Flow Injection Method for Preconcentration and Polarographic Determination of Copper in Water

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Abstract

The analytical application of a simple polarographic flow through cell, which was previously designed for the continuous polarographic analysis of organic compounds in pharmaceuticals and urine, is proposed in this work for the determination of copper in diluted water samples. The cell contains a conventional dropping mercury electrode (DME), a mercury pool and a platinum wire as the working, reference and counter electrodes, respectively. Enrichment of the analyte, previous to the polarographic continuous determination, was necessary and was achieved by using a microcolumn containing Chelex-100, located in the loop of the injection valve. The flow through detector can be used either amperometrically, under continuous flow operation, or voltammetrically in quiet solution, under continuous flow-stopped flow mode. Under continuous flow operation of the cell, after a preconcentration time of 3 min, the preconcentration factor was calculated to be 90, with a limit of detection of 9.5 ng/mL and a sampling rate of $15\,h^{-1}$. The repeatability of the analytical signals, expressed as RSD, was always lower than 2.1%. Validation of the method was carried out by analysis of certified reference materials, and the recovery was $101.96 \pm 1.38\%$.

Keywords: Flow injection, Polarographic flow through cell, Copper, Chelex-100, Water

In previous articles [1, 2] we described the design of a new electrochemical flow cell containing a conventional dropping mercury electrode (DME) as working electrode. Despite the previously discussed improvements and advantages of our design over other polarographic flow cells, one limitation is the sensitivity, which is comparable to DC polarography, thus impeding application to determination of the analyte at trace level. In order to increase the sensitivity of the method, in this work a continuous preconcentration unit (Chelex-100) was used, thus allowing the analysis of water samples in which copper is present at $ng\,mL^{-1}$ level. In this context, by controlling appropriately the preconcentration time, the sensitivity of the present method becomes comparable to that offered by anodic stripping voltammetry.

By using the one-channel FIA manifold containing a peristaltic pump and the flow through cell shown in Figure 1, the analyte can be determined either voltammetrically or amperometrically, depending on the nature of the analytical information requested. Figure 2 shows the two different signals obtained. In the first case (Fig. 2a) the DC polarogram was recorded after the pump was halted when the entire volume of the cell was filled with the sample injected. Under these conditions the reduction is diffusion-controlled as shown by the linear dependence of the wave height with $h^{1/2}$. These typical current–voltage curves in quiet solution can not be obtained with previous cell designs based on a flow through polarographic detector immersed in an electrolyte bulk solution in which are placed the other two electrodes [3–6]. The second type of signal (Fig. 2b) was obtained under continuous flow conditions, by applying a constant potential (-0.6 V) for transient reduction of copper. Contrarily, in this case convection dictates the mass-transport to the electrode. Independently of the target analyte the former situation should be selected if mechanistic information about the electrode process is required, while the latter, which is considerably faster, is the indicated one for analytical purposes.

Selection of the optimum conditions were made by using the univariate method. (Table 1).

Taking into account our previous experience in solid-liquid separation [7–9] and preconcentration, and also the suggestions made by other users [10, 11], a Chelex-100 microcolumn was selected to preconcentrate and separate copper from very diluted water samples. This chelating resin has shown very good performance for preconcentration of transition metal ions when the aqueous sample is adjusted to pH 6.5 previously loading onto a microcolumn using a flow rate of 3–4 mL/min.

The preconcentration time, required to preconcentrate a measurable amount of copper, depends on its concentration level in the sample. However, by using a preconcentration time of 3 min, the sensitivity is quite sufficient to determine copper at ng/mL level. Considering that the concentrated analyte is eluted with the first $100\,\mu L$ of carrier solution (nitric acid 1 M) then the calculated preconcentration factor under these conditions is at least 90.

The effect of the delay coil length was investigated, a short delay coil of 20 cm was used to minimize the dispersion effect on the samples. It was observed that injection of the samples (and blanks) gave rise to a physical perturbation in the flow profile [1, 2]. This perturbation was recorded as a parasite signal, which appears simultaneously with the analytical peak. The height and width of the parasite signal depend directly on the injection volume (*IV*)/delay coil length (*L*) ratio. Attempts to decrease this interference resulted in proportional decrease in the sensitivity of the analytical measurements (Faradaic current). Consequently, in the selected conditions (Table 1), the interference signal reached a constant value of $0.38\,\mu A$. On the other hand, it was found that the peak current increases linearly with increasing flow rate in the range 0.6 to 3.5 mL/min. The decrease in the signal with decreasing flow rate is due not only to the increased dispersion of the injected sample but also to the diminished rate of convective transport of the analyte to the DME. Because the flow stream impacts directly on the drop flowing from the DME, flow rates
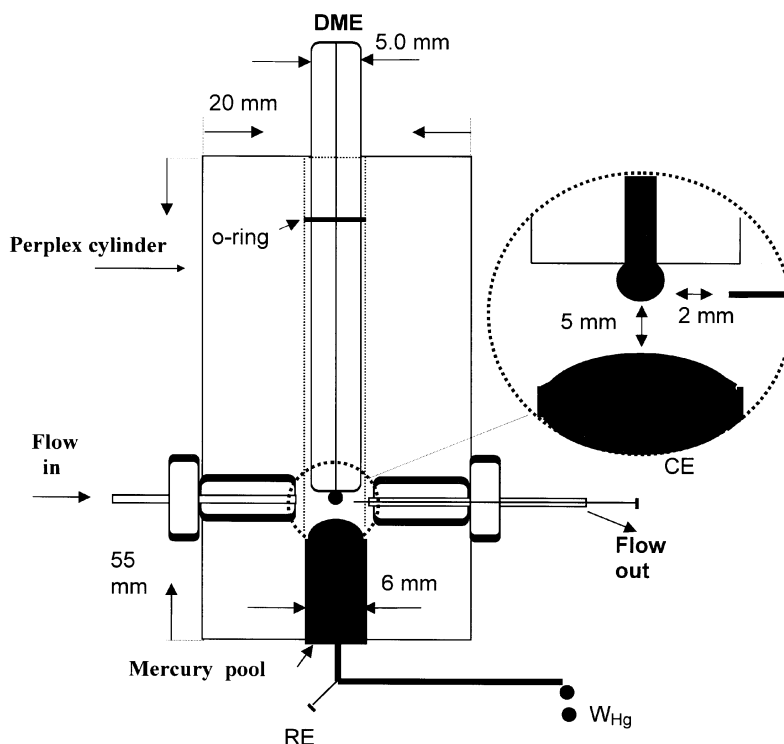
Fig. 1. Flow through polarographic cell. DME: dropping mercury electrode; RE: reference electrode; CE: counter electrode; W_{Hg}: mercury waste.

over 4.0 mL/min interfered with the drop stability giving rise, consequently, to less reproducible signals.

The effect of the cell volume on the analytical signal was investigated by changing the distance between the DME surface and mercury pool from 2 up to 5 mm, by moving the mercury pool, but always keeping the location of the DME in the optimum position (Fig. 1). Because the flow stream always impacts the drop of the DME, the height of the signal was almost constant between this volume range in a wide range of flow rates. The correct location of the DME into the cell (Figure 1) is when the flow stream directly impacts the mercury drops. Contrarily, as was discussed earlier [2], if the mercury drop was over the flow stream the signal was considerably less sensitive, and its height became dependent of the cell volume.

The drop times of the mercury electrode do not affect significatively the sensitivity of the signal, which increases slightly with decreasing drop times. However, the repeatability of the measurement decreases considerably with lower drop times [1, 2]. A drop time of 7.5 s was selected; consequently one drop is sufficient to eliminate the maximum of the analytical signal.

Because the area of the DME is time-dependent, the arrival of the analyte to the cell must be synchronized in order for the sample zone to meet, in each injection, the equal electrode area. In this context, to get the maximum reproducibility in the measurements, a long drop time (7.5 s) was selected and also the time elapsed (delay time, Table 1) between injection of the sample and the fall of the mercury drop was studied. The peak height varies with this time according to the electrode area that the sample zone meets when it passes through the cell. Consequently, the instant of injection must be synchronized with the electrode area for getting reproducibility in the analytical measurements.

The peak height of the flow injection signal was recorded with different potentials applied to the DME. A potential of −0.6 V was selected, for FIA determination of copper.

Under the optimum conditions stated in Table 1, and by using a preconcentration time of 3 min, a linear relation was observed between the peak height and copper concentration in the range 32 and 750 ng/mL. The equation ($n = 6$) of the regression line obtained was:

$$I(\mu A) = 28.17[\text{copper}]_{\mu g/mL} + 0.38$$

The correlation coefficient for this plot was equal to 0.9991. The detection limit, determined by the 3σ criterion, was 9.5 ng/mL, where "σ" corresponds to the standard deviation of the parasite signal obtained after 11 injections of blanks. The repeatability of the measurements, expressed as the relative standard deviation of 11 replicate injections of solutions containing 100 ng/mL of copper was 2.1 %. This value reflects the precision of the combined preconcentration/elution-electrochemical detection process. Under the selected experimental conditions, the sample rate was found to be 15 h^{-1}.

In order to check the analytical application of the present method validation was achieved by analysis of certified reference materials (CRM). The CRM GBW 08607 "Metal Element in Water" from Laboratory of the Government Chemist, LGC, UK, which contains a certificate copper concentration of 1.02 μg/mL was diluted and analyzed by the proposed method. The recovery obtained was 101.96 ± 1.38 %, indicating that the method can be applied to water analysis.

Determination of copper was then carried out in a river water sample (collected in August 1999, Colorado River, Metropolitan region, Chile). The concentration found was: 45 ± 3 ng mL^{-1} which was consistent with that determined by AAS. The recovery for an addition of 100 ng mL^{-1} of copper in this sample was 96 ± 2 %.

All these analytical features indicate that the proposed flow through cell is reliable and sensitive for continuous polarographic determination of low concentrations of copper. The analytical
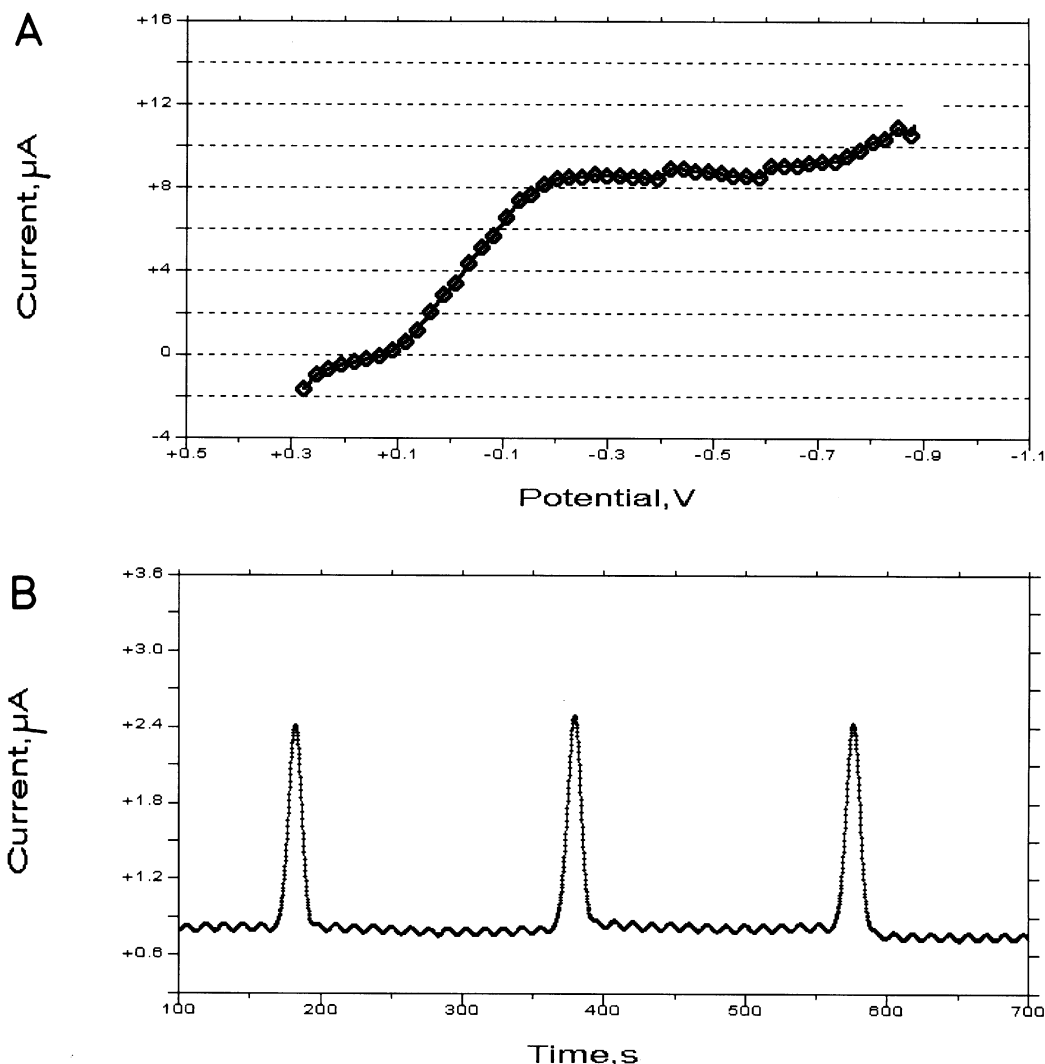
Fig. 2. Types of analytical signals obtained. A) Voltammetric signal obtained under continuous flow-stopped flow mode. B) Amperometric FIA-signals obtained under continuous flow mode, $E = -0.6$ V.

responses do not present irregularities associated with the use of a DME together with a mercury pool, as was observed previously in cell designs based on the use of both mercury electrodes simultaneously [12, 13].

Experimental

Chemicals: All chemicals used, except as noted, were of analytical reagent grade. Deionized water (NANOpure ultrapure water system, Barnstead) was used throughout. Standard solutions of copper were prepared by dilution of aqueous 1000 mg/L stock solution. A 1 M Nitric acid solution was used as carrier acting as supporting electrolyte and eluting solution. All solutions (samples and carrier) were deoxygenated with oxygen-free nitrogen before aspiration starts by using a similar assembly to that described previously [13]. An iminodiacetic acid chelating resin Chelex-100 was used for preconcentration of the analyte from the water samples.

A CV-50 W voltammetric analyzer (Bioanalytical Systems, Lafayette, IN, USA) was used as potentiostat/amperometric detector.

The flow injection manifold consisted of a four channel peristaltic pump (Masterflex 7523-37 digital console drive containing a Masterflex 7519-20 cartridge pump; Cole Palmer Instrument Company), a Rheodyne (Model 5041) injection valve and a microcolumn made of Tygon tubing (1.5 cm long, 2.5 mm i.d.) were also used. The features of the cell were described previously [1, 2].

Table 1. Study of Variables.

Variable	Studied range	Selected value
FIA		
Preconcentration time [min]	1–6	3
Delay coil (L) [cm]	10–200	20
Flow rate (q) [mL min^{-1}]	0.5–3.5	2.4
Delay time [s]	0–22	0
Flow cell		
Cell volume [μL]	30–220	39
Potential ($-E$) [V]	0–0.9	0.6
Drop Time (t) [s]	2.4–10	7.5

Procedure: The Chelex-100 microcolumn was located in the loop of the valve, in which the analyte was preconcentrated by passing the sample solution through the loop for a preset interval (T_p), at a flow rate of $3.0 \, mL \, min^{-1}$. The carrier solution was 1 M nitric acid. After the preconcentration time, which depends on the concentration of the analyte in the samples, valve *IV* was switched to the injection position allowing the nitric acid solution to pass through the microcolumn at a flow rate of $2.4 \, mL \, min^{-1}$. The concentrated copper was eluted quantitatively from the column and conduced to the cell. When the eluted zone arrives to the cell the flow was stopped in order to achieve voltammetric measurements. Contrarily, if normal FIA determinations are required, the amperometric transient signals were recorded by applying to the cell a potential of $-0.6 \, V$.

Acknowledgement

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