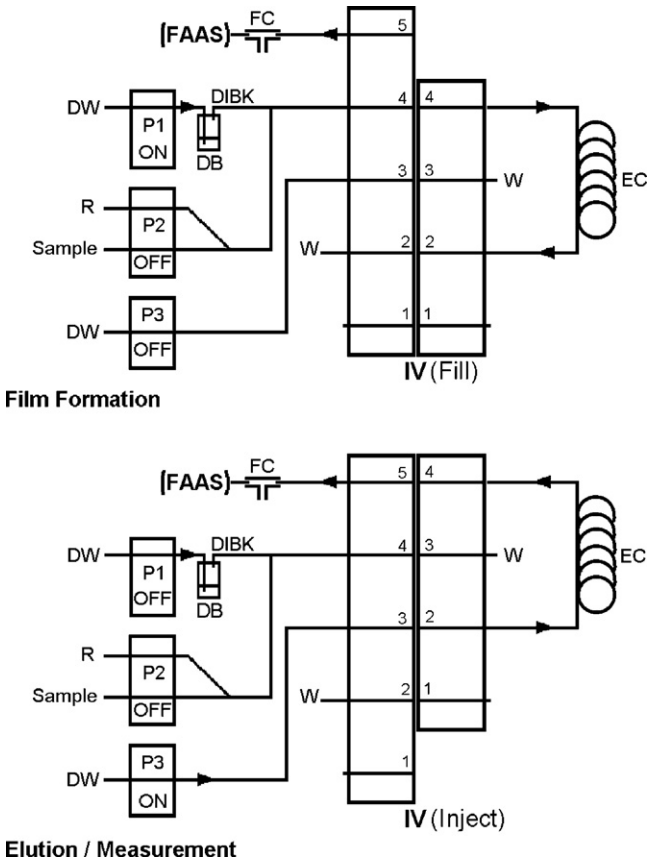

Fig. 1. Schematic diagram of the FI–WFE manifold and the two operation sequences, for metal determination. R, 0.2% (m/v) DDTC; P1, P2, P3, peristaltic pumps; IV, injection valve; DB, displacement bottle; EC, extraction coil; FC, flow compensation adapter; DW, distilled water; W, waste.

In that case the nebulizer's free uptake rate was 5.5 ml min^{-1}. A flow spoiler was employed into the spray chamber for better nebulization conditions. The spectrometer was set to work in the FI-FAAS mode and peak height was used for signal evaluation. The electrothermal atomization mode of the above PerkinElmer atomic absorption spectrometer equipped with zeeman background corrector was used as a standardized method for cadmium determination in the water samples.

A PerkinElmer Norwalk, Connecticut, U.S.A. model FIAS-400 flow injection analysis system was coupled to the flame atomic absorption spectrometer for automatic processing of the method and operated in normal mode. The whole system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 application program. The FIAS-400 system, which is shown schematically in Fig. 1, consisted of three peristaltic pumps P1, P2, P3, a 5-port 2-position (Fill/Inject) injection valve and it was connected to the spectrometer's nebulizer using a short PTFE capillary 20.0 cm length, 0.5 mm i.d., in order to minimize the eluent dispersion. A flow compensation (FC) unit was used just before the nebulizer inlet, in order to compensate the lack of nebulizer free uptake flow rate as described elsewhere [22]. Peristaltic pump tubing of "Tygon" type was adopted to deliver the aqueous solutions and a displacement bottle (Tecator, Hoganas, Sweden http://www.foss.dk) was used to deliver the organic solvent, diisobutyl ketone. The extraction coils of 0.75 mm i.d. in different lengths in the range 150–400 cm were coiled on 30 mm i.d. cylinder. All other conduits used for various connections were of 0.5 mm i.d. PTFE tubing.