Nickel and zinc determination by flow-injection solid-phase spectrophotometry exploiting different sorption rates

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Received 25 October 1999; received in revised form 20 December 1999; accepted 21 December 1999

Abstract

Flow-injection solid-phase spectrophotometry is applied for sequential determination of nickel and zinc, exploiting their different sorption rates on 1-(2-thiazolylazo)-2-naphthol (TAN) immobilized on C18-bonded silica. The Zn(II) sorption rate on the solid support is constant for flow rates ranging from 0.70 to 2.2 ml min⁻¹, but for Ni(II) the sorption rate decreases with increasing flow rate. A flow system was designed to perform sequential measurements at two different flow rates (0.85 and 1.9 ml min⁻¹). The absorbance was measured at 595 nm, where both TAN-immobilized complexes showed maximum absorption. The coefficients of variation were estimated (n = 10) as 1.1 and 1.7% (at 1.9 ml min⁻¹) and 1.2 and 2.1% (at 0.85 ml min⁻¹) for zinc and nickel, respectively. This strategy was applied to determine zinc and nickel in copper-based alloys and the results agreed with certified values at the 95% confidence level. The sample throughput was estimated as 36 h⁻¹. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Solid-phase spectrophotometry; Sorption rates; Flow-injection analysis; Nickel; Zinc; Copper-based alloys

1. Introduction

Since flow injection analysis (FIA) was introduced, several procedures to determine more than one analyte at a time have been proposed [1–3]. Ingenious flow networks exploiting different strategies, such as splitting zones [4], sandwich technique [5], gradient exploitation [6] and binary sampling [7] were designed with this aim. When more than one component needs to be determined by FIA, the flow manifold can become complex, particularly when two or more reagents per analyte are required [1–3]. Otherwise, when only one chromogenic reagent is employed, the complexity is transferred to the detection or data treatment steps or both.

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In flow-injection solid-phase spectrophotometry (FI-SPS), the solid support is placed into the light path of the flow cell and detection is performed simultaneously with the analyte retention. Since the chromogenic reagents can be immobilized on the solid support, the manifolds are usually simpler than those designed for measurements in solution. In addition, selectivity can be increased by choosing the solid support and the bonded reagent to implement different reaction and retention rates for the analyte and concomitant species.

An interesting trend in FI-SPS is the determination of multicomponents, matching the characteristics of SPS [8,9] such as high sensitivity and low reagent consumption with the advantage of performing the determination of more than one species with the same flow manifold. The same approaches employed for the spectrophotometric determination of multicomponents in solution [1–3] can be applied for measurements in the solid-phase. However, the proposed procedures have exploited mainly multiwavelength detection with mathematical data processing [10–13].

Nickel and zinc are important components in copper-based alloys, affecting the physical characteristics of the material [14]. These metal ions react with 1-(2-thiazolylazo)-2-naphthol (TAN) immobilized on C18 bonded silica at near pH ranges, yielding complexes with close absorption maxima. However, while zinc retention is practically unaffected by the flow rate, the efficiency of nickel retention is remarkably affected by this parameter. In this work, a flow manifold is presented to perform sequential measurements at two flow rates and the different retention efficiency of the metal ions on C18–TAN were exploited for the determination of zinc and nickel in copper-based alloys.

2. Experimental

2.1. Apparatus

The set up consisted of a Cary 1E spectrophotometer (Varian, Australia) with a homemade 78 µl flow cell with 1.0 mm optical path [9]. A Reglo peristaltic pump (Ismatec, Switzerland) equipped with tygon tubes was employed as propeller device. The flow manifold was assembled with a homemade sliding-bar commutator [15], employing sample loops and flow lines of 0.8 mm i.d. polyethylene tubes.

2.2. Reagents and solutions

All solutions were prepared with analytical grade reagents and freshly distilled deionized water. Zinc and nickel reference solutions (0.10–1.00 mg l⁻¹) were prepared by dilution of 1000 mg l⁻¹ stock solutions. The buffer solution was 1.0 mol l⁻¹ hexamine whose pH was adjusted to 6.2 with hydrochloric acid. TAN solution was prepared by dissolving 1.0 mg 1-(2-thiazolylazo)-2-naphthol in 1 ml ethanol and completing the volume to 100 ml with a 5% (m/v) Triton X-100 solution. As the TAN reagent shows low solubility in water, it is necessary the addition of the Triton X-100 surfactant to maintain the reagent in solution. Hydrochloric acid solutions (0.1–0.5 mol l⁻¹) were prepared by appropriate dilutions. TAN reagent was immobilized on C18-bonded silica (60–100 µm) obtained from Sep-Pak cartridges (Waters) and employed as the solid support. Solutions containing 5% (m/v) ascorbic acid and 5% (m/v) sodium thiosulfate were employed for the masking of copper.

2.3. Sample preparation

A mass of 100 mg of each alloy was placed in conical flasks and 1.0 ml concentrated nitric acid plus 0.2 ml concentrated hydrochloric acid were added. The flasks were warmed to complete dissolution. After cooling, the solutions were transferred to 250 ml volumetric flasks and the volumes were completed with water. The CEPED 2150 sample was transferred to a 50-ml volumetric flask. After dilution, 5 ml sample aliquots were transferred to 25 ml volumetric flasks and then 2 ml ascorbic acid solution, 5 ml hexamine buffer solution pH 6.2 and 2 ml thiosulfate solution were added. The volume was then made up with water. Zinc and nickel reference solutions were processed in the same way.
2.4. Flow diagram and procedure

The flow cell was filled with ca. 35 mg of C_{18} beads and glass wool was placed at the inlet and outlet of the cell to avoid removal of the solid-phase by the carrier stream. The chromogenic reagent was immobilized on the solid support by pumping the TAN solution through the cell at 1.5 ml min^{-1} for 2 min. Then, the flow cell was sequentially washed with 0.5 mol l^{-1} hydrochloric acid and deionized water to remove the unadsorbed TAN. The flow cell was inserted in the optical path of the spectrophotometer, near the detector window for improved precision [9].

The flow diagram of the system is presented in Fig. 1. An intermittent carrier stream (C_2) and the sample loops L_1 and L_2 are employed to perform sequential measurements at flow rates of 1.9 and 0.85 ml min^{-1}. In the position shown, the buffered sample inside the loop L_1 is transported by the carrier at 1.9 ml min^{-1} (C_1 + C_2) towards the flow cell. Simultaneously, the loop L_2 is filled with another sample aliquot. By sliding the commutator central bar, the carrier C_2 is directed towards its storing vessel and the sample loop L_2 is inserted into the analytical path. The sample aliquot is transported by the carrier C_1 towards the flow cell at 0.85 ml min^{-1}. Signals due to zinc and nickel complexes retained on the solid support are measured at 595 nm. After reaction and detection, the acidic carrier, which also acts as the eluent stream, removes the analytes from the solid-phase, without removing the TAN reagent. In the flow manifold, the flow line B is maintained as short as possible (ca. 20 cm) to minimize the sample dispersion in the carrier/eluent stream.

3. Results and discussion

3.1. Chemical variables

The TAN reagent immobilized on C_{18} was stable in neutral and acidic solutions, allowing the use of the solid phase for at least 1 month. In this period, more than 100 measurements were performed without affecting the retention of the analytes. When necessary, the reagent was immobilized as previously described without removing the solid phase from the flow cell. Zinc(II) and nickel(II) complexes with TAN adsorbed on C_{18} showed absorption maxima at 596 and 594 nm, respectively. Thus, measurements were carried out at the same wavelength using a single beam spectrophotometer.

The effect of the acidity on the reaction and retention of Zn(II) and Ni(II) on C_{18}–TAN was studied within the range of pH 4.5–8.5. No significant variation in the retention efficiency was observed for the 5.8–6.7 pH range for Zn(II) and for the 5.8–7.3 pH range for Ni(II). Thus, in further experiments, a hexamine buffer solution of pH 6.2 was previously added to the sample solutions.

Hydrochloric acid solutions with concentrations ranging from 0.05 to 0.5 mol l^{-1} were evaluated as eluents. Transient signals sequentially obtained at the flow rates of 0.85 and 1.9 ml min^{-1} are shown in Fig. 2. The acid concentration affected directly the analyte removal efficiency and inversely the signal magnitude for both species. Thus, a 0.20 mol l^{-1} HCl solution was chosen as a compromise between sensitivity and sample throughput. The removal of the TAN reagent at this eluent concentration was not perceptible and the baseline was stable during the measurements.

For copper-based alloys, under the employed conditions, interference was observed only for...
copper. This drawback was overcome by reducing the Cu(II) ions using ascorbic acid and complexing the reduced ions with thiosulfate [16].

3.2. Hydrodynamic variables

The flow system was designed to carry out sequential measurements at two different flow rates (0.85 and 1.9 ml min\(^{-1}\)). It was employed a sliding bar commutator that allowed the insertion of sample aliquots at both rest positions (Fig. 1). Thus, the effect of changes in the solid-phase on the accuracy was avoided and sample throughput was improved. The removal of the analytes from the solid-phase was performed after each measurement to avoid the saturation of the adsorption sites that could affect the sensitivity and the linear range. This was carried out by employing the eluent solution as carrier. Thus, a transient signal was obtained after each sample insertion, due to analyte retention in the buffered sample zone and removal by the acidic carrier.

The effect of the flow rate on the retention of zinc and nickel ions is shown in Fig. 3. While the zinc signal was practically unaffected by the flow rate within the 0.70–2.2 ml min\(^{-1}\) range (signal variation lower than 6%), for nickel the retention is remarkably affected by the flow rate (Fig. 3b). These results are caused by the differences in the rates of reaction and retention of these ions on the C\(_{18}\)–TAN support. Flow rates of 0.85 and 1.9 ml min\(^{-1}\) were chosen to emphasize the differences in the sorption rates of the analytes without impairing sample throughput. Flow rates higher than 2.2 ml min\(^{-1}\) produced fluid leakage in the joints due to the increase in backpressure.

Considering that the same solution is employed as carrier and eluent stream, it is important to minimize the sample dispersion in the carrier. For this reason, the flow line B (Fig. 1) was maintained as short as possible (ca. 20 cm). Sample volume is other important parameter, and its effect is shown in Fig. 4. The signal magnitude increases with the sample volume due to the increase of the analyte amount and of the retention efficiency, since the sample dispersion in the acidic carrier is minimized. For additional measurements, the sample volume was maintained as 625 \(\mu\)l.
3.3. Features of the method

The ratio of the analyte concentrations in the sample can affect the precision and the accuracy of the results obtained by the proposed procedure. This hindrance is commonly observed in analytical methods based on the additive property of the absorbance. In solid-phase spectrophotometry, this drawback can be more critical because the number of sorption sites can be limited. However, when the sum of the analyte concentrations was lower than $2.5 \, \mu\text{g ml}^{-1}$, the absorbances due to zinc(II) and nickel(II) complexes were additive at both flow rates. The results shown in Table 1 demonstrate that synergistic effects were not observed for the concentration range evaluated (zinc/nickel ratio from 0.3 to 6.2). Similar results were obtained for the flow rate of $1.9 \, \text{ml min}^{-1}$ showing the viability of the proposal for the determination of zinc and nickel in copper-based alloys.

The absorbance signals varied linearly with the concentration of zinc(II) plus nickel(II), and equations obtained by linear regression were employed to determine the concentration of both analytes. The analytical curves obtained at flow rates of $1.9$ and $0.85 \, \text{ml min}^{-1}$ were

$$A_{1.9} = (0.161 \pm 0.002) C_{\text{Zn}} (\mu\text{g ml}^{-1}) + (0.050 \pm 0.001) C_{\text{Ni}} (\mu\text{g ml}^{-1})$$

and

$$A_{0.85} = (0.187 \pm 0.001) C_{\text{Zn}} (\mu\text{g ml}^{-1}) + (0.132 \pm 0.003) C_{\text{Ni}} (\mu\text{g ml}^{-1})$$, respectively. The confidence intervals presented for the slopes were estimated at 95% confidence level and the linear regression coefficients were both of 0.999. The coefficients of variation were estimated ($n = 10$) as 1.1 and 1.7% (at $1.9 \, \text{ml min}^{-1}$) and 1.2 and

### Table 1

<table>
<thead>
<tr>
<th>$\text{Zn} (\mu\text{g ml}^{-1})$</th>
<th>$\text{Ni} (\mu\text{g ml}^{-1})$</th>
<th>Difference (%)</th>
</tr>
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<tbody>
<tr>
<td>0.30</td>
<td>0.30</td>
<td>5.4</td>
</tr>
<tr>
<td>0.30</td>
<td>1.00</td>
<td>1.2</td>
</tr>
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<td>0.60</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>0.60</td>
<td>0.60</td>
<td>5.9</td>
</tr>
<tr>
<td>0.90</td>
<td>0.30</td>
<td>0.0</td>
</tr>
<tr>
<td>1.00</td>
<td>0.30</td>
<td>7.7</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>–5.5</td>
</tr>
<tr>
<td>1.00</td>
<td>0.50</td>
<td>–4.2</td>
</tr>
<tr>
<td>1.70</td>
<td>0.60</td>
<td>–0.5</td>
</tr>
<tr>
<td>2.00</td>
<td>0.50</td>
<td>8.5</td>
</tr>
<tr>
<td>2.15</td>
<td>0.40</td>
<td>–2.6</td>
</tr>
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</table>

* The flow rate was $0.85 \, \text{ml min}^{-1}$. 

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![Graph](image)

Fig. 4. Effect of the sample volume on the analytical signal for (a) zinc; and (b) nickel. Flow rate, $1.9 \, \text{ml min}^{-1}$.

![Graph](image)

Table 1

Difference between signals obtained for zinc and nickel solutions prepared in conjunct and the sum of signals for single zinc and nickel solutions.

![Graph](image)

Fig. 5. Recorder outputs for (a) zinc; (b) nickel; and (c) zinc plus nickel. Sequential measurements at the flow rates of $1.9$ and $0.85 \, \text{ml min}^{-1}$ were carried in duplicate. Numbers indicate concentrations in $\mu\text{g ml}^{-1}$. 

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L.S.G. Teixeira et al. / Talanta 51 (2000) 1027–1033 1031
Mean values and uncertainties \((n = 3)\) for zinc and nickel determination in certified copper-based alloys

<table>
<thead>
<tr>
<th>Reference material(^a)</th>
<th>Zinc (% m/m)</th>
<th>Nickel (% m/m)</th>
</tr>
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<tr>
<td></td>
<td>Certified value</td>
<td>Found</td>
</tr>
<tr>
<td>NIST 52 C</td>
<td>2.12 ± 0.02</td>
<td>2.37 ± 0.06</td>
</tr>
<tr>
<td>NIST 184</td>
<td>2.69 ± 0.01</td>
<td>2.74 ± 0.05</td>
</tr>
<tr>
<td>CEPED 1883</td>
<td>2.22 ± 0.02</td>
<td>1.96 ± 0.07</td>
</tr>
<tr>
<td>CEPED 2150</td>
<td>0.41 ± 0.01</td>
<td>0.45 ± 0.01</td>
</tr>
</tbody>
</table>

\(^a\) NIST, National Institute of Standards and Technology, USA; CEPED, Research and Development Center of Bahia, Brazil.

Certified values for the analyzed copper-based alloys

<table>
<thead>
<tr>
<th>Sample(^a)</th>
<th>Concentrations (% m/m)</th>
</tr>
</thead>
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<td></td>
<td>Cu</td>
</tr>
<tr>
<td>NIST 52C</td>
<td>89.25</td>
</tr>
<tr>
<td>NIST 184</td>
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</tr>
<tr>
<td>CEPED 1883</td>
<td>84.09</td>
</tr>
<tr>
<td>CEPED 2150</td>
<td>89.25</td>
</tr>
</tbody>
</table>

\(^a\) NIST, National Institute of Standards and Technology, USA; CEPED, Research and Development Center of Bahia, Brazil.

2.1 (at 0.85 ml \(\text{min}^{-1}\)) for zinc and nickel, respectively.

The recording of analytical runs obtained for solutions containing zinc, nickel and zinc plus nickel are shown in Fig. 5. From this record, it can be deduced that a throughput of 36 samples per hour can be achieved with good baseline stability. The proposed procedure allowed reduction of both the reagent consumption and the generation of waste. Considering that more than 100 determinations can be performed without altering the sensitivity, a reagent consumption lower than 1 \(\mu\)g per determination was achieved.

The results of determination of zinc and nickel in copper-based alloys by the proposed procedure are shown in Table 2. These results agreed with the certified values presented in Table 3 at the 95% confidence level.

Acknowledgements

The authors acknowledge the financial support of the Brazilian agencies CNPq, FAPESP, FINEP and CAPES.

References