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Development of on-line single-drop micro-extraction sequential injection system for electrothermal atomic absorption spectrometric determination of trace metals

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ABSTRACT

A novel automatic sequential injection (SI) single-drop micro-extraction (SDME) system is proposed as versatile approach for on-line metal preconcentration and/or separation. Coupled to electrothermal atomic absorption spectrometry (ETAAS) the potentials of this SI scheme are demonstrated for trace cadmium determination in water samples. A non-charged complex of cadmium with ammonium diethyldithiophosphate (DDPA) was produced and extracted on-line into a 60 μL micro-drop of di-isobutyl ketone (DIBK). The extraction procedure was performed into a newly designed flow-through extraction cell coupled on a sequential injection manifold. As the complex Cd(II)-DDPA flowed continuously around the micro-droplet, the analyte was extracting into the solvent micro-drop. All the critical parameters were optimized and offered good performance characteristics and high preconcentration ratios. For 600 s micro-extraction time, the enhancement factor was 10 and the sampling frequency was 6 h^{-1}. The detection limit was 0.01 $\mu g\,L^{-1}$ and the precision (RSD at 0.1 $\mu g\,L^{-1}$ of cadmium) was 3.9%. The proposed method was evaluated by analyzing certified reference material.

1. Introduction

Despite the valuable advances in separation and quantification the conventional liquid–liquid extraction (LLE) is still the most widely used sample pretreatment technique in routine analyses for improvement of sensitivity and/or selectivity of analytical methods. The implementation of LLE in flow manifolds simulating the same sequences performed in batch procedures contributes advantages inherent in automatic methods. Recently, efforts have been focused on the miniaturizing of the LLE procedure by reducing the organic solvent, leading to the development of micro-extraction methodologies [1,2].

The first attempt to miniaturize LLE in a flowing stream assembly was carried out by Liu and Dasgupta [3] reporting a flow-through drop-in-drop micro extraction system where a 1.3 μL drop of an organic solvent was immersed into a larger flowing aqueous drop to accomplish the extraction of ion-paired species. Further research led to the development of the so-called single-drop microextraction (SDME) where a droplet of organic solvent was suspended at the tip of a microsyringe needle and immersed into the aqueous sample [4]. Psillakis and Kalogerakis [5] and recently Xu et al. [6] overviewed the principles of SDME as well as its latest developments and applications. The implementation of SDME in a continuous flow micro-extraction mode (CF-SDME) was firstly described by Liu and Lee for trace nitroaromatic compounds and chlorobenzens in environmental samples [7]. The proposed procedure differs from other SDME approaches in the fact that the solvent is continuously surrounded by fresh aqueous solution, thus leading to improved extraction efficiencies.

Hitherto, the majority of the reported SDME papers have been focused on preconcentration of organic pollutants, and only few efforts have been devoted to metal extraction using SDME coupled to electrothermal vaporization (ETV)-ICP-MS [8–10] and electrothermal atomic absorption spectrometry (ETAAS) [11–13]. Pena et al. [14] proposed the combination of sequential injection analysis (SIA) with electrothermal atomic absorption spectrometry (ETAAS) for determination of Cr(VI) in waters using a home-made micro-extraction vial but for limited sample volume and extended cycling times, when high preconcentration factors are demanded.

Recently, Kokosa developed an automatically performing liquid phase micro-extraction method on liquid samples in discrete vials for GC, HPLC and GC/MS [15]. Thus, still there is need for automation of on-line continuous flow micro-extraction procedure coupled with atomic spectrometric techniques.

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On the other hand, the significant advantages of sequential injection (SI) systems are the ability for even small volumes (down to a few tenths of micro-liters) handling of solutions with great success, thanks to the use of syringe pump and advanced software [1,16,17]. Moreover, they are much economical regarding to the sample, reagents and hence the waste production.

The aim of present work is to develop a new completed automatic sequential injection single-drop micro-extraction (SI-SDME) system for metal determination in water samples using ETAAS, based on the on-line complex formation of metals with chelating agents. For this purpose a newly designed flow-through micro-extraction cell was manufactured, while the effectiveness and efficiency of the proposed SI-SDME system has been demonstrated for cadmium determination, due to its high toxicity and the very low concentration levels in the environmental water samples. Ammonium diethyldithiophosphate (DDPA) was also selected as chelating agent due to its good selectivity for cadmium in strong acidic medium [18].

2. Experimental

2.1. Apparatus

The SI manifold and its operation for on-line SDME and cadmium determination by ETAAS is depicted schematically in Fig. 1.

A FIAlab®-3000 sequential injection system (Alitea FIAlab, USA) equipped with an internally incorporated six-port multiposition valve (MV) and a syringe pump (SP, Cavro, Sunnyvale, CA) with a capacity of 1000 μL was used. The FIAlab®-3000 system was controlled by a personal computer and the FIAlab for windows v. 5.9.245 application program, written by FIAlab instruments (http://www.flowinjection.com).

A PerkinElmer, Norwalk, Connecticut, USA (http://las.perkinelmer.com) model 5100 PC atomic absorption spectrometer with Zeemann 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 measurements. Pyrolytically coated THGA graphite tubes (PerkinElmer) with integrated L'vov platform were used. A cadmium electrodeless discharge lamp (EDL) was used as 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 (GF) temperature program for the Cd determination in DIBK includes preheating/drying steps at 90/110 °C for gradual drying of the organic solvent and a pyrolysis step at 400 °C. Argon 99.996% was used as purge and protective gas. Integrated absorbance (peak area) was used exclusively for signal evaluation.

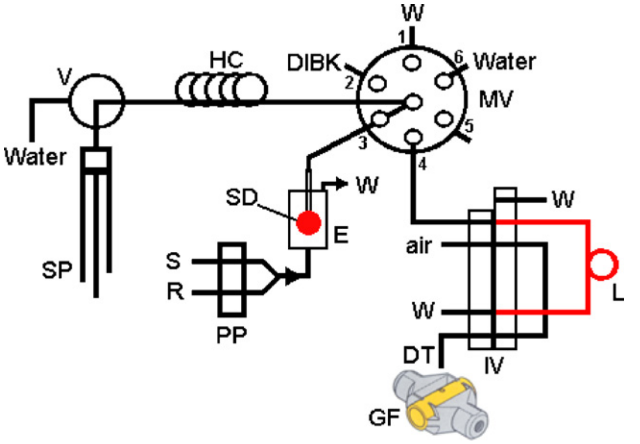

Fig. 1. SI-SDME manifold of the on-line solvent micro-extraction system coupled to ETAAS for cadmium determination. For details see text and Table 1. S, sample; R, DDPA solution; W, waste; PP, peristaltic pump; SP, syringe pump; MV, multi-position valve; IV, injection valve in "Load" position; V, valve in "OUT" position; HC, holding coil; L, loop; E, micro-extraction cell; SD, solvent droplet; DT, delivery tube; GF, graphite furnace ETAAS.

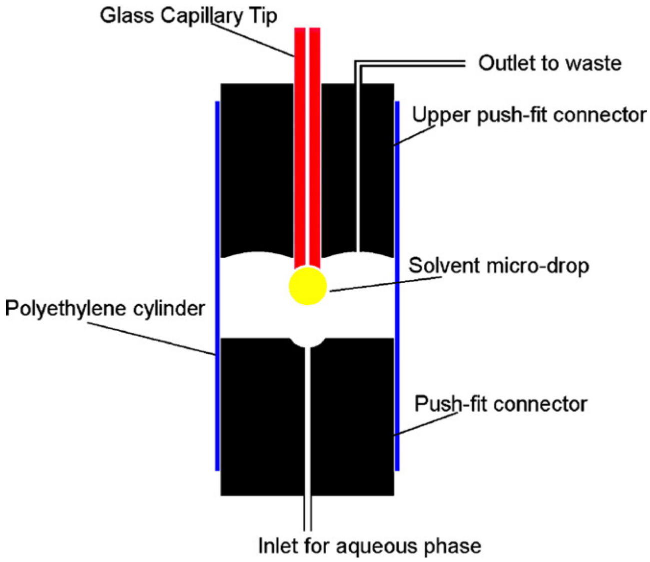

Fig. 2. Schematic diagram of the micro-extraction flow-through cell and the capillary tip.

A PerkinElmer Norwalk, Connecticut, USA model FIAS-400 flow injection analysis system was coupled to the SI system and to the ETAAS for automatic processing of the whole procedure. The FIAS-400 system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 software program. The FIAS-400 system consisted of two peristaltic pumps (only one is used for the proposed manifold) and a 5-port 2-position injection valve.

A 35 μL extract loop (L) of PTFE tubing was employed with the injection valve IV in order to grab and transfer an accurate portion of the DIBK micro-drop into the graphite tube for atomization. A 30 cm length/0.3 mm i.d. delivery tube (DT) was used to connect the FI manifold with the atomizer. An air compressor (air flow rate: 0.1 mL min^{-1}) was used in association with the injection valve, IV for loop evacuation into the graphite tube.

2.2. The micro-extraction flow-through cell and the capillary tip

The micro-extraction flow-through cell (E) and the capillary tip were constructed in the laboratory and are presented schematically in Fig. 2. The flow-through cell was made of a polyethylene cylinder 3.0 cm length/9.0 mm internal diameter/11.0 mm external diameter. At the two ends of the cylinder there are push-fit connectors. The capillary tube, for organic micro-drop suspension, passes through the upper push-fit connector and was made of a glass tube with 0.15 mm i.d./4.5 mm o.d. The glass material (hydrophilic) is necessary for suspension of the organic solvent drop into the flowing aqueous solution. As it is proved from preliminary experiments a hydrophobic material like PTFE cannot be used as capillary tube because the organic solvent (hydrophobic material), wets the end of the capillary tube and glides towards the exit of the cell. Thus, in this case it is impossible to be generated a suspended micro-drop. The above configuration of the flow-through cell together with the capillary tube facilitates the generation and suspension of a stable DIBK micro-drop. With this extraction cell