Chem. Anal. (Warsaw), **41**, 569 (1996)

Spectrophotometric Determination of Chromium Based on Ion-Pair Formation

by V. Maheswari and N. Balasubramanian*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Key words: chromium, rhodamine 6G, spectrophotometry

A sensitive spectrophotometric method for the determination of trace amounts of chromium(VI) is described. Chromium(VI) forms chlorochromate anion in the presence of acid and chloride ion. The formed anion is extracted in toluene as ion-pair with a cationic dye – rhodamine 6G. At 535 nm absorption maximum molar absorptivity is 2×10^4 l mol^{-1} cm^{-1}. The colour is stable for 4 h and the system obeys the Beer's law in the range 0–8 μg of chromium(VI). Chromium(III) is determined after oxidation to chromium(VI) with potassium permanganate. The method has been applied for the determination of chromium in standard alloy steels, pharmaceutical preparations, geological samples and industrial effluents.

Opracowano czułą spektrofotometryczną metodę oznaczania śladowych ilości chromu(VI). Chrom (VI) tworzy w obecności kwasu i jonów chlorkowych jon chlorochromianowy. Tak utworzony jon jest ekstrahowany toluenem jako para jonowa z kationowym barwnikiem rodaminą 6G. Przy maksimum absorpcji przy 535 nm molowy współczynnik absorpcji wynosi 2×10^4 l mol^{-1} cm^{-1}. Kolor jest trwały w ciągu 4 godzin, a układ spełnia prawo Beera w zakresie od 0 do 8 μg chromu(VI). Chrom(III) oznacza się po jego utlenieniu za pomocą nadmanganianu potasu. Opracowaną metodę zastosowano do oznaczania chromu w certifikowanych próbkach stali, preparatach farmaceutycznych, próbkach geologicznych i ściekach przemysłowych.

The importance of chromium is due to its use in various industries like leather, textile, pigment, chemical manufacture and metal finishing. Chromium(III) is essential for maintaining physiological functions [1], whereas chromium(VI) is toxic and

* Author for correspondence.

carcinogenic [2]. Hence the determination of chromium(VI) is extremely important. Analytical techniques widely used for trace determination of chromium in various matrices include spectrophotometry [3], atomic absorption spectrometry [4], and inductively coupled plasma atomic emission spectrometry [5]. Techniques such as atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry require a preliminary separation step such as solvent extraction or ion-exchange to determine individual amounts of chromium(III) and chromium(VI). Diphenylcarbazide is the commonly used specific reagent for the spectrophotometric determination of chromium(VI) [6,7]. The disadvantage of the method is its poor colour stability, demanding the absorbance measurements to be completed within 30 min [8]. The extraction of chlorochromate anion with cationic dyes like methylene blue [9] ($\varepsilon = 8.33\times10^4$ l mol^{-1} cm^{-1}), iodonitroterazolium chloride [10] ($\varepsilon = 8.8\times10^4$ l mol^{-1} cm^{-1}) and tetrazolium violet [10] ($\varepsilon = 1.22\times10^5$ l mol^{-1} cm^{-1}) have been recently reported for the determination of chromium(VI) at trace levels. Although these methods have high sensitivity, the blank absorbance values are high A = (0.20–0.35).

In the present investigation, rhodamine 6G is used to form an ion-pair with chlorochromate anion which is extracted into toluene. Chromium(III) is determined after oxidation it to chromium(VI) by potassium permanganate and destroying the excess permanganate using sodium azide.

EXPERIMENTAL

Apparatus and reagents

Absorbance measurements were made with Carl Zeiss PMQ II spectrophotometer with 1 cm glass cells.

Standard chromium(VI) solution (1000 μg ml^{-1}) was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 100 ml water. Suitable volume of this solution was diluted to obtain the working standard.

Standard chromium(III) solution (1000 μg ml^{-1}) was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 50 ml water, adding 1 ml of saturated sodium sulphite solution, acidifying with 1 ml of 2.5 mol l^{-1} sulphuric acid, boiling for 2 min to remove the excess SO_2 gas and diluting with water to 100 ml. Suitable volume of this solution was diluted to obtain the working standard.

Ammonium tetrathiomolybdate (1 mg Mo in 1 ml) was prepared by dissolving 1.8 g of ammonium heptamolybdate tetrahydrate in a mixture of 15 ml aqueous ammonia and 5 ml of water and bubbling H_2S through the solution until it is saturated. The temperature was raised to 60°C and H_2S was passed again till the formation of the red coloured complex. The mixture was cooled in ice and filtered through a Buchner funnel, the product was washed with isopropanol and dried by sucking air. The reagent was prepared by dissolving 0.271 g of ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$] in 100 ml water. This reagent is stable for 30 days if stored in refrigerator.

The following reagents were prepared by dissolving appropriate amounts of reagents in distilled water: sodium chloride 15%, rhodamine 6G 0.1%, potassium permanganate 0.1%, sodium azide 1.0%, sodium fluoride 1.0%, sulphuric acid 0.5 and 5 mol l^{-1}.

Toluene was used for extraction.

All chemicals used were of analytical reagent grade and distilled water was used for preparing reagent solutions.

Procedures

Determination of chromium(VI): Transfer the sample solution (< 10 ml) containing not more than 8 μg of chromium(VI) into a 60 ml separatory funnel. Add 1.5 ml of 5 mol l^{-1} sulphuric acid, 5 ml of 15% sodium chloride and 5 ml of 0.1% rhodamine 6G. Add 5 ml of toluene and equilibrate for 2 min. Separate the organic layer, and dry it by adding 1 g of anhydrous sodium sulphate and measure the absorbance at 535 nm using 1 cm glass cells against a reagent blank run through the entire procedure. Establish the concentration of chromium(VI) by reference to the calibration graph prepared with 0–8 μg of chromium(VI) following the above procedure.

Determination of chromium(III): To 10 ml of sample solution containing not more than 8 μg of chromium(III), add 1 ml of potassium permanganate and 1.5 ml of 5 mol l^{-1} sulphuric acid. Boil the solution for 3 min, cool and add 1 ml of 1% sodium azide. Transfer this solution into a 60 ml separatory funnel, add 5 ml of 15% sodium chloride and 5 ml of 0.1% rhodamine 6G. Add 5 ml of toluene and equilibrate for 2 min. Separate the organic layer, add 1 g of anhydrous sodium sulphate and measure the absorbance at 535 nm using 1 cm glass cells against a reagent blank run through the entire procedure. Establish the concentration of chromium(III) by reference to the calibration graph prepared with 0–8 μg of chromium(III) following the above procedure or 0–8 μg of chromium(VI) following the procedure described for chromium(VI).

Analysis of mixture containing chromium(III) and chromium(VI): For determination of chromium(VI) take an aliquot (10 ml) of the mixture, follow the procedure recommended for chromium(VI) determination and establish the concentration of chromium(VI). For determination of total chromium take another aliquot (10 ml) and follow the procedure described for chromium(III) to establish the concentration of total chromium [chromium(III) + chromium(VI)]. The difference between the two values will be a measure of chromium(III) concentration in the mixture.

RESULTS AND DISCUSSION

Preliminary investigations were carried out using 5 μg of chromium(VI) and 0.1% rhodamine 6G solution. The ion-pair formed in hydrochloric acid medium [$Rh6G^{+}\cdot CrO_3Cl^{-}$] was extracted in toluene. Conditions were optimised by measuring the absorbance at 535 nm.

The ion-pair was found to extract only in the presence of hydrochloric acid. It was observed that the absorbance of the blank was high A = (0.08–0.10) when hydrochloric acid was used. This may be due to heavy metal contamination at trace levels. Hence, in order to decrease the blank absorbance, it was decided to use sulphuric acid and sodium chloride instead of hydrochloric acid for the extraction of the ion-pair and the result indicated low blank value A = (0.02–0.04). The extraction was found to be maximum and constant in the acidity range from 0.2 to 0.55 mol l^{-1} with respect to sulphuric acid. Five ml of 15% sodium chloride and 5 ml of 0.1% rhodamine 6G were sufficient to provide maximum absorbance. The continuous variation and the mole ratio methods showed that the extracted species was 1:1 ion-pair of the rhodamine 6G cation and the chlorochromate anion.

Among the various solvents investigated for the extraction of the ion-pair, benzene and toluene proved to be satisfactory as the extraction of the ion-pair was found to be maximum. Solvents like chloroform, chlorobenzene, cyclohexanone, cyclohexanol, 1-butanol, 4-methylpentanone-2 and 4-methylbutylacetate were not tried since they are known to extract free rhodamine 6G. Carbon tetrachloride and

cyclohexane do not extract the ion-pair. Considering the carcinogenicity of benzene [11] and higher blank absorbance compared with toluene, the latter was chosen for further studies. The extracted ion-pair showed an absorption maximum at 535 nm.

Determination of chromium(III) was carried out by its oxidation to chromium(VI) and subsequent extraction as described above. Potassium permanganate was used for the oxidation of chromium(III) to chromium(VI) in 0.25 mol l^{-1} sulphuric acid by boiling the solution for 3 min [12]. Excess permanganate was decomposed by the addition of sodium azide.

The absorption spectrum of the system for different concentrations of chromium(VI) is shown in Fig. 1. A linear calibration graph was obtained over the range 0–8 μg of chromium(VI). The precision of the method was established by determining the concentration of ten samples containing 5 μg of chromium(VI) and it showed a relative standard deviation of 2.2%. The calibration graph has a correlation coefficient of 0.991. The molar absorptivity of the colour system is 2×10^4 l mol^{-1} cm^{-1} and the colour was stable in the organic phase for 4 h.

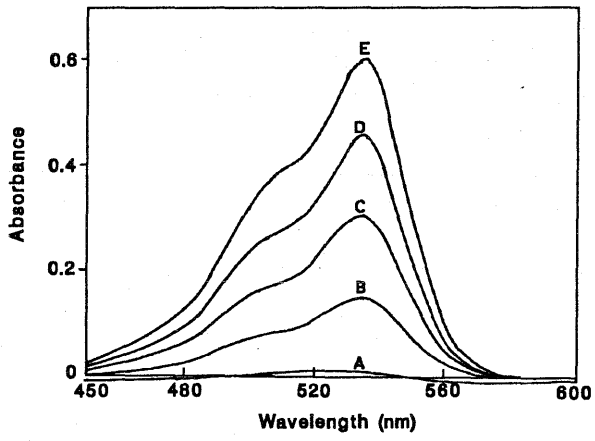

Figure 1. Absorption spectrum, measured against toluene: A – reagent blank; B, C, D and E – 2, 4, 6 and 8 μg of Cr(VI), respectively

Effect of interfering species

The interfering effect of various ions at milligram levels on the determination of chromium(VI) by the proposed method was examined. The results are shown in Table 1. The tolerance limits of interfering species were established at those concentrations which do not cause more than ±2.0% error in the recovery of chromium(VI) at 5 μg level.

The interference of iron(III) at 1 mg level can be masked by the addition of 1 ml of 1% sodium fluoride. The interference of iron(II) at 1 mg level can be eliminated by the addition of 1 ml of potassium permanganate and boiling the solution for 3 min to oxidize the formed chromium(III) to chromium(VI). Then 1 ml of 1% sodium azide

was added followed by 1 ml of 1% sodium fluoride. The interference of tungsten(VI) at 1 mg level was eliminated by adding 1 ml of 0.5 mol l^{-1} sulphuric acid and removing tungstic acid by centrifugation. The interference of manganese(VII) at 1 mg level can be eliminated by the addition of 1 ml of 1% sodium azide. The interference due to As(III), Bi(III), Hg(II), Sb(III), Sn(II), Sn(IV) and Te(IV) at 1 mg level can be eliminated by the addition of 1 ml of ammonium tetrathiomolybdate and 1 ml of 0.5 mol l^{-1} sulphuric acid. The solution was filtered to remove the metal sulphides collected on the formed molybdenum sulphide. The filtrate was treated with 1 ml of 0.1% potassium permanganate and heated to boiling to convert the formed chromium(III) to chromium(VI). Excess of permanganate was destroyed by the addition of 1 ml of 1% sodium azide.

Table 1. Interference studies [chromium(VI) 5 μg]

Interferents (1 mg)	Remarks
Ag^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Ce^{4+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Ge^{4+}, In^{3+}, Mg^{2+}, Mn^{2+}, MoO_4^{2-}, Ni^{2+}, Pb^{2+}, Sr^{2+}, SeO_3^{2-}, SiO_3^{2-}, Th^{4+}, Tl^{3+} VO_4^{3-}, Zn^{2+}, citrate, tartrate, EDTA, fluoride, phosphate, azide	no interferece
AsO_3^{3-} (50), Bi^{3+} (50), Fe^{2+} (10), Fe^{3+} (50), Hg^{2+} (10), MnO_4^{-} (100), Sb^{3+} (10), Sn^{2+} (10), Sn^{4+} (500), TeO_3^{2-} (50), WO_4^{2-} (10)	negative interference

Tolerance limits in μg are given in brackets.

Application of the method

The results of the determination of chromium content in standard alloy steels, pharmaceutical preparations, geological samples and industrial effluents are shown in Tables 2–5.

Alloy steels (Table 2) were brought into solution by the addition of 10 ml 1:1 hydrochloric acid, 4 ml of 1:1 sulphuric acid and evaporating the solution to about 5 ml. Two ml of nitric acid were added and evaporated till crystallization of salts occurred. Ten ml of water were added, warmed and the solution was filtered to remove silica and tungsten [13]. The filtered solution was treated with 10 ml of hydrochloric acid to extract iron with 10 ml of 4-methylpentanone-2. The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of the sample solutions were used for analysis following the procedure for chromium(III) determination.

Table 2. Determination of chromium in standard alloy steels

No.	Sample	Cr content %	Vol. of aliquot ml	Cr content		Average %
				µg	%	
1	Tisco mild steel, India (0.05 g in 100 ml) [Mn 0.685%, Cu 0.366%, Si 0.109%, C 0.101%]	0.580	1.0 1.5 2.0	2.9 4.3 5.7	0.580 0.573 0.570	0.574
2	BCS No.491, 16% Mn-steel (0.05 g in 200 ml) [Mn 16.000%, Mo 0.600%, Ni 0.050%, Al 0.046%]	1.450	1.0 1.5 2.0	3.6 5.5 7.1	1.440 1.467 1.420	1.442
3	Analysen-Kontrol Probe* 2-CrCoMoVW2/634 (0.10 g in 100 ml)** [W 11.920%, Co 2.730%, V 1.981%, Mo 0.953%]	4.231	0.5 1.0 1.5	2.1 4.3 6.3	4.200 4.300 4.200	4.233
4	BCS/SS No. 261/1 (0.05 g in 250 ml)** [Ni 13.100%, Nb 0.910%, Mn 0.830%, Si 0.500%, Cu 0.120%, Mo 0.110%]	17.400	1.0 1.5 2.0	3.4 5.2 6.9	17.000 17.333 17.250	17.194
5	Analysen-Kontrol Probe* 2-CrNiZr/91 (0.05 g in 250 ml)** [Ni 10.470%, Mn 0.863%, Si 0.473%, Zr 0.053%]	18.530	1.0 1.5 2.0	3.7 5.5 7.3	18.500 18.333 18.250	18.361

*Samples obtained from Bundesanstalt für Materialprüfung, Berlin-Dahlem, Germany.
**Solutions diluted 10 times before determination.

Representative samples of the finely ground multivitamin–multimineral tablets (Table 3) containing chromium(III) were treated with 5 ml of nitric acid and evaporated to dryness. The residue was leached with 5 ml of 0.5 mol l^{-1} sulphuric acid [14]. The solution was treated with 5 ml of hydrochloric acid to extract iron with 10 ml of 4-methylpentanone-2. The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of the sample solutions were used for analysis following the procedure for chromium(III) determination.

Table 3. Determination of chromium in pharmaceutical preparations

No.	Sample	Composition of tablet (weight per tablet)	Certified value Cr, mg/tablet	Vol. of aliquot ml	Cr found	
					µg	mg/tablet*
1	Aquamin [Pfimex International Ltd., India] (5.00 g in 50 ml)	iron 3.00 mg; magnesium 35.00 mg; zinc 1.5 mg; iodine 15 µg; copper 300 µg; manganese 500 µg; chromium 20 µg (1.00 g)	0.0200	1.0 2.0 3.0	1.9 4.0 5.9	0.0196
2	Fourts B [Fourts Laboratories Pvt. Ltd., India] (0.65 g in 100 ml)	thiamine mononitrate 10 mg; riboflavin 10 mg; pyridoxine hydrochloride 3 mg; niacinamide 50 mg; vitamin C 150 mg; zinc sulphate 8 mg; selenium 100 µg; chromium 150 µg (0.65 g)	0.1500	2.0 3.0 4.0	3.0 4.4 5.9	0.1483
3	Centrum (Lederle, USA) (7.50 g in 50 ml)	iron 18 mg; magnesium 100 mg; copper 2 mg; zinc 15 mg; manganese 2.5 mg; potassium 40 mg; chromium 25 µg; vitamin C 60 mg; vitamin B_1 1.5 mg; vitamin B_2 1.7 mg (1.50 g)	0.0250	1.0 2.0 3.0	2.5 4.9 7.4	0.0247

*Average of three determinations.

Geological samples (Table 4) were brought into solution by the addition of 2 ml of sulphuric acid, 10 ml of hydrofluoric acid and evaporating the solution to nearly dryness to remove silica as SiF_4 [13]. The solution was treated with 5 ml of 1:1 hydrochloric acid and iron was extracted with 10 ml of 4-methylpentanone-2. The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of the sample solutions were used for analysis following the procedure for chromium(III) determination.

Table 4. Determination of chromium in geological samples*

No.	Sample	Chromium content** $\mu g\ g^{-1}$	Volume of aliquot ml	Chromium found μg	Average $\mu g\ g^{-1}$
1	Anorthosite AN-G [SiO_2 46.30%, Al_2O_3 29.80%, CaO 15.90%, Fe_2O_3 3.36%, MgO 1.80%] (2.5 g in 50 ml)	50.0	1.0 2.0 3.0	2.4 4.9 7.6	49.2
2	Basalt BE-N [SiO_2 38.20%, CaO 13.87%, MgO 13.15%, Fe_2O_3 12.84%, Al_2O_3 10.07%] (0.5 g in 50 ml)	360.0	1.0 1.5 2.0	3.6 5.2 7.1	358.0

*Obtained from Geostandards, C.R.P.G., B.P. 20, 54501 Vandoeuvre Cedex, France.
**Certified values.

Tannery effluent was diluted fifty times and chromium plating plant effluent was diluted ten times before analysis (Table 5). Suitable aliquots of the sample solutions were used for analysis following the procedure for the determination of chromium(III) and chromium(VI). The solutions were also analysed following the diphenylcarbazide method [6] for comparison. The results obtained were comparable.

Table 5. Determination of chromium in industrial eluents

No.	Sample	Volume of aliquot ml	Proposed method				Diphenylcarbazide method			
			total Cr ppm	Cr(VI) ppm	Cr(III)* ppm	total Cr# in the effluent ppm	total Cr ppm	Cr(VI) ppm	Cr(III)* ppm	total Cr# in the effluent ppm
1	Chromium plating effluent[a]	1.0 1.5 2.0	3.9 3.9 3.8	3.0 2.8 2.9	0.9 1.0 0.9	38.3	3.7 3.9 3.8	2.8 3.1 2.9	0.9 0.8 0.9	38.0
2	Tannery effluent[b]	0.5 1.0 1.5	4.6 4.7 4.7	ND ND ND	4.6 4.7 4.7	233.3	4.7 4.6 4.5	ND ND ND	4.7 4.6 4.5	230.0

[a]Diluted ten times before determination.
[b]Diluted fifty times before determination.
*Cr(III) concentration = total Cr concentration - Cr(VI) concentration.
#Average of three determinations.
ND – not detected.

Results summarised in Tables 2–5 clearly show that the method developed works satisfactorily for the analysis of chromium in standard alloy steels, pharmaceutical preparations, geological samples and industrial effluents.

Conclusion

The developed procedure for the determination of chromium(VI) is simple, rapid and sensitive ($\varepsilon = 2\times10^4$ l mol^{-1} cm^{-1}). The calibration range is linear over the range 0–8 μg of chromium(VI). The relative standard deviation is 2.2% for ten determinations of chromium(VI) at 5 μg level. The developed colour is stable for 4 h. The method finds use for the determination of chromium(III) after oxidation with potassium permanganate. The method is useful for the determination of chromium in alloy steels, pharmaceutical preparations, geological samples and industrial effluents. The sensitivity of the method is comparable to the widely used diphenylcarbazide method. The proposed method has the advantage of greater colour stability (4 h) compared with the diphenylcarbazide method (30 min).

Acknowledgement

One of us (VM) is thankful to CSIR New Delhi for the award of Research fellowship.

REFERENCES

1. Versiek J. and Cornelis R., *Anal. Chim. Acta*, **116**, 217 (1980).
2. Eckert J.M., Judd R.J., Lay P.A. and Symons A.D., *Anal. Chim. Acta*, **255**, 31 (1991).
3. Willems G.J., Blaton N.M., Peeters O.M. and De Ranter C.J., *Anal. Chim. Acta*, **88**, 345 (1977).
4. Barnes L., *Anal. Chem.*, **38**, 1083 (1966).
5. Greenfield S., McGeachin H.McD. and Smith P.B., *Talanta*, **22**, 553 (1975).
6. *Standard Methods for the Examination of Water and Wastewater*, 18th edn., American Public Health Association, Washington D.C. 1992, pp. 3-59–3-60.
7. Marchart H., *Anal. Chim. Acta*, **30**, 11 (1964).
8. Saltzman B.E., *Anal. Chem.*, **24**, 1016 (1952).
9. Kamburova M., *Talanta*, **40**, 713 (1993).
10. Kamburova M., *Talanta*, **40**, 707 (1993).
11. *The Handbook of Environmental Chemistry*, Vol.3, Part B (O. Hutzinger, Ed.), Springer, Berlin 1982, p. 149.
12. Marczenko Z., *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood, Chichester 1986, p. 236.
13. Snell F.D., *Photometric and Fluorimetric Methods of Analysis*, Part I, Wiley, New York 1978, p. 704, 732.
14. Sundaramurthi N.M. and Shinde Vijay M., *Analyst*, **116**, 541 (1991).

Received December 1995
Accepted February 1996