

TECHNICAL COMMUNICATIONS

Indirect Spectrophotometric Determination of Chromium

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A sensitive spectrophotometric method for determining trace amounts of chromium(VI) is described. In the presence of acetate buffer, chromium(VI) oxidizes hydroxylamine quantitatively to nitrite at pH 4.0 ± 0.5 . The nitrite diazotizes *p*-nitroaniline to form a diazonium salt that, in acidic medium, couples with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form an azo dye with a molar absorptivity of 4.1×10^4 L/mol-cm at 545 nm. The color is stable for 5 h, and the system obeys Beer's law in the range 0–8 μ g chromium(VI) in a final volume of 10 mL. The detection limit of chromium(VI) is 0.6 μ g. Chromium(III) can be determined after it is oxidized with bromine water in alkaline medium to chromium(VI). Extraction of the azo dye in alkaline medium with methyl isobutyl ketone followed by addition of methanolic hydrochloric acid permitted determination of chromium(VI) down to 10 ng/mL. The method has been used to determine chromium in alloy steels, pharmaceutical preparations, and industrial effluents.

Chromium compounds are widely used in leather, textile, and chemical manufacture; in metal finishing; and in many other industries. The determination of chromium is of considerable interest because of the contrasting biological effects of its 2 common oxidation states, chromium(III) and chromium(VI). Chromium(III) is an essential nutrient for maintaining normal physiological functions (1), whereas chromium(VI) is toxic (2). Spectrophotometric methods for chromium(III) have been developed with reagents such as 4-(2-pyridylazo)resorcinol (3) and arsenazo III (4). The reactions with these reagents require a heating step for color development. Several spectrophotometric methods based on oxidation of organic compounds by chromium(VI) have been reported (5, 6). Spectrophotometric determination of chromium(VI) based on formation of ion associates with iodonitrotetrazolium chloride, tetrazolium violet (7), and methylene blue (8) has the disadvantage of high blank value. The most commonly used reagent for chromium(VI) determination is diphenylcarbazide (9, 10). Although the formed complex is stable for only 20 min,

addition of phosphate buffer increases the stability to 30 min (11).

In the present investigation, chromium(VI) is used to quantitatively oxidize hydroxylamine to nitrite. Chromium(VI) is determined indirectly by using the generated nitrite to diazotize *p*-nitroaniline and coupling the formed diazonium salt with *N*-(1-naphthyl)ethylenediamine dihydrochloride (NEDA) to form an azo dye. Chromium(III) is determined after it is oxidized to chromium(VI) by hypobromite and the excess bromine is destroyed by acidification followed by addition of sulfosalicylic acid. Lower concentrations of chromium(VI) can be determined by extracting the azo dye in alkaline medium with methyl isobutyl ketone (MIBK) and then adding methanolic hydrochloric acid to the organic layer.

METHOD

Apparatus

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

Reagents

All chemicals used were analytical reagent grade. Distilled water was used for preparing reagent solutions.

(a) *Standard chromium(VI) solution (1000 μ g/mL).*—Prepared by dissolving 0.2829 g $K_2Cr_2O_7$ in 100 mL water. Suitable volume of this solution was diluted to obtain the working standard.

(b) *Standard chromium(III) solution (1000 μ g/mL).*—Prepared by dissolving 0.2829 g $K_2Cr_2O_7$ in 50 mL water, adding 1 mL saturated sodium sulfite solution, acidifying with 1 mL 5N sulfuric acid, and then boiling 2 min to remove excess SO_2 and diluting with water to 100 mL. Suitable volume of this solution was diluted to obtain the working standard.

(c) *Acetate buffer (pH 4.0).*—Prepared by dissolving 13.6 g sodium acetate in 80 mL water. Solution pH was adjusted to 4.0 with acetic acid, and the mixture was diluted to 100 mL with water.

(d) *p-Nitroaniline (0.05% in 4N H_2SO_4).*—Prepared by dissolving 0.05 g *p*-nitroaniline in 80 mL 5N sulfuric acid and diluting to 100 mL with water.

(e) *Methanolic hydrochloric acid.*—Prepared by mixing 50 mL methanol with 25 mL HCl (specific gravity, 1.18).

(f) *Others.*—The following reagents were prepared by dissolving appropriate amounts of reagents in distilled water: hydroxylamine hydrochloride (0.1 and 0.5%), NEDA (0.1 and 0.5%), bromine water (saturated), sulfosalicylic acid (5.0%),

EDTA (1.0%), sodium fluoride (1.0%), KOH (4.5N), sulfuric acid (1N and 5N), and HCl (5N).

(g) *MIBK*.—For extraction.

Determination of Chromium(VI)

To 3 mL sample solution containing not more than 8 µg chromium(VI), add 1 mL acetate buffer and 1 mL 0.1% hydroxylamine hydrochloride in a 10 mL calibrated flask. Allow mixture to stand for at least 2 min. Add 1 mL *p*-nitroaniline and allow mixture to stand for at least 2 min. Then add 1 mL 0.1% NEDA and dilute mixture to 10 mL with water. Using 1 cm glass cells, measure absorbance at 545 nm against a reagent blank run through the entire procedure. Establish concentration of chromium(VI) by reference to calibration graph prepared with 0–8 µg chromium(VI).

Determination of Chromium(III)

To 3 mL sample solution containing not more than 8 µg chromium(III), add 0.5 mL saturated bromine water and 0.5 mL 4.5N KOH in a 10 mL calibrated flask. Allow mixture to stand for 5 min. Add 0.5 mL 5N sulfuric acid and 0.5 mL 5% sulfosalicylic acid. Then add 1 mL acetate buffer and 1 mL 0.1% hydroxylamine hydrochloride. Allow mixture to stand for at least 2 min. Add 1 mL *p*-nitroaniline and allow mixture to stand for at least 2 min. Then add 1 mL 0.1% NEDA and dilute mixture to 10 mL with water. Using 1 cm glass cells, measure the absorbance at 545 nm against a reagent blank run through the entire procedure. Establish concentration of chromium(III) by reference to calibration graph prepared with 0–8 µg chromium(III).

Analysis of Mixture Containing Chromium(III) and Chromium(VI)

Analyze an aliquot (3 mL) of mixture according to the procedure for chromium(VI) and establish the concentration of chromium(VI). Analyze another aliquot (3 mL) according to the procedure described for chromium(III) to establish the concentration of total chromium [chromium(III) + chromium(VI)]. The difference between the 2 values is the concentration of chromium(III) in the mixture.

Determination of Chromium(VI) and Chromium(III) in Water Samples

To 50 mL sample solution containing not more than 4 µg chromium(VI), add 2.5 mL acetate buffer and 1 mL 0.5% hydroxylamine hydrochloride in a 100 mL beaker and allow the mixture to stand for at least 2 min. Add 2.5 mL *p*-nitroaniline and allow the mixture to stand for at least 2 min. Then add 1 mL 0.5% NEDA. Transfer solution into 125 mL separatory funnel and add 5 mL 4.5N KOH. Equilibrate contents for 1 min with 3.5 mL *MIBK*. Separate organic layer into 5 mL calibrated flask and dilute the organic layer to 5 mL with methanolic HCl. Using 1 cm glass cells, measure the absorbance at 545 nm against a reagent blank run through the entire procedure. Establish the concentration of chromium(VI) by reference to calibration graph prepared with 0–4 µg chromium(VI). For samples containing both chromium(III) and chromium(VI), establish

the concentration of chromium(VI) by following the procedure described above. To oxidize chromium(III) to chromium(VI), add 0.5 mL bromine water and 0.5 mL 4.5N KOH to 50 mL sample solution and allow the mixture to stand for 5 min. Add 0.5 mL 5N sulfuric acid and 0.5 mL sulfosalicylic acid. Add 2.5 mL acetate buffer and 1 mL 0.5% hydroxylamine hydrochloride and allow mixture to stand for at least 2 min. Add 2.5 mL *p*-nitroaniline and allow mixture to stand for at least 2 min. Then add 1 mL 0.5% NEDA, transfer solution to separatory funnel, and add 5 mL 4.5N KOH. Complete determination by following the extraction procedure to establish the total chromium concentration [chromium(III) + chromium(VI)]. The difference between total chromium and chromium(VI) is the chromium(III) concentration.

Results and Discussion

Preliminary investigations were performed with 5 µg chromium(VI) and 0.1% hydroxylamine hydrochloride solution. The nitrite generated by oxidation of hydroxylamine with chromium(VI) was used to diazotize *p*-nitroaniline. The diazonium salt formed was coupled with NEDA. Conditions were optimized by measuring the absorbance of the azo dye at 545 nm.

The oxidation of hydroxylamine to nitrite by chromium(VI) was effective in the pH range 3.5–4.5, which could be maintained by adding 1 mL acetate buffer. The following conversion was completed within 2 min:



This reaction is similar to oxidation of hydroxylamine to nitrite by iodine (12–14). The nitrite formed can be determined easily by a diazo-coupling reaction (15). The equation shows that 5 µg chromium(VI) reacts with hydroxylamine to generate 3.2 µg nitrite. Quantitative oxidation of hydroxylamine to nitrite by chromium(VI) was confirmed by performing the diazo-coupling reaction with standard nitrite solution, prepared from sodium nitrite dried at 105°C for 1 h. Five micrograms chromium(VI), on treatment with hydroxylamine and after the diazo-coupling reaction in a total aqueous volume of 10 mL, gives an absorbance of $0.39 \pm 0.01A$ at 545 nm, comparable with 0.40A, the absorbance at 545 nm from the diazo-coupling reaction of 3.2 µg standard nitrite solution in a total aqueous volume of 10 mL. The nitrite formed by oxidation of hydroxylamine by chromium(VI) was determined by treating it with 1 mL 0.05% *p*-nitroaniline in 4N sulfuric acid to form *p*-nitrophenyldiazonium chloride. Diazonium chloride formation was complete within 2 min at room temperature. Coupling of *p*-nitrophenyldiazonium chloride with NEDA occurred with 2.0N to 6.0N sulfuric acid, and 1 mL 0.1% NEDA was sufficient to provide maximum absorbance by forming the dye, which showed an absorption maximum at 545 nm. The color system was stable for 5 h, after the absorbance decreased gradually.

Chromium(III) was determined after it was oxidized to chromium(VI). Various oxidizing reagents (16, 17), like persulfate with silver ion as catalyst in acid solution, permanganate in 0.5N sulfuric acid, hydrogen peroxide in 2N NaOH, and hy-

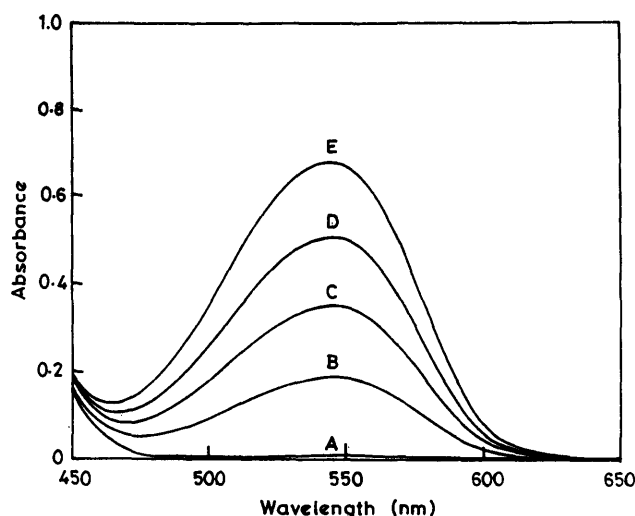


Figure 1. Absorption spectrum measured against water: A, reagent blank; B, C, D, and E, 2, 4, 6, and 8 µg Cr(VI), respectively.

pobromite, were used. For all these methods, excess oxidizing agent must be destroyed prior to estimation of chromium(VI), because oxidizers interfere in the determination. Excess persulfate and peroxide were destroyed by boiling, and permanganate was destroyed by adding sodium azide. In the present study, bromine water in alkaline medium was used to oxidize chromium(III) to chromium(VI), and the excess hypobromite was destroyed after acidification followed by addition of 5% sulfosalicylic acid.

Extraction of azo dye from a large volume of aqueous solution into a suitable organic solvent permits determination of lower concentrations of chromium(VI). At pH 9.0–12.0 the azo

dye was extracted quantitatively in the yellow form into organic solvents such as isoamyl alcohol, 1-butanol, and MIBK. The desired solution pH for extraction was maintained by adding 5 mL 4.5N KOH. Adding methanolic HCl to the organic layer restored the original pink color of the dye, which has an absorption maximum at 545 nm. A low blank value was obtained with MIBK as solvent; 3.5 mL MIBK was sufficient to extract the dye. The absorbance of the organic layer was measured at 545 nm against the reagent blank after addition of 1.5 mL methanolic HCl. The color was stable for 3 h in the organic phase.

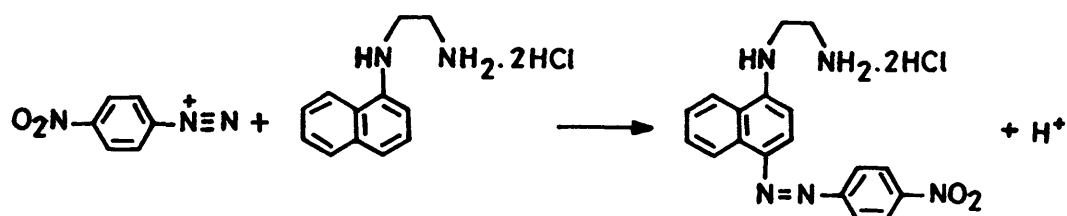
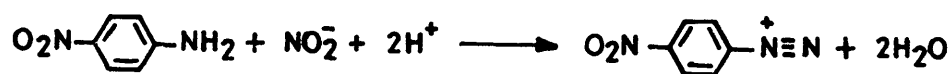
Figure 1 shows the absorption spectrum of the color system in aqueous phase for different concentrations of chromium(VI). A linear calibration graph was obtained for 0–8 µg chromium(VI) in a final volume of 10 mL. The detection limit of chromium(VI) is 0.6 µg. Method precision was established by determining the concentration of 10 samples containing 5 µg chromium(VI); the relative standard deviation was 2.3%. The calibration graph has a correlation coefficient of 0.999. The molar absorptivity of the color system is 4.1×10^4 L/mol-cm.

Species Responsible for Color

On treatment with hydroxylamine at pH 4.0 ± 0.5 , chromium(VI) generates nitrite, which diazotizes *p*-nitroaniline. The resulting diazonium chloride is coupled with NEDA in acidic medium to form the azo dye 4-(4-nitrophenylazo)-*N*-(1-naphthyl)ethylenediamine dihydrochloride (Figure 2).

Effect of Interfering Species

The effect of various ions at milligram levels on the determination of chromium(VI) was examined (Table 1). Tolerance limits of interfering species were established at those concen-



4-(4-nitrophenylazo)-*N*-1-naphthylethylenediamine dihydrochloride

Figure 2. Species responsible for color.

Table 1. Interference studies using 5 µg chromium(VI)

Potential interferents (1 mg)	Effect
Ag ⁺ , Al ³⁺ , AsO ₃ ³⁻ , AsO ₄ ³⁻ , Ba ²⁺ , Bi ³⁺ , Ca ²⁺ , Cd ²⁺ , Cr ³⁺ , Co ²⁺ , Hg ²⁺ , In ³⁺ , Mg ²⁺ , Mn ²⁺ , MoO ₄ ²⁻ , Ni ²⁺ , Pb ²⁺ , Sr ²⁺ , SeO ₃ ²⁻ , Sn ⁴⁺ , Sb ⁵⁺ , TeO ₃ ²⁻ , Ti ³⁺ , Th ⁴⁺ , Zn ²⁺ , F ⁻ , PO ₄ ³⁻ , EDTA, oxalate	No interference
Fe ³⁺	Positive interference
Ce ⁴⁺ , Cu ²⁺ , Fe ²⁺ , Ge ⁴⁺ , MnO ₄ ⁻ , Sb ³⁺ , Sn ²⁺ , VO ₃ ³⁻ , WO ₄ ²⁻ , citrate, tartrate	Negative interference

trations that do not cause more than $\pm 2.0\%$ error in recovery of chromium(VI) at 5 µg.

Cerium(IV) above 500 µg; copper(II) and manganese(VII) above 100 µg; iron(II), germanium(IV), antimony(III), tin(II), and vanadium(V) above 10 µg; and tungsten(VI) above 5 µg caused low recovery of chromium(VI). Iron(III) above 10 µg caused positive interference. The interference of iron(III) and copper(II) at 1 mg can be masked by addition of 1 mL 1% EDTA. The interference of iron(II), antimony(III), and tin(II) at 1 mg can be overcome by addition of 1 mL 1% EDTA followed by the addition of 1 mL bromine water. To this solution was added 0.5 mL 4.5N KOH. The mixture was allowed to stand for 5 min. Excess bromine water was destroyed by addition of 0.5 mL 5N sulfuric acid and 0.5 mL 5% sulfosalicylic acid. The interference caused by up to 1 mg germanium(IV) can be eliminated by addition of 1 mL 1% sodium fluoride. Interference of tungsten(VI) at 1 mg can be overcome by adding 1 mL 1N sulfuric acid and removing tungstic acid by centrifugation. The interference of cerium(IV), manganese(VII), and vanadium(V) up to 1 mg can be overcome by extraction of chromium(VI) as chromyl chloride in 5 mL MIBK after addition of 5N HCl to provide an overall acidity of 0.3N to 0.5N (18). Chromium(VI) in the organic layer can be stripped by equilibration with 5 mL water for determination.

Application of the Method

The chromium contents of standard alloy steels, pharmaceutical samples, and industrial effluents, determined by the proposed method, are shown in Tables 2–4, respectively.

Alloy steels were dissolved in a mixture of 10 mL 5.5N HCl, 4 mL 18N H₂SO₄; the solution was evaporated to about 5 mL. Nitric acid (2 mL) was added, and the mixture was allowed to evaporate until salts crystallized. Water (10 mL) was added. The solution was warmed, filtered (7, 8, 19), and treated with 10 mL HCl and 10 mL MIBK to extract iron. The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of sample solutions were analyzed according to the procedure for chromium(III).

Samples of the finely ground multivitamin–multimineral tablets containing chromium(III) were treated with 5 mL nitric acid, and the mixtures were evaporated to dryness. The residue was leached with 5 mL 1N H₂SO₄ (20). The solution was treated with 5 mL HCl and 10 mL MIBK to extract iron. The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of sample solutions were analyzed according to the procedure for chromium(III).

Tannery effluent was diluted 50 times, and chromium-plating effluent was diluted 10 times before analysis. Suitable aliquots of sample solutions were analyzed according to the

Table 2. Determination of chromium in alloy steels

Sample (wt/vol)	Chromium, %	Volume of solution, mL	Chromium found		Average, %
			µg	%	
Tisco mild steel, India (0.05 g/100 mL) [Mn 0.685%, Cu 0.366%, Si 0.109%, C 0.101%]	0.580	1.0	2.85	0.570	0.579
		1.5	4.45	0.593	
		2.0	5.75	0.575	
BCS No. 491, 16% Mn-steel (0.05 g/200 mL) [Mn 16.000%, Mo 0.600%, Ni 0.050%, Al 0.046%]	1.450	1.0	3.60	1.440	1.433
		1.5	5.40	1.440	
		2.0	7.10	1.420	
Analysen-kontrol probe ^a 2-CrCoMoVW 2/634 (0.10 g/100 mL) ^b [W 11.920%, Co 2.730%, V 1.981%, Mo 0.953%]	4.231	0.5	2.10	4.200	4.178
		1.0	4.20	4.200	
		1.5	6.20	4.133	
BCS/SS No. 261/1 (0.05 g/250 mL) ^b [Ni 13.100%, Nb 0.910%, Mn 0.830%, Si 0.500%, Cu 0.120%, Mo 0.110%]	17.400	0.5	1.70	17.000	17.278
		1.0	3.50	17.500	
		1.5	5.20	17.333	
Analysen-kontrol probe ^a 2-CrNiZr/91 (0.05 g/250 mL) ^b [Ni 10.470%, Mn 0.863%, Si 0.473%, Zr 0.053%]	18.530	0.5	1.80	18.000	18.278
		1.0	3.70	18.500	
		1.5	5.50	18.333	

^a From Bundesanstalt für Materialprüfung, Berlin-Dahlem, Germany.

^b Solution diluted 10 times before determination.

Table 3. Determination of chromium in pharmaceutical preparations

Sample (w/v)	Composition of tablet (w/tablet)	Certified value of chromium, mg/tablet	Volume of solution, mL	Chromium found	
				mg	mg/tablet
Aquamin [Pfimex International Ltd, India] (5.00 g/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	1.9	0.0190
			1.5	3.1	0.0207
			2.0	3.9	0.0195
					0.0197 ^a
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; chromium, 150 µg (0.65 g)	0.1500	1.0	1.5	0.1500
			2.0	2.9	0.1450
			3.0	4.4	0.1467
					0.1473 ^a
Centrum [Lederle, USA] (7.50 g/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	2.4	0.0240
			2.0	5.1	0.0255
			3.0	7.4	0.0247
					0.0247 ^a

^a Average of 3 determinations.

procedure for determining chromium(III) and chromium(VI). Solutions were also analyzed according to the diphenylcarbazine method (9). Results from the 2 methods were comparable.

Results summarized in Tables 2–4 show that the method works satisfactorily for analysis of chromium in alloy steels, pharmaceutical preparations, and industrial effluents.

Conclusions

The procedure for determining chromium(VI) is simple, rapid, and sensitive (molar absorptivity, 4.1×10^4 L/mol-cm). The calibration graph is linear over the range of 0–8 µg chromium(VI) in a final volume of 10 mL. The detection limit of chromium(VI) is 0.6 µg. The relative standard deviation is 2.3% for 10 determinations of chromium(VI) at 5 mg. The developed color is stable for 5 h. The method can determine chromium(III) after oxidation with bromine water in alkaline medium. Chromium down to 10 ng/mL can be determined by extraction of the dye in alkaline medium with MIBK followed by addition of methanolic HCl to organic layer. The method is useful for determining chromium in alloy steels, pharmaceutical preparations, and industrial effluents. The sensitivity of the

method is comparable with that of the widely used diphenylcarbazine method (molar absorptivity, 4.0×10^4 L/mol-cm). The proposed method has the advantage of greater color stability (5 h) compared with the diphenylcarbazine method (30 min). The method has the added advantage of determining individual amounts of chromium(VI) and chromium(III), whereas the usual element-specific techniques require a preliminary separation step to distinguish between the 2 oxidation states. Usually, separation is by solvent extraction or ion-exchange; in either case an additional sample preparation step is required before actual determination.

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Table 4. Determination of chromium in industrial effluents

Sample	Volume of solution, mL	Results from proposed method			Results from diphenylcarbazine method		
		Cr(III), ppm	Cr(VI), ppm	Total Cr, ppm ^a	Cr(III), ppm	Cr(VI), ppm	Total Cr, ppm ^a
Tannery effluent ^b	0.5	230	ND ^c	232.7	235	ND	234.0
	1.0	235	ND		233	ND	
	1.5	233	ND		234	ND	
Chromium-plating effluent ^d	1.0	10	29	38.6	9	28	38.0
	1.5	9	30		8	31	
	2.0	9	29		9	29	

^a Average of 3 determinations.^b Diluted 50 times before determination.^c ND, not detected.^d Diluted 10 times before determination.

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