

Extractive Spectrophotometric Determination of Chromium(III) in Steels Using 4-(2-Pyridylazo)resorcinol and Xylometazoline Hydrochloride

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Chromium(III) forms a 1 : 3 orange - red anionic complex with 4-(2-pyridylazo)resorcinol (PAR) when heated in an acetate buffer medium (pH 4.0–5.5) on a water-bath, and this complex can be extracted quantitatively with the xylometazolonium (XMH) cation into chloroform. This ion association system exhibits a maximum absorbance at 530 nm, with a molar absorptivity of $4.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and obeys Beer's law in the range 0–1.0 $\mu\text{g ml}^{-1}$ of chromium(III). Job's method of continuous variations revealed that the composition of the extracting species is 1 : 3 : 1 for Cr(III) - PAR - XMH. EDTA, when added after the formation of the complex between Cr(III) and PAR, can effectively mask the interference from Ca(II) (1000 μg), Ba(II) (1000 μg), Sr(II) (1000 μg), Tl(II) (1000 μg), Cd(II) (1000 μg), Mg(II) (500 μg), Hg(II) (500 μg), Al(III) (500 μg), Bi(III) (400 μg), V(V) (200 μg), Mn(II) (200 μg), Mo(VI) (200 μg), Cu(II) (150 μg) and W(VI) (150 μg) without any interference in the determination of chromium. This makes the method highly selective.

Keywords: Chromium(III) determination; extractive spectrophotometry; steels; 4-(2-pyridylazo)resorcinol; xylometazoline hydrochloride

Several workers^{1–3} have studied the formation of the complex between chromium(III) and 4-(2-pyridylazo)resorcinol (PAR) in aqueous media and the application of this complex to the spectrophotometric determination of chromium. Yotsuyanagi *et al.*³ reported the extraction of the Cr(III) - PAR anionic complex with a quaternary ammonium cation (tetradecyldimethylbenzylammonium chloride, TDBA⁺). However, in their procedure, the use of higher concentrations of TDBA⁺ to achieve the quantitative extraction of chromium delays the separation of the two phases and produces high reagent blank values, which requires the rigorous maintenance of experimental conditions. These conditions make it unsuitable for the determination of chromium in steel samples.

In our investigations we have observed that the Cr(III) - PAR anionic complex can be quantitatively extracted as an intense orange - red ion pair into chloroform in the pH range 4.0–5.5 using the xylometazolonium (XMH) cation as a counter ion. Even with large concentrations of XMH, good separation of the phases can be achieved within 1 min without any significant absorbance due to the reagent blank. When EDTA is added after the complex formation, the interference of many metal ions is effectively suppressed, without causing any errors in the determination of chromium. This has been exploited as a selective spectrophotometric method for the determination of chromium in steels. The average molar absorptivity of this method is $4.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, which is higher than those reported earlier for chromium complexes with diphenylcarbazide^{4–6} ($\epsilon = 41\,700$), dichromate⁷ ($\epsilon = 750$), EDTA^{8,9} ($\epsilon = 140$), Eriochrome Cyanine R¹⁰ ($\epsilon = 26\,400$), PAN¹¹ ($\epsilon = 12\,800$), TAN¹² ($\epsilon = 14\,600$), PAR² ($\epsilon = 29\,870$) and PAR - zephiramine³ ($\epsilon = 47\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$).

Experimental

Apparatus

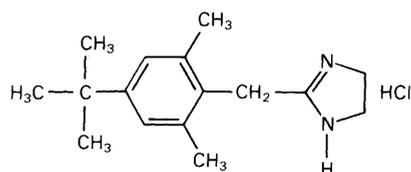
Absorbance measurements were made with a Systronics digital spectrophotometer, Model 106, Type MK(II). pH measurements were made with a Systronics pH meter, Model 335.

Reagents and Standards

Chromium(III) solution. A $1 \times 10^{-2} \text{ M}$ stock solution is prepared by dissolving 1.248 g of AnalaR chrome alum [$\text{K}(\text{SO}_4)_2\text{Cr} \cdot 12\text{H}_2\text{O}$] (E. Merck) in water in a 250-ml calibrated flask. A few drops of sulphuric acid are added to prevent hydrolysis of the chromium and the solution is diluted to the mark with doubly distilled water. The concentration is checked titrimetrically.¹³

4-(2-Pyridylazo)resorcinol. A $1 \times 10^{-3} \text{ M}$ solution is freshly prepared by dissolving the monosodium salt (Riedel), recrystallised twice from a 1 : 1 V/V ethanol - water mixture, in de-mineralised water.

Xylometazoline hydrochloride.



A $1 \times 10^{-2} \text{ M}$ stock solution is prepared by dissolving 0.2810 g of pure sample (Fair-deal, Bombay) in 100 ml of doubly distilled water.

Buffer solution. A buffer solution of pH 5 is prepared by mixing 30 ml of 0.2 M acetic acid and 70 ml of 0.2 M sodium acetate in a 100-ml calibrated flask.

EDTA solution, $1 \times 10^{-2} \text{ M}$. Prepared as described elsewhere.¹⁴

Cerium(IV) ammonium sulphate solution, $2 \times 10^{-2} \text{ M}$. Prepared as described elsewhere.¹⁴

Chloroform. Doubly distilled chloroform (BDH Chemicals) is used in all the investigations and all extractions are carried out in a fume-cupboard.

General Extraction Procedure

Pipette an aliquot (*ca.* 5 ml) of the sample solution containing 2–10 μg of chromium into a 25-ml calibrated flask. Add 5.0 ml of acetate buffer (pH 5.0) and 4.0 ml of $1 \times 10^{-3} \text{ M}$ PAR and

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heat on a water-bath at 90 °C for 2 h. After cooling to room temperature, transfer quantitatively into a 125-ml separating funnel and add 1.0 ml of 1×10^{-2} M EDTA and 4.0 ml of 1×10^{-3} M XMH. Dilute to 25 ml and equilibrate with 10 ml of chloroform for 1 min. When the two phases have separated, run the organic layer into a 1-cm quartz cell. Measure the absorbance at 530 nm against a similarly prepared reagent blank.

Results and Discussion

Solvent Selection

Chloroform, butanol, nitrobenzene, ethyl methyl ketone and isobutyl methyl ketone (IBMK) all extract the ion pair. However, chloroform gives the maximum absorbance and is therefore recommended as a solvent.

Optimum Conditions

The ion pair is best extracted in the pH range 4.0–5.5. A 10-fold excess of PAR and a 20-fold excess of XMH to chromium(III) are sufficient to attain the maximum absorbance and quantitative extraction. Variations of the reagent concentrations between 10^{-5} and 10^{-2} M do not cause any difficulty either in the separation of the phases or in the absorbance of the reagent blank. A 1-min equilibration time is sufficient to attain maximum absorbance and quantitative extraction.

Absorption Spectra and Beer's Law

The absorption spectra of the Cr(III) - PAR - XMH ion association system and its reagent blank are shown in Fig. 1. This shows the maximum absorbance of the system to be at 530 nm. The system obeys Beer's law up to $1.0 \mu\text{g ml}^{-1}$ of chromium at 530 nm.

Interference Studies

Up to 4 ml of 1×10^{-2} M EDTA are tolerated in this method when added after the formation of the Cr(III) - PAR complex. Interfering ions such as Ca(II) (1000 μg), Ba(II) (1000 μg), Sr(II) (1000 μg), Tl(II) (1000 μg), Cd(II) (1000 μg), Mg(II) (500 μg), Hg(II) (500 μg), Al(III) (500 μg), Bi(III) (400 μg), V(V) (200 μg), Mn(II) (200 μg), Mo(VI) (200 μg), Cu(II) (150 μg) and W(VI) (150 μg) can be effectively masked if the

extractions are carried out in the presence of 1 ml of 1×10^{-2} M EDTA. As these ions form labile complexes with PAR, they are decomposed completely by EDTA in 2 min, even at room temperature. However, Fe(III), Ni(II), Co(II) and Pd(II), which form inert complexes with PAR, seriously interfere in the determination of chromium. In the presence of these interfering ions, this method can be successfully applied after the separation of chromium. The recommended procedure for the separation of Cr(III), as given under Analytical Application, involves the oxidation of Cr(III) to Cr(VI) by cerium(IV) ammonium sulphate,¹⁵ followed by the extraction of Cr(VI) from 2 M HCl with two aliquots of IBMK as HCrO_3Cl ,¹⁶ stripping the Cr(VI) quantitatively with two portions of water and then reducing Cr(VI) to Cr(III) by heating with hydrogen peroxide.

Experimental results for the analysis of synthetic mixtures containing metal ions normally present with chromium in complex materials are given in Table 1.

Precision

The precision of the method was evaluated by analysing samples containing different concentrations of chromium (each determination was carried out six times). A standard deviation in the range 0.058–0.118 for 2–10 μg of chromium in 10.0 ml of chloroform was obtained, which indicates that the method is both precise and reproducible.

Composition of the Cr(III) - PAR - XMH Ion Association Complex

The composition of the ion pair was determined by Job's method of continuous variations and a ratio of 1:3:1 for Cr(III) - PAR - XMH was obtained. As PAR (H_2R) exists equally as H_2R and HR^- in the pH range 4–6,¹⁷ the extracting species can be represented as $\text{Cr}(\text{R})(\text{HR})_2^- \cdot \text{XMH}^+$. The conditional formation - extraction constant of this Cr(III) - PAR system in the presence of XMH was determined by the Likussar and Boltz¹⁸ method and was found to be 1.34×10^{13} .

Analytical Application

Procedure for the Determination of Chromium in Steels

Dissolution of the sample

Dissolve a known mass (0.5–1.0 g) of the sample in 100 ml of HCl (1:1); cautiously add 20 ml of HNO_3 (1:1) and then boil gently for 5 min (or for steels containing tungsten, until the solution becomes bright yellow). Dilute to 150 ml and heat to boiling. Filter the precipitate, wash it thoroughly with HCl (1:4) and quantitatively collect the filtrate and washings. Add 10 ml of H_2SO_4 (5 M) to the filtrate and evaporate it until fumes of H_2SO_4 appear, then cool and add 100 ml of water. Digest the filtrate until all soluble salts are in solution. If any tungstic acid separates (as with high-speed steels), filter again and wash thoroughly with dilute sulphuric acid (1:99).

Separation of chromium

Transfer the filtrate into a 500-ml beaker, add 10 ml of 0.02 M cerium(IV) ammonium sulphate and boil until the volume is reduced to 50 ml. After cooling, transfer the solution into a 250-ml separating funnel, add 50 ml of 6 M HCl and dilute to ca. 150 ml with distilled water, then add 20 ml of IBMK and shake for 1 min. After the complete separation of the two phases, remove the aqueous phase and repeat the extraction with another 20 ml of IBMK. Combine the two organic extracts and shake with 50 ml of 2 M HCl (three or four times) to back-extract any traces of iron present in the organic layer

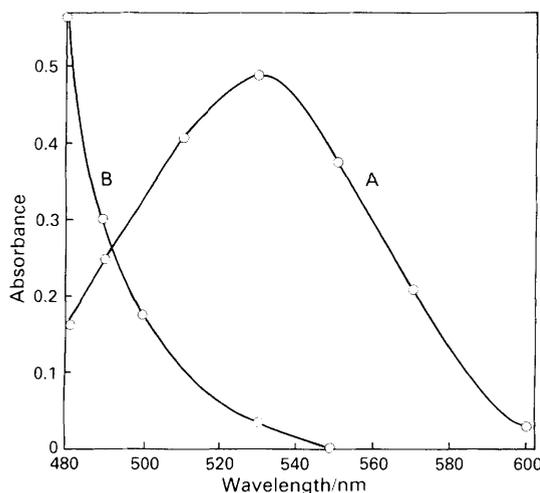


Fig. 1. Absorption spectra of the chromium(III) - PAR - XMH ion associate in chloroform at pH 5.0. A, Cr(III) + PAR + XMH vs. reagent blank (PAR + XMH); B, PAR + XMH vs. chloroform. Conditions: Cr(III) = 5×10^{-6} M; PAR = 4×10^{-4} M; and XMH = 4×10^{-4} M

Table 1. Determination of chromium in some synthetic mixtures

Sample No.	Composition/ μg	Chromium added/ μg	Chromium, %	Chromium found, mean \pm s.d. *
1	Al(III) (400) + V(V) (200) + Mo(VI) (200) + W(VI) (150) + Mn(II) (150). Total: 1 100	10.0	0.91	10.10 \pm 0.095
2	Al(III) (300) + Mn(II) (200) + V(V) (150) + Cu(II) (100) + Bi(III) (100). Total: 850	5.0	0.59	4.90 \pm 0.053
3†	Ni(II) (10 000) + Mo(VI) (8000) + Al(III) (4000) + Mn(II) (2000) + Co(II) (1000). Total: 25 000	5.0	0.02	4.95 \pm 0.074
4†	Ni(II) (25 000) + Mo(VI) (20 000) + Al(III) (10 000) + V(V) (10 000) + Mn(II) (5000). Total: 70 000	5.0	0.0071	4.90 \pm 0.085
5†	Fe(III) (3500) + Mo(VI) (1000) + Mn(II) (800) + V(V) (1000) + Bi(III) (500). Total: 6800	5.0	0.074	4.95 \pm 0.045
6†	Fe(III) (4000) + Ni(II) (1000) + Co(II) (500) + V(V) (1000) + Cu(II) (500) + Al(III) (1000) + Mn(II) (600). Total: 8600	5.0	0.058	4.90 \pm 0.070

* Average of six determinations.

† Chromium determined after prior separation by the procedure given under Analytical Application.

Table 2. Determination of chromium in steels

Sample No.	Composition, %	Certified chromium content, %	Chromium found, % (mean \pm s.d. *)
1	BCS No. 224/1. Chromium - vanadium steel, C(0.50), Si(0.30), S(0.008), P(0.022), Mn(0.66), V(0.19)	1.06	1.07 \pm 0.010
2	BCS No. 405. Chromium - vanadium steel, Mo(0.017), Si(1.38), S(0.058), P(0.19), Mn(1.28), Ni(0.12), Cu(0.015), V(0.32)	0.21	0.21 \pm 0.004
3	BCS No. 219/3. Nickel - chromium - molybdenum steel, Ni(2.52), Mo(0.60), C(0.31), Si(0.20), S(0.010), P(0.019), Mn(0.74), Cu(0.19)	0.76	0.76 \pm 0.011
4	BCS No. 241/1. High-speed steel, W(19.61), Mo(0.52), Co(5.67), C(0.85), Si(0.33), S(0.033), P(0.021), Mn(0.30), Sn(0.025)	5.03	5.00 \pm 0.019

* Average of six determinations.

and to separate the aqueous layer. Shake the organic layer with two portions of 20 ml of distilled water to back-extract the Cr(VI) quantitatively. Combine the two aqueous layers and boil for 2 min, then add 4 ml of 5 M H₂SO₄ and 2 ml of H₂O₂ (30%) to reduce Cr(VI) to Cr(III) and continue boiling for 10 min. After the solution has cooled to room temperature, transfer it into a 250-ml calibrated flask and dilute to the mark. Place an aliquot from the above solution in a 125-ml separating funnel and determine the chromium present as under General Extraction Procedure.

The results obtained for the determination of chromium in some synthetic mixtures and in steel samples using the described procedure are given in Tables 1 and 2.

Conclusions

The Cr(III) - PAR complex anion can be extracted as an ion pair into chloroform with the xylometrazolium cation (XMH), giving an intense orange - red extract with a molar absorptivity of $4.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 530 \text{ nm}$. In the presence of EDTA this extraction becomes selective and can be used for the precise determination of chromium in steel. In contrast to cationic extractants such as TDBA and CDBA, XMH can be used as an effective extractant over a wide concentration range without any difficulties either in the separation of the phases or in the absorbance of the reagent blank.

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