Development of an on-line solvent extraction system for electrothermal atomic absorption spectrometry utilizing a new gravitational phase separator. Determination of cadmium in natural waters and urine samples

Aristidis N. Anthemidis,* George A. Zachariades and John A. Stratis

Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University, Thessaloniki 54124, Greece. E-mail: anthemid@chem.auth.gr; Fax: +30 2310997719; Tel: +30 2310997707

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A novel flow injection (FI) on-line solvent extraction preconcentration/separation system coupled to electrothermal atomic absorption spectrometry (ETAAS), which can tolerate high aqueous to organic flow rate ratios, was developed. The organic extract was effectively separated from a large volume of aqueous phase in a newly designed gravitational phase separator. The performance of the system was illustrated for ultra-trace cadmium determination using ammonium diethylidithiophosphate (DDPA) as chelating agent and isobutyl methyl ketone (IBMK) as extractant. The ETAAS determination and solvent extraction are successfully synchronized through a parallel-operated sequence. The obtained enrichment factor was 24.6 with a sampling frequency of 30 h⁻¹. The detection limit was 2.8 ng l⁻¹ and the precision (RSD at 0.2 μg l⁻¹ Cd) was 3.2%.

The proposed method was evaluated by analyzing certified reference materials and applied to the analysis of natural waters and urine samples.

Introduction

Undoubtedly, solvent extraction is a well-established preconcentration technique, although in batch mode it is time consuming, laborious and hence potentially prone to contamination problems when ultra trace determinations are required. On the other hand flow injection (FI) on-line preconcentration systems can overcome the above drawbacks because they offer automated sample handling, improved precision, lower reagent consumption and increased sampling frequency.¹

Despite the favorable advantages of the coupling of atomic absorption spectrometry with on-line solvent extraction, the number of contributions in this field is rather few compared to other on-line preconcentration systems due to the fact that the flow rate ratios of aqueous/organic phase and hence the enrichment factors are limited to about 10–20.¹ On the other hand, the segmented (total) flow rates that the gravitational and membrane type phase separators can handle are restricted, due to the occasional entraining of aqueous phase into the separated concentrate when high segmented flow rate is used, resulting in an inferior performance of the system.² In addition the main drawback of the membrane type phase separator is the short life time of the membrane, and thus operations are interrupted periodically.³

Recently, Tao and Fang² developed an on-line gravitational phase separator for electrothermal atomic absorption spectrometry, which is however limited to the implementation of sample flow rates higher than 5.5 ml min⁻¹ and flow rate ratios higher than 25. On the other hand, Wang and Hansen⁴ proposed a modification of the above phase separator suitable only for sequential injection systems, which are less frequently used compared with flow injection systems because they are limited by the syringe pump’s volume (<10 ml).⁵

In the present work a novel FI on-line solvent extraction system, with high reliability in a wide range of flow rate ratios and unlimited operational lifetime, was developed for ETAAS. For this purpose, a new gravitational phase separator (G-PS) was designed and elaborated. The effectiveness and efficiency of the proposed FI solvent extraction system was demonstrated for cadmium determination due to its high toxicity even in extremely low concentrations. Ammonium diethylidithiophosphate (DDPA) was selected as the chelating agent because of its great ability to form stable complexes even in strong acidic medium with several metals and its selectivity for cadmium, copper and lead.⁶,⁷ However, to the best of our knowledge DDPA has not been employed in flow injection solvent extraction systems for these metals.

Experimental

Instrumentation

A PerkinElmer model 5100 PC atomic absorption spectrometer with Zeeman effect background correction and a transversely heated graphite tube atomizer (THGA), equipped with AS-71 furnace auto-sampler and a circulating cooling unit, was employed throughout the measurements. Pyrolytically coated THGA graphite tubes (PerkinElmer) with integrated L’vov platform were used. A cadmium electrodeless discharge lamp (EDL) was used as a radiation source operated at 5 W. The wavelength was set at 228.8 nm resonance line and the monochromator spectral bandpass at 0.7 nm. The graphite furnace temperature program for the Cd determination in IBMK includes preheating/drying steps at 90/110 °C for gradual drying of the organic solvent and a pyrolysis step at 400 °C. An air compressor was used in association with the injection valve, IV₃, for G-PS evacuation with an air flow rate of 0.1 l min⁻¹.

The FI manifold for on-line solvent extraction and its operation is presented schematically in Fig. 1. It consisted of two peristaltic pumps (Watson Marlow model 205U/BA and Gilson minipuls 3) and four six-port two-position injection valves (LabPro, Rhodyne, USA). A 35 μl extract loop (L) of PTFE tubing was employed with the injection valve IV₂ in order to define the accurate volume of the collected extract for
atomization. A 20 cm length/0.3 mm id delivery tube (DT) was used to connect the FI manifold with the atomizer. A VICI AG (Valco International) trisection “Tee” type confluence connector with 0.50 mm id bore size made of PEEK was employed as segmentor. The extraction coil (EC) was made of a PTFE tubing 300 cm length, 0.75 mm id, 2.5 cm id coiled.

Two displacement bottles (Tecator, Hoganas, Sweden) were used for the propulsion of organic solvent (IBMK) streams due to IBMK being non-compatible with peristaltic tubes.

Phase separator

The gravitational phase separator (G-PS), which was characterized by the absence of consumable parts, was constructed in our laboratory, and is presented schematically in Fig. 2. The separating chamber was made of glass (hydrophilic) in a cylindrical shape, and the push-fit connections at the two ends of polytetrafluoroethylene (PTFE), which is a hydrophobic material. The above connections have internal conical cavities of ca. 30 μl in order to facilitate the separation of the hydrophobic organic solvent. The upper PTFE connection has a single outlet (0.3 mm id) for the separated organic phase, while the lower one has an inlet (1.0 mm id) for the segmented flow and an outlet (1.0 mm id) for the waste flow. During the collection time the low-density organic phase (i.e. IBMK) was raised to the upper region of the G-PS, while the aqueous phase was collected to the lower one due to the different densities of the two phases.

The above configuration facilitates the use of high flow rate ratio of aqueous/organic phase and high total flow rate in order to achieve high preconcentration factors and extraction efficiency. The performance of the phase separator was stable and the collected phases were completely separated during all experiments.

Reagents

All chemicals used were of analytical reagent grade and were supplied by Merck (Darmstadt, Germany). Double de-ionized water was used throughout. All standard solutions were prepared immediately before use, by stepwise dilution of a 1000 mg l⁻¹ Cd(II) stock standard solution (Merck Titrisol) to the required sub μg l⁻¹ levels. The chelating reagent, 1.2% mV⁻¹ DDPA solution was prepared daily by dissolving appropriate amount of DDPA (Aldrich) in deionized water followed by extraction with IBMK for further purification.

Procedure

The operation sequences for FI on-line solvent extraction preconcentration and ETAAS determination of cadmium is summarized in Table 1, and runs through five steps. In step 1 (extraction/preconcentration, Fig. 1a), the sample was merged downstream with the complexing reagent (R) and the resulting aqueous stream was segmented with the IBMK one. The formed complex was extracted into the extraction coil (EC). The organic phase (extract) was separated from the aqueous one into the G-PS, due to the different densities of the two phases. The extract was raised to the upper region of the G-PS.
and was collected for 38 s. In step 2, water was propelled into the G-PS by activating pump P2, and thus the extract goes up and fills the loop L (35 μl) of the injection valve IV2. After that, the delivery tube (DT) mounted at the furnace autosampler was moved into the dosing hole of the graphite tube. In step 3 (extract delivery, Fig. 1b), the injection valve IV2 was switched to the “B” position, so that 35 μl of the extract was propelled by an air stream (Air1) and introduced into the graphite tube. Meanwhile the G-PS chamber was evacuated to waste by an air stream (Air1). Afterwards the autosampler arm was moved back to the wash position and the atomization program was started. In step 4, loop L and the DT were washed by an IBMK stream. In step 5, loop L and the DT were evacuated and the segmented flow in the extraction coil was preconditioned. All steps except 3 were performed in parallel during the ETAAS atomization program of the previous sample. The integrated absorbance measurements were proportional to the cadmium concentration in the sample, and were used for all measurements. Three replicate measurements were made in all instances.

**Results and discussion**

**Optimization of chemical and extraction parameters**

The pH value of the sample plays a significant role in the overall performance of the on-line solvent extraction, affecting the complex formation and the extraction efficiency in the IBMK. Therefore, in this study the effect of pH was studied in the range 0.0–7.5 by adjusting it with dilute nitric acid or ammonia. The maximum signal was obtained within a pH range 0.4–3.2. Thus the samples and standards were fixed to pH = 2.0. This pH value enables the use of the method directly in many aqueous samples after common acid preservation, without any laborious precise pH adjustment.

The effect of the DDPA concentration was studied in the range 0.05–1.5% mV⁻¹. The maximum integrated absorbance was observed over the range 0.8–1.5 mV. In further experiments, 1.2% mV⁻¹ DDPA were selected.

In FI on-line solvent extraction systems, the extraction time, which is defined by the dimensions of the extraction coil and the total (segmented) flow rate, has a strong effect on the residence time and thus, on the extraction efficiency. The influence of the extraction coil length was studied in the range 50–500 cm (0.75 mm id). The signal was increased up to 300 cm, which corresponds to 4.3 s residence time and remained almost constant over this value. Thus, a length of 300 cm was employed for this study, because longer extraction coils increase the back pressure of the manifold and derange the extraction efficiency.

The degree of preconcentration in FI solvent extraction systems is determined by the flow rate ratio of aqueous/organic phase and generally, higher ratios result in greater preconcentration factors. However, there is an upper limit to this ratio, which is dependent on the segmented flow rate. Too high segmented flow rate causes significant derangement of the two phases segmentation into the extraction coil and a limited contact between the aqueous and organic phase resulting in lower extraction efficiency. The effect of the total segmented flow rate on the integrated absorbance was studied in the range 9.6–27.0 ml min⁻¹, keeping the flow rate ratio of aqueous to organic phase constant at Qaq/Qorg = 1. The integrated absorbance increased up to 18.4 ml min⁻¹ and above this value started to decrease due to derangement of the segmentation.

The effect of aqueous to organic phase flow rate ratio on the absorbance was studied from 10 to 52, varying the aqueous phase flow rate and keeping the organic one constant. As expected increasing the flow rate ratio the sensitivity increased up to 40, but at higher ratios the integrated absorbance was decreased due to the effect of the too high segmented flow rate (>18.4 ml min⁻¹). The value Qaq/Qorg = 40 corresponds to total flow rate of about 18.4 ml min⁻¹, thus for practical purposes and smooth operation a 40 flow rate ratio was adopted for the proposed method. For higher preconcentration lower organic flow rate must be employed.

**Interference studies**

The effect of potential interferents encountered in natural waters and biological samples on the proposed method were examined using 0.2 μg l⁻¹ Cd(II) solution with individual potential interferents added. The results showed that, Al(III), Co(II), Cr(III), Cr(IV), Fe(III), Mn(II), Pb(II) and Zn(II) are tolerated up to 5 mg l⁻¹ while Cu(II), Hg(II) are tolerated up to 1 mg l⁻¹. Moreover, the potential interferences from some common matrix cations such as Ca(II), Mg(II) and Ba(II) and some anions as Br⁻, I⁻, SO₄²⁻, HCO₃⁻, NO₃⁻ were also investigated at concentrations up to 1000 mg l⁻¹ and NaCl up to 30 g l⁻¹. No interferences were investigated within ±5% error range.

**Analytical performance and analysis of natural waters and urine samples**

The performance data of the FI on-line solvent extraction ETAAS method for cadmium determination are presented in Table 2.

The accuracy of the proposed method was checked, by the analysis of the following certified reference materials: NIST CRM 1643d (National Institute of Standards and Technology, Trace elements in water) and NRCC CASS 3 (National Institute of Standards and Technology, Trace elements in water).
Research Council Canada, Coastal seawater). The proposed method was applied to the analysis of drinking water, river water (Aliakmon River, Greece), coastal seawater (Kavala Gulf, Greece), and human urine samples. Water samples were filtered through (0.45 μm) filters and acidified to pH ~2.0 with dilute HNO₃. Urine sample (250 ml) was taken from a 35 year old healthy person and was digested with a mixture of HNO₃/HCl (1:1), using closed Teflon beakers in a pressurized bomb, at 130–140 °C, as it is described elsewhere. After cooling, the mixture was properly diluted and the pH was adjusted to pH = 2.0 with HNO₃. The obtained solutions were used for cadmium determination.

The results are presented in Table 3. The determined concentrations of cadmium were in good agreement with the certified values and the recovery ranged between 93–99%, showing the good performance of the method in all type of samples.

Conclusions

One of the most important features of the proposed G-PS is the capability to successfully manage very high aqueous/organic flow rate ratios and thus to attain high preconcentration factors. In all cases the obtained extract was completely separated. Also, it offers the ability to collect as much extract as required for accurate measuring, by varying the collection time of the extract. In addition, the above G-PS is easily manufactured in the laboratory without using expendable parts (e.g., membranes) in contrast to membrane type phase separators.

Although the obtained results in this work are related to cadmium determination, the system could be readily applied to the determination of other metals using various ligands, extractable by IBMK or other organic solvents. Additional work is in progress on testing the proposed phase separator and its performance employing various organic solvents with a lower or higher density than water, for on-line trace metals determination using ICP-AES.

References