

Article

Determination of Iron in Alkaline Salts by ICP-AES Using 1-(2-Thiazolylazo)-p-Cresol (TAC) for Preconcentration and Separation

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O presente trabalho descreve o uso de 1-(2-thiazolylazo)-p-cresol (TAC) para separação, preconcentração e determinação de traços de ferro (ng g^{-1}) em sais alcalinos usando a técnica ICP-AES. O método proposto é baseado na extração líquido-líquido do complexo formado entre o cátion ferro(III) e o 1-(2-thiazolylazo)-p-cresol (TAC). Foram estudados parâmetros tais como: quantidade de TAC, efeito de pH, influência do solvente orgânico, mineralização da fase orgânica e re-extração. Os resultados demonstraram que o complexo ferro(III)-TAC, formado na faixa de pH de 4,0 a 10,0, pode ser quantitativamente extraído de soluções salinas, usando como solvente extractor álcool isoamílico, tetracloreto de carbono, clorofórmio ou metil isobutil cetona. A solução para determinação de ferro pode ser obtida por uma re-extração usando soluções de ácido clorídrico 1 mol/L ou ácido nítrico 1 mol/L ou também por uma mineralização da fase orgânica, com uma evaporação do solvente orgânico e digestão do resíduo com ácido nítrico concentrado. O procedimento foi usado para determinação de ferro em amostras de vários sais alcalinos. A técnica da adição padrão foi aplicada e as recuperações obtidas revelaram que o procedimento proposto tem uma boa exatidão.

The present paper describes the use of 1-(2-thiazolylazo)-p-cresol (TAC) for separation, preconcentration and determination of iron traces (ng g^{-1}) in alkaline salts by the ICP-AES technique. The proposed method is based on the liquid-liquid extraction of the complex formed between iron(III) and 1-(2-thiazolylazo)-p-cresol (TAC). Parameters such as: TAC amount, pH effect, influence of the organic solvent on the extraction, back extraction and mineralization of the organic phase were studied. The results show that the iron(III)-TAC complex, formed in the pH range from 4.0 to 10.0, can be quantitatively extracted from saline solutions (up to 30% NaCl) using isoamyl alcohol, carbon tetrachloride, chloroform or methyl isobutyl ketone as extracting solvent. The solution for the iron determination can be obtained by a back extraction using 1 mol/L hydrochloric acid or 1 mol/L nitric acid solutions or also by mineralization of the organic phase, which was accomplished by evaporation of the organic solvent and digestion of the residue with concentrated nitric acid. The procedure was used for iron determination in several alkaline salt samples. The standard addition technique was applied and the recoveries obtained revealed that the proposed procedure has a good accuracy.

Keywords: *iron determination, ICP-AES, saline salts*

Introduction

The determination of iron traces in alkaline salts by ICP-AES (inductively coupled plasma atomic emission spectrometry) is difficult because the aspiration of solu-

tions with high salt concentrations into the plasma can cause problems such as: blockage of the nebulizer, considerable background emission, transport and chemical interferences, with consequent drop in sensitivity and precision¹⁻⁴. Thus, trace determination in saline solutions,

always needs a prior separation. Several papers for determination of iron and other metal ions in saline matrices have been described in the literature⁵⁻¹⁰. Berman *et al.*⁵ proposed a procedure for the simultaneous determination of iron, manganese, copper, zinc and nickel in sea water by a combination of ion-exchange preconcentration and ICP-AES. The sample is passed through a Chelex-100 column and trace metals are eluted by shaking the resin with 5 mol/L nitric acid. Brooks *et al.*⁶ determined cobalt, copper, iron, lead, nickel and zinc in saline waters by simultaneous extraction of their ammonium pyrrolidine dithiocarbamate (APDC) complexes into methyl isobutyl ketone (MIBK) and subsequent analysis by atomic absorption spectrometry. A procedure for the determination of iron, manganese, copper, zinc, cadmium, lead, vanadium and nickel in sea water was described by Sugimae⁷. In it, the trace elements are complexed with diethyldithiocarbamic acid (DDTC) and extracted with chloroform, followed by a decomposition of the extract and determination by using the ICP-AES technique. McLeod *et al.*⁸ proposed a method for preconcentration and determination of iron, copper, nickel, cadmium, vanadium and zinc from sea water by ICP-AES. It was based on liquid-liquid extraction with dithiocarbamate, using chloroform as the extraction solvent and back extraction with nitric acid. Nakashima *et al.*⁹ reported the use of graphite furnace atomic absorption spectrometry in combination with the silica immobilized 8-hydroxyquinoline miniature column flow system for the preconcentration of iron and other metal ions from sea water. Watanabe¹⁰ described a preconcentration method for iron and other metal ions from sea water prior to the determination by ICP-AES. The method involved complexation of the metal ions with 8-hydroxyquinoline followed by adsorption on a column of C₁₈-bonded silica gel.

In this paper, a procedure for separation, preconcentration and determination of iron in alkaline salts by ICP-AES, based on the liquid-liquid extraction of the iron(III)-TAC (1-(2-thiazolylazo)-p-cresol) complex, followed by a back extraction or a mineralization process of the organic phase is proposed. The TAC reacts instantaneously with iron(III) forming a stable complex. This reagent was used for iron determination by molecular absorption spectroscopy^{11,12} and also by cathodic adsorptive stripping voltammetry¹³. TAC has been proposed several times as a spectrophotometric reagent. Methods for determination of zirconium¹⁴, bismuth¹⁵, yttrium¹⁶ were described. In our laboratory, it was employed for the spectrophotometric determination of titanium¹², nickel¹⁷, indium¹⁸ and lead¹⁹ using several masking agents to increase the selectivity.

Experimental

Apparatus

An Applied Research Laboratories model 3410 mini-torch sequential inductively coupled plasma spectrometer with an IBM PC-AT computer was used. The emission intensity measurements were made under the conditions shown in Table 1. A 300 ANALYSER pH meter was also used.

Reagents

All reagents were of analytical reagent grade unless otherwise stated. Double distilled water was used for the preparation of the solutions. The nitric acid and hydrochloric acid were Suprapur from Merck. The laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

Iron(III) solution (10.00 µg/mL). Prepared by dilution of a 1000 µg/mL iron solution (for atomic absorption, Aldrich) using a 5% hydrochloric acid solution. *TAC solution* (1.00 %). Prepared by dissolving 1.00 g (Aldrich) in 100 mL of ethanol. *Buffer solution* (pH 4.75). Prepared by mixing 68.0 g of sodium acetate trihydrate and 29.4 mL of glacial acetic acid in 1 l of demineralized water.

General Procedure

In a 250 mL separation funnel, transfer 100 mL of a solution containing iron(III) in the range of 2.0 to 100.0 µg, 2.5 mL of acetate buffer (pH 4.75) and 1.0 mL of 1% TAC solution. Mix and after 5 min make the extraction using 30 mL of the organic solvent.

Table 1. Operating parameters for the inductively coupled plasma spectrometer.

Incident output power	650 W
Reflected power	<5 W
Nebulizer	Glass, Meinhard
Plasma gas flow rate	7.5 L min ⁻¹
Auxiliary gas flow rate	0.8 L min ⁻¹
Aerosol carrier gas flow rate	0.8 L min ⁻¹
Solution uptake rate	2.5 mL min ⁻¹
Wavelength	259.93 nm
Signal integration time	5 s
Integration for determination	3

Results and Discussion

Characteristics of TAC and iron(III)-TAC complex

The TAC reacts instantaneously with the iron(III) cation, forming a stable complex with a composition of 1:2 cation-reagent. TAC and its iron complex have low solubility in water, but are very soluble in organic solvents, allowing the extraction of TAC and its complex. The TAC is not selective for the iron determination, However, pH control increases the selectivity.

TAC amount

In order to test the reagent amount for quantitative extraction of iron, different amounts of TAC from 500 μg to 20 mg were added to a series of 100 mL solutions containing 20.0 μg of iron and the general procedure was applied, using 30 mL of isoamyl alcohol. The results showed that the extraction was quantitative, for a TAC amount greater than 800 μg . In the proposed procedure, a TAC amount of 10 mg is recommended to guarantee the complete complexation of the iron present in the samples, considering that it can also react with other metal cations.

pH effect on the extraction

The pH effect on the extraction of the iron(III)-TAC complex was studied and the results showed that it is maximum and quantitative in a pH range from 4.0 to 10.0. The extraction is not quantitative at pH lower than 4.0, due to competition between the hydrogen ion and the iron(III) cation. With the increase of the hydrogen ion concentration, the competition leads to a less favorable complex formation and consequent extraction of TAC. The pH control was done using acetate buffer with pH 4.0 and 6.0, borate buffer with pH 8.0 and ammonium buffer with pH 10.0. For pH 2.0 and 12.0, solutions of hydrochloric acid and sodium hydroxide were used respectively. In the proposed procedure an acetate buffer with pH 4.75 is recommended because at this pH, the TAC reagent is more selective and the buffer index of the acetate buffer is maximum.

Effect of electrolytes on the extraction of the iron(III)-TAC complex

The influence of electrolytes on the extraction of the iron(III)-TAC complex was studied and the results showed that it is quantitative even in the presence of 100 mL of 30%, w/v, sodium chloride solution or of 100 mL of 30%, w/v, potassium nitrate. The salting out effect allowed a more rapid extraction.

Effect of the organic solvent

In order to investigate the influence of the organic solvent on the extraction of the iron(III)-TAC complex, several organic solvents with different properties were

tested. The results demonstrated that the solvents isoamyl alcohol, carbon tetrachloride, chloroform and methyl isobutyl ketone allow quantitative extraction.

Back extraction of iron to aqueous medium

The introduction of the organic solvents used in this work into the plasma (low-power) presents considerable operational difficulties due to the loading of the plasma with large quantities of organic vapor, destabilizing the plasma, often to the point of extinction. Thus, solutions of 1 mol/L nitric acid and 1.0 mol/L hydrochloric acid were tested for the back extraction of the complexed iron. The results showed that for both solutions the back extraction is quantitative. The recoveries (mean of 3 determinations) were 99.90% using nitric acid solution and 92.50% for hydrochloric acid solution. These results were obtained using isoamyl alcohol as solvent for the extraction of the complex.

Mineralization of the organic solvent

Another way to obtain an appropriate solution for iron determination by ICP-AES is to evaporate the organic solvent containing TAC and its iron complex, followed by digestion by heating the residue with 5.0 mL of concentrated nitric acid and dilution with 2%, v/v, hydrochloric acid solution. The obtained recovery (mean of 3 determinations) was 99.9%.

Analytical characteristics

The proposed procedure can be applied to preconcentration and separation of iron, in the range of 1.0 to 100.0 μg , contained in a solution volume of 50 to 500 mL, by using 30 mL of organic solvent, making a single extraction.

The calibration graph (0-2.0 $\mu\text{g/L}$) of iron was obtained with solutions prepared from 1 mg/L stock solution. The correlation coefficient was 0.9998.

The detection limit for the proposed procedure was 7.6 $\mu\text{g/L}$. The precision of the method, evaluated as the relative standard deviation obtained after analyzing a series of seven replicates, was 3.2% to 10.0 μg of iron contained in a solution volume of 250 mL.

Application

For the mineralization process of the organic solvent phase, carbon tetrachloride and chloroform are better because these have lower boiling points and higher vapor pressures than isoamyl alcohol, thus are evaporated more easily. However, for back extraction the isoamyl alcohol is better due to its lower density compared with water.

The proposed method was applied to iron determination in previously dried alkaline salts. The standard addition technique was applied and the obtained recoveries revealed

Table 2. Determination and recovery of iron in alkaline salt samples.

Sample	Concentration of the salt (%)	Concentration added (ng/g salt)	Iron found (ng/g salt)*	Recovery (%)
NaCl <i>Reagen</i>	30	0	502 ± 17	---
		667	1194 ± 21	104
NaCl <i>Carlo Erba</i>	30	0	237 ± 12	---
		667	893 ± 17	98
KNO ₃ <i>Vetec</i>	25	0	444 ± 12	---
		400	864 ± 17	105
KCl <i>Carlo Erba</i>	25	0	148 ± 9	---
		400	513 ± 15	91

* at 95% confidence level.

that the proposed procedure has a good accuracy. The results are shown in Table 2.

Conclusions

The proposed method is very important and fortunate, for the analytical problem of the determination of metal traces in alkaline salts by ICP-AES, and the fact that iron is frequently present at trace levels in these samples. The procedure for preconcentration and separation is simple, and can be also applied to the determination of iron using other analytical techniques for which the trace separation from saline matrices is nearly always inevitable.

The obtained recovery, measured through the standard addition technique, revealed that the proposed procedure has good accuracy.

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References

- Boumans, W.J.M. In *Inductively Coupled Plasma Emission Spectroscopy. Part 1: Methodology, Instrumentation and Performance*, Interscience, New York, **1987**.
- Bekjarov, G.; Kmetov, V. *Fresenius Z. Anal. Chem.* **1989**, 335, 971.
- Budic, B.; Hudnik, V. *J. Anal. At. Spectrom.* **1994**, 9, 53.
- Montaser, A.; Golightly, D.W. In *Inductively Coupled Plasma in Analytical Atomic Spectrometry*, VHC Publishers, New York, 1990.
- Berman, S.S.; McLaren, J.W.; Willie, S.N. *Anal. Chem.* **1980**, 52, 488.
- Brooks, R.R.; Presley, B.J.; Kaplan, I.R. *Talanta* **1967**, 14, 809.
- Sugimae, A. *Anal. Chim. Acta* **1980**, 121, 331.
- McLeod, C.W.; Otsuki, A.; Okamoto, K.; Haraguchi, H.; Fuwa, K. *Analyst* **1981**, 106, 419.
- Nakashima, S.; Sturgeon, R.E.; Willie, S.N.; Berman, S.S. *Fresenius Z. Anal. Chem.* **1988**, 330, 592.
- Watanabe, H.; Goto, K.; Taguchi, S.; McLaren, J.W.; Berman, S.S.; Russel, D.S. *Anal. Chem.* **1981**, 53, 738.
- Ueda, K. *Nippon Kagaku Kaishi* **1981**, 7, 1111.
- Ferreira, S.L.C.; Costa, A.C.S.; Andrade, H.A.S. *Mikrochimica Acta* **1993**, 111, 119.
- Fárias, P.A.M.; Ohara, A.K.; Ferreira, S.L.C. *Anal. Lett.* **1992**, 25, 1929.
- Gusev, S.I.; Gavrilova, N.F.; Kurepa, G.A.; Poplevina, L.V. *Zh. Anal. Khim.* **1974**, 29, 1955.
- Tsurumi, K.; Furuya, H.; Kamata, H. *Nippon Kagaku Kaishi* **1977**, 10, 1469.
- Tsurumi, K.; Furuya, H.; Kamata, H. *Anal. Lett.* **1980**, 13A(4), 319.
- Ferreira, S.L.C. *Talanta* **1988**, 35, 485.
- Ferreira, S.L.C.; Costa, A.C.S.; Andrade, H.A.S. *Mikrochimica Journal* **1991**, 44, 63.
- Ferreira, S.L.C.; Andrade, M.G.M.; Lopo, I.P.; Costa, A.C.S. *Anal. Lett.* **1991**, 24, 1675.