

FLOW INJECTION CONTINUOUS LIQUID-LIQUID EXTRACTION
USING A HOLLOW FIBER MEMBRANE SEPARATOR FOR
DETERMINATION OF COPPER IN WATER

Keywords: Flow injection, continuous liquid-liquid extraction, hollow fiber, copper, water.

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ABSTRACT

A simple flow injection photometric method for the determination of copper was developed based on the formation and liquid-liquid extraction of the analyte-bathocuproine-perchlorate ternary complex. The analytical reaction of complex formation is integrated with the continuous liquid-liquid extraction procedure. A hollow fiber-type membrane separator was specially constructed for the determination. The analytical properties like sensitivity, precision, accuracy and rapidity were evaluated. The sensitivity of the method depends on the injection volume. By using an injection volume of 0.6 ml, the detection limit (3σ) found

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was 15 ng ml⁻¹ copper, with a determination range of 48 - 3000 ng/ml. The repeatability of the method, expressed as the relative standard deviation, was in all instances less than 3.0%. The sampling rate was of 20 h⁻¹. The accuracy of the method was tested with certified reference materials, and the mean error was calculated to be less than 5 %. The method was successfully applied to the determination of copper in river water.

INTRODUCTION

The incorporation of separation techniques in flow injection analysis had contributed considerably to the enhancement of analytical features in a large number of determinations, not only in the enhancement of sensitivity and selectivity but also in the improvement of precision, sample throughput and other features of analytical methods. On the other hand, from a practical point of view, by using FIA the time-consuming manipulation required in manual extraction procedures, which in addition are more subjected to contamination problems, are avoided.

When the continuous extraction system involves the mixing of both liquid phases providing alternate and regular segments of the immiscible liquids in a single channel, the manifold necessary must include an efficient phase separator which provides at least one channel of the outlet stream containing only one phase, thus avoiding interference with the detection process. In this context, a number of possibilities has been described¹ and in practice it has been demonstrated that membrane separators have been more accurate than T-shaped separators. Among the different possibilities reported in the literature relative to membrane phase separators, the most widely used alternative has been the sandwich-type membrane separator. This type of separator has been involved in the indirect determination by FIA-AAS of anionic surfactant in wastewater,² in continuous solvent extraction in a closed-loop system,³ and also in other

analytical applications which have been reviewed by Valcárcel and Luque de Castro.¹ In this work we considered to use a hollow fiber-type separator which has been less exploited from an analytical point of view. Recently, a miniaturized supported hollow fiber liquid membrane device was developed for sample preparation and connected on-line to a liquid chromatograph⁴. In the context of liquid membrane technology for extraction in industrial processes, Valenzuela et al.⁵ recently studied the transport of copper from El Teniente's mine waters (VI Region, Chile) by solvent extraction in a membrane tubular extractor using a hollow fiber system. Previously, Kim⁶ and Matsumoto et al.⁷ studied the extraction efficiency of tubular reactors containing a package of hollow fibers.

Metals are widely and heterogeneously distributed in the environment, depending both on natural conditions and human activity. Because several countries, among them central Chile, are characterised by large copper mining activities, variable levels of copper are expected to be found in different ecosystems. Consequently, analytical methods which can be an alternative to other more expensive instrumental methods and which could be able to determine in a reliable way this parameter in wide concentration levels are in great demand.

This paper describes a simple, precise and accurate method for determination of copper in waters which involves the formation of the copper-bathocuproine-perchlorate ternary complex that is integrated to the continuous liquid-liquid extraction into dichloroethane and the subsequent photometric detection is performed at 478 nm. The method was validated by analysis of certified reference materials and it was applied to the determination of copper in river water.

EXPERIMENTAL

Instruments and apparatus

Absorbances were measured in the organic phase at 478 nm with a Shimadzu UV-160 spectrophotometer equipped with a Hellma 178.010-OS flow

cell. An Orion Research model 701 digital ion analyzer with glass and saturated calomel electrodes was used for pH measurements. Two four-channel Ismatec fixed-speed peristaltic pumps fitted with Tygon tubes, displacement bottles for pumping 1,2-dichloroethane, Teflon flow injection tubes of 0.56 mm i.d., a Rheodyne 5041 injection valve, and two Teflon[®] PTFE 3-way connectors were also used. The hollow fiber-type membrane separator was as follows: a microporous polytetrafluoroethylene hollow fiber membrane (Japan Gore Tex) 75 cm long with an inner diameter of 1mm; outer diameter 1.8 mm and 2 μ m as maximum pore size was inserted into a helically coiled glass tube of 2.0 mm inner diameter. The coiled glass contains one inlet and one outlet for flow of the DCE acceptor stream. The segmented phase flows through the hollow fiber membrane.

Reagents

All chemicals used were 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 solutions. A 5×10^{-3} M solution of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) was prepared in dichloroethane (DCE). A buffer/reducing agent solution was prepared daily containing a Britton-Robinson buffer system of pH=10 and hydroxylamine Chlorhydrate (1 %). The Britton-Robinson buffer was prepared by diluting 2.3 ml acetic acid (100%), 2.7 ml phosphoric acid (85%) and 0.8 g of boric acid in 1000 ml of water. To an aliquot of this solution was added 0.2 M NaOH until a pH of 10 was reached. A 1 M sodium perchlorate solution was also used acting as carrier solution and counter ion.

Manifold and procedure

The schematic diagram of the proposed FIA system is depicted in figure 1. The manifold contained one injection valve with an injection volume of 0.6 mL.

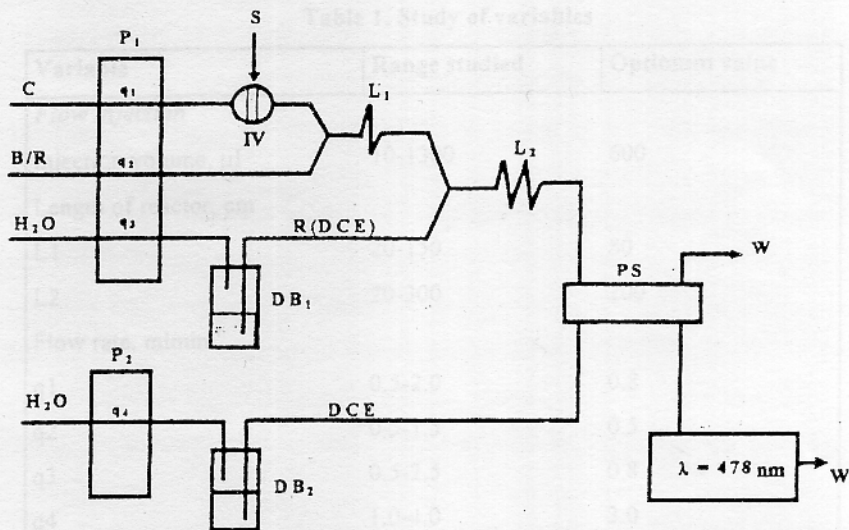


Figure 1. Manifold for implementation of the method. S denotes the sample, C carrier solution, B/R buffer reductor mixture, P peristaltic pump, q flow rate, IV injection valve, R(DCE) reagent dissolved in dichloroethane, DB displacement bottle, L reactor, PS phase separator, W waste.

The sample zone injected into a sodium perchlorate carrier stream is merged and mixed in L_1 (80 cm, 0.56 mm i.d.) with the buffer/reducing agent system of pH 10 at a flow rate of 1.3 ml/min, and the continuous liquid-liquid extraction integrated with the analytical reaction between Cu(I), perchlorate and bathocuproine (R) occurred subsequently in L_2 (200 cm, 0.56 mm i.d.) at a flow rate of 2.1 ml/min (flow rate of the organic phase 0.8 ml/min). After this process the sample zone reached the phase separator unit in which the coloured complex contained in the organic phase passes through the membrane to reach the acceptor phase of pure DCE, while it is kept in the stopped flow mode. After 120 sec. the flow of the acceptor stream is restarted and the reaction product is conducted to the spectrophotometric detector. The signal obtained at 478 nm was used to calculate the copper content in the sample.

RESULTS AND DISCUSSION

Some batch spectrophotometric procedures to determine metals using ferriin-type reagents have been previously described by our team.⁸⁻¹¹ This basically has involved the formation of the ternary complex under the appropriate physicochemical conditions, the manual conventional extraction into DCE and the subsequent analytical measurement by using both classical and derivative spectrophotometry. Recently, we automated partially this batch procedure by using flow injection analysis and derivative spectrophotometry as detection.¹² The method was successfully applied to the simultaneous determination of iron and cobalt in mixtures, however the sensitivity was limited because that method does not include a preconcentration step. In that case a soluble version of the ferriin-type reagent (ferrozine) was used.

One of the aims of the present work was to include a separation process with the purpose to increase both sensitivity and selectivity of this type of analytical spectrophotometric method. The chemical system used in this work involves the ternary complex formation between the Cu-bathocuproine binary complex and perchlorate or other anion present in the buffer system (borate, acetate, phosphate) which is extractable in DCE. As bathocuproine is dissolved in DCE and different anions are present in the aqueous phase, the analyte has to be transferred to the organic phase as the ion pair Cu-anion to form alternatively the ternary complex Cu(I)-bathocuproine-anion directly in the bulk of the organic phase or at the liquid-liquid interface before reaching the bulk of the organic phase. In any case, the separation of the analyte is integrated with its reaction of ternary complex formation.¹³⁻¹⁵

By using the manifold depicted in figure 1, the analytical signal obtained appears as a typical flow injection peak. The chemical and flow injection variables were optimized by the univariate method, and the best analytical conditions for the determination of copper were selected. Table 1 shows the optimum values found for the variables studied.

Table 1. Study of variables

Variable	Range studied	Optimum value
<i>Flow injection</i>		
Injection volume, μl	10-1300	600
Length of reactor, cm		
L1	20-150	80
L2	20-300	200
Flow rate, mlmin^{-1}		
q1	0.5-2.0	0.8
q2	0.5-1.5	0.5
q3	0.5-2.5	0.8
q4	1.0-4.0	3.0
Phase separator length, cm	10-100	75
<i>Chemical</i>		
Bathocuproine conc., mM	0.1-1.0	0.8
NaClO_4 conc., M	0.01-2.5	1.0
Hydroxylamine conc., %	0-2.5	1.0
PH	0.5-13	10

The sample volume is selected depending on the concentration of the copper in the samples. However, for optimization studies 0.6 ml of sample was used. This volume allows the determination of copper between about 50 to 3000 ng/ml. For lower concentrations the sample volume must be increased, but in detriment of the sampling frequency.

The optimum lengths of the reactors are $L1 = 80$ y $L2 = 200$ and the inner diameter of these tubes is 0.56 mm. The optimum values for length of the reactors were selected in favour of obtaining the maximum sensitivity for the

analyte, taking into account that the reduction of copper by hydroxylamine is very fast and the integrated step extraction/complex formation demands a higher development time. Consequently the signal was more sensitive to the length of L2 than of L1. In the case of L1, the height of the signal is maintained constant until reaching 80 cm, then begins to decay due to the physical dispersion of the sample zone into the manifold. With respect to L2, a plot of peak height vs the extraction coil length showed that the FIA signal increased with the increasing extraction coil length up to 200 cm; in the range 200-250 the peak height was not affected by the length of the extraction coil, whereas at larger values the signal started to decrease slightly.

The effect of the flow rate was also studied for the organic and the aqueous phase. In general, increasing flow rates of any of the channels decreased the absorbance of the signal because the residence time of the sample zone inside the phase separator decreased concomitantly, making the mass transport through the membrane less favourable. In any case, in order to increase the preconcentration factor, the flow of the organic phase was kept slower than that for the aqueous phase.

It was observed that an increment in the length of the separator favours the sensitivity of the signal but decreases the sample rate. This effect occurs because the residence time of the analyte in the separator is longer, resulting in more complete extraction and transfer through the membrane. A separator containing a hollow fiber 75 cm long was selected as a compromise between sensitivity and sample rate. In that condition the volume of the acceptor stream was approximately 400 μl , which indicates that a preconcentration effect will be observed if the sample volume is larger than 400 μl . It was observed that when the separator unit contains an acceptor stream of pure DCE the transfer process through the membrane was faster, in spite of some dilution of the complex in the organic phase. To avoid an excessive dilution, the acceptor stream was kept in the stopped-flow mode while the segmented phase containing the sample zone

passes through the hollow fiber inserted inside the separator unit. Afterwards, this stream was restarted to drive the reaction product to the detector. In this context, the situation was similar to dialysis, except for the immiscibility of the phases involved. Sahlestrom and Karlberg¹⁶ proposed a similar system in which a membrane sandwich-type module received and allowed the streams of the two immiscible phases to drive it independently. The difference with the present system is that, in the case of Sahlestrom and Karlberg, the analyte or its reaction product were transferred across the membrane without a previous contact of the phases, which is key in the present method, thus avoiding the chief shortcoming related to low separation already commented on by Valcarcel and Luque de Castro.¹

As it is common in this type of analytical reactions, the signal was very sensitive to the chemical variables. The concentration of bathocuproine was varied from 0.1 to 1.3 mM. The baseline was not affected between this range, it always was stable because the reagent dissolved in DCE is colorless. Contrarily, the FIA signal increased rapidly until reaching a constant value at about 0.7 mM bathocuproine. On the other hand, the signal increased rapidly with the hydroxylamine concentration reaching a constant value when its concentration was over 0.8%. Hence, concentrations of 0.8 mM and 1% were selected for bathocuproine and hydroxylamine, respectively. In the case of perchlorate, the peak height was almost constant between the concentration range 0.5 to 2.0 mM.

The plot of analytical signal vs pH shows a plateau over the range 5.5-11.5. Hence, the pH value was kept at 10 by using a Britton Robinson buffer.

Features of the method and application

Table 2 shows the analytical features of the method obtained under the selected experimental conditions.

In order to investigate the analytical application of this method, the effect of several foreign ions that usually are present in natural water matrix were

Table 2. Features of the method

Analytical Feature	
Limit of detection, ngml^{-1}	15
Determination range, ngml^{-1}	48-3000
Repeatability ($n=11$), RSD%	
200 ngml^{-1}	2.24
1000 ngml^{-1}	1.62
Sample throughput	20

Table 3. Determination of copper in certified reference materials

Certified Reference Material	Determined Conc., μgml^{-1} ^(c)	Certified Conc., μgml^{-1}
Metal Element in water. GBW 08607 ^(a)	1.03 ± 0.09	1.02 ± 0.01
HPS Certified waste water. CWW-TM D ^(b)	1.04 ± 0.03	1.000 ± 0.005

^(a) From Laboratory of the Government Chemist, LGC, UK

^(b) From High Purity Standards, USA

^(c) Mean of five determinations.

examined by analysis of synthetic samples containing: 300 ngml^{-1} Zn, 300 ngml^{-1} Cu, 300 ngml^{-1} Fe, 50 μgml^{-1} Ca, 50 μgml^{-1} Mg, and 0.5 % NaCl. The recovery was 104.3 ± 2.8 %. Validation of the method was achieved by analysis of certified reference materials (table 3).

Determination of copper was then carried out in a river water sample (Collected on April 1998, Los Almendros River, Chile). The concentration found was: $1.01 \pm 0.02 \mu\text{gml}^{-1}$ which was consistent with that determined by AAS ($0.97 \pm 0.04 \mu\text{gml}^{-1}$).

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