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Rapid Spectrophotometric Determination of Chromium with Trifluoperazine Hydrochloride

by H.D. Revanasiddappa* and T.N. Kiran Kumar

Department of Studies in Chemistry, University of Mysore,
Manasagangothri, Mysore – 570 006, India

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A rapid and sensitive spectrophotometric method for the determination of trace amounts of chromium(VI) is described. The method is based on the oxidation of trifluoperazine hydrochloride (TFPH) by chromium(VI) in the presence of orthophosphoric acid. The red coloured species obtained give an absorption maximum at 505 nm. The system obeys Beer's law over a range of 2 to 18 μg of Cr(VI) in the final volume of 10 mL. The molar absorptivity of the colour system is 2.08×10^4 L mol^{-1} cm^{-1} and the developed colour is stable for 2 h. The detection limit of Cr(VI) is 0.0033 μg mL^{-1}. Chromium(III) can be de-termined after oxidation to chromium(VI) with bromine water in alkaline medium. The method has been used for the determination of chromium in alloy steels, industrial effluents and pharmaceutical samples.

Opisano szybką i czułą metodę spektrofotometrycznego oznaczania śladów chromu(VI). Metoda jest oparta na utlenianiu chlorowodorku trifluoroperazyny (TFPH) przez Cr(VI) w środowisku H_3PO_4. Powstają produkty zabarwione na czerwono. Maksymalną absorpcję światła uzyskuje sie dla fali 505 nm. Prawo Beer'a jest spełnione w zakresie 2–28 μg Cr(VI) w końcowej objętości 10 mL. Molowy współczynnik absorpcji wynosi 2.08×10^4 L mol^{-1} cm^{-1}, a uzyskany czerwony kolor jest trwały przez 2 godz. Granicę wykrywalności dla Cr(VI) oszacowano na 0.0033 μg mL^{-1}. Chrom(III) można oznaczyć po utlenieniu do chro-mu(VI) wodą bromową w środowisku zasadowym. Opracowaną metodę wykorzystano do oznaczania chromu w stali oraz próbkach przemysłowych i farmaceutycznych.

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* Corresponding author.

The determination of trace amounts of chromium is of considerable importance because of the contrasting biological effect of its two common oxidation states, chromium(III) and chromium(VI). Chromium(III) is an essential nutrient for maintaining normal physiological function[1], whereas chromium(VI) is toxic [2]. Chromium compounds are extensively used in leather, textile and many other industries. Owing to the increasing commercial importance of chromium a wide variety of reagents have been proposed for its spectrophotometric determination. Some spectrophotometric methods for the determination of chromium as chromium(III), based on azo reagents [3–5]. The reaction with these reagents require a heating step for colour development. Other spectrophotometric methods are based on the oxidation of organic compounds [6–8] and on the formation of ion-associates [9,10]. The later method has the disadvantage of high blank value. The most widely used reagent for chromium(VI) determination is diphenylcarbazide [11,12] but it suffers serious interference from Fe(III), Mo(VI), Cu(II) and Hg(II) [11,13], and also the formed complex is stable for only 30 min in the presence of phosphate buffer [14]. Some indirect methods have been developed for the determination of chromium(VI) [15,16].

The determination of traces of chromium is important in the studies of biological processes and for industrial purpose, development of a simple, rapid, sensitive and inexpensive spectrophotometric method is highly desirable.

N-alkyl derivatives of phenothiazines have attracted the attention of analytical chemists as versatile spectrophotometric reagents [17] and redox indicators. These compounds are first oxidized to a red radical cation, which may be further oxidized to a colourless sulfoxide derivative [18]. Trifluoperazine hydrochloride, TFPH, chemically 10-[3-(4-methyl-1-poperazinyl) propyl]-2-trifluoromethyl phenothiazine, is one of such compounds.

The aim of the present work is to provide a simple, sensitive and inexpensive method for the determination of chromium(VI) based on the oxidation of trifluoperazine hydrochloride in phosforic acid medium. Chromium(III) is determined after oxidation to chromium(VI) by bromine in the alkaline medium and the excess bromine is removed by the addition of sulfosalicylic acid. The proposed method has been successfully used for the determination of chromium in alloy steels, industrial effluents and pharmaceutical preparations.

EXPERIMENTAL

Apparatus

Jasco model UVIDEC–610 and Elico model SL–171 spectrophotometers with 1 cm matched quartz cells were used for all absorbance measurements.

Reagents

All chemicals used were of analytical-reagent grade and distilled water was used for dilution of reagents and samples.

Standard chromium(VI) solution (1000 µg mL^{-1}). Dissolve 0.2829 g of $K_2Cr_2O_7$ in 100 mL of water, and dilute this to obtain the working standard of suitable concentration.

Standard chromium(III) solution (1000 µg mL^{-1}). Prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 50 mL water, adding 1 mL saturated sodium sulfite solution, acidifying with 1 mL, 2.5 mol L^{-1} sulfuric acid, and then boiling 2 min to remove excess SO_2 and diluting with water to 1000 mL. A suitable volume of this solution was diluted to obtain the working standard.

Trifluoperazine hydrochloride (TFPH). A 0.5% (m/v) aqueous solution of TFPH was prepared and stored in an amber bottle in a refrigerator.

Others. The following reagents were prepared by dissolving the requisite amount in distilled water: orthophosphoric acid (10 mol L^{-1}), hydroxylamine hydrochloride (0.1%), bromine water (saturated), sulfosalicylic acid (5%), KOH (4.5 mol L^{-1}), sulfuric acid (0.5 and 2.5 mol L^{-1}), HCl (5 mol L^{-1}).

Procedures

Determination of chromium(VI). An aliquot of the sample solution containing 2–18 µg (0.2 to 1.8 ppm) of chromium(VI) was transferred into a series of 10 mL calibrated flasks. 5 mL of 10 mol L^{-1} orthophophoric acid and 0.5 mL of 0.5% TFPH solution were added, the contents were diluted to the mark with distilled water, mixed well and the absorbance was measured at 505 nm against the corresponding reagent blank.

Determination of chromium(III). An aliquot of the sample solution containing 2–18 µg (0.2 to 1.8 ppm) of chromium(III) was transferred into a series of 10 mL calibrated flasks. 0.5 mL saturated bromine water and 0.5 mL of 4.5 mol L^{-1} KOH solution were added to each flasks and allowed the mixture to stand for 5 min. Then, 0.5 mL of 2.5 mol L^{-1} sulfuric acid and 0.5 mL of 5% sulfosalicylic acid were added and followed the above procedure [chromium(VI)] for the colour development and recorded the absorbance at 505 nm against the corresponding reagent blank.

Analysis of mixture containing chromium(III) and chromium(VI). Analyze separately, an aliquot (18 µg) of the mixture according to the procedure for chromium(VI) and establish the concentration of chromium(VI). Analyze another aliquot (18 µg) according to the procedure described for chromium(III) to establish the concentration of total chromium[Cr(III) + Cr(VI)]. The difference between the two values is the concentration of chromium(III) in the mixture.

RESULTS AND DISCUSSION

Preliminary investigations were performed with 5 µg of chromium(VI) to establish the optimum conditions for the formation of the chromium-TFPH species. These showed that chromium(VI) reacts with TFPH at room temperature (30°C) in the orthophosphoric acid medium to form a red species, which is believed to be a radical cation

[19,20]. This was confirmed by the ion-exchange technique. The red species was retained by a cation-exchange resin but not by an anion-exchange resin column.

Effect of acids. The stability of the coloured species depends on the nature of the acid medium. The red species is unstable in either sulfuric acid or hydrochloric acid medium, and does not give maximum colour intensity in acetic acid medium. Orthophos-phoric acid medium is recommended because the red colour is stable for 2 h and sub-ject to less interference from foreign ions. The maximum colour development obtained in the range 3–6 mol L^{-1} phosphoric acid and hence the acid strength of 5 mol L^{-1} was found to be sufficient for the subsequent studies.

Effect of reagent concentration. The effect of the concentration of TFPH was studied by measuring the absorbance at 505 nm for a solution containing a fixed concentration of chromium(VI) [1ppm] and varying amounts of TFPH. 0.5 mL of 0.5% TFPH in a total volume of 10 mL was found to be sufficient.

Effect of temperature. The absorbance of the coloured radical cation remains the same in the temperature range 5–45°C. A departure of the temperature from this range decreases the absorbance values.

Analytical data. A linear calibration graph was obtained for 2–18 μg chromium(VI) in the final volume of 10 mL. The detection limit (D_L) of chromium(VI) is 0.0033 μg mL^{-1} [$D_L = 3.3\ \sigma/S$, where, σ is the standard deviation of the blank (n = 5), and 'S' is the slope of the calibration curve]. The precision of the proposed method was established by determining the concentration of 10 samples containing 10 μg chromium(VI); the relative standard deviation was 1.5%. The correlation coefficient of calibration graph equals 0.999. The molar absorptivity of the colour system is 2.08×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.0025 μg cm^{-2}.

Effect of diverse ions. In order to assess possible analytical applications of the method, the effect of some ions which often accompany chromium was studied by adding different amounts of the diverse ions to a 1 ppm chromium(VI) solution which gave the absorbance readings error smaller than ±2% (Tab. 1). The major advantage of this method is that TFPH can be used as a selective reagent for the determination of chromium in the presence of large amounts of Fe(III), Mo(VI), Ni(II) and Mn(II), which are associated with chromium in steels. The results also indicate that Fe(II), iodide and iodate, interfere seriously.

Table 1. Effect of diverse ions on determination of 1 ppm of Cr(VI)

Ion added	Tolerance limit, ppm	Ion added	Tolerance limit, ppm
Cu^{2+}	1000	MoO_4^{2-}	900
Ni^{2+}	2000	VO_4^{3-}	2
Co^{2+}	90	WO_4^{2-}	110
Pb^{2+}	200	Flouride	1500
Al^{3+}	3000	Sulfate	400
Ca^{2+}	1500	Iodide	0.4
Fe^{2+}	0.4	Oxalate	2000
Fe^{3+}	400	Sulfite	100
Na^{+}	3000	Nitrate	400
K^{+}	3000	Iodate	0.2
Mn^{2+}	1200	Chloride	1500
Zn^{2+}	1000	Tartrate	200
Ba^{2+}	3500	Bromide	1000

Applications

The proposed method was applied to the determination of chromium in standard alloy steels, industrial effluents and pharmaceutical samples. The results are presented in Tables 2, 3, 4, respectively.

Alloy steels were dissolved in approximately 8 mL of aqua regia. The solutions were evaporated nearly to dryness on a sand bath, then sulfuric acid (1–2 mL, 1:1) was added and evaporated until salts crystallized. 10 mL of water was added. The solution was warmed, filtered and diluted to know volume. The suitable aliquots of the sample solutions were analyzed, according to the procedure, for chromium(III).

The tannery effluent was diluted 50 times, and the chromium plating effluent was diluted 10 times before analysis. The suitable aliquots of the sample solution were analyzed according to the procedure for the determination of chromium(III) and chromium(VI). The solutions were also analyzed according to the standard diphenylcarbazide method.

Table 2. Determination of chromium in alloy steels

Sample (m/v)	Certified chromium, %	Volume of solution, ml	Chromium found[a], %	RSD, %
GKW Steel, India (0.05g 100mL) [C 0.54%, Mn 0.89%, S 0.018%, P 0.034%, Si 0.33%, V 0.13%]	1.02	1.0 1.5 2.0	1.016 ± 0.012 1.018 ± 0.015 1.014 ± 0.014	1.18 1.47 1.38
Stainless steel No.304 (0.05g/100ml)[b] [Ni 8.12%, Fe (70-71%)]	18.0	1.0 1.5 2.0	17.97 ± 0.09 17.98 ± 0.08 18.00 ± 0.07	0.50 0.44 0.38

[a] At each level, mean ± standard deviation (n = 5).

[b] Solution diluted 20 times before determination.

Table 3. Determination of chromium in industrial effluents

Sample	Proposed method		Diphenylcarbazide method	
	chromium found, ppm[a]		chromium found, ppm[a]	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tannery effluent [b]	323.9 ± 0.24	ND[c]	324.0 ± 0.30	ND[c]
Chromium plating effluent [d]	32.1 ± 0.15	69.7 ± 0.27	31.9 ± 0.19	69.6 ± 0.34

[a] Mean ± standard deviation (n = 5).

[b] Solution diluted 50 times before analysis.

[c] ND, not detected.

[d] Solution diluted 10 times before analysis.

The samples of the finely powdered multivitamin-multimineral tablets containing chromium(III) were treated with 5 mL nitric acid, and the mixture was dried by evaporation. The residue was leached with 5 mL of 0.5 mol L^{-1} H_2SO_4. The solution was diluted to a known volume with water. The suitable aliquots of the sample solution were analyzed according to the procedure for chromium(III).

The statistical analysis of the results by the F- and t-test showed no significant difference in the accuracy and the precision between the proposed and the reference methods and the certified values of the samples. The values of Student's t-test and the F-test were ≤ 1.8 and 1.6, respectively, (the tabulated t-value for the 95% confidence level and $n = 5$ is 2.78, and for F-value is 6.39). The precision of the proposed method was evaluated by doing replicate analysis of the samples containing chromium at thrpee different concentrations. The low values of the RSD reflect the high precision of the proposed method.

Table 4. Determination of chromium in pharmaceutical preparations

Sample (m/v)	Composition of tablet m/tablet	Certified value of chromium mg/tablet	Volume of solution mL	Chromium found[a] mg/tablet	RSD %
Optisulin [Sai Mira Innopharm Pvt. Ltd, India] (0.30 g 100 mL)	Zinc sulfate monohydrate, 27.50 mg; vitamin B_6, 3 mg; vitamin B_{12}, 15 mg; folic acid, 1 mg; (0.3 g)	0.500	1.0 1.5 2.0	0.495 ± 0.008 0.498 ± 0.009 0.497 ± 0.005	1.61 1.80 1.00
Chromoplex [Aristo Pharmaceuticals Ltd, India] (0.55 g/100 mL)	Zinc sulfate monohydrate, 27.50 mg; vitamin B_1, 10 mg; vitamin B_{12}, 15 mg; nicotinamide, 50 mg; calcium pantothenate, 12 mg; folic acid, 1 mg; vitamin C, 150 mg; (0.550 g)	0.200	1.5 2.5 3.0	0.198 ± 0.003 0.199 ± 0.002 0.198 ± 0.004	1.51 1.00 2.02
Fourts B [Fourts Laboratories Pvt. Ltd, India] (0.65 g/100 mL)	Thiamine mononitrate, 10 mg; riboflavin, 10 mg; pyridoxine hydrochloride, 3 mg; niacinamide, 50 mg; vitamin C 150 mg; zinc sulfate, 8 mg; selenium, 100 µg; (0.65 g)	0.150	1.5 2.0 2.5	0.149 ± 0.003 0.148 ± 0.002 0.150 ± 0.001	2.01 1.36 0.66

[a] At each level, mean ± standard deviation (n = 5).

CONCLUSIONS

The proposed method for the determination of chromium(VI) offers the advantage of simplicity, rapidity and sensitivity without the need for heating or extraction. The developed colour is stable for 2 h, has the advantage of greater colour stability compared with diphenylcarbazide method (30 min). The method has also the advantage of determining individual amounts of chromium(VI) and chromium(III). The proposed method has been successfully applied to the determination of chromium in alloy steels, industrial effluents and pharmaceutical preparations.

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