Simultaneous determination of iron and copper in pregnant liquid solutions

C. Paipa, E. Poblete, M. Inés Toral *

Department of Chemistry, Faculty of Sciences, University of Chile, P.O. Box 653, Santiago, Chile

Abstract

A new method for the determination of Fe_{total} and Cu is proposed. The method is based on the formation of the iron and copper complexes with 5-sulfosalicylic acid (SSA), the optimal conditions were found, using SSA 5.1 g L^{-1} in the presence of ammonia 7.5 g L^{-1} (pH = 10). Under these conditions the selected analytical wavelengths were 488.5 and 423.5 nm for the determination of iron and copper, respectively, by using the zero crossing approach. The detection and quantification limits were 0.02 mg L^{-1} and 0.07 mg L^{-1} for iron and 1.14 mg L^{-1} and 3.80 mg L^{-1} for copper. The proposed method was applied to the determination of both analytes in pregnant liquid solutions and the recovery was between 98% and 100% and in all cases the relative standard deviation was minor to 2%.

Keywords: Determination of Fe(II); Fe(III); Total iron and copper; Pregnant liquid solution

1. Introduction

There are many situations where the copper and iron concentration in aqueous solutions has to be determined quantitatively. The leaching solutions from hydrometallurgical processing of copper sulphides have a high concentration of several metallic sulphates (Barret et al., 1993), usually, it is necessary to determine quantitatively the Fe(III), Fe(II), Fe_{total} and Cu concentrations. Depending on the acidity of the solution could happen the hydrolysis and precipitation of Fe(III) compounds such as jarosites MFe_{3}(SO_{4})_{2}(OH)_{6}, where M^{+} = H^{+}, Na^{+}, K^{+}, NH_{4}^{+} or Ag^{+} (Barret et al., 1993; Dutrizac, 1979; Das et al., 1996 and Sasaki et al., 1995). It is important to control the kinetic of Fe(III) precipitates formation, because these compounds could inhibit seriously the reagent and products transport on the surface of the sulphide mineral particles. For this reason, it is necessary to determine quantitatively the iron in presence of copper. Besides, it is important to know iron and copper concentration. Many colorimetric determinations of iron are well known; i.e. Fe(II)-1,10-phenantroline red–orange complex, in this method copper is a serious interferent (APHA, 1998). Recently, it has been described a simple and fast method for the quantitative simultaneous determination of Fe(III) and Fe_{total} with SSA in acid mine drainages (AMD) and other solutions (Karamanev et al., 2002). Recently, this method was compared with Fe-1,10-phenantroline and atomic absorption spectroscopy methods, and an statistical analysis demonstrated that the SSA method gives more exact and representative results (Paipa et al., 2005). In this context, the objective of this work is to develop a simple and rapid method for the simultaneous determination of the Fe_{total} and Cu, in pregnant liquid solutions (PLS) from hydrometallurgical processes.

2. Experimental

2.1. Apparatus

A Shimadzu UV-PC 1603 spectrophotometer with 10 mm cells was used for absorbance measurements and
to obtain derivative absorption spectra on the range between 300 and 700 nm using a smoothing factor of 40,000 and a scale factor of $10^4$. The spectral data are processed by software Shimadzu kit version 3.7 (P/N 206-60570-04).

2.2. Procedure for the determination of Fe(III) at pH = 2

Into a 100 mL volumetric flask, add an aliquot containing less than 2 g of iron and 25 g of copper. Then add 6 mL of 10% (w/v) 5-sulfosalicylic acid solution, stir during 30 s and complete volume with Ultrapure Millipore® Water. Stir during 30 s and measure the absorbance at 500 nm.

2.3. Procedure for the simultaneous determination of total iron and copper

Into a 100 mL volumetric flask, add an aliquot containing less than 2 g of iron and 25 g of copper. Then add 6 mL of 10% (w/v) sulfosalicylic acid solution and 3 mL of 25% (w/v) ammonia solution, stir during 30 s and complete volume with Ultrapure Millipore® Water. Stir during 30 s and evaluate the first derivative spectra for iron and copper at 488.5 nm and 423.5 nm, respectively against a reagent blank.

3. Results and discussion

It is known that SSA forms a yellow complex with Fe(II) and Fe(III) in basic media. The spectral bands have the same shape and high and in both cases these spectra depend on iron concentration, this fact can be attributed to that both complexes have the same molar absorptivity ($5201 \text{ L mol}^{-1} \text{ cm}^{-1}$). Under this condition, the determination of Fe$_{total}$ is possible.

The Cu(II) also forms complex with SSA at pH = 10. As the spectral bands of both complexes are overlapped, the derivative spectrophotometrical technique was adopted, because it permits to solve and determine binary mixture of constituents (Toral et al., 2005). On the other hand, Fe(III) can be determined at pH = 2 and Fe(II) can be determined by difference between Fe$_{total}$ and Fe(III), because the Cu(II)-SSA complex does not absorb on this pH.

3.1. Optimization of chemical variables

A pH study shows that, the SSA forms a red–violet complex with Fe(III) in acid media and a yellow complex with Fe(II) and Fe(III) in basic solutions. In the same condition was studied the formation of the Cu(II)-SSA complex. A pH = 10 was selected for the simultaneous determination of iron and copper.

The effect of SSA concentration on the formation of both complexes in presence of ammonia solution was carried out. An excess of SSA concentration does not modify the analytical signal. In order to have an excess of reagent, 6 mL of 10% w/v SSA were used.

4. Selection of spectral variables

4.1. Derivative order

In digital derivative spectrophotometry, is possible to use two ways. In the first way, the $\Delta \lambda$ values can be varied, this modality is very useful when the spectra are strongly overlapped. The second way was proposed by Savitzky and Golay (1964), which uses the least squares procedure for to smooth and to differentiate the numeric spectral data. In this case the numeric spectral data are processed by software incorporated in a computer on-line with the spectrophotometer. In this condition the higher signal/noise ratio is found and this technique is very useful in order to decrease the noise of the baseline, which does not require a complex computational data treatment to obtain information of quality. The last way was adopted in this work. Under this differentiation procedure $\Delta \lambda$ is constant and corresponds to scan range.

In order to optimize the derivative order, between the first to the fourth derivative spectra of the solution, containing separately the respective complexes were recorded (Fig. 1 a–d). Comparing the derivative spectra, the first derivative presents the highest sensitivities and also presents a good resolution for this simultaneous determination. In this context, the first derivative technique was selected. Higher derivative orders were discarded because when the noise is attenuated, the sensitivity also decreases.

5. Selection of the smoothing and scale factor

By using the first derivative of the spectrum, the smoothing factor was varied taking into account values, which are defined by defect depending on the $\Delta \lambda$ value selected. For a $\Delta \lambda$ value of 400 nm the smoothing factor can be studied taking the following values: 5000; 10,000; 20,000 and 40,000. These numbers are in relation to the range of wavelengths used when the spectrum was scanned. When the smoothing factor increases, the heights of derivative signal decreases, but the noise decreases more significantly, obtaining higher signal/noise ratios. A value of 40,000; was selected, because in these conditions the signal/noise ratio was favored and the sensitivities were sacrificed in order to decrease the error. A factor scale of $10^4$, was selected because it allows that the reading of the values be appropriated for the analytic measurements.

6. Selection of wavelength

The first derivative spectrum of Fe$_{total}$-SSA presents a zero crossing at 488.5 nm consequently when this compound is together with Cu(II)-SSA, all the absorption at this wavelength can be attributed to the absorption of Cu(II)-SSA. Similarly, Cu(II)-SSA presents a zero crossing at 423.5 nm, in which Fe$_{total}$-SSA can be determined in mixtures. The effect of the concentration of the analytes over both zero crossing was studied and was found that the
values of zero crossing are independent of concentration and the signals of both complexes does not present interference. In this context 423.5 nm and 488.5 nm were selected for the determination of copper and iron, respectively.

7. Analytical parameters

Calibration curves (95% confidence limit) of the first derivative values obtained versus the respective analyte concentrations were obtained for both complexes.

The detection limits and quantitation limits were obtained according to the criteria $3 \sigma / S$ and $10 \sigma / S$, respectively, where $S$ is the slope of the calibration curve and $\sigma$ is the standard deviation corresponding to the response of 11 blanks. The repeatability, expressed as relative standard deviation (RSD), was obtained by using 11 replicates of standards samples containing 10 mg L$^{-1}$ of iron and 150 mg L$^{-1}$ of copper. The determination range was defined between the quantification limit and the loss of linearity. In this context, it is possible to obtain an acceptable linearity degree with accuracy and precision in the results when the proposed method is applied. All analytical features are shown in Table 1.

8. Study of interferents

A study of the effect of foreign ions on the simultaneous determination of 10 mg L$^{-1}$ of iron and 150 mg L$^{-1}$ of copper was made to define the tolerance limit; this was accepted as ±5% of error in the determination of these analytes. The tolerance limits shows that only the EDTA interferes.

9. Application of the proposed method

The application of the simultaneous determination of iron and copper in synthetic mixture with different iron/copper ratio was carried out. A good accuracy and repeatability was found, the method is applicable when copper is in major proportion. The recovery percentage was between 99.5% and 100.8%, for relationships of Cu/Fe among 50–1 and 4–1.

The validation of the method was carried out by using a sample of the Quality Control Standard 19$^\circ$ (QCS 19) (High Purity Standards), this sample contains 100 µg mL$^{-1}$ of Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ti, Ti, V, Zn and trace of HF in 4% HNO$_3$ v/v.

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Fig. 1. Derivative spectra of Fe$_{total}$-SSA and Cu(II)-SSA complexes at pH = 10; (A) Fe$_{total}$, 20 mg L$^{-1}$; (B) Cu, 250 mg L$^{-1}$. (a) First derivative, (b) second derivative, (c) third derivative and (d) fourth derivative.
The recovery percentages for iron and copper were between 99% and 100%.

The method was applied in real pregnant liquid solution (PLS) samples from a confidential source. The results for Cu; Fe_{total}; Fe(III) and Fe(II) were: 2.59; 2.90; 2.69 and 0.21 g L^{-1}, respectively. The total concentrations are in agreement with atomic absorption spectroscopy results.

In conclusion a new simple and fast method for the simultaneous determination of Fe(II), Fe(III), Fe_{total} and Cu was developed.

Acknowledgements

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References


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu</th>
<th>Fe_{total}</th>
<th>Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit (mg L^{-1})</td>
<td>1.14</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>Determination limit (mg L^{-1})</td>
<td>3.80</td>
<td>0.07</td>
<td>0.30</td>
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<tr>
<td>Determination range (mg L^{-1})</td>
<td>3.80–250</td>
<td>0.07–20</td>
<td>0.30–20</td>
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<tr>
<td>Relative standard deviation (%)</td>
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<td>1.22</td>
<td>1.18</td>
</tr>
<tr>
<td>Equations</td>
<td>DU = 0.394 C + 3.23 (\lambda = 423.5 nm)</td>
<td>DU = 9.052 C – 1.40 (\lambda = 488.5 nm)</td>
<td>A = 0.030 C + 0.003 (\lambda = 500.0 nm)</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Where, DU is derivative units, C corresponds to compound concentration in mg L^{-1}.