Comparative study of alternative methods for the simultaneous determination of Fe^{+3} and Fe^{+2} in leaching solutions and in acid mine drainages

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Abstract

In leaching solutions coming from the hydrometallurgical processing of copper sulphides, it is necessary to determine the concentrations of Fe_{total}, Fe^{+2} and Fe^{+3}. It is known that the 5-sulfosalicylic acid (SSA) forms a red-violet complex with Fe^{+3} in acid media and a yellow complex with Fe^{+2} and Fe^{+3} in presence of ammonia at pH = 10. In this study, the results obtained by the SSA method are statistically compared with those obtained by 1,10-phenanthroline method, dichromate titration method and atomic absorption spectrometry. A statistical analysis demonstrated that the SSA method gives more exact and representative results than the other studied methods. The acid mine drainages and the leaching solutions, present an extremely complex matrix because to the high content of copper and arsenic, showing relationships that vary from 1:30 up to 1:1, depending on the stages of the hydrometallurgical process. Under these considerations, the SSA method allows the determination of Fe^{+3} directly in samples that have an iron content in the range 0.005 g L^{-1}–18 g L^{-1} with a relative standard deviation (RSD) <2%.

1. Introduction

The leaching solutions from hydrometallurgical processing of copper sulphides have a high concentration of several metallic sulphates. Usually, it is necessary to determine quantitatively the iron ions concentration of both oxidation states, which could be sometimes imprecise because two techniques are required; furthermore, copper is a very usual interferent in the colorimetric

determination of iron. The Fe^{+2} determination is carried out by 1,10-phenanthroline method (APHA, 1998). The Fe_{total} determination is realised using potassium dichromate volumetric method and Atomic Absorption Spectrometry (AAS) technique. In this sense, in all of these cases the determination of Fe^{+3} is not direct and for instance, a quantitative determination of both oxidation states could be imprecise. Recently, a simple and fast method has been described for the quantitative simultaneous determination of Fe^{+3} and Fe_{total} with SSA in acid mine drainages (AMD) and other solutions (Karamanev et al., 2002). The objective of this work was to compare the sulfosalicylic acid method with the other two described methods, with the aim of validating its use in monitoring of Fe(II) and Fe(III) in leaching

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solutions and in AMD which came from bio/hydromet-allurgical processes.

2. Experimental

In order to compare results, the following analytic methods were used for the direct determination of Fe^{+2}: Method of the *o*-phenanthroline (1,10-phenan-throline) (APHA, 1998) and the titration method with potassium dichromate, and indirectly ($[Fe_{total}]–[Fe^{+3}]$) by means of the method of the sulfosalicylic acid (SSA) like it is described.

For the direct determination of Fe^{+3} the method of the SSA was used, and indirectly Fe^{+3} also was determined by means *o*-phenanthroline method and potassium dichromate method ($[Fe_{total}]–[Fe^{+2}]$). For the determination of Fe_{total} the three previous methods were compared with those of Atomic Absorption Spectrometry (AAS) (APHA, 1998).

The procedure used in the SSA method was as follows: Into a 100 mL volumetric flask, add an adequate volume of the sample. Then add 3 mL of 10% (w/v) sulfosalicylic acid solution and complete volume with Ultrapure Millipore® Water. Stir during 2 min and measure de absorbance at 500 nm. Then add 3 mL of ammonia solution 25% (w/v) and stir during 2 min and measure the absorbance at 425 nm (Karamanev et al., 2002). The other methods have been broadly described in the literature (APHA, 1998).

3. Results and discussion

A comparative study of the employed analytical methods by means of control chart was carried out (Fig. 1). The obtained results allowed to establish that the average values obtained by the dichromate method were significantly different for the determination of Fe_{total} and Fe^{+3}. On the other hand, in the determination of Fe^{+2} with a confidence level of 99%, the precision of the three methods is statistically comparable. However, from the three subjected methods to statistical control, the *o*-phenanthroline method presents the biggest relative error ($Fe^{+2} = -3.76\%$, $Fe^{+3} = -2.28\%$ and $Fe_{total} = -4.00\%$) and SSA method presents the smaller relative error ($Fe^{+2} = 0.88\%$, $Fe^{+3} = -0.08\%$ and $Fe_{total} = -0.09\%$).

A regression among the variable measured "concentration" (*y* axis) and the "true concentration" (*x* axis) allows to study an analytic method to detect and to quantify its possible errors and also as correcting them. In Fig. 2, the correlation is presented from the methods subjected to statistical control. For the dichromate method a significant evidence of a fixed systematic error exists for the determination of Fe(II) and Fe(III), since
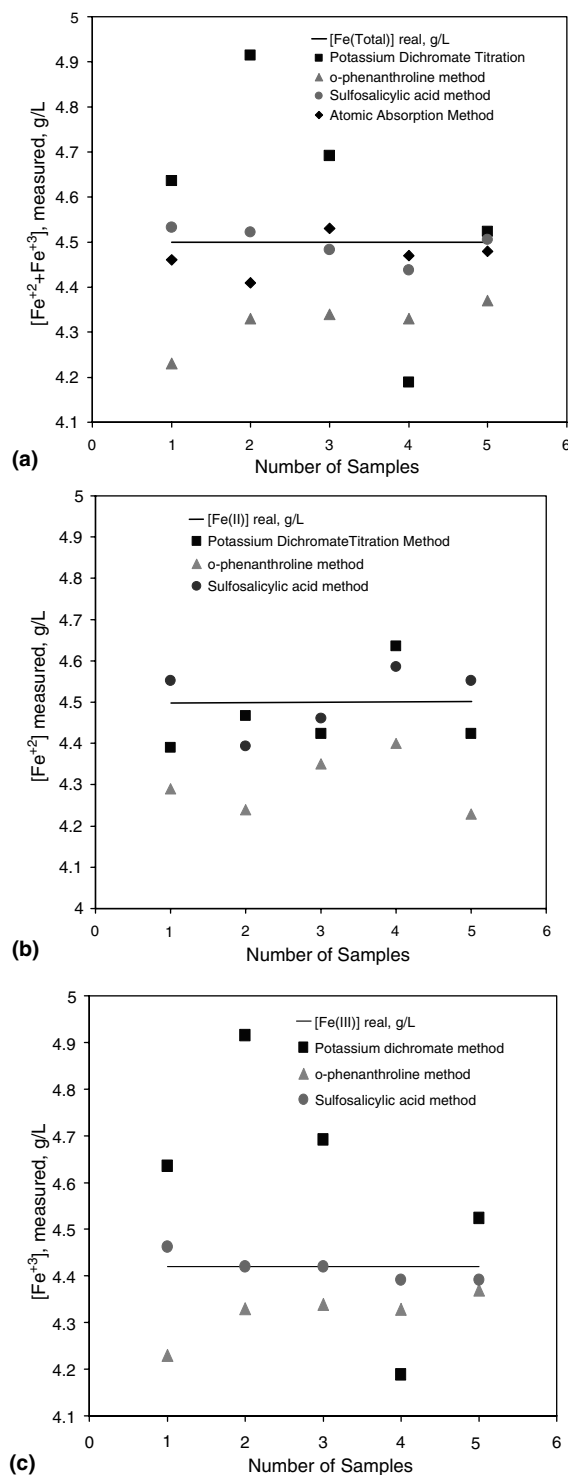

(a)

(b)

(c)

Fig. 1. Control chart of the media for the determination of (a) Fe_{total}, (b) Fe^{+2} and (c) Fe^{+3} for the methods subjected to statistical control.

the confidence limit for the true intercept does not include the zero value as much in the determination of Fe(II) 3.3452 ± 2.7422, as in Fe(III) 0.7578 ± 0.4549 for a significance level of 95%. On the other hand, the *o*-phenanthroline method and the sulfosalicylic acid method, include the zero value and therefore, significant
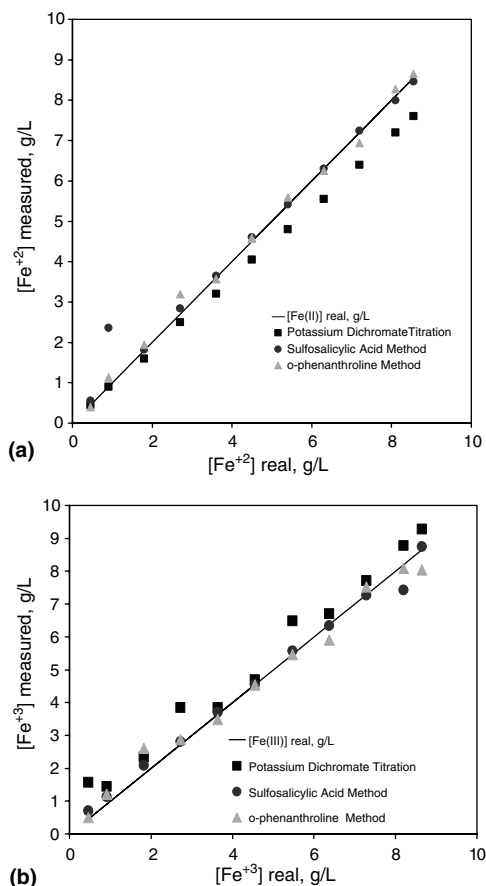
Fig. 2. Detection and estimation of the systematic error in the determination of mixtures Fe^{+2}, Fe^{+3} among 1.8 and 9 g L^{-1} of each analyte. (a) Fe^{+2} and (b) Fe^{+3}.

evidence of fixed systematic error does not exist. The analysis of the confidence limits of the true slope, allowed to conclude that significant evidence of a relative systematic error does not exist in the methods subjected to control, since the confidence limits of the slope include the value 1 for a significance of 95% for critical values of the test t.

On the other hand, the addition of standard method and calibration graph in aqueous medium were compared. The statistical treatment of comparison of this slopes allow establishing the matrix influence. A significant difference was found for the determination of Fe_{total} for the o-phenanthroline method in presence of 30 g L^{-1} of Cu(II). This specie is a majority constituent of the leaching solutions and of the acid mine drainages, being in concentration levels that reach 30 g L^{-1} with a pH between 1 and 2. Applying the critical values in a "two tailed" t-test with a 95% of confidence, a 3.18 t value was found. On the other hand, the t experimental value was of 3.88 which corroborate the copper interference. Therefore, the analysed samples cannot be contrasted directly with the standards prepared in water by the o-phenanthroline method.

On the other hand, in the analysis of the method of SSA, it was found that both slopes are practically similar and as a result it can be contrasted the sample directly with the standards prepared in water. The same thing happens when the studied interference is the As(V), also studied by our group. Under these last considerations the method of the SSA is adapted statistically for the analysis of Fe^{+2}, Fe^{+3} and Fe_{total} in leaching solutions and acid mine drainages.

Finally, it was decided to compare the SSA method and the $ortho$-phenanthroline method in samples taken from a respirometric equipment. Oxygen uptake was determined during the experiments using electrochemical respirometer SAPROMAT. Six reaction vessels maintained at a constant temperature in a thermostatic bath compose the system. Each reaction flask is connected to an electrochemical cell and to a contact manometer in a closed system. Oxygen consumption in the reaction vessels produces a decrease of pressure in the system that is compensated by the same amount of oxygen generated by an electrochemical reaction. The electrochemical current that is directly proportional to oxygen uptake is integrated and recorded continuously. For this experiment, $Thiobacillus$ $ferrooxidans$ was inoculated in 100 mL of the MC media, which contains 3 g L^{-1} of Fe(II). And then the experiment was made in duplicate. Periodical samples were taken and immediately analyzed by the two methods for comparing their results with the curve obtained in the respirometer which gave us mg of O_2 and by a conversion we could obtain Fe(III) oxidized against the time by the bacterial culture.

The results shown that the $ortho$-phenanthroline method has a higher relative error than SSA method, specifically at higher [Fe(III)] concentrations. The direct measurement of Fe(III) is very important because it constitutes a parameter of monitoring the oxidative capacity of the bacteria.

4. Conclusions

The fact of having a system of analysis under statistical control, allowed to establish that the method of the SSA is which gives more exact and representative results among the studied methods. The acid mine waters and the leaching solutions, present an extremely complex matrix because the content of the interference, as copper for example, is in relationships which could vary from 1:30 up to 1:1 depending on the stages of the hydrometallurgical processing. Under these considerations, the method of the SSA allows the determination of Fe(III) directly in samples that have an iron content understood between 0.005 g L^{-1} and 18 g L^{-1} with a relative standard deviation (RSD) <2%. This wide lineal range, includes samples coming from all the stages of the hydrometallurgical processing of copper.

Acknowledgments

References

APHA, 1998. Standard methods for the examination of water and wastewaters.

Karamanev, D.G., Nikolov, L.N., Mamatarkova, V., 2002. Rapid simultaneous quantitative determination of ferric and ferrous ions in drainage waters and similar solutions. Minerals Engineering 15, 341–346.