

Spectrophotometric Determination of Chromium in Steel with 4-(2-Thiazolylazo)-Resorcinol (TAR) Using Microwave Radiation

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Um método espectrofotométrico foi desenvolvido para determinação de Cr(III) com 4-(2-thiazolilazo)-resorcinol. Cr(III) reage lentamente com TAR em pH 5,7 formando um complexo vermelho. A formação do complexo pode ser acelerada pela irradiação de energia de microondas na mistura reacional. A absorvância atinge seu máximo após 5 min de irradiação e permanece estável por pelo menos 24 h. Brometo de N-cetil-N,N,N-trimetilamônio (CTAB) foi usado para aumentar a sensibilidade e solubilização do sistema. O método permitiu a determinação de cromo na faixa de concentração entre 0,050 e 3,0 $\mu\text{g mL}^{-1}$ ($9,62 \times 10^{-7}$ a $5,77 \times 10^{-5}$ mol L⁻¹) com absorvidade molar de $2,73 \times 10^4$ L⁻¹ mol⁻¹ cm⁻¹ e limite de detecção de 17 ng mL⁻¹ ($3,3 \times 10^{-7}$ mol L⁻¹) em 545 nm. A seletividade foi melhorada com o uso de EDTA e citrato como agentes mascarantes. Fe(III) interfere e deve ser extraído previamente, se presente na amostra. O método proposto foi aplicado com sucesso na determinação de cromo em amostras de aço. A precisão (R.S.D. < 2%) e a exatidão obtidas foram satisfatórias.

A spectrophotometric method for the determination of Cr(III) with 4-(2-thiazolylazo)-resorcinol was developed. Cr(III) slowly forms a red complex with TAR at pH 5.7. Irradiating the reacting mixture with microwave energy can accelerate the complex formation. The absorbance reached its maximum with 5 min of irradiation and remained stable, at least, for 24 h. N-cetyl-N,N,N-trimethylammonium bromide (CTAB) was used for increasing the sensitivity and solubility of the system. The method allowed the determination of chromium ranging from 0.050 to 3.0 $\mu\text{g mL}^{-1}$ (9.62×10^{-7} to 5.77×10^{-5} mol L⁻¹) with a molar absorptivity of 2.73×10^4 L⁻¹ mol⁻¹ cm⁻¹ and a detection limit of 17 ng mL⁻¹ (3.3×10^{-7} mol L⁻¹) at 545 nm. The selectivity was improved by using EDTA and citrate as masking agents. Fe(III) interferes and must be extracted previously, if present in the sample. The proposed method has been successfully applied to the determination of chromium in steel. The precision (R.S.D. < 2%) and accuracy were satisfactory.

Keywords: chromium, TAR, spectrophotometric, microwave radiation, steel

Introduction

The most important application of chromium in the metallurgic industry is its use as an alloying element in steels. In these materials, chromium contributes to increase the hardness, tempering and oxidation resistance.¹

Very few methods for chromium determination are based on the complex formation with Cr(III) in aqueous solution.² However spectrophotometric determination of chromium(III) invariably involves heating the reactants with reflux. This is probably due to the slow reactions of

chromium(III) aquocomplexes, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.³ The time required for heating the reactants varies from 5 to 130 min, depending on the reagent employed. Characteristics of previously spectrophotometric methods for chromium determinations are summarized in Table 1.²⁻⁶

Thiazole azo compounds have attracted much attention, as they are sensitive chromogenic reagents in addition to being important complexing agents. These dyes have been useful in spectrophotometric determinations due to their good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify.⁷ Among various thiazolylazo derivatives, 1-(2-thiazolylazo)-2-naphthol (TAN)⁸ and 4-(2-

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Table 1. Characteristics of previously spectrophotometric methods for chromium determination

Reagent	Linear range/ mg L ⁻¹	Molar absorptivity/ L mol ⁻¹ cm ⁻¹	Relative standard deviation/ %	Heating time/ min	Ref.
EDTA	6.0-160	–	0.6	30	2
5-Br-DMPAP	0.02- 0.56	7.8 x 10 ⁴	2	5	3
PAR	–	4.7 x 10 ⁴	–	135	4
PAN	0.3-2.0	1.28 x 10 ⁴	1.25	35	5
Br-PADAP	–	7.93 x 10 ⁴	–	40	6

thiazolylazo)resorcinol (TAR)⁹ have been reported for spectrophotometric determination of chromium(III). The previously method reported by Subrahmanyam and Eshwar⁹ with TAR requires 45 min of heating in a boiling water bath and addition of tert-butyl alcohol because some precipitate was observed after the complex formation.

Microwave energy has been applied to the field of chemistry in recent years, primarily dealing with rapid sample dissolution in analytical chemistry and acceleration of reactions in organic chemistry.^{10,11} In addition, microwave irradiation can be used to accelerate some colour-forming reactions for spectrophotometric determinations.¹² Spectrophotometric determination of chromium in catalyst using EDTA as the colour-forming reagent and microwave radiation has been proposed by the authors.¹³

In this paper, a simple and rapid method involving microwave radiation is described for the determination of chromium using TAR as spectrophotometric reagent. The method was used for the determination of chromium in steel samples.

Experimental

Reagents

All reagents were of analytical grade quality and freshly distilled and deionized water was used.

1.92 x 10⁻² mol L⁻¹ chromium stock solution (1000 µg mL⁻¹) was prepared by dilution of standard solution (Merck, CrCl₃ in 4.2% HCl) with water. Chromium reference solutions were prepared by dilution of the stock solution with water.

4.51 x 10⁻⁴ mol L⁻¹ 4-(2-thiazolylazo)resorcinol (TAR) was prepared by dissolving 0.1 g TAR (Aldrich) in 100 mL of ethanol.

Complexing solution. Prepared by dissolving 1.0 g of ethylenediamine tetraacetic acid (EDTA, Merck) and 1.0 g of sodium citrate (Merck) in 100 mL of water.

N-cetyl-N,N,N-trimethylammonium bromide (CTAB) solution 0.025 mol L⁻¹ was prepared by dissolving 1.0 g of CTAB (Merck) in 100 mL of water.

Buffer solution (pH 5.7) was prepared by mixing a trihydrate sodium acetate solution 1.0 mol L⁻¹ and glacial acetic acid 1.0 mol L⁻¹ until the required pH.

Hydroxylammonium chloride solution 2% (m/v) was prepared by dissolving 2.0 g of hydroxylammonium chloride (Merck) in 100 mL of water.

Apparatus

Spectrophotometric measurements were made in a Varian Cary 1E UV-Vis spectrophotometer with 1.00 cm glass cells. The pH measurements were performed with a ANALYSER 300 pH meter. A domestic microwave oven (Sanyo 700) with 2450 MHz frequency and 700 W (maximum power) was used for heating the sample solutions.

Sample preparation

A 0.25 g amount of each steel sample was previously weighed and placed in a conical flask to which 10 mL of concentrated nitric acid and 2 mL of concentrated hydrochloric acid were added. The system was heated up to promote the sample dissolution. The dissolved sample was placed in a volumetric flask and the volume was filled to 250 mL with water. Aliquots of 5.00 mL were placed into 100 mL separating funnels. Then, 50.0 mL of HCl 7 mol L⁻¹ were added and shaken with 25.0 mL of methyl isobutyl ketone (MIBIK) for 5 min for iron extraction and allowed the phases to separate. The aqueous solution was adjusted with NaOH to pH 5.7, transferred to a 100.00 mL volumetric flask and the volume was filled to 100 mL with water. The chromium(III) was determined under the optimized experimental conditions.

Procedure

Appropriated aliquot of each sample or standard solution containing chromium ranging from 2.5 to 150.0 µg was placed into a 250 mL beaker and 2.0 mL of hydroxylammonium solution were added to guarantee quantitative chromium reduction to Cr(III). Then 10.0 mL

of buffer solution, 2.0 mL of TAR solution and 5.0 mL of CTAB solution were added. The volume of the system was filled to approximately 40 mL with water and placed on the center of the microwave oven. So, the solution was heated up with the microwave oven operating on full power (700 W) for 5 min to promote the complexing reaction. After cooling to room temperature, 5 mL of the complexing solution was added. The resulting solution was placed in a volumetric flask and the volume was filled to 50 mL with water. The absorbance was measured at 545 nm in 1.00 cm glass cells, against a blank prepared in the same way but without chromium.

Results and Discussion

Characteristics of chromium(III)-TAR complex

Under the conditions used, chromium(III) ions form a reddish complex with TAR at pH 5.7 with absorption maximum at 545 nm. The absorption maximum of the reagent in the same conditions is at 418 nm. The reaction between TAR and Cr(III) is too slow at room temperature to be observed. However the absorbance reached its maximum in 4 min and remained stable, at least for 24 h, when the chromium(III)-TAR complex was formed with the aid of microwave energy. In addition, use of CTAB promotes an increase in analytical sensitivity and allows the complex solubilization in aqueous medium.

Effect of the pH

Chromium(III)-TAR system showed a maximal and constant absorbance at pH ranging from 5.3 to 6.5. An acetate/ acetic acid buffer at pH 5.7 was used to control the medium acidity. The effect of the buffer concentration on the chromium(III)-TAR complex was studied and according to the results no effect in the absorbance signal was observed within acetate concentration ranging from 0.10 to 2.5 mol L⁻¹. The concentration of 1.0 mol L⁻¹ was select for this procedure.

Effect of the surfactant amount

The results showed that CTAB must be present in the system in a concentration of at least 2.5 x 10⁻³ mol L⁻¹ to avoid precipitation. The presence of the surfactant avoids the use of organic solvent to prevent complex and reagent precipitations. In addition, the presence of CTAB in the system promoted an increasing of 20% in absorbance signal. It was observed that when this surfactant was present in the range from 2.5 x 10⁻³ to 1.0 x 10⁻² mol L⁻¹ no effect

was observed in the absorbance signal. The concentration of 2.5 x 10⁻³ mol L⁻¹ was select for this procedure.

Composition of chromium(III)-TAR complex

A study of the complex by mole ratio method showed that TAR forms a 1:2 (metal-to-ligand) complex with Cr(III). Under the conditions employed, 2.0 mL of 4.51 x 10⁻⁴ mol L⁻¹ TAR solution was required to obtain maximal and constant absorbance signal when 3.0 μg mL⁻¹ (3.77 x 10⁻⁵ mol L⁻¹) of chromium were used.

Effect of heating with microwave irradiation

Chromium(III) did not react with TAR at room temperature due to inertness of [Cr(H₂O)₆]³⁺. However, a complex is formed on heating the reactants. Under experimental conditions it was studied the effect of microwave irradiation on the coordination reaction between TAR and Cr(III). Because the microwave energy in the oven is not uniformly distributed, the location of the beaker with the reational system was the same during experiments. In this way, the beaker was placed on the center of the microwave oven and the solution was heated with the microwave oven operating on full power (700 W) at different times (1 to 7 min). As constant absorbance was recorded on irradiation for 4 min, all determinations were carried after irradiation for 5 min. The complex was stable for at least 24 h.

Effect of the addition order of the reagents

According to the results obtained, the order of addition of the reagents affects the complex formation. It was observed that the EDTA must be added only after microwave irradiation, when the complex was already been formed in order not to mask the chromium(III) reaction with TAR. Another fact observed relative to the order of addition of reagents is the effect of the hydroxylammonium as a reductant. The hydroxylammonium solution must be always added before the buffer addition.

Effect of interfering ions

TAR is not a selective reagent for chromium determination. However the mixture of citrate and EDTA as masking agents allowed the spectrophotometric determination with less interference. The effect of this combination on the chromium(III)-TAR complex formation was studied and it was observed that in the concentrations used in the procedure, the mixture did not affect the

stability of the system for at least 3 h when it was added after the microwave irradiation.

To study the effect of various metals on the determination of chromium with TAR, a solution containing both chromium and the foreign metal was treated according to the procedure. The reaction selectivity was investigated by determining 25.0 μg of chromium in the presence of 2500 μg of other ions using the mixed EDTA and citrate complexing solution. The tolerance limit was taken as $\pm 2\%$ change in absorbance. It was found that for these amounts, Zn(II), Pb(II), Ag(I), W(VI), Mn(II), Mo(VI), Si(IV), Sb(III), Cd(II), Al(III), Co(II), Cd(II), Pb(II), Ni(II), V(IV), Zr(IV), W(VI), Bi(III) and Hg(II) did not interfere. Chloride, bromide, iodide, sulfate, nitrate, carbonate, acetate and fluoride did not interfere. The interference of copper was circumvented with addition of thiourea. Fe(III) interfered and must be extracted, as chloride complex, using methyl isobutyl ketone (MIBK), as previously described.

Application

In the proposed procedure, Beer's law was obeyed from 0.050 to 3.0 $\mu\text{g mL}^{-1}$ (9.62×10^{-7} to 5.77×10^{-5} mol L⁻¹), with a molar absorptivity of 2.73×10^4 L mol⁻¹ cm⁻¹ at 545 nm. The analytical curves were made as described in the experimental procedure and good correlation coefficients ($R = 0.9999$, $n = 7$) were found. The detection limit (99.7 % confidence level) and the standard deviation ($n = 10$) were estimated as 17 $\mu\text{g L}^{-1}$ (3.3×10^{-7} mol L⁻¹) and 1.9 %, respectively.

The method was applied to chromium determination in steel reference samples and the results are shown in

Table 2. The results, as means of three determinations on each of the four steel samples, were compared with the certified values. The application of the paired *t*-test (95 % confidence level) did not show significant differences.

Conclusions

The method using TAR as spectrophotometric reagent to determine chromium in the presence of CTAB is selective, rapid, and simple. Many interferences can be completely masked with EDTA and citrate and the complex showed good stability after microwave irradiation. Fe(III) interfered and must be removed, as chloride complex, using methyl isobutyl ketone (MIBK). The sensitivity is comparable to other analytical methods allowing chromium determination at mg L⁻¹ level. The method was successfully applied to determine chromium in steel samples and the results showed good agreement with certified values.

Acknowledgements

The authors acknowledge the financial support from CNPq, FINEP and CAPES.

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Table 2. Chromium determination in steel reference samples and sample compositions (% , m/m)

Sample composition	Steel Sample			
	IPT 50	IPT 17	IPT 97	IPT 98
C	0.916	0.415	0.165	0.050
Si	0.326	0.260	0.231	0.26
Mn	0.280	0.724	1.11	1.88
P	0.031	0.014	0.015	0.042
S	0.015	0.021	0.026	0.016
Cr	4.49	0.820	1.22	16.75
Co	0.260	0.039	0.012	0.125
Mo	5.54	0.259	0.064	1.92
Ni	0.33	1.76	0.227	11.01
V	2.00	-	0.024	0.053
W	6.40	-	-	0.053
Cu	0.091	0.074	0.129	0.292
Certified Value (Cr)	4.49	0.820	1.22	16.75
This Method ^a (Cr), $n = 3$	4.39 ± 0.07	0.803 ± 0.02	1.18 ± 0.02	16.7 ± 0.2

^a at 95% level confidence.

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Received: January 27, 2003

Published on the web: November 28, 2003