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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 $\mu g\,L^{-1}$ Zn(II), 5–200 $\mu g\,L^{-1}$ Cd(II), 10–200 $\mu g\,L^{-1}$ Pb(II), 20–400 $\mu g\,L^{-1}$ Cu(II) were obtained with detection limit of 3.6, 0.1, 0.7 and 4.3 $\mu g\,L^{-1}$, respectively. Relative standard deviation were 4.2, 2.6, 3.1 and 4.7% for seven replicate analyses of 27 $\mu g\,L^{-1}$ Zn(II), 13 $\mu g\,L^{-1}$ Cd(II), 13 $\mu g\,L^{-1}$ Pb(II) and 27 $\mu g\,L^{-1}$ 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.

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 number 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. Monosegemented 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 HNO_3 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 (H_2O_2, 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

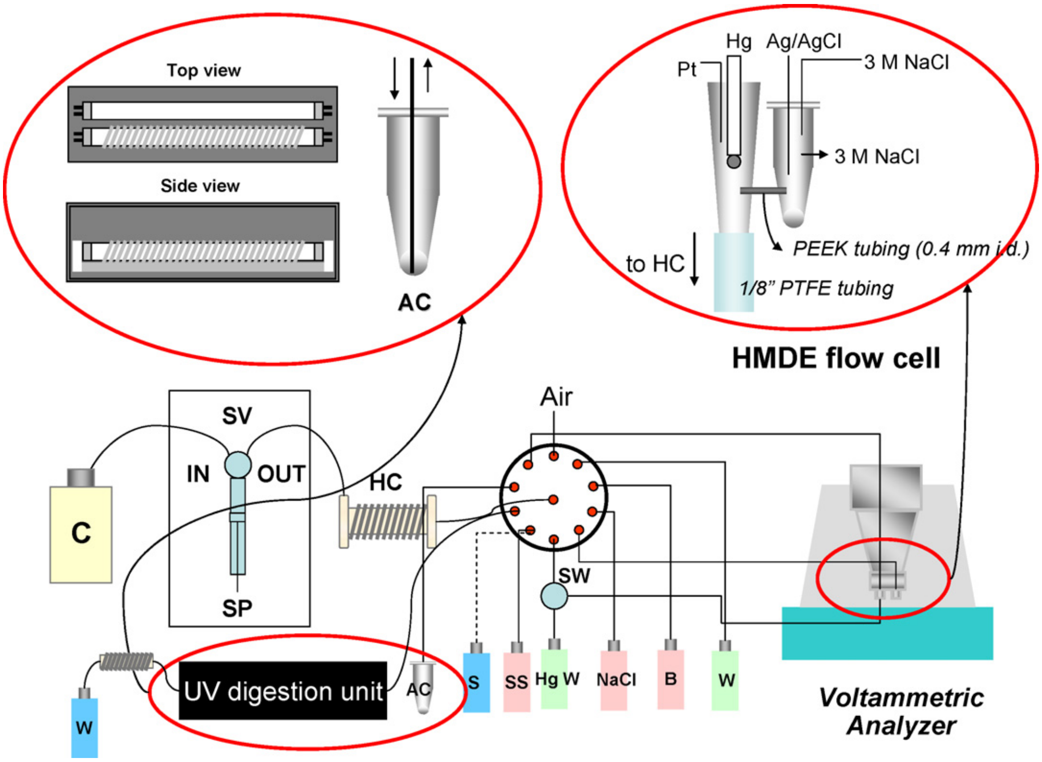

Fig. 1. Sequential injection UV digestion voltammetric system; C = carrier (Milli-Q water); SV = syringe valve; SP = syringe pump; HC = holding coil; SW = 3-way switching valve; AC = auxiliary chamber; S = sample; SS = single standard; Hg W = mercury waste; NaCl = 3 M sodium chloride; B = 3 M acetate buffer; W = waste.

perform UV digestion of sample for 10 min. After that the digested sample was aspirated back to the holding coil (HC) and deliver to store in an auxiliary chamber (AC), waiting for analysis in the next step. Then, the UV reactor was cleaned with water.

The sequences for the determination of metals by an in-line standard calibration or an in-line standard addition are briefly described as below. In case of the external calibration curves, various concentrations of metals standard in buffer solutions were

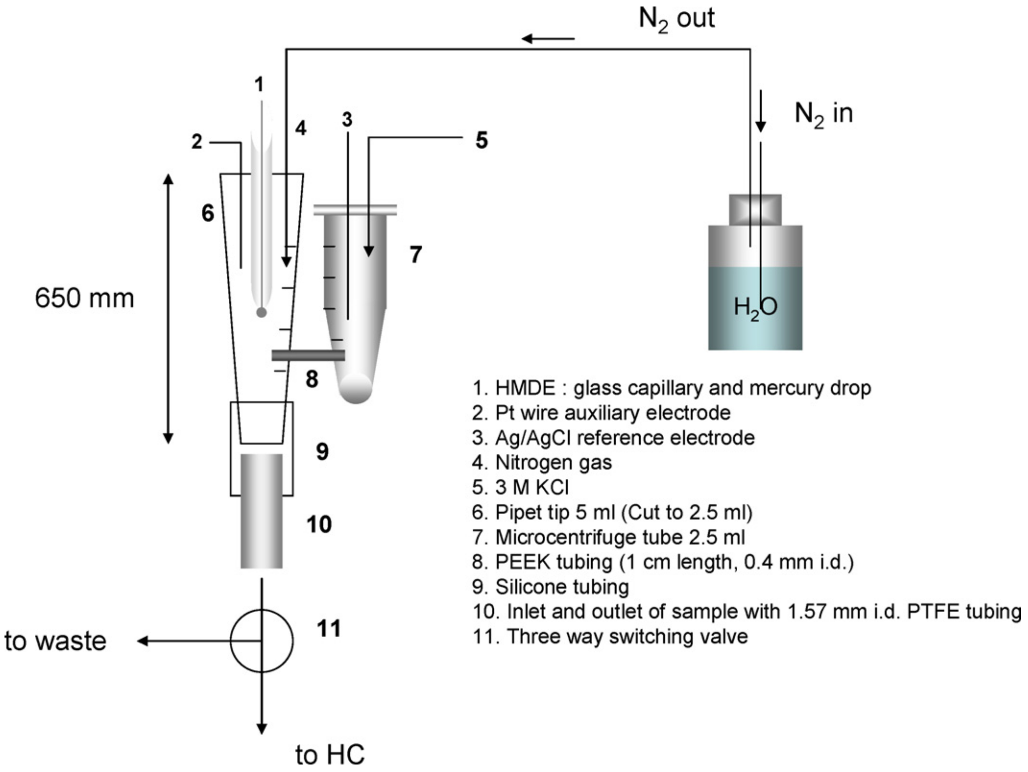

Fig. 2. The developed small scale voltammetric cell.

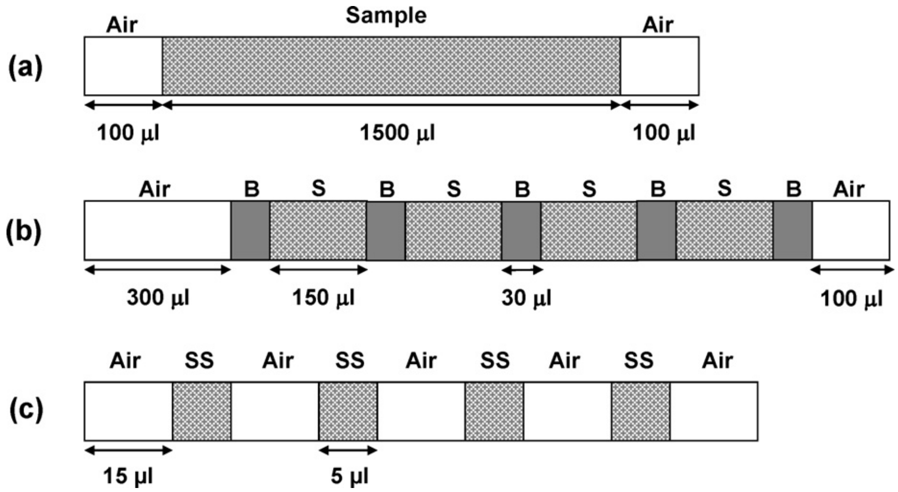

Fig. 3. Sequence of solutions in a holding coil for; (a) in-line UV digestion; (b) in-line buffer dilution; (c) in-line single standard calibration or standard addition; S = sample; SS = single standard; B = 3 M acetate buffer.

aspirated. For the in-line calibration curves or the in-line standard addition, the air monosegmented of buffer (B) and sample (S) or water was sequentially aspirated to form stacked zones as shown in Fig. 3(b). The stacked zone was then propelled to put in a small scale voltammetric cell for electrodeposition of the metals by applying a potential of −1.1 V versus Ag/AgCl to the WE for a specified deposition time. The solution in the cell was moved up and down during the deposition step to promote mass transfer to the electrode. Then, the stripping step was performed under stopped flow condition. A voltammogram was recorded using the following condition: sweep mode, square wave; sweep potential, −1.10 to 0.2 V; sweep rate, 0.25 V/s. To construct the in-line standard addition curves, the 5 μL of stock standard (SS) each in the monosegment were dispensed to the measurement chamber (see profile in Fig. 3(c)). The solution in the chamber was mixed with SS added before starting the analysis. The concentration of each metal in this system could be varied from the volume of added single standard concentrations. Finally, the used mercury drop was flushed out from the small scale voltammetric cell and dispensed to mercury waste container through a 3-way switching valve. The 3 M NaCl solution was dispensed into a reference chamber to renew the salt bridge between the two chambers and then the measurement chamber and auxiliary chamber were cleaned with water.

3. Results and discussion

3.1. Small scale voltammetric cell design

In this study, a small scale voltammetric cell was designed and fabricated for use with the HMDE without modification of the mercury capillary. The modified voltammetric cell (as shown in Fig. 2) was connected to the tip of mercury capillary tubing. For the deoxygenation step, the commercial nitrogen purging system was modified by connecting the gas tubing from original system to the polypropylene bottle which fills with Milli-Q water. Then, humidified nitrogen gas was connected to the measurement chamber by the PTFE tubing. So, the nitrogen purging time was controlled by the voltammograph software in a similar manner to the batch system.

Preliminary experiments using the small scale voltammetric cell indicated that the upper part of the voltammetric cell should not to be tight to the glass capillary of the HMDE, and the hole at the bottom of voltammetric cell had to be wide enough for efficient removal of mercury waste. The first small scale voltammetric cell developed, the measurement chamber is made from microcentrifuge tube of 2.5 mL with cover. The cover was drilled to the same size of the capillary tube diameter. Poor reproducibility of peak current for all metals studied was observed due to the irreproducibility of mercury drop size. In addition, the lower part of the microcentrifuge tube which was drilled and connected to the SI system by 0.51 mm i.d. PTFE tube are not sufficient for mercury waste removal through the bottom hole of the chamber. To solve these problems, 5 mL disposable pipet tip was then used as a measurement chamber. The upper and lower part of the disposable pipet tip was cut to obtain the chamber of approximate volume of 3 mL. A fresh mercury drop was used for each measurement and a suitable position for the glass capillary should be at the center of the chamber. Silicone and 1/8″ o.d. PTFE tubes were used for connecting of the small scale voltammetric cell to the SI system. The hole at the bottom of the cell was used to allow the inlet and outlet of the solution. And also used for removal of mercury waste after each analysis, avoiding its accumulation inside the voltammetric cell. The used mercury drop and the solution were then flushed out to the mercury waste bottle through the 3-way switching valve (see Fig. 2) before starting the measurement chamber cleaning step.

The inner diameter of PEEK tube that act as the salt bridge between measurement chamber and reference chamber had to be narrow in order to preventing NaCl leakage or contamination of the reference chamber by the sample solution but it should be wide enough for low resistance liquid junction between the two chambers. PEEK tube of internal diameter of 0.4 mm was found to provide reproducible voltammograms of all the metals.

3.2. Optimization of sequential injection and electrochemical parameters

Most of the electrochemical parameters are followed by our previous study [9,11] with mercury thin film electrode. However, some parameters have been re-investigated to fit with the hanging mercury drop electrode used in this work.

3.2.1. Influence of solution movement on peak current

In batch ASV, peak currents increase with the increase of convection rate of the solution due to the decrease of the diffusion layer, thus increasing the mass transport. The similar trend is observed in flow ASV system [24], i.e., an increase in flow rate increased mass transport and sensitivity in the determination. The movement of solution during the deposition step should help increase the sensitivity in the same manner as in the batch ASV. The solution was

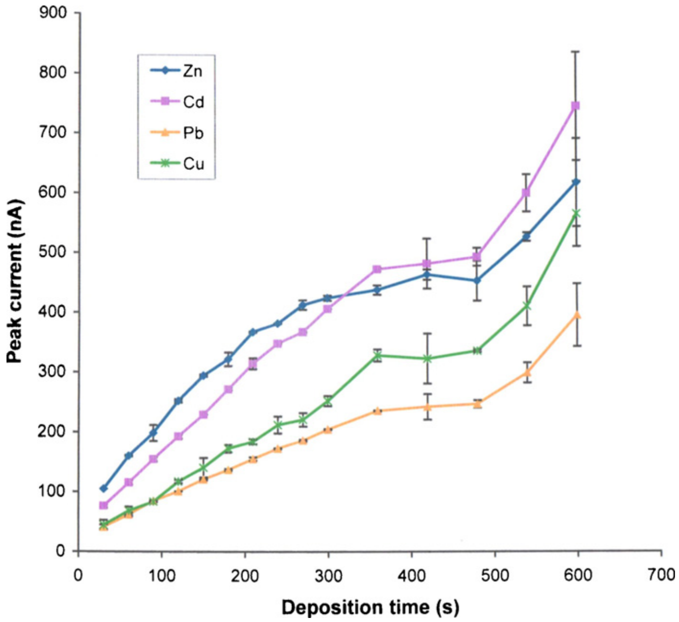

Fig. 4. Effect of deposition time on the peak currents of Zn(II), Cd(II), Pb(II) and Cu(II). (conditions: concentration of each metal ion 100 μg L^{-1}; voltammetric parameters: deposition potential −1.1 V, stripping potential −1.1 to 0.2 V, sweep mode: square wave, voltage step: 0.009918 V, amplitude 0.03998 V, frequency 50 Hz, sweep rate 0.4959 V/s).

moved up and down in the measurement chamber during the deposition step by employing syringe pump. The currents obtained were compared with the quiescent solution at the same deposition times (30 and 180 s deposition time). The results showed that peak current of the metals increased about 65–85% with the movement of the solution.

3.2.2. Influence of deposition time on peak current

The relationship between peak current and deposition time is shown in Fig. 4. Linearities for all metals were observed from deposition time of 0–300 s. Linearities for Cd(II) and Pb(II) were obtained along the concentration of 10–100 μg L^{-1} and deposition time of 30, 60, 120 and 180 s. That means there is no saturation of the metals on Hg surface. As expected, the sensitivity (peak current) could be increased with an increase in deposition time. However, the comparison of signals obtained in batch and the developed SI system showed that the ratio of the slope of calibration graphs (a plot of peak currents versus concentration of the metals in range of 10–100 μg L^{-1}), of batch to SI systems at deposition time of 30, 60, 120 and 180 s, are 5.5, 6.2, 6.9, 7.1 for Cd(II) and 5.6, 5.9, 6.4, 6.6 for Pb(II), respectively. The lower sensitivity obtained in SI system probably due to mass transport of metal ions toward electrode surface in the developed SI-ASV (by up-down movement of solution) is less efficient than in the batch ASV (by convection). Nevertheless, the developed SI-ASV gave sufficient sensitivity to determine metal ions in range of 10–100 μg L^{-1} with deposition time of 180 s.

3.2.3. Sequence of solutions for good mixing

Monosegmented flow helped in mixing of the solutions in-line by the effect of turbulent flow in the monosegment while the monosegment zone was moving. Sequence of solutions (mixed standard/sample and buffer) affected on the homogenization of the mixture zone in a monosegment as similar to the previous study [27]. Long zones of each solution would result in incompleted mixing, which lead to lower peak current obtained comparing to an off-line mixing of the solutions. Once the sequence was created, the stacked zones were moved to the measurement chamber and during the transportation turbulent flow in the monosegment occurred which caused mixing of the stacked zones. It was found that the sequence as shown in Fig. 3(b) which had a total volume of a final monosegment zone of 750 μL provided good mixing. Peak currents of all the metals were comparable to those obtained from off-line mixing.

3.3. In-line UV digestion

In order to release bound metals, an in-line UV digestion was carried out as described in Section 2.4. Some parameters affecting on the digestion were investigated. It was observed that the UV digestion unit caused interference to the voltammetric instrument, so it must be placed far away (at least 60 cm) from the voltammograph unit. Bubbles were evolved during the digestion and caused irreproducibility and low accuracy in the voltammetric analysis. In order to solve this problem, an auxiliary chamber was used for collecting the digested solution from the UV digestion unit. It was fabricated from a 2.5 mL microcentrifuge tube by drilling two holes on the cover lid (one for insert the PTFE tubing to the bottom of the chamber and one for open to the atmosphere). After filling the digested solution into the chamber, the bubbles were released to the atmosphere and then the solution was aspirated into SI system for metal determination. The chamber was cleaned with deionized water after finishing the determination of the metals.

3.3.1. Effect of some parameters on digestion efficiency

The parameters affecting digestion efficiency, i.e., type, concentration and volume of oxidant, and digestion time were investigated. The release of metal ions from the complexes with strong organic ligand (i.e. EDTA) at mole ratio of 1:10 metal:EDTA was used to evaluate digestion efficiency. HCl and/or H_2O_2 was added to 5 mL of the test solution and mixed well before it was aspirated into the system.

Type of oxidant is the most important factor influencing the digestion efficiency in this system. It was found that with the addition of 25 μL of 30% (v/v) H_2O_2 and without acid, Pb(II) and Cu(II) could not be detected, while with only 5 μL of conc. HCl, low recovery of Cu(II) was observed. However, the mixture of 30% (v/v) H_2O_2 and conc. HCl showed good recoveries (>95%) for all the metals.

Concentration or volume of oxidant used did not significantly affect to the digestion efficiency. The percentage of labile metals after UV digestion are nearly 100% when 10 μL 30% (v/v) H_2O_2 and 5 μL conc. HCl was used as oxidant. Anyway, volume of H_2O_2 of 25 μL was chosen to ensure better digestion efficiency in case of the present of complexing agent or organic matters in sample higher than in this experimental condition.

The digestion time of 4, 6, 8, 10 and 15 min were studied, when using 25 μL H_2O_2 and 5 μL conc. HCl added to 5 mL of test solution (1:10 metal:EDTA). The good digestion efficiencies of $\geq$85% were observed with digestion time of 4 min. However, the voltammograms showed incomplete digestion of Zn(II) (high background current at potential of Zn(II) peak) until digestion time of $\geq$8 min was used. Therefore, digestion time of 10 min was chosen.

Accuracy and precision of the in-line UV digestion under the optimum condition were investigated. By spiking the metal ions at 25, 50 μg L^{-1} for Cd(II) and Pb(II) and 50, 100 μg L^{-1} for Zn(II) and Cu(II), the percentage recoveries are in range of 87–106% for Cd(II) and Pb(II) and 82–107% for Zn(II) and Cu(II). Reproducibilities for UV digestion of test solution in five replicates are 3.6%, 2.2%, 4.4% and 5.0% for Zn(II), Cd(II), Pb(II) and Cu(II), respectively.

3.3.2. Digestion performance

Some complexing ligands such as EDTA (strong organic ligand), humic acid or HA (dissolved organic matter), Triton X-100 (surfactant) were added to the metal solutions to be used as model

Table 1
Comparison of percentage recoveries of metal ions in model water samples containing different complexing agents, obtained from using UV-digestion method and wet digestion method.

No.	Organic matter concentration (mg L^{-1})			Recovery of metal ions (%)							
	EDTA	HA	TritonX	Zn(II)		Cd(II)		Pb(II)		Cu(II)	
				UV digestion	Wet digestion	UV digestion	Wet digestion	UV digestion	Wet digestion	UV digestion	Wet digestion
1	5	–	–	81.1 ± 2.3	113.8 ± 5.9	104.4 ± 0.9	110.3 ± 2.5	104.7 ± 4.2	97.4 ± 12.7	97.3 ± 5.7	114.7 ± 6.9
2	10	–	–	77.8 ± 2.0	94.0 ± 3.8	104.9 ± 1.1	112.8 ± 2.1	103.1 ± 1.4	101.0 ± 12.7	98.1 ± 9.7	109.9 ± 2.8
3	25	–	–	86.3 ± 1.6	89.2 ± 13.6	100.6 ± 2.5	107.8 ± 6.6	94.0 ± 1.5	108.6 ± 2.0	101.9 ± 1.3	106.6 ± 4.2
4	–	5	–	90.1 ± 4.2	115.0 ± 14.7	102.7 ± 3.6	103.8 ± 14.8	97.7 ± 4.5	91.2 ± 13.6	101.7 ± 6.7	115.6 ± 3.5
5	–	10	–	100.4 ± 2.2	77.5 ± 6.5	100.1 ± 5.6	113.2 ± 0.8	93.7 ± 1.2	108.6 ± 8.2	99.9 ± 12.9	105.6 ± 4.8
6	–	25	–	100.9 ± 2.9	115.4 ± 4.2	102.4 ± 5.5	99.6 ± 6.6	96.3 ± 4.0	98.0 ± 4.1	104.6 ± 4.0	106.5 ± 7.2
7	–	–	5	95.2 ± 2.9	76.3 ± 6.9	103.0 ± 4.0	119.4 ± 1.1	104.2 ± 2.3	99.5 ± 3.2	106.3 ± 15.5	98.5 ± 9.9
8	–	–	10	85.8 ± 1.6	118.8 ± 3.6	115.5 ± 7.9	113.9 ± 3.3	105.5 ± 1.7	101.2 ± 1.2	104.1 ± 4.9	111.9 ± 16.3
9	–	–	25	99.1 ± 4.2	91.2 ± 11.7	100.5 ± 5.5	110.0 ± 3.8	99.7 ± 1.0	94.8 ± 10.7	100.2 ± 9.1	123.9 ± 9.2
10	5	5	5	88.3 ± 3.5	85.0 ± 12.5	102.0 ± 4.7	113.0 ± 11.8	100.6 ± 7.2	107.8 ± 5.4	107.6 ± 5.9	117.9 ± 17.4
11	10	10	10	83.4 ± 6.4	92.9 ± 8.8	108.0 ± 0.3	109.9 ± 3.8	93.6 ± 3.3	112.8 ± 2.0	106.2 ± 4.0	116.5 ± 4.9
12	25	25	25	85.6 ± 0.9	93.2 ± 1.7	104.6 ± 2.0	114.2 ± 2.7	104.8 ± 4.3	93.7 ± 1.2	109.2 ± 6.7	107.9 ± 8.3

water samples. Performance of the proposed system was tested. The wet acid digestion method of aqueous samples [28] for total metal analysis (USEPA 3010a) was used as a standard digestion method for comparison. It was found that the released metal ions from both the digestion procedures were in good correlation as shown in Table 1. According to *t*-test at 99.8% confident limit, the results obtained from both methods were in good agreement ($t_{\text{critical}} = 4.025$, $t_{\text{calculate}} = 1.387$, 3.862, 0.477 and 3.365 for Zn(II), Cd(II), Pb(II) and Cu(II), respectively). Therefore, the SI in-line digestion procedure could be effectively used for digestion of water sample.

3.4. Analytical features of the proposed system

Using the operational sequences for SI-monosegmented flow together with the conditions as described in section 2.4, in-line single standard calibration in range of 10–300 $\mu g\,L^{-1}$ for Zn(II), 5–200 $\mu g\,L^{-1}$ for Cd(II), 10–200 $\mu g\,L^{-1}$ for Pb(II) and 20–400 $\mu g\,L^{-1}$ for Cu(II) were constructed by plotting of peak current versus concentration of metal ions ($\mu g\,L^{-1}$). Under the selected conditions, linear calibration graph could be obtained for Zn(II), Cd(II), Pb(II) and Cu(II) with the calibration equations, $y = 0.0013x + 0.003$, $R^2 = 0.9992$ for Zn(II); $y = 0.0012x - 0.0006$, $R^2 = 0.9991$ for Cd(II); $y = 0.0008x - 0.0002$, $R^2 = 0.9982$ for Pb(II); $y = 0.0009x + 0.0139$, $R^2 = 0.9983$ for Cu(II); respectively. The detection limits (the concentration corresponding to three times of standard deviation of blank) were obtained at 3.6 $\mu g\,L^{-1}$ for Zn(II), 0.1 $\mu g\,L^{-1}$ for Cd(II), 0.7 $\mu g\,L^{-1}$ for Pb(II) and 4.3 $\mu g\,L^{-1}$ for Cu(II) for deposition time of 180 s. The relative standard deviations for seven replicate determinations of 27 $\mu g\,L^{-1}$ for Zn(II), 13 $\mu g\,L^{-1}$ for Cd(II), 13 $\mu g\,L^{-1}$ for Pb(II) and 27 $\mu g\,L^{-1}$ for Cu(II) were 4.2%, 2.6%, 3.1% and 4.7%, respectively.

3.5. Validation of the proposed system

The system under the selected conditions was applied for analysis of standard reference material of trace metals in natural water (SRM 1640, NIST) as giving the results in Table 2. It was found that there is no evidence of significant difference between the concentration obtained by SI-ASV and certified value at 95% confidence level ($t_{\text{critical}} = 4.30$, $t_{\text{calculate}} = 0.49$, 2.49, 4.04 and 2.87 for Zn(II), Cd(II), Pb(II) and Cu(II), respectively). Batchwise ASV was also performed. No significant different of the results from Batch-ASV and certified value at 98% confidence level ($t_{\text{critical}} = 6.96$, $t_{\text{calculate}} = 5.13$, 4.00, 1.69 and 3.49 for Zn(II), Cd(II), Pb(II) and Cu(II), respectively). The developed SI-ASV with a small scale voltammetric cell could detect the metals concentrations at the same level as batch-ASV, although sample volumes of 0.750 mL and 10 mL were used for SI-ASV and batch-ASV, respectively. Comparison to batch ASV, the developed method provided higher degrees of automation and lower waste production.

3.6. Analysis of real samples

The system was applied for analysis of bottled mineral drinking water and tap water samples. Concentration of Cd(II) and Pb(II) in those water samples were below detection limit of the method. By spiking 25, 50 and 100 $\mu g\,L^{-1}$ of each metals into a sample, recoveries were found in range of 83–116% for Zn(II), 93–112% for Cd(II), 87–105% for Pb(II) and 80–120% for Cu(II).

The proposed system was employed for determination of Cd(II), Pb(II) and Cu(II) in ground water samples collected from nearby the zinc mining area. In this study, zinc was not determined and the deposition potential of 800 mV was used in order to avoid interference due to the formation of Zn–Cu intermetallic compounds in the amalgam [29]. The samples were collected in a clean polyethylene bottles (1 L) with adding of HCl to acidify sample to pH 1. No sample pretreatment was made except filtering of the sample just before the analysis. The obtained results are presented in Table 3. Voltammograms of sample without and with subjected to UV digestion is depicted in Fig. 5. It should be noticed that peak potential of copper was close to that of mercury so the baseline of the peak was high, leading to high %RSD of the obtained peak current. It was found that concentration of labile metals obtained from direct-ASV system was less than the concentration of metals obtained from UV-ASV system. This indicated that there were some organic matters or complexing agent in ground water samples that could form complexes or adsorb metal ions. To investigate the performance of the in-line UV digestion system, wet digestion was performed on 6 samples for comparison. The results showed that the released metal ions from both of the digestion procedures were

Table 2
Concentrations of Zn(II), Cd(II), Pb(II) and Cu(II) in SRM 1640, determined by the proposed SI-ASV and batch ASV methods, using standard addition method.

Metal ions	Concentration of metals ($\mu g\,L^{-1}$)		
	Certified value	SI-ASV	Batch-ASV
Zn(II)	53.5 ± 1.1	51.9 ± 5.7	60.9 ± 2.5
Cd(II)	22.82 ± 0.96	22.1 ± 0.5	24.9 ± 0.9
Pb(II)	27.93 ± 0.14	24.2 ± 1.6	29.3 ± 1.4
Cu(II)	85.3 ± 1.2	92.3 ± 4.2	93.4 ± 4.0

Table 3
Concentrations of Cd(II), Pb(II) and Cu(II) in ground water samples, determined by the proposed SI-ASV, using in-line standard addition method.

Sample No.	Concentration found (μgL^{-1}) by method					
	Direct-ASV[a]			UV-ASV[b]		
	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)
1	1.3 ± 0.1	5.0 ± 2.3	21.8 ± 4.9	1.8 ± 0.4	9.6 ± 0.9	80.0 ± 1.8
2	ND	4.2 ± 0.6	ND	0.5 ± 0.0	5.3 ± 1.7	21.3 ± 9.6
3	1.5 ± 0.1	4.7 ± 0.9	37.7 ± 3.3	2.3 ± 0.6	9.1 ± 0.8	55.1 ± 0.6
				1.5 ± 0.2	*4.5 ± 0.1*	*53.5 ± 17.4*
4	1.1 ± 0.5	3.1 ± 1.1	14.1 ± 6.4	1.7 ± 0.2	14.9 ± 0.3	52.4 ± 3.0
5	ND	14.2 ± 1.4	33.6 ± 5.2	0.3 ± 0.1	44.1 ± 1.3	40.4 ± 4.7
				0.4 ± 0.1	*36.9 ± 0.7*	*24.5 ± 1.2*
6	1.0 ± 0.7	2.2 ± 0.0	34.5 ± 2.6	2.8 ± 0.1	2.8 ± 0.5	54.5 ± 0.5
7	2.7 ± 0.6	68.8 ± 0.8	ND	4.3 ± 0.2	70.6 ± 2.1	13.5 ± 2.6
				5.0 ± 0.6	*81.5 ± 1.2*	*18.0 ± 0.1*
8	ND	3.1 ± 0.3	10.8 ± 2.8	1.3 ± 0.2	4.7 ± 1.2	27.6 ± 8.9
9	1.2 ± 0.0	6.9 ± 1.4	16.6 ± 1.5	2.2 ± 0.3	12.3 ± 2.1	49.9 ± 2.5
10	0.6 ± 0.2	9.5 ± 0.9	17.6 ± 6.0	1.7 ± 0.1	15.6 ± 0.8	32.8 ± 4.0
				2.1 ± 0.1	*13.1 ± 0.4*	*27.6 ± 8.1*
11	2.9 ± 0.1	4.0 ± 0.6	22.4 ± 1.3	4.0 ± 0.2	8.6 ± 0.2	72.6 ± 4.5
12	2.4 ± 0.1	2.4 ± 0.2	34.8 ± 6.8	2.0 ± 0.4	2.4 ± 0.1	52.3 ± 3.4
				1.7 ± 0.1	*2.0 ± 0.9*	*27.3 ± 10.5*
13	0.8 ± 0.6	13.7 ± 0.7	104.2 ± 21.6	2.6 ± 0.5	14.5 ± 2.1	233.7 ± 46.7
14	0.9 ± 0.0	14.2 ± 1.6	107.6 ± 15.7	1.4 ± 0.1	15.6 ± 2.5	130.0 ± 7.9
15	ND	4.9 ± 0.5	43.4 ± 3.3	0.6 ± 0.2	6.8 ± 1.4	61.8 ± 15.6
16	0.3 ± 0.2	5.1 ± 0.0	57.7 ± 9.4	0.7 ± 0.1	9.7 ± 2.5	82.4 ± 6.9
17	0.7 ± 0.2	4.5 ± 0.3	25.7 ± 15.7	0.4 ± 0.1	8.3 ± 0.1	34.1 ± 1.3
				0.5 ± 0.1	*7.1 ± 0.6*	*46.5 ± 12.2*
18	1.0 ± 0.1	3.2 ± 0.1	97.6 ± 31.4	1.1 ± 0.0	11.3 ± 0.4	121.8 ± 19.6
19	ND	3.3 ± 0.3	33.4 ± 1.6	0.9 ± 0.0	6.7 ± 0.5	44.2 ± 12.8
20	0.5 ± 0.3	3.9 ± 0.1	24.9 ± 2.5	1.1 ± 0.1	7.3 ± 0.6	62.0 ± 8.8

Italic values: determined by SI-ASV after batchwise wet digestion [28].

[a] Direct-ASV: determined by SI-ASV without sample digestion.

[b] UV-ASV: determined by SI-ASV after in-line UV digestion of sample.

in good correlation. According to *t*-test at 95% confidence limit, the results obtained from both the methods were in good agreement ($t_{critical} = 2.57$, $t_{calculate} = 0.015$, 0.664 and 0.548 for Cd(II), Pb(II) and Cu(II), respectively). To perform the recovery study, eight samples were spiked with metals at 10 $\mu g\,L^{-1}$ for Cd(II) and Pb (II) and 20 $\mu g\,L^{-1}$ for Cu(II). Satisfactory results for the concentration level studied were obtained for Cd(II), Pb(II) and Cu(II) which percentages recoveries of 97–111, 93–115 and 83–118% were obtained, respectively. The proposed system allowed the speciation of free and bound metals to be carried out quickly and more efficiently.

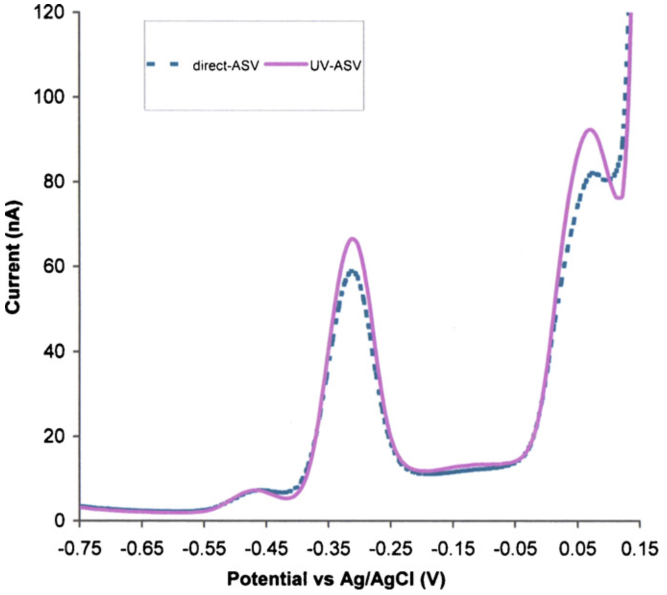

Fig. 5. Voltammograms of ground water sample without and with UV digestion before the voltammetric measurement.

4. Conclusion

A cost-effective sequential injection system was assembled and applied to perform a monosegmented flow anodic stripping voltammetric analysis with a small scale voltammetric cell using a hanging mercury drop electrode (HMDE) as a working electrode and an in-line UV digestion for determination of Zn(II), Cd(II), Pb(II) and Cu(II) in water samples. The low-cost small scale voltammetric cell was firstly proposed here and it provides several advantages, e.g. convenient to perform analysis with the HMDE, avoiding tedious washing of glass cell and electrodes after each determination, involving small amounts of solution, compatible with automated operation of SI system and providing good precision and accuracy of the results. The system developed further by incorporating a homemade UV digestion unit was successfully applied for speciation of labile and bound forms of some trace metals in ground water samples. Performance of the in-line UV digestion system was tested in the determination of metal ions in model water samples which contained some dissolved organic matters. The results obtained are comparable to those by the standard method based on wet acid digestion (USEPA 3010A) which was used for comparison. The in-line UV digestion system offers high degrees of automation, less contamination, low consumption of reagent and sample, and low waste production when comparing to batchwise wet acid digestion method.

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