Flow system with in-line separation/preconcentration coupled to graphite furnace atomic absorption spectrometry with W–Rh permanent modifier for copper determination in seawater

Zilvanir F. Queiroz a, Fábio R.P. Rocha b, Günter Knapp c, Francisco J. Krug d,∗

a Instituto de Química de São Carlos, Universidade de São Paulo, P.O. Box 390, 13560-970, São Carlos, SP, Brazil
b Departamento de Química, Universidade Federal de São Carlos, P.O. Box 626, 13560-970, São Carlos, SP, Brazil
c Department of Analytical Chemistry, Graz University of Technology, A-8010 Graz, Austria
d Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Caixa Postal 96, 13400-970, Piracicaba SP, Brazil

Received 18 July 2001; received in revised form 29 April 2002; accepted 7 May 2002

Abstract

A flow system was coupled to a graphite furnace with a platform coated with tungsten–rhodium permanent chemical modifier for in-line separation and preconcentration of copper by employing a minicolumn loaded with 1-(2-tiazolylazo)-2-naphthol (TAN) immobilized on C18-bonded silica fixed in the tip of the autosampler arm. Elution was made by sampling 35 μl of 0.50 mol l⁻¹ HCl with further delivering into a coated platform. Remarkable improvements in both selectivity and sensitivity were observed. Copper(II) was effectively separated from solutions containing up to 20 g l⁻¹ Na⁺; 10 g l⁻¹ K⁺, Ca²⁺ and Mg²⁺; 1.0 g l⁻¹ Fe³⁺ and Zn²⁺. For a sample flowing at 3.0 ml min⁻¹ and a loading of 60 s, the detection limit was estimated as 5 ng l⁻¹ Cu(II) at the 99.7% confidence level, and an enrichment factor of 33 was calculated. Coefficient of variation was estimated as 4% for a 0.30 g l⁻¹ copper solution (n = 20). The W–Rh permanent chemical modifier was used to improve system stability, analytical performance and atomizer lifetime. More than 1500 firings were carried out with the same atomizer without significant variations in sensitivity and precision. On account of the reagent immobilization, its consumption was lower than 0.2 g per determination. In addition, TAN purification was unnecessary. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Copper; Seawater; Electrothermal atomic absorption spectrometry; Permanent chemical modifier; Separation; In-line preconcentration

1. Introduction

Although very low detection limits have been reported in electrothermal atomic absorption spectrometry (ETAAS), the direct determination of trace metals in seawater is difficult even with sophisticated background correctors and/or chemical modifiers. Because the low concentrations of copper in seawater and the effect of the sample matrix, separation of the analyte and preconcentration are often required [1]. Among the several methods used to separate the analyte from the matrix, in-line procedures with sorption methods have been preferred with ETAAS [1–3]. Many different types of chelating resins have been developed for trace metal determinations [4,5] and flow techniques with minicolumns are of increasing interest due to their simple design and capability of automation [6–8]. Continuous flow techniques with large eluent volumes can not be used in furnace atomic absorption
spectrometry (FAAS). On the other hand, for ETAAS, a discrete elution step with a small volume, in general lower than 100 μl, need to be applied. Depending on the system design, there is no limitation in terms of sampling rate, because the preconcentration can be accomplished in parallel and synchronized with the atomization process in a discontinuous mode [9]. From already proposed designs, minicolumns with the solid support inserted in the tip of the autosampler arm has been successfully employed [7,10,11].

Solid-phase sorption has already been proposed for in-line separation and preconcentration of copper from seawater [7,10–16]. However, most of the suggested procedures require the formation of complexes in solution and their retention on a solid-phase [7,10,12,14,15]. Thus, continuous reagent purification is required for reducing the blank values. Cathodic stripping voltametry was proposed for copper determination in unpolluted seawater using a combination of dimethylglyoxime and 8-hydroxyquinoline [17]. This method presents enough sensitivity, but the seawater samples need UV-digestion during 3 h for avoiding interferences caused by natural organic compounds.

Chan and Huang [18] reported that copper in seawater can be determined using a transversely heated graphite furnace with Zeeman-effect background corrector. However, a purification step was required to remove trace metals from the chemical modifier (12.5% (w/v) NH4NO3). Although a loss in sensitivity of about 50% is expected when Zeeman-effect background correction is applied [19], the detection limit was estimated as 0.06 μg l−1.

In electrothermal atomic absorption spectrometry, the use of modifiers has become an essential part of the stabilized temperature platform furnace (STPF) concept. Usually, the modifier is added prior to or together with each sample injection. This approach hinders the use of minicolumns in the autosampler tip and increases the analysis time. These limitations may be overcome by placing the modifier on the graphite platform in a permanent form. This consists in an important and recent development in chemical modification techniques, which has increased sample throughput and reduced reagent blanks. The use of a permanent modifier avoids the generation of undesirable chemical species during atomization. Moreover, it is compatible with in-line and in situ enrichment [20] and increases the atomizer lifetime. A tungsten-rhodium permanent chemical modifier was proposed to increase the tube lifetime for the determination of Pb, Cd, and Se in waters [21].

The present work describes a flow system for in-line separation and preconcentration for the determination of copper in seawater by graphite FAAS (GFAAS). A pyrolytic graphite platform coated with a tungsten-rhodium permanent chemical modifier was employed for improving the analytical performance and atomizer lifetime. A minicolumn loaded with 1-(2-thiazolylazo)-2-naphthol (TAN) immobilized on C18-bonded silica [22] was used for copper retention.

2. Experimental

2.1. Samples and reagent solutions

All solutions were prepared with analytical grade chemicals and distilled/deionized water further purified with a Milli-Q Plus system (Millipore, Bedford, USA) to 18 mΩ cm−1. All vessels, autosampler cups and glassware were soaked with 10% (v/v) HNO3 for 24 h, rinsed three times with water, dried and stored in a Class-100 laminar flow hood. All solutions were stored in polypropylene bottles.

Nitric and hydrochloric acid were purified in quartz sub-boiling stills (H. Kürner, Rosenheim, Germany) [23]. A 1.000 g l−1 stock solution was prepared from metallic copper dissolved in nitric acid. Reference solutions within 0.100 and 1.000 μg l−1 in 0.10% (v/v) HNO3 were prepared by stepwise dilution.

TAN solution was prepared by dissolving 1.0 mg of 1-(2-thiazolylazo)-2-naphthol (Sigma) in 1 ml of ethanol and completing the volume to 100 ml with a 5% (v/v) Triton X-100 solution. The buffer was a 0.50 mol l−1 hexamethylenetetramine (Merck) solution, purified in a column (5 cm long, 50 mm i.d.) packed with cation (Bio-Rad, AG 50W-X8, hydrogen form) and anion (Bio-Rad, AG 1-X8, chloride form) exchange resins (200–400 mesh). The pH was adjusted to 6.5 with hydrochloric acid. Optimization of sample flow rate, loading time and complexation pH were carried out with a 0.300 μg l−1 Cu solution.

The effect of concomitants was investigated with solutions containing up to 20 g l−1 Na+ (from NaCl), 10 g l−1 K+ (from KCl), 10 g l−1 Ca2+ (from CaCO3),
$10 \text{ g} \text{l}^{-1} \text{ Mg}^{2+}$ (from MgO), $1.0 \text{ g} \text{l}^{-1} \text{ Fe}^{3+}$ (from Fe$_2$O$_3$) and $1.0 \text{ g} \text{l}^{-1} \text{ Zn}^{2+}$ (from metallic Zn) in $0.10\% \text{ (v/v)} \text{ HNO}_3$. Nitric and hydrochloric acids within $0.10$ and $0.50 \text{ mol} \text{l}^{-1}$ were investigated for elution of copper.

The chemical modifier (1.00 $\mu$g ml$^{-1}$ W) was prepared by dissolving 180 mg of Na$_2$WO$_4 \cdot 2\text{H}_2\text{O}$ (Merck) in 100 ml of water. A 0.800 $\mu$g ml$^{-1}$ Rh solution was obtained by dissolving 30.8 mg of (NH$_4$)$_3$RhCl$_6 \cdot 1.5\text{H}_2\text{O}$ (Johnson Matthey) in 10 ml of 10% (v/v) HCl. A 5.00 g l$^{-1}$ Cu in $0.50 \text{ mol} \text{l}^{-1}$ HCl solution was employed for the evaluation of the tungsten–rhodium deposit as permanent chemical modifier.

Seawater samples were collected in different areas in southwest and northeast of Brazilian shore, filtered through a 0.2 $\mu$m PTFE membrane, acidified to about pH 2 with $1.0\% \text{ (v/v)} \text{ HNO}_3$ and stored in polypropylene bottles (Nalgene, New York, USA). A certified reference material of open ocean seawater (NASS-4, National Research Council, Canada) was used for method validation.

2.2. Instruments and apparatus

A Varian SpectrAA-220 spectrometer (Varian, Australia) equipped with a GTA 110 graphite furnace, furnished with a longitudinally heated plateau graphite tube atomizer (Part No. 6310001100) and pyrolytic platform (Part No. 6310001300) was used. A copper hollow cathode lamp of the same manufacturer was used as radiation source. Data were based on integrated absorbance at 324.8 nm and results were based on at least three replicates.

The flow system (Fig. 1) was similar to that already described [24]. It was designed to perform the analytical cycles involving column conditioning, sample loading, column washing, eluent sampling, copper elution into atomizer and complementary elution. The valve schedule is presented in Table 1.

Initially, the autosampler arm was in the position 1 (Fig. 1). For column conditioning (Table 1, step 1), valve $V_2$ was switched on and the buffer solution flowed through the C$_{18}$-TAN minicolumn. For preconcentration (step 2), valve $V_1$ was switched on and the acidified sample was mixed with the buffer solution.

Fig. 1. Flow diagram of the system designed for separation and preconcentration of copper: C, $C_{18}$-TAN minicolumn coupled to the autosampler of the spectrometer; $V_i$, three-way solenoid valves; S, sample or reference solutions; B, buffer solution ($0.50 \text{ mol} \text{l}^{-1}$ hexamine, pH 6.5); E, eluent ($0.50 \text{ mol} \text{l}^{-1}$ HCl); W, waste; x, y, confluence points. Numbers between parentheses indicate flow rates in ml min$^{-1}$. 
Table 1

<table>
<thead>
<tr>
<th>Step</th>
<th>V1</th>
<th>V2</th>
<th>V3</th>
<th>V4</th>
<th>t (s)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>Column conditioning</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>60</td>
<td>Preconcentration</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>10</td>
<td>Column washing</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>Elution</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>Complementary elution</td>
</tr>
</tbody>
</table>

The status 0 and 1 represent that the valves (Fig. 1) are switched off and on, respectively.

(Fig. 1, confluence x), loading the C_{18}-TAN minicolumn during 60 s, the effluent being directed towards waste (W). For column washing (step 3), valves V1 and V2 were switched off and valve V3 was switched on, allowing the column rinsing with water for removing interfering matrix compounds and excess of reagents. In the step 4, valve V1 was switched off and the autosampler arm was moved to the position 2 to perform the eluent sampling step, which was carried out by sequentially aspirating 15 μl of air (from the empty modifier cup) and 35 μl of 0.50 mol l\(^{-1}\) HCl from an autosampler cup into the column. After, the autosampler arm was automatically moved to the position 3, for delivering the eluate into the tungsten–rhodium coated platform of the atomizer. When the autosampler arm moved back to the resting (position 1), an optical sensor sent the message to start the heating cycle of the atomizer. Finally, a complementary elution with 0.50 mol l\(^{-1}\) HCl (step 5) was performed by switching the valve V4 on, in order to remove any remaining copper from the column. The complementary elution step and another preconcentration cycle can be started simultaneously with the heating cycle of the atomizer.

2.4. Permanent tungsten–rhodium modifier

The modification of the platform surface was performed by sequentially delivering 30 μl of the solutions containing W and Rh. The injected volume was somewhat smaller than that recommended by Lima et al. [21], due to differences in platforms geometry and area, but the heating programs for platform coating were kept the same. The number of 30 μl aliquots of W or Rh was also investigated, so that the total mass of each metal was varied from 30 to 240 μg. For comparison, pyrolysis and atomization temperature curves and addition/recovery experiments were carried out by using pyrolytic carbon platforms with and without the coating.

3. Results and discussion

3.1. Adsorption and elution of copper

TAN has low solubility in water and can be efficiently adsorbed on C_{18}-bonded silica. The immobilized reagent is stable in neutral and acidic solutions [22]. TAN can react with several metallic ions, but the reactivity decreases when the reagent is immobilized, because some groups of the complex agent are used for the immobilization on the solid support. Thus, it is expected a higher selectivity for copper. The reversible retention of copper by TAN immobilized on C_{18}-bonded silica is represented in Fig. 2.

Retention of Cu\(^{2+}\) on C_{18}-TAN was studied at various pH values (4.0–8.5) and no significant variation in the retention efficiency occurred in this range. At constant sample flow rate (3.0 ml min\(^{-1}\)), absorbance signals increased linearly for preconcentration times within 15 and 180 s (\(A = -0.0530 + 0.003275t\) (s), \(r = 0.997\)). For a 60 s preconcentration time and flow rates lower than 3 ml min\(^{-1}\), the absorbance is related to the flow rate (\(q\), ml min\(^{-1}\)) according to the equation:

\[
A = -0.0132 + 0.102q - 0.0162q^2, r = 0.999.
\]

Similar elution efficiencies were obtained for hydrochloric and nitric acids but the sensitivity was higher in the former media (Fig. 3). Although hydrochloric acid can be aggressive to the untreated graphite platform, no significant changes were observed with the modified surface. The effects caused by the concentration and the volume of the eluent were evaluated and it was found that 35 μl of 0.5 mol l\(^{-1}\) HCl was sufficient for elution of ca. 65% of the retained copper.

After modification of the graphite platform surface with W-Rh, the optimum pyrolysis temperature was determined. The heating program for copper in hydrochloric acid is shown in Table 2.

3.2. Tungsten–rhodium coating

Similar sensitivities were found when the mass of Rh varied from 150 to 240 μg (mass of W equal to...
and the decrease of the absorbance signal after 1500 heating cycles indicates the degradation of the graphite tube. The coefficient of variation of measurements carried out with 0.20 μg l⁻¹ Cu (preconcentration mode) was about 4% when the permanent modifier was used and 7% with untreated platforms.

For measurements in hydrochloric acid medium, the maximum pyrolysis temperatures were 1000 and 1300 °C without and with the modifier, respectively. Although this higher pyrolysis temperature was attained with W–Rh coated platform, yielding better analyte/matrix separation, pronounced interferences were yet observed for copper determination in the seawater matrix.

Table 2
Heating program for Cu determination with W–Rh coated platform

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature (°C)</th>
<th>t (s)</th>
<th>Ar flow-rate (ml min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>30.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>10.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>170</td>
<td>20.0</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>1100</td>
<td>10.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>1300</td>
<td>15.0</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>2200</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>2200</td>
<td>6.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>2600</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>2600</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>
3.3. Selectivity

Sodium, potassium, calcium, magnesium and chloride are the most important concomitants in seawater, which can interfere in the electrothermal atomization of copper. The method described herewith is very selective for copper. Table 3 shows that 20 g l$^{-1}$ Na$^+$; 10 g l$^{-1}$ K$^+$; Cd$^{2+}$ or Mg$^{2+}$; 1.0 g l$^{-1}$ Fe$^{3+}$ and Zn$^{2+}$ did not interfere on the atomization of copper (signal variation lower than 5%). No significant signal variations were observed for solutions containing up to 3.0 g l$^{-1}$ Cl$^-$. Recovery experiments were carried out by spiking known amounts of Cu(II) to the seawater samples, under different conditions (Table 4). Better results were obtained with the W–Rh permanent modifier.

Table 3

<table>
<thead>
<tr>
<th>Concentrants</th>
<th>Without separation (5.0 μg Cu l$^{-1}$)</th>
<th>With separation (0.3 μg Cu l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>$&lt; 2 \times 10^7$</td>
<td>$&gt; 5 \times 10^7$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>$&lt; 2 \times 10^7$</td>
<td>$&gt; 5 \times 10^7$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$&lt; 1 \times 10^7$</td>
<td>$&gt; 3 \times 10^7$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$&lt; 1 \times 10^7$</td>
<td>$&gt; 3 \times 10^7$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$&lt; 1 \times 10^7$</td>
<td>$&gt; 3 \times 10^7$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>$&lt; 1 \times 10^7$</td>
<td>$&lt; 3 \times 10^7$</td>
</tr>
</tbody>
</table>

However, recoveries as low as 43% for direct atomization of 20 μg l$^{-1}$ copper indicate the need for separation. Moreover, this concentration is unusually high for copper in seawater, emphasizing the need of preconcentration. Recoveries between 93.2 and 99.6% were obtained after addition of 50 to 500 ng l$^{-1}$ Cu(II) to seawater samples from polluted and unpolluted places by employing the procedure for in-line separation and the permanent chemical modifier. Absorbance signals for unspiked samples ($n = 3$) were: 0.0082 ± 0.0010 (seawater 1); 0.1076 ± 0.0045 (seawater 2); 0.0386 ± 0.0048 (seawater 3) and 0.0383 ± 0.0040 (seawater 4). Blank signals estimated for a 0.10% (v/v) HNO$_3$ solution were comparable to the signals obtained for unpolluted seawater.

Accuracy of the procedure was assessed with the NASS-4 seawater reference material. The concentration found with the proposed method was 0.230 ± 0.030 μg l$^{-1}$ ($n = 3$) which was in agreement with the certified value 0.228 ± 0.011 μg l$^{-1}$ at the 95% confidence level.

3.4. Analytical figures of merit

The proposed method presented linear response for copper concentrations up to 0.70 μg l$^{-1}$. The detection limit based on 20 preconcentration cycles of a blank consisted of 0.10% (v/v) HNO$_3$ (absorbance =
Table 4
Results for addition/recovery experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Direct atomization</th>
<th>In-line separation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recovery (%) (^a) (without modifier)</td>
<td>Recovery (%) (^a) (with modifier)</td>
</tr>
<tr>
<td>Seawater 1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Seawater 2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Seawater 3</td>
<td>20.0</td>
<td>43.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawater 4</td>
<td>22.6</td>
<td>43.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Determinations obtained in triplicates for two spiked concentrations.

\(^a\) Samples collected from different areas in southwest and northeast of Brazilian shore.

\(^b\) Spiking: \(20.0 \mu\text{g} l^{-1} \text{Cu}\).

pointed out the simplicity of the system design with the minicolumn in the tip of the autosampler arm, which permits to explore the original spectrometer software.

A single minicolumn packed with 9.0 mg of C\(_{18}\)-bonded silica was used for 340 preconcentration cycles without changes in sensitivity. TAN consumption was lower than 0.2 \(\mu\text{g}\) per determination, reducing considerably the production of undesirable wastes. Previous purification of the reagent is not required, because it takes place when the reagent is immobilized on the solid support. When signal decreasing is observed, it is recommended to repeat the immobilization of the reagent. This takes about 20 min, so that the sampling rate is not significantly lessened. After this procedure, similar sensitivities (variations <10\%) were always observed.
4. Conclusions

The association of the flow system for separation/preconcentration with a tungsten–rhodium coated platform resulted in a sensitive and selective analytical procedure for Cu determination. The proposed procedure is suitable for the accurate determination of Cu in unpolluted seawater, without previous sample treatment.

Acknowledgements

The authors acknowledge the Brazilian agencies CAPES, FAPESP, CNPq and PRONEX/CNPq by the grants and financial support. E.A.G. Zagatto and E.N.V.M. Carrilho are thanked by critical comments. F. Barbosa Jr. is thanked for his help in some experiments.

References