



Sequential injection anodic stripping voltammetry with monosegmented flow and in-line UV digestion for determination of Zn(II), Cd(II), Pb(II) and Cu(II) in water samples

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ABSTRACT

A cost-effective sequential injection system incorporating with an in-line UV digestion for breakdown of organic matter prior to voltammetric determination of Zn(II), Cd(II), Pb(II) and Cu(II) by anodic stripping voltammetry (ASV) on a hanging mercury drop electrode (HMDE) of a small scale voltammetric cell was developed. A low-cost small scale voltammetric cell was fabricated from disposable pipet tip and microcentrifuge tube with volume of about 3 mL for conveniently incorporated with the SI system. A home-made UV digestion unit was fabricated employing a small size and low wattage UV lamps and flow reactor made from PTFE tubing coiled around the UV lamp. An in-line single standard calibration or a standard addition procedure was developed employing a monosegmented flow technique. Performance of the proposed system was tested for in-line digestion of model water samples containing metal ions and some organic ligands such as strong organic ligand (EDTA) or intermediate organic ligand (humic acid). The wet acid digestion method (USEPA 3010a) was used as a standard digestion method for comparison. Under the optimum conditions, with deposition time of 180 s, linear calibration graphs in range of 10–300 $\mu\text{g L}^{-1}$ Zn(II), 5–200 $\mu\text{g L}^{-1}$ Cd(II), 10–200 $\mu\text{g L}^{-1}$ Pb(II), 20–400 $\mu\text{g L}^{-1}$ Cu(II) were obtained with detection limit of 3.6, 0.1, 0.7 and 4.3 $\mu\text{g L}^{-1}$, respectively. Relative standard deviation were 4.2, 2.6, 3.1 and 4.7% for seven replicate analyses of 27 $\mu\text{g L}^{-1}$ Zn(II), 13 $\mu\text{g L}^{-1}$ Cd(II), 13 $\mu\text{g L}^{-1}$ Pb(II) and 27 $\mu\text{g L}^{-1}$ Cu(II), respectively. The system was validated by certified reference material of trace metals in natural water (SRM 1640 NIST). The developed system was successfully applied for speciation of Cd(II) Pb(II) and Cu(II) in ground water samples collected from nearby zinc mining area.

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1. Introduction

Determination of trace metals in environmental samples is important due to their toxicity to the living things. However, there are only some parts of metals that are toxic or bioavailable to the humans and animals. The toxicity of metal ions varies with its physicochemical form. Typically, in water the most toxic forms are the hydrated metal ions and labile complexes (i.e., dissociation can readily occur), and the least toxic forms are strongly bound metal complexes and metal adsorbed on colloidal particles (indeed, in unpolluted natural waters, metals are usually present in one of these latter two forms) [1]. Therefore, the development in speciation analysis for identifying and measuring the species of these metals present in environment is more concern. There are a num-

ber of speciation procedures for identifying and quantifying the individual forms of heavy metals. The selection of the speciation technique depends on which individual form is of interest and what kind of sample is investigated. In this work, speciation of trace elements contaminated in water in the forms of labile dissolved metals and metals bound to various kinds of substances or particles, either organic or inorganic ones are of interested.

It is well known that electroanalytical methods, notably voltammetric techniques, allow the differentiation of free ions or labile metal ion complexes on one hand and species that are stable bound to colloidal species or inert species on the other hand [2]. Labile species are species that can be detected by anodic stripping voltammetry (ASV), such as hydrated metal ions, and metal ions dissociated from weakly bound complexes or weakly adsorbed on colloidal particles. The inert fraction consists of the species that do not dissociate the metal under the conditions used such as metals bound to dissolved organic matter (DOM), so can not be directly detected by ASV. The total metal species can be measured following prolonged sample pretreatment process such as wet digestion, UV digestion [3–5] to convert bound metals to the labile ones and

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hence the inert species can be calculated by subtracting of the total metal content with the labile metal content [1]. The most popularly used method for destruction of DOM is wet acid digestion [4]. However, the large amounts of reagent added cause high contamination to the sample. UV digestion is a clean method, effective and can easily be incorporated in an automated trace metal analyzer. Thus, it is a more preferable method for destruction of organic matter prior to voltammetric analysis [4].

The combination of flow-based techniques [6–12] such as flow injection analysis (FIA) and sequential injection analysis (SIA) with voltammetric methods [9,11,13] increases the automation degrees and sample throughput of the method. The most often used working electrode in flow-based system is solid electrode or various thin film electrodes because they provides good mechanical stability to withstand the flow of solution. However, these electrodes have major drawback on low reproducibility and accuracy due to carry over of contaminated analyte on the electrode. On the other hand, mercury drop electrode offers renewable surface, high sensitivity and reproducibility. The use of hanging or static mercury electrodes in flow systems requires the suitable design of the flow cell and the adequate flow conditions to keep the drop stable and firmly hold by the capillary tube. Therefore, up to now there are a few papers describing the construction of home-made flow cells for static mercury drop electrode (SMDE) [14–18] or hanging mercury drop electrode (HMDE) [19–23] and applied them for determination of metal ions by stripping voltammetry. In this work, we proposed the use of a small scale voltammetric cell with HMDE in SI system which provides good stability and reproducibility of the electrode and higher degrees of automation comparing to conventional batch-wise voltammetric analysis. The SI with monosegmented flow analysis (MSFA) approach was introduced to promote good mixing of the solution zones sandwiched between two air segments, resulting from a turbulent flow in the monosegment [24–26]. With this approach sample dilution, single stock standard calibration and standard addition could be made in-line [24,26].

In the present work, we developed the SI-ASV system incorporated with UV digestion unit to perform in-line digestion of sample and quantification of some metals. A low-cost small scale voltammetric cell and home-made UV digestion unit were fabricated and tested for their performances. Monosegmented flow was used to gain benefit in convenient handling of sample preparation and determination of the metals. The developed system provided sensitive, reproducible and clean method for speciation of labile and bound metals with semi-automatic operation and low chemical consumption.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade. Deionized water (obtained from a system of Milli-Q, Millipore, Sweden) was used throughout. An acetate buffer solution (0.6 M, pH 4.6), which served as a supporting electrolyte was prepared by dissolving sodium acetate 3-hydrate (Ajax Finechem, Australia) (40.82 g) in water before adding of acetic acid (Carlo Erba, Italy) (17.2 mL) and making up to final volume of 500 mL with water. Working standard solutions of Zn(II), Cd(II), Pb(II) and Cu(II) were daily prepared by appropriate dilution the stock standard solutions (1000 mg L⁻¹ of the metal, atomic absorption standard solutions, Merck, Germany) with 0.1 M HNO₃ solution. The purified humic acid (Sigma–Aldrich, Germany), ethylenediaminetetraacetic acid disodium salt dihydrate (Sigma–Aldrich, Germany) and *t*-octylphenoxypolyethoxyethanol (Sigma–Aldrich, Germany) were used as complexing ligands on the study of performance of an in-

line UV digestion system. Hydrogen peroxide (H₂O₂, 30%) (BDH, England) and hydrochloric acid (HCl, 37%) (Merck, Germany) were used for digestion of sample.

2.2. Instrumentation and apparatus

A sequential injection-anodic stripping voltammetric (SI-ASV) system was assembled as depicted in Fig. 1, consisted of a syringe pump (Model XL-3000, CAVRO, USA) and a 10-port selection valve (Valco Instrument Co. Inc., Texas, USA), a holding coil (Tygon® tubing, 1.25 mm i.d., 4.5 m), an UV digestion unit and a voltammetric analyzer (757 VA computrace, Metrohm, Switzerland) equipped with a home-made small scale voltammetric cell. The sequential injection system was controlled by an in-house created software based on Visual Basic 6.0 [27]. The 757 PC software version 2.0 was used with the voltammetric analyzer for voltammetric measurement and data evaluation. The small scale voltammetric cell (EC) was connected via a 3-way switching valve (UpChurch Scientific, USA) and a coil tube to the selection valve of the SI system. The used mercury was flushed out from the cell to the mercury waste bottle through this line.

2.3. Small scale voltammetric cell

A simple small scale voltammetric cell as depicted in Fig. 2, consisted of two chambers: measurement chamber and reference chamber. The measurement chamber was constructed from part of disposable pipet tip (5 mL, Appendorf, Germany) which was cut the upper and lower side to obtain a chamber with approximate volume of 3 mL. The hanging mercury drop working electrode (HMDE) and the platinum wire auxiliary electrode were put in the measurement chamber. Silicone and PTFE tubes were used for connecting the cell to the SI system. The oxygen removal was done by bubbling the nitrogen gas into the solution in the measurement chamber. The electrochemical cell was completed with the modified Ag/AgCl reference electrode (RE) which was made from microcentrifuge tube of 2.5 mL as a chamber filling up by 3 M NaCl and Ag/AgCl wire was put in the RE chamber. The PEEK tube (0.4 mm i.d. × 10 mm) was used as salt bridge for connecting between measurement chamber and RE chamber. The liquid junction between these two chambers was renewed for each measurement by dispensing 100 μL of 3 M NaCl solution to the reference chamber.

2.3.1. Homemade UV digestion unit

A homemade UV digestion unit employing a small size and low wattage (6 W) UV lamps (length 226.3 mm, wavelength 253.7 nm, TAS UV Curing Co. Ltd., Pathumthani, Thailand) has been fabricated. The flow reactor was made of PTFE tubing (0.79 mm i.d., 200 cm long) coiled around the UV lamp and wrapped around the coil with an aluminium foil. The reactor was connected to one port of the selection valve of the SI system (Fig. 1).

2.4. Procedure

An in-housed developed software [27] was employed for control the instrument using a script program containing various steps of operational sequences. Before running the operational sequences for sample analysis, the “Start-up” program was firstly executed, in order to fill the tubings connected to all ports of the selection valve with their respective solutions.

Operational sequences for in-line UV digestion procedure are briefly described as follow. First, air (100 μL) was aspirated to separate sample solution from the carrier solution. Then, sample (1500 μL) and air (100 μL) were aspirated to form stacked zones as shown in Fig. 3(a). The monosegmented zone was then propelled to place in the reactor of the UV digestion unit and irradiated to

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