Article

Spectrophotometric Determination of Aluminium in Iron Ores Using Solid-Phase Extraction

Sérgio Luis Costa Ferreira[a], Valfredo Azevedo Lemos[a], Antônio Celso Spinola Costa[a], Djane Santiago de Jesus[b], and Marcelo Souza de Carvalho[c]

[a]*Universidade Federal da Bahia, Instituto de Química,*

40170-290 Salvador - Ba, Brazil

e-mail:slcf@ufba.br;

[b]*Centro Federal de Educação Tecnológica da Bahia, SSA - Bahia*

[c]*Instituto de Engenharia Nuclear, CNEN - Rio de Janeiro, Brazil*

No presente trabalho, um procedimento para separação e determinação de alumínio em matrizes de ferro é proposto. Este é baseado na extração em fase sólida do ferro sob a forma de tiocianatos complexos, pela espuma de poliuretano. Os seguintes parâmetros foram estudados: efeito de pH e da concentração de tiocianato sob a extração do ferro, tempo de agitação necessário para extração quantitativa, quantidade de espuma requerida, separação de alumínio de ferro e de outros elementos, influência de ânions sob a sorção de ferro pela espuma e características analíticas do procedimento para determinação de alumínio usando o azul de metiltimol (MTB) como reagente cromogênico.

Os resultados demonstraram que na faixa de pH de 1,5 a 4,7, com tiocianato na concentração de 0.80 mol L^{-1}, tempo de agitação de 1 min e usando 1 g de espuma de poliuretano para extração, é possível separar alumínio(40 µg) de: grandes quantidades de ferro (10 mg), 800 µg de cobre(II), cobalto(II), zinco(II), mercúrio(II), manganês(II), estanho(IV) e tungstênio(V); 100 µg de chumbo(II) e titânio(IV) e 50 µg de vanádio(V). Cálcio(II), bário(II), estrôncio(II) e magnésio(II) não são separados por este processo; entretanto, não reagem com o MTB nas condições estabelecidas para determinação de alumínio. Os ânions nitrato, cloreto, sulfato e acetato não afetam a extração do ferro. Fosfato e EDTA devem estar ausentes.

O azul de metiltimol possibilita a determinação espectrofotométrica de alumínio, com absortividade molar de 1,32 x 10^4 L mol^{-1} cm^{-1}(em 528 nm), sensibilidade de calibração de 0,491 mL $µg^{-1}$, limite de detecção de 5 ng mL^{-1}, intervalo dinâmico de aplicação de 15 ng mL^{-1} a 1,00 µg mL^{-1} e coeficiente de variação de 0,73%.

O procedimento proposto foi aplicado para determinação de alumínio em padrões de minérios de ferro e ligas metálicas. Os resultados encontrados não exibiram diferenças significativas em relação aos valores certificados.

In the present paper, a procedure for separation and determination of aluminium in iron matrices is proposed. It is based on the solid-phase extraction of the iron, in the form of thiocyanate complexes, by a polyurethane(PU) foam. The followings parameters were studied: effect of pH and of the thiocyanate concentration on the iron extraction, shaking time required for quantitative extraction, amount of PU foam necessary for complete extraction of iron, aluminium separation from other cations, influence of anions on the iron sorption by PU foam and analytical characteristics of the procedure for aluminium determination using methylthymol blue as chromogenic reagent.

The results show that, in the pH range from 1.5 to 4.7, with a thiocyanate concentration of 0.80 mol L^{-1}, by extraction using 1 g of polyurethane foam and a shaking time of 1 min, aluminium (40 µg) can be separated from large amounts of iron (10 mg), 800 µg of copper(II), cobalt(II), zinc(II), mercury(II), tin(IV), manganese(II) and tungsten(V); 100 µg of titanium(IV) and lead(II); and 50

µg of vanadium(V). Calcium(II), barium(II), strontium(II) and magnesium(II) can not be separated by this process, but do not react with MTB under the conditions used for aluminium determination. The anions nitrate, chloride, sulfate and acetate do not affect the iron extraction. Phosphate and EDTA must be absent.

The methylthymol blue allowed the spectrophotometric determination of aluminium with molar absorptivity of 1.32×10^4 L mol^{-1} cm^{-1} (528 nm), calibration sensitivity of 0.491 mL g^{-1}, detection limit of 5 ng mL^{-1} and dynamic interval of application of 15 ng mL^{-1} to 1.00 µg mL^{-1} and variation coefficient of 0.73%.

The proposed procedure was applied for aluminium determination in iron ores and metal-base alloy standards. The obtained results did not show significant difference from the certified values.

Introduction

The spectrophotometric determination of aluminium[1,2] in iron ores requires most of the time a previous separation stage of aluminium from iron, because the organic reagents available for aluminium determination also react with iron(III). The classical method for separation of these cations is based on the liquid-liquid extraction of iron(III)[3,4] in strong hydrochloric acid solution (6-10 mol L^{-1}) in the form of chloro complexes, using ethyl ether or methyl-iso-butylketone as extractor solvents. Other procedures often used are based on the separation of iron(III) as chloro-complex[5,6] or thiocyanate complex[7] on an anion-exchange column, liquid-liquid extraction from thiocyanate complex iron(III)[8] using tributylphosphate as extractor solvent and precipitation of iron(III) with cupferron[9].

In the present paper a method is proposed for separation of iron from aluminium, based on the solid-phase extraction of iron(III) as a thiocyanate complex, using polyurethane foam as sorbent. This procedure allowed the separation of aluminium from iron and other elements commonly present in the iron ores.

The PU foam has been used as a solid sorbent for a wide variety of inorganic and organic compounds from different media. It was proposed firstly by Bowen[10] in 1970. Braun[11-13] and Palagyi[14] have revised the literature on the use of PU foam in procedures of separation and preconcentration.

The use of PU foam for iron extraction has been proposed by several authors[15-19]. Gesser and co-workers[15,16] reported the extraction of iron(III) hydrochloric acid as HFeCl$_4$ by the polyurethane foam. From their results, they inferred that polyether polyurethane could be regarded as a solvent of moderate dielectric constant in which some dissociation of sorbed species was possible.

The first detailed study about separation and preconcentration of iron(III) and cobalt(II) in the aqueous thiocyanate medium was published in 1978 by Braun and Farag[17]. They demonstrated that no more than 20 min was necessary to achieve quantitative (99%) extraction of iron (III) from

0.2 mol L^{-1} thiocyanate solutions using squeezing process. Carvalho *et al.*[18] described the use of the PU foam-thyocianate system for separation of cobalt(II) from iron(II) during the cobalt determination in steel materials. Maloney *et al.*[19] proposed a procedure for simultaneous extraction of zinc(II), cobalt(II), iron(III) and cadmium(II) from thiocyanate medium by PU foam. The extraction mechanism of the iron(III) by the PU foam as thiocyanate complexes was studied by Moody[20] and co-workers.

Aluminium(III)[21,22] reacts with methylthymol blue [MTB] (3,3'-bis[N,N'-di(carboxymethyl)-aminomethyl]thymolsulfon-phthalein), in the range of pH from 3.5 to 5.5, with formation of a complex with absorption maximum at 528 nm and molar absorptivity of 1.32×10^4 L mol^{-1} cm^{-1}. Iron(III) also reacts with MTB forming a complex with absorption maximum at 500 nm.

Experimental

Apparatus

Spectrophotometric measurements were made using a VARIAN Cary 1E spectrophotometer with matched 1.00-cm quartz cells.

An Applied Research Laboratories model 3410 mini-torch sequential inductively coupled plasma spectrometer with an IBM PC-AT computer was used for ICP-AES analysis.

A Rigaku-B3 wavelength dispersive X-Ray fluorescence spectrometer, with a rhodium tube operated at 40 Kv and 30 mA, a LiF crystal, and a scintillation counter, was used.

A 300 ANALYSER pH meter was used to measure the pH values.

A VKS-100 Mechanical Shaker, 100 cpm was used for extraction.

Reagents

All reagents were of analytical-reagent grade unless otherwise stated. Doubly distilled water was used for the

preparation of solutions. The nitric acid and hydrochloric acid were of Suprapur quality (Merck). The laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, the glassware was washed with demineralized water and dried in a dust-free environment.

Aluminium solution (10.00 µg mL⁻¹). Prepared by diluting a 1000 µg mL⁻¹ aluminium solution (atomic absorption Aldrich) using a 5% hydrochloric acid solution.

Iron (III) solution (100.0 µg mL⁻¹). Prepared by diluting a 1000 µg mL⁻¹ iron solution (atomic absorption Aldrich) using a 5% hydrochloric acid solution.

Potassium thiocyanate solution (4.0 mol L⁻¹). It was prepared by dissolving the reagent (Carlo Erba) in water.

Buffer solution (pH 4.25). Prepared by mixing 32.7 g of trihydrate sodium acetate and 44.7 mL of glacial acetic acid in 1 L of water.

Methylthymol blue solution (0.10 % m/v). It was prepared by dissolving a monosodium reagent (Merck) in water.

Polyurethane foam. A commercial, open cell, polyether-type PUF (Vulcan of Brazil - VCON 202, 42% resilience and 10-12 cells/linear cm) was comminuted with water, and used as described by Carvalho[18, 23-24].

Separation procedure

Into a volumetric flask of 100 mL, add an aliquot solution containing aluminium(III) and iron (up to 20 mg), 20 mL of 4.0 mol L⁻¹ thiocyanate solution, and 20 mL of acetate buffer solution. Make up the volume with water. Transfer an aliquot of 50 mL of the earlier solution to a stoppered polypropylene flask and add a mass of 1 ± 0.05 g of comminuted PU foam (previously treated with 0.80 mol L⁻¹ thiocyanate solution). Shake the system mechanically for 5 min and separate the PU foam by filtration. In the filtrate, add again 1 g of comminuted PU foam and shake for 2 min. Separate the PU foam by filtration. Determine the aluminium in the filtrate as in the procedure described in the next section.

Spectrophotometric determination of aluminium using MTB reagent

Into a volumetric flask of 25 mL, add aluminium(III) solution in the range from 3.75 to 25.0 µg, 5.0 mL of methylthymol blue solution and 5.0 mL of acetate buffer solution. Make up the volume with water and measure the absorbance at 528 nm against a reagent blank.

Results and Discussion

In order to determinate the conditions required for separation of aluminium from iron several parameters were studied.

pH effect on the sorption of iron for its separation from aluminium

The pH effect on the iron sorption by the PU foam was studied. The results show that the extraction was maximum and constant in the pH range from 1.5 to 4.7, as can be seen in Fig. 1. The pH control was done using acetate buffer with pH 3.75 to 5.75, hexamine buffer pH 6.5. For range from pH 1.5 to 3.2 solutions of hydrochloric acid were used. The aluminium is not extracted by polyurethane foam in all the range of studied pH. The proposed procedure recommends the extraction with the pH solution (4.25 ± 0.25), because the appropriate pH range for spectrophotometric determination of aluminium by using MTB is 3.75 to 5.75.

Effect of the thiocyanate concentration on the iron extraction

In order to test the thiocyanate concentration required for a quantitative extraction, 500 µg of iron(III) was extracted by PU foam, in experiments where the thiocyanate concentration was changed from 0.02 to 2.00 mol L⁻¹. The results in Fig. 2, show that the extraction efficiency increases with the thiocyanate concentration, reaching a constant value over 0.50 mol L⁻¹ KSCN, where the system exhibits the highest distribution coefficient (D = 2.7 x 10⁴ mL g⁻¹). The proposed procedure recommends a thiocyanate concentration of 0.80 mol L⁻¹ to guarantee the sorption of iron(III) and other ions present in iron ore samples. Aluminium is not extracted by polyurethane foam even at high thiocyanate concentrations.

Effect of the sample volume on the iron extraction

In order to evaluate the effect of the sample volume on the efficiency of iron(III) extraction, several solutions with volumes of 10, 20, 25, 50, 100 and 200 mL, all containing a fixed mass of 500 µg of iron and 0.80 mol L⁻¹ thiocyanate

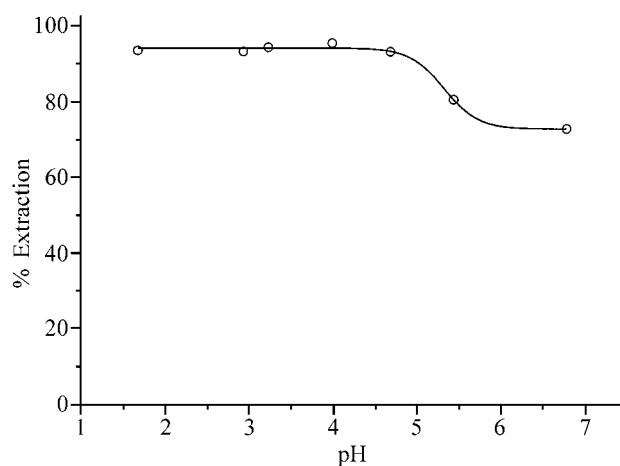**Figure 1.** pH effect on the iron(III) extraction: 500 µg; PU foam mass: 0.10 g. Thiocyanate concentration: 0.50 mol L⁻¹. Agitation time: 5 min.
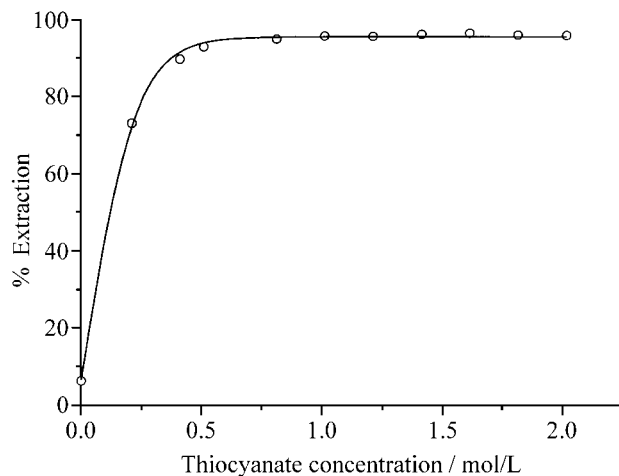
Figure 2. Effect of the thiocyanate concentration on the iron extraction iron(III): 500 µg; PU foam mass: 0.10 g. pH: 4.25. Agitation time: 5 min.

were prepared. Then, the iron was extracted by using 100 mg of PU foam with an agitation time of 5 min. The results demonstrated that the extraction was constant and quantitative for solution volumes in the range of 10 to 50 mL.

Effect of the shaking time

The effect of the shaking time on the efficiency of extraction of iron was studied. The results in Fig. 3 demonstrated that for a quantitative extraction of 500 µg of iron, with 0.80 mol L^{-1} thiocyanate, 1 min was enough. In the procedure proposed, a 5 min time is recommended to guarante maximum extraction.

Amount of PU foam necessary for complete extraction

The effect of the amount of PU foam on the iron extraction was also evaluated. It was found that 100 mg of PU foam was the minimal quantity required for a quantitative extraction of 500 µg of iron. This test was done using
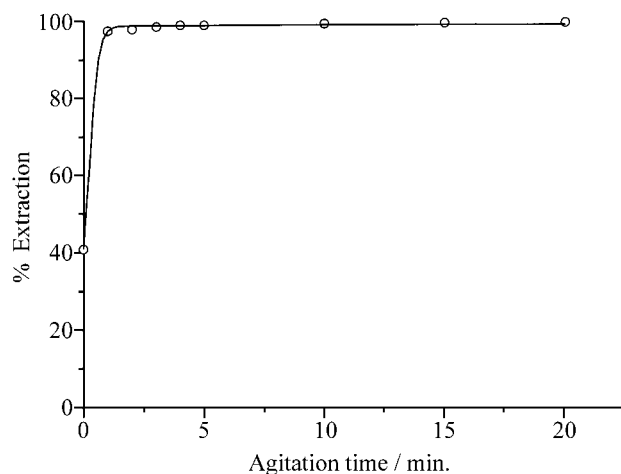

Figure 3. Effect of shaking time on the iron extraction iron(III): 500 µg; PU foam mass: 1.00 g. Thiocyanate concentration: 0.80 mol L^{-1}. pH: 4.25

a PU foam with a sorption capacity of 0.090 mmol of iron/g of PU foam, as determine by the sorption isotherm[24]. In this way, a mass of PU foam in the range of 0.95 to 1.05 g is recommended to guarante a complete extraction.

Efficiency of separation of aluminium from iron

In order to test the efficiency of the separation procedure, for aluminium determination with the MTB reagent, several portions of aluminium (0, 100, 200, 300, 400 and 500 µg) were mixed with 10000 µg of iron(III) and the proposed procedure was applied. Aluminium was determinated with the MTB reagent as described in the experimental part. The relation between aluminium present and aluminium found is linear with an equation:

$$Al_{(found)} = (1.006 \pm 0.027)Al_{(present)} + (0.009 \pm 0.284)$$

with a correlation coefficient of 0.9996. These data demonstrate the efficiency of separation of the proposed method.

Separation of aluminium from other ions

Solutions containing aluminium(III) and several cations were prepared, and the efficiency of the separation procedure was tested. The results demonstrated that, at pH 4.25 and thiocyanate concentration of 0.80 mol L^{-1}, aluminium (40 µg) can be perfectly separated from 800 µg copper(II), cobalt(II), zinc(II), mercury(II), manganese(II), tin(IV), tungsten(V), 100 µg of lead(II) and titanium(IV) and 50 µg of vanadium(V). The cations calcium(II), magnesium(II), strontium(II), iron(II) and barium(II) are not separated by this process, but do not react with MTB under the conditions used for aluminium determination. The anions nitrate, chloride, sulfate and acetate do not affect the iron extraction for the PU foam. EDTA and phosphate must be absent. In this experiment, the metal determinations were done using ICP-AES analysis. X-Ray fluorescence spectrometry was used to measure directly metal thiocyanate complexes on the PU foam discs.

Application

The analytical curves for the aluminium(III)-MTB system were done according to the procedure described in the experimental part. The system showed a molar absorptivity of $(1.32 \pm 0.02) \times 10^4$ L mol^{-1} cm^{-1} (at 528 nm), calibration sensitivity[25] of 0.491 mL μg^{-1}, for a dynamic interval of application of 15 ng mL^{-1} to 1.00 µg mL^{-1}, detection limit of 5 ng mL^{-1} and a variation coefficient of 0.73 %.

The analytical characteristics of the iron sorption for separation from aluminium are summarized in Table 1. These were determinated based on the extraction of iron at pH 4.25, with a thiocyanate concentration of 0.80 mol L^{-1}.

The proposed procedure was applied to aluminium determination in several standards of iron ores and metal-

Table 1. Analytical Characteristics of the iron(III) extraction with polyurethane foam.

Distribution coefficient	2.7×10^4 (L/kg)
Shaking time for extraction	1 min
Sorption capacity of the PU foam	0.090 (mmols g^{-1})
Coefficient of variation	1.35 (%)

base alloys. Samples were dissolved using nitric and hydrochloric acids. The results are described in Tables 2 and 3.

The results of the Tables 2 and 3 demonstrated that there were no significant differences, between the certified value and the found value with the procedure of separation and determination of aluminium proposed, at the 95% confidence level.

Conclusions

Aluminium can be easily separated from iron and other metallic ions, based on the iron extraction by the PU foam in a range of pH 1.5 to 4.7 and thiocyanate concentration higher than 0.50 mol L^{-1}.

The extraction process using PU foam has typical advantages of the solid-phase extraction, when it is compared with other separation techniques, because the utilization of PU foam dispenses with the need for organic solvents which are frequently toxic, and avoid the problem of formation of emulsions. The PU foam is commercially available and inexpensive. A comparison with the classical

method for separation has the advantage that hydrochloric acid with at high concentrations is not required.

The results obtained in the aluminium determination in the certified samples, demonstrated that the proposed method has satisfactory accuracy and precision.

The use of solid-phase extraction with PU foam is an effective means overcoming iron interference in the spectrophotometric procedures, and can be applied for aluminium determination by other analytical methods.

Acknowledgments

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Table 2. Aluminium determination in iron ore standards.

	Certified values			Results found by the proposed method[*] Al_2O_3 (%)
Standard	Fe (%)	MnO (%)	Al_2O_3 (%)	
Iron ore IPT-21a	68.48	0.017	0.75	0.72 ± 0.02 (3)
Iron ore IPT-23a	65.81	0.116	1.21	1.19 ± 0.09 (3)
Iron ore IPT-27a	61.87	0.316	1.76	1.78 ± 0.02 (3)
Manganese ore IPT-52	2.40	59.53	10.6	10.50 ± 0.60 (3)

*- 95% confidence level.
(N)- Determination number.

Table 3. Aluminium determination in metal-base standards.

	Certified values (%)						Results found by the proposed method Al(%)
Standard	Fe	Cu	Zn	Pb	Ni	Al	
Magnesium-base alloy NBS171	0.0018	0.011	1.05	0.003	0.001	2.98	2.96 ± 0.07 (3)
Copper-base alloy NBS164	2.52	63.76	21.89	0.22	0.046	6.21	6.38 ± 0.15 (3)
Zinc-base alloy NIST 94C	0.018	1.01	94.83	0.018	0.006	4.13	4.04 ± 0.04 (3)

*- 95% confidence level.
(N)- Determination number.

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