

Determination of copper in natural waters by batch and oscillating flow injection stripping potentiometry

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Abstract

Copper trace analysis in natural waters rich in chloride ions and organic matter was performed by means of a copper-selective electrode (Cu-ISE), inductively coupled plasma-atomic emission spectrometry (ICP-AES), anodic stripping voltammetry (ASV), batch potentiometric stripping analysis (PSA) and oscillating flow injection stripping potentiometry (OFISP). The results obtained by the first two analytical methods showed that copper was present mainly in the form of various complexes with inorganic (mainly chloride) ions and organic ligands. The organic constituents impeded the application of ASV in the quantitative determination of labile copper concentration in the water samples mainly due to adsorption of organic matter onto the working electrode. Consistent analytical data concerning the labile fraction of copper were obtained by both batch PSA and OFISP in hydrochloric acid medium when standard addition or direct calibration were used. However, discrepancies between the batch PSA results obtained by the two calibration methods mentioned above in nitric acid medium were observed. Unlike batch PSA, OFISP appears to be versatile with respect to the sample matrix in both standard addition and direct calibration approaches. On the basis of this and the other well-known advantages of OFISP it was concluded that this analytical technique is suitable for fast and inexpensive trace heavy metal analysis in natural waters with unknown matrices.

Keywords: Copper; Trace metal analysis; Natural waters; Ion-selective electrodes; Inductively coupled plasma spectrometry; Anodic stripping voltammetry; Flow injection

1. Introduction

Electroanalytical methods have been successfully applied in the trace metal analysis in samples of widely different origin [1]. With the growing concern

regarding heavy metals pollution of natural waters, the importance of these methods has increased considerably in the last decade. Electroanalysis appears to provide the best opportunity for experimentally modelling the bioavailability of heavy metals and their complexes with organic and inorganic ligands [1].

Among the electroanalytical methods, those using a stripping cycle (e.g., anodic stripping voltammetry (ASV) and potentiometric stripping analysis (PSA))

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have emerged as very suitable for trace metal speciation [2–6]. The preconcentration step in these methods takes place in the pretreated sample solution, thus excluding the necessity for more complex preconcentration steps (e.g., solvent extraction or dialysis) which inevitably increase the risk of contamination.

However, problems may arise when the samples contain chemical species which can react, e.g. by complexation or precipitation with the analyte (Cu^{2+}) in the cases of ASV and PSA and/or with the oxidant (e.g., Hg^{2+}) in the case of PSA. Natural waters, which are usually rich in chloride ions, are typical examples of samples with matrices interacting chemically both with the analyte and the oxidant. In chloride medium, depending on the concentrations of metal and chloride ions, the following copper and mercury complexes may coexist $[\text{CuCl}]$, $[\text{CuCl}_2]^-$, $[\text{CuCl}]^+$, $[\text{CuCl}_2]$, $[\text{CuCl}_3]^-$, $[\text{CuCl}_4]^{2-}$, $[\text{HgCl}]^+$, $[\text{HgCl}_2]$, $[\text{HgCl}_3]^-$ and $[\text{HgCl}_4]^{2-}$. For this reason, if calibration curves are used, the matrix content of the standard solutions should match with that of the sample. This is not necessary if the standard addition method is used. However, this method requires some additional measurements with each sample which slows down the sample throughput and impedes automation of analysis. Additional difficulties may be encountered in the case of ASV because of the adsorption of organic matter, in which natural waters are usually rich, onto the mercury electrode [7–9]. An adsorbed organic layer is likely to diminish the amount of electroplated metal and may cause nonlinearity in the stripping current-deposition time relationship [10]. The use of potentiometric stripping analysis (PSA) largely overcomes this drawback of ASV because an adsorbed organic layer on the electrode would exhibit similar resistance to mass transfer of the analyte during the electrolytical deposition step and the oxidant during the chemical stripping step [1,11–13]. While dissolved oxygen is a major interferent in ASV, causing in some cases (e.g., Cu and Pb analysis) an apparent increase in the stripping current, in PSA it only shortens the stripping time if another oxidant (e.g., Hg(II)) is used [14]. The presence of organic dipoles in the sample may generate “tensammetric” peaks in pulsed ASV which can be mistaken for metal stripping peaks [15] while such problems are not

expected to occur with PSA. On the basis of the above considerations, and taking into account the fact that PSA requires simpler equipment compared to ASV, it can be concluded that PSA may be regarded as the technique of choice for trace metal analysis in natural waters.

The analytical signal in PSA, unlike that in ASV, is independent of the electrode size, so that reduction of the electrode area is feasible. This feature of the technique is important in respect of system miniaturisation. For this reason PSA has been successfully used as a detection technique in flow injection (FI) systems [16–20]. Under FI conditions the potentiostatic deposition process and the chemical stripping process are performed in different media which offers additional advantages (e.g., improved sensitivity and reproducibility, easy and fast background potential correction) in comparison to the batch mode [20]. Considerable enhancement of PSA sensitivity can be achieved through flow reversal. Multiple passes of the sample plug over the working electrode, gives much increased electroplating efficiency. Based on this principle a technique called oscillating flow injection stripping potentiometry was introduced in the analytical practice [20].

In the present paper the applicability of both OFISP and batch PSA in the analysis of traces of Cu(II) in filtered (through a Millipore 0.45 μm filter) water samples from the Myponga Reservoir in South Australia where CuSO_4 is utilised to control the potential algal blooms is reported. The main chemical

Table 1
Selected analytical results for the reservoir water analysed

Free copper(II) ions ($\mu\text{g l}^{-1}$) ^a	4.4
Total copper ($\mu\text{g l}^{-1}$) ^b	359
Calcium (mg l^{-1}) ^b	19
Magnesium (mg l^{-1}) ^b	12
pH	7.60
Alkalinity as CaCO_3 (mg l^{-1}) ^c	52
Dissolved organic carbon (mg l^{-1}) ^d	13
Chloride (mg l^{-1}) ^e	120

^a Copper(II) ion-selective electrode with the method described in [26].

^b Inductively coupled plasma (ICP) method [27].

^c Titration method [27].

^d Skalar Sk12 Analyser, using gas chromatography flame ionisation detector [28].

^e Automated hexacyanoferrate(III) method [27].

constituents in these samples, determined by various methods in the State Water Laboratory of the Engineering and Water Supply Department of South Australia, are presented in Table 1. The relatively high chloride concentration is expected to affect considerably speciation of copper. A comparison with the results obtained by other frequently utilised methods for trace metal analysis (e.g., batch ASV, inductively coupled plasma-atomic emission spectrometry (ICP-AES) and copper ion-selective electrode) is also presented.

2. Experimental

2.1. Equipment

2.1.1. Batch ASV analysis

A 174A polarographic analyser (Princeton Applied Research, USA) was employed for ASV measurements. Voltammograms were recorded on a Omni-graphic 2000 X–Y chart-recorder (Houston Instrument, Division of Bausch and Lomb, USA). A linear waveform with 100 mV s^{-1} scan rate was used during the stripping step. The cell assembly contained a magnetic stirrer, a 3 mm diameter glassy carbon electrode, (Chemtronics, Australia) employed as working electrode, a platinum wire, used as auxiliary electrode, and a Ag/AgCl/3 M KCl double-junction electrode (HNU ISE 40-02-00, HNU Systems, USA) as reference.

2.1.2. Batch PSA

The equipment employed in this study comprised a CV-1B cyclic voltammetry unit (Bioanalytical Systems, USA) as the potentiostat, a 701A Digital Ionalyzer (Orion Research, USA) for potential measurement and a PCL-712 Multi-Lab Card (Advantech, Taiwan) for data acquisition and control. An IBM compatible 386-SX personal computer was used to control the measurement system. The same cell assembly was used as in the ASV setup. The experimental setup is described in detail in [21].

2.1.3. Oscillating flow injection stripping potentiometry (OFISP)

The PSA equipment used was as described earlier. The flow injection system included a Minipuls 3

peristaltic pump (Gilson SA, France) fitted with Tygon pump tubing. Polypropylene connectors and PTFE tubes (0.5 mm i.d.) were utilised throughout. A 4-way rotary valve with a sample loop size of 100 μl was employed as an injection device, with sample injection controlled by a pneumatic actuator, activated by a solenoid unit (Rheodyne 5041, 5701 and 7163, respectively; Rheodyne, USA). The experimental setup is described in detail in [20].

2.2. Reagents

All chemicals used were of analytical grade and Milli-Q reagent water (Millipore, USA) was used throughout the experiments. During the mercury pre-coating of the glassy carbon electrode, a 0.1 M hydrochloric acid solution of 30 mg l^{-1} Hg(II) ($\text{Hg}(\text{NO}_3)_2$, Ajax chemicals, Australia) was used. The electrodeposition and chemical stripping in the case of batch PSA were performed in 0.1 M hydrochloric acid or 0.1 M nitric acid solutions containing 10 mg l^{-1} Hg(II). In the case of OFISP, the chemical stripping was carried out in 0.1 M hydrochloric acid or 0.1 M nitric acid solutions of 1 mg l^{-1} Hg(II). Standard solutions of Cu(II) ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Ajax Chemicals) in 0.1 M hydrochloric acid were prepared by serial dilution of a 1000 mg l^{-1} stock solution.

Solution deaeration was carried out by bubbling CIG (Commonwealth Industrial Gases) high purity nitrogen gas.

2.3. Experimental procedure

2.3.1. Batch ASV analysis

The glassy carbon working electrode was polished using a BAS PK-4 polishing kit (Bioanalytical Systems, USA), then rinsed with A.R. ethanol and dried in air. It was then preplated with a mercury film from a 30 mg l^{-1} solution of $\text{Hg}(\text{NO}_3)_2$ in 0.1 M HCl at -900 mV for 5 min.

Direct calibration was performed using 50 ml 0.1 M hydrochloric acid as electrolyte solution. Five additions of 50 μl of a 100 mg l^{-1} copper standard solution to the analytical cell were made by means of a 50–200 μl adjustable micropipette (Socorex, Switzerland) thus increasing the concentration of Cu(II) from 0 to $500 \mu\text{g l}^{-1}$. Initial deaeration was carried

out for 15 min in the cell and deaeration after each standard addition was carried out by bubbling nitrogen gas for 1 min. During both the electro deposition and the stripping steps, a stream of high purity nitrogen gas was maintained over the surface of the solutions and a 1 min plating time at -900 mV was employed throughout. All measurements were made in triplicate using peak current as the analytical parameter.

2.3.2. Batch PSA

The procedures for mercury precoating of the glassy carbon electrode, initial deaeration and direct calibration in 0.1 M HCl and 0.1 M HNO_3 media were performed in the same way as in the case of ASV. The electrodeposition and the chemical stripping steps took place at the same stirring rate. During the later step the concentration of Hg(II) used as oxidant was 10 mg l^{-1} . A 50 ml aliquot of acidified water samples (0.1 M HCl and 0.1 M HNO_3) and 0.05 ml of 10000 mg l^{-1} $\text{Hg}(\text{NO}_3)_2$ solution (10 mg l^{-1} final concentration) were transferred to the analytical cell. Electrodeposition and chemical stripping were performed according to the procedure outlined above. The copper concentration was interpolated directly from the corresponding calibration curve. The standard addition method was also applied to determine the copper concentration in $50 \mu\text{l}$ of acidified water samples (0.1 M HCl and 0.1 M HNO_3). Five additions of $50 \mu\text{l}$ of a 100 mg l^{-1} copper standard solution to the analytical cell containing the sample were performed. A 50 – $200 \mu\text{l}$ adjustable micropipette (Socorex, Switzerland) were used for this purpose. The Cu(II) concentration was determined as the intercept of the calibration curve with the abscissa. All measurements were done in triplicate using peak area as the analytical parameter. All stripping potentiograms were background corrected against a blank.

2.3.3. Oscillating flow injection stripping potentiometry (OFISP)

Two different carrier/stripping solutions, 0.1 M HCl and 0.1 M HNO_3 , each with 1 mg l^{-1} Hg(II), were selected in this study. Calibration curves were obtained using 0 – $1000 \mu\text{g l}^{-1}$ Cu(II) standards at 0.267 ml window width and 2.0 ml min^{-1} plating flow rate with four oscillations. Static stripping

(stopped flow conditions) was used to obtain maximum sensitivity. Acidified water samples (0.1 M HCl and 0.1 M HNO_3) were injected. The copper concentration was interpolated directly from the corresponding calibration curve. Three additions of $100 \mu\text{l}$ of a 100 mg l^{-1} copper standard solution to the sample were done by a 50 – $200 \mu\text{l}$ adjustable micropipette (Socorex, Switzerland). After each standard addition, FI measurements were performed. The Cu(II) concentration was determined as the intercept of the calibration curve with the abscissa. All measurements were done in triplicate using peak area as the analytical parameter. All stripping potentiograms were background corrected against a blank.

3. Results and discussion

3.1. Comparison of ICP-AES and Cu-ISE results

The total copper content of the sample determined by ICP-AES and the concentration of the free (hydrated) Cu(II) ions determined by the Cu-ISE are presented in Table 1. These results support the fact that the matrix in the water samples from the Myponga Reservoir plays a very important role in respect of the distribution of copper in the form of various complexes with inorganic and organic ligands.

3.2. Influence of the chloride concentration on the PSA and ASV signal

Because of the relatively high chloride concentration in the water samples (Table 1), the complexation of these ions with copper is expected to influence considerably the electrochemical measurements. Similarly to ASV [22], the higher the chloride concentration in the sample the greater the negative shift in the PSA copper peaks that will be observed (Fig. 1). Initially, the stripping potentiometric peak is suppressed with the addition of chloride, which is similar to the situation in ASV and is due to the diminished plating rate because of the complexation of Cu(II) with chloride ions. Further increase in the chloride concentration, however, causes an increase in the stripping signal (Fig. 1). This increase is most probably due to the formation of chloride complexes

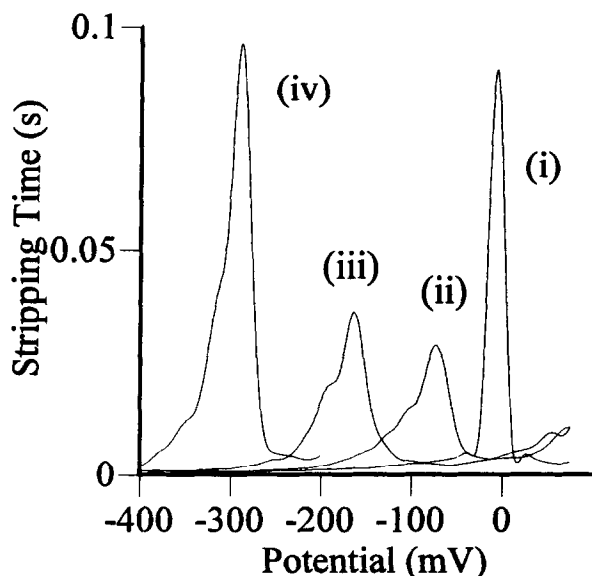


Fig. 1. Influence of the chloride concentration in standard solutions of (i) 0.1 M HNO₃, (ii) 0.1 M HNO₃ + 0.01 M Cl⁻, (iii) 0.1 M HNO₃ + 0.1 M Cl⁻ and (iv) 0.1 M HNO₃ + 1 M Cl⁻ containing 100 μg l⁻¹ copper and 10 mg l⁻¹ Hg(II) on the position of the stripping peak after 1 min electrodeposition.

of mercury. As a result of these complexation processes, the Hg(II) flux at the electrode/solution interface decreases because the concentration of the hydrated Hg(II) ions decreases considerably and also because the diffusion coefficients of the corresponding chloride complexes of Hg(II) are lower than that of the hydrated ion. The matrix effects during stripping can be minimised if medium exchange is carried out before stripping. FI PSA is a very suitable technique for implementing medium exchange stripping.

3.3. Influence of the oxidant (Hg(II)) concentration on the potentiometric stripping process

The concentration of the Hg(II) ion governs the oxidation rate of the amalgamated analyte, and thus the sensitivity of PSA. The stripping time was found to be inversely proportional to the Hg(II) concentration in the solution (Fig. 2(b)). This result is in excellent agreement with the findings of other researchers [12] and with theoretical predictions [23,24]. On the basis of the results presented in Fig. 2(b) it can be concluded that the sensitivity of PSA

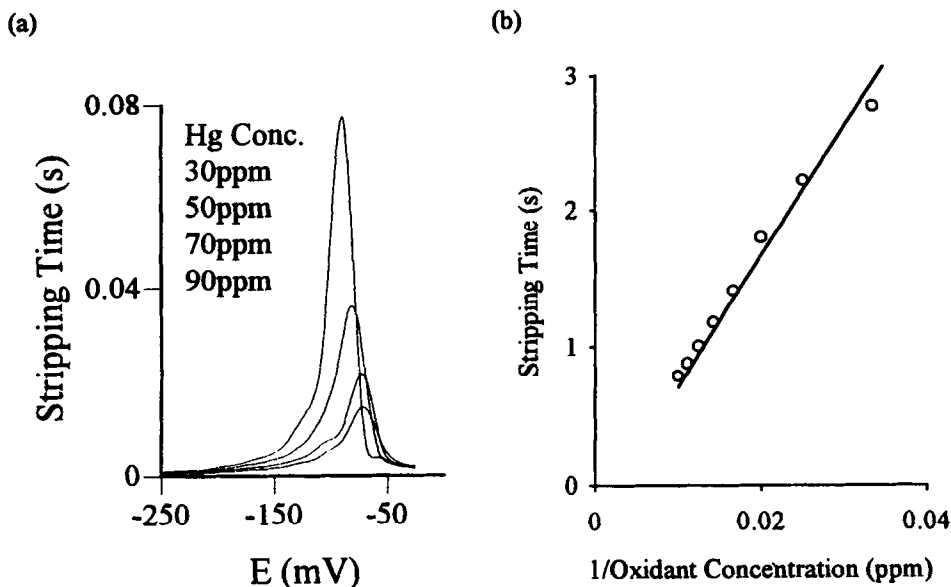


Fig. 2. (a) Stripping time versus reciprocal of the Hg(II) concentration, (b) stripping potentiograms obtained in 0.1 M HCl solutions of 500 μg l⁻¹ Cu(II) and Hg(II) concentration in the range 30–90 mg l⁻¹ after 1 min electrodeposition (25-point polynomial smoothing was applied).

can be considerably improved by lowering the oxidant (Hg(II)) concentration in the stripping solution. However, under such conditions the contribution of both the residual dissolved oxygen and other minor impurities to the chemical stripping of the amalgamated analyte may become significant. Such effects express themselves in poorly reproducible results and non-linear calibrations [11,25]. Linear calibrations of Cu(II) up to 1 mg l^{-1} were observed under batch conditions with Hg(II) concentrations as low as 10 mg l^{-1} . In the flow injection mode, where the sample solution has been flushed out after the electroplating step, a further decrease in the oxidant concentration (1 mg l^{-1} Hg(II)) is possible.

The influence of the oxidant (Hg(II)) on the position and shape of the batch stripping potentiograms obtained for a $500 \mu\text{g l}^{-1}$ Cu(II) in 0.1 M HCl solution is illustrated in Fig. 2(a). A cathodic shift in the position of the stripping peaks with decreasing Hg(II) concentration was observed. This effect can be explained by the fact that by decreasing the Hg(II) concentration, the portion of chloride ions complexing with Hg(II) will be reduced thus increasing the concentration of free chloride ions. This in turn will decrease the concentration of free Cu(II) ions leading to the cathodic shift experimentally observed.

3.4. Matrix effects in FI- and batch PSA

3.4.1. Batch PSA

The positions of the stripping potentiograms of samples and standard solutions in both 0.1 M HNO₃ and 0.1 M HCl media are shown in Fig. 3. In both media the sample peaks are shifted to more negative potentials compared to the corresponding standard solutions, thus illustrating the matrix effect. This effect is only slightly less pronounced in 0.1 M HCl acid medium than in 0.1 M HNO₃ acid medium despite the fact that the chloride ions are one of the main constituents in the matrix.

Unlike the slight dependence of the peak shift on medium, a pronounced matrix effect on the calibration curves was observed. This fact can be illustrated by comparing the direct and the standard addition calibration curves obtained in the two media mentioned above, i.e., 0.1 M HCl and 0.1 M HNO₃ (Fig. 4). In 0.1 M HCl medium (Fig. 4(a)) the direct calibration and the standard addition calibration

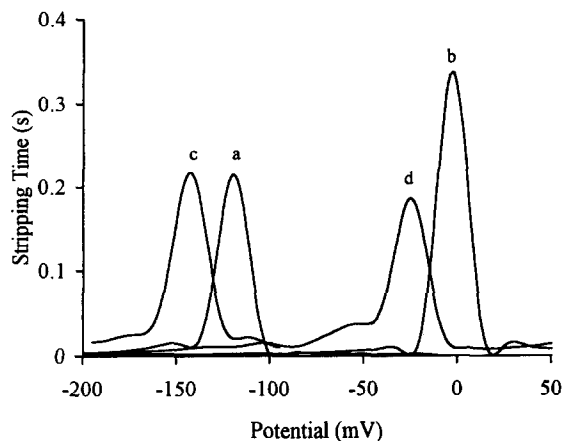


Fig. 3. Batch stripping potentiograms obtained in 10 mg l^{-1} Hg(II) standard Cu(II) ($300 \mu\text{g l}^{-1}$) (a) 0.1 M HCl or (b) 0.1 M HNO₃ solutions and in 10 mg l^{-1} Hg(II) (c) 0.1 M HCl or (d) 0.1 M HNO₃ sample solutions (25-point polynomial smoothing was applied).

curves are parallel to each other. The 95% confidence intervals of Cu(II) determined by the two methods are 334 ± 40 and $366 \pm 14 \mu\text{g l}^{-1}$, respectively. This result suggests that in hydrochloric acid medium direct calibration is applicable. However, when direct and standard addition calibration is performed in 0.1 M HNO₃ medium, the corresponding calibration curves have different slopes (Fig. 4(b)). The concentrations of Cu(II) determined by the two methods are 238 ± 28 and $326 \pm 41 \mu\text{g l}^{-1}$, respectively. Obviously the result obtained by the standard addition method agrees well with the result obtained in 0.1 M HCl medium. However, this is not true in the case of the direct calibration method, confirming the conclusion that direct calibration under batch conditions can be used successfully only when the medium matches the matrix.

3.4.2. Oscillating flow injection stripping potentiometry (of ISP)

As might have been expected, under FI conditions the matrix effect can be practically eliminated. This assumption was experimentally proven by the fairly good overlapping of the stripping potentiograms of samples and standard solutions in both 0.1 M HNO₃ and 0.1 M HCl media (Fig. 5). The concentration of Hg(II) in the corresponding 0.1 M HNO₃ and 0.1 M HCl carrier/stripping solutions was 1 mg l^{-1} . The

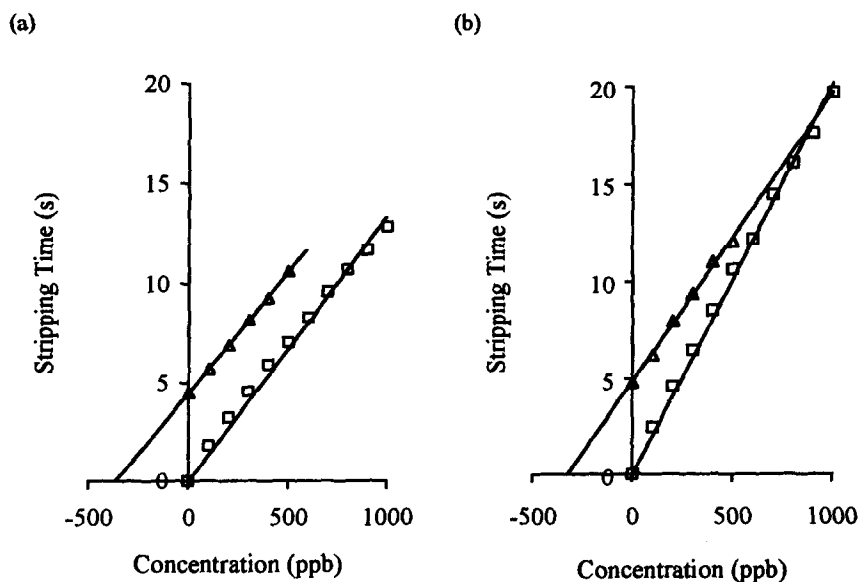


Fig. 4. Standard addition (Δ) and direct calibration (\square) curves obtained under batch conditions in (a) 0.1 M HCl or (b) 0.1 M HNO₃ solutions containing 10 mg l⁻¹ Hg(II) after 1 min electrodeposition.

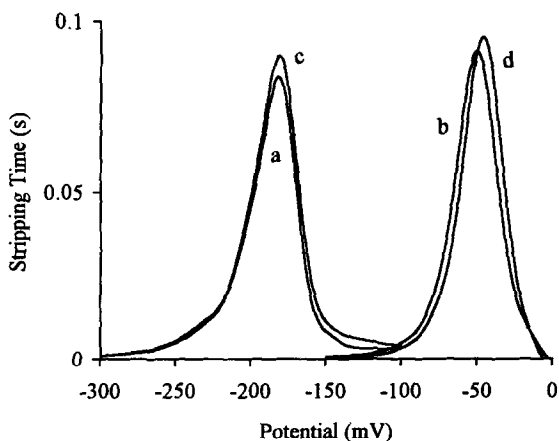


Fig. 5. Oscillating flow injection stripping potentiograms obtained in 1 mg l⁻¹ Hg(II) 0.1 M HCl or 0.1 M HNO₃ carrier/stripping solutions after the injection of 100 μ l standard Cu(II) (300 μ g l⁻¹) solution (a and b, respectively) or sample (c and d, respectively). (0.267 ml window width, four oscillations and 2.0 ml min⁻¹ flow rate during electrodeposition and stopped flow during stripping; 25-point polynomial smoothing was utilised).

direct calibration and standard addition curves obtained in each acid medium were parallel to each other, showing the lack of matrix influence (Fig. 6(a) and (b)). The values of Cu(II) concentration determined by the two methods in both media are close to

each other (Table 2). This result shows that the direct calibration method can be successfully applied even if the matrix is unknown, emphasising the versatility of the FI approach in utilising PSA in the analysis of natural waters.

3.5. Comparison between PSA and ASV

The copper concentration determined by batch ASV using the direct calibration approach is lower than the value obtained using batch PSA (Table 2). The reason for this effect may be found in the fact that during electrodeposition surface-active dissolved organic species present in the sample can adsorb onto the electrode surface. This will affect the electrodeposition step since the transport of metal ions to the electrode surface is restricted. The analytical signal obtained in ASV is directly dependent on the number of ions deposited in a given time, and is diminished as a consequence. However, in PSA such surface processes not only affect the transport of metal ions to the electrode surface during the electrodeposition step, but also slow the transport of oxidant ions to the electrode surface during the stripping step. It turns out that these two effects are partially self-compensatory in PSA, stripping time thus being in practice

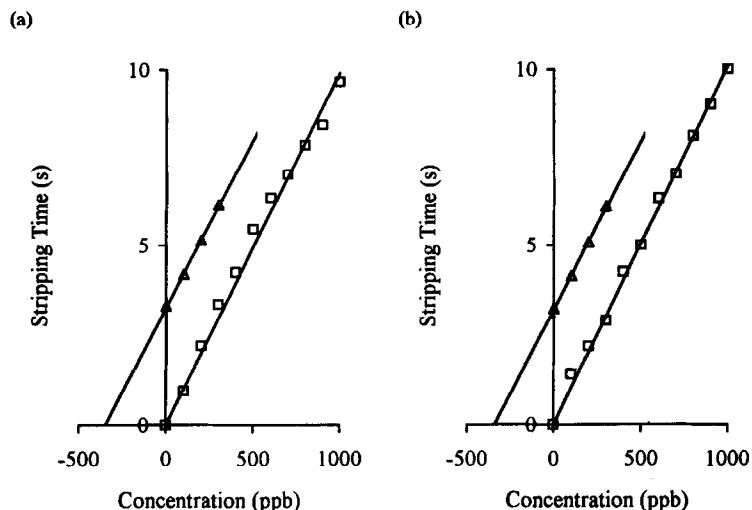


Fig. 6. Standard addition (Δ) and direct calibration (\square) curves obtained under OFISP conditions in (a) 0.1 M HCl or (b) 0.1 M HNO₃ (The experimental conditions are the same as for Fig. 5).

Table 2

The 95% confidence interval of copper concentration^a in $\mu\text{g l}^{-1}$ determined in water samples from the Myponga Reservoir

Method	Batch PSA		FI-PSA		Batch ASV
Medium	0.1 M HNO ₃	0.1 M HCl	0.1 M HNO ₃	0.1 M HCl	0.1 M HCl
Direct calibration	238 \pm 28	334 \pm 40	322 \pm 28	335 \pm 32	244 \pm 19
Standard addition	326 \pm 41	366 \pm 14	341 \pm 21	349 \pm 19	350 \pm 31

^aThe concentration values are the mean values of triplicate readings interpolated directly from the corresponding calibration curves (direct calibration) or determined as the intercept of the standard addition curves (standard addition method) and the 95% confidence interval values presented were estimated based on the method outlined in [29] and calculated using Minitab (Version 7.2, Minitab, USA).

less influenced by surface-active organic species than stripping current [11,12].

4. Conclusions

On the basis of the results obtained, it was confirmed that PSA offers considerable advantages in the quantitative determination of traces of Cu(II) in natural waters compared to ASV (which is the electroanalytical method most frequently used for this purpose). The most important among them are the simplicity of the equipment needed, the possibility for miniaturisation and relative insensitivity to organic constituents in the natural water capable of adsorbing onto the working electrode. When implemented as a detection technique in an oscillating flow injection system, PSA, offers additional advan-

tages such as versatility, easy and relatively inexpensive automation of analysis, use of small sample volumes, high sample throughput, and the possibility of on-line sample pretreatment. The versatility of FI-PSA compared to batch PSA can be attributed mainly to the fact that under FI conditions standard addition calibration can be successfully used without matching the matrix constituents in the standard solutions. This is an important advantage because, in the general case, the exact content of the medium is not known. The periodic alternations of the flow direction increases substantially, compared to traditional FI applications, the contact time between the working electrode and the sample. This approach allows retention of the high sensitivity characteristic of batch PSA. All these features of OFISP characterise this analytical technique as a powerful tool in trace metal analysis. The analytical results obtained for a

reservoir water sample using the OFISP, constitute a successful application of this new technique.

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