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Article

Rapid Spectrophotometric Determination of Trace Amounts of Chromium Using Variamine Blue as a Chromogenic Reagent

B. Narayana* and Tom Cherian

Department of Studies and Research in Chemistry, Mangalore University. Mangalagangothri-574199, India

Um método espectrofotométrico simples, rápido e sensível foi desenvolvido para a determinação traço de cromo usando azul de Variamina como reagente cromogenico. O método proposto consiste na reação de cromo(VI) com iodeto de potássio, em meio ácido, liberando iodeto que então oxida o azul de Variamina formando um composto de cor violeta com o máximo de absorção em 556 nm. A lei de Beer é obedecida na faixa de 2-12 μg mL^{-1} para Cr(VI). A absortividade molar, a sensibilidade de Sandell, o limite de detecção e de quantificação do método foram encontrados como sendo 0,911×10^{4} L mol^{-1} cm^{-1}, 1,14×10^{-2} μg cm^{-2}, 0,02 μg mL^{-1} e 0,07 μg mL^{-1} respectivamente. As condições analíticas e ótimas da reação foram avaliadas. O efeito de íons interferentes na determinação é descrita. O cromo(III) pode ser determinado depois da oxidação à cromo (VI), com brometo em solução aquosa alcalina. O método desenvolvido foi aplicado com sucesso na análise de cromo em ligas de aço, efluentes industrias, águas naturais e amostras de solo.

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of trace amounts of chromium using variamine blue as a chromogenic reagent. The proposed method is based on the reaction of chromium(VI) with potassium iodide in acid medium to liberate iodine, which oxidizes variamine blue to form a violet colored species having an absorption maximum 556 nm. Beer's law is obeyed in the range 2-12 μg mL^{-1} of Cr(VI). The molar absorptivity, Sandell's sensitivity, detection limit and quantitation limit of the method were found to be 0.911×10^{4} L mol^{-1} cm^{-1}, 1.14×10^{-2} μg cm^{-2}, 0.02 μg mL^{-1} and 0.07 μg mL^{-1} respectively. The optimum reaction conditions and other analytical conditions were evaluated. The effect of interfering ions on the determination is described. The chromium(III) can be determined after it is oxidized with bromine water in alkaline medium to chromium(VI). The developed method has been successfully applied to the analysis of the chromium in alloy steels, industrial effluents, natural water samples and soil samples.

Keywords : chromium determination, spectrophotometry, variamine blue

Introduction

Chromium is one of the most widely distributed heavy metals in the earth's crust. It is normally found in two oxidation states ie Cr(III) and Cr(VI). Chromium is required in small quantities as an essential trace metal, nutrient and its deficiency may result in several physiological disorders. Most of the biological tissues contain Cr(III) which is usually nontoxic, where as Cr(VI) is a highly toxic form of the metal to the organisms. It is known that an increase in the content of this element in soils makes them infertile and that the toxic effect depends to some extent on the oxidation state of chromium. On the other hand, the introduction of chromium salts into soils have some positive effects due to activation of some biochemical processes.[1] Cr(III) is an essential nutrient for maintaining normal physiological function,[2] where as Cr(VI) is toxic.[3] The determination of chromium by spectrophotometric method based on oxidation of organic compounds[4-6] and on formation of ion associates[7] has the disadvantage of a high blank value. The most widely used reagent for chromium(VI) determination is diphenylcarbazide,[8,9] but it suffers serious interference from Fe(III), Mo(VI), Cu(II) and Hg(II)[10] and also the formed complex is stable for 30 minutes in the presence of a phosphate buffer.[11] Other reagents have been suggested for spectrophotometric determination of chromium using 4-(2-pyridylazo) resorcinol,[12] phenylarsenazo,[13] gallacetophenone oxime, [14] citrazinic acid,[15] trifluoroperazine hydrochloride,[16] and leuco xylene cyanol FF.[17] Of these reagent, some have been reported to be carcinogenic, while few others are less selective and are time consuming. The need for a sensitive

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* e-mail: nbadiadka@yahoo.co.uk

simple reliable method for the determination of chromium is therefore clearly recognized.

In the present investigation, a facile , sensitive and selective method has been reported for the determination of chromium(VI) with a new reagent Variamine Blue(VB). Chromium(III) is determined after it is oxidized to chromium(VI) by bromine water. The proposed method has been used to determine chromium in alloy steels, industrial effluents, natural water samples and soil samples.

Experimental

Apparatus

A secomam Anthelie NUA 002 UV-Visible spectrophotometer with 1 cm quartz cell was used for the absorbance measurements and a WTW pH 330, pH meter was used.

Reagents

All chemicals used were of analytical grade and distilled water was used for dilution of reagents and samples. Standard chromium(VI) stock solution (1000 μg mL^{-1}) was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 100 mL of water. The stock solution was further diluted as needed. Standard chromium(III) stock solution(1000 μg mL^{-1}) was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 50mL of water, adding 1mL saturated sodium sulfite solution, acidifying with 1mL of 2.5 mol L^{-1} sulfuric acid, and then boiling for 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. HCl 2 mol L^{-1}, KI 2%, sodium acetate 2 mol L^{-1} and bromine water (saturated) were used. A 0.05% solution of variamine blue was prepared by dissolving 0.05 g of variamine blue in 25 mL of ethanol and made up to 100 mL with distilled water and stored in an amber bottle

Determination of chromium(VI)

An aliquot of a sample solution containing 2-12 μg mL^{-1} of chromium(VI) was transferred in to a series of 10 mL calibrated flasks. Potassium iodide (2%, 1 mL) then hydrochloric acid (2 mol L^{-1} ,1 mL) were added and mixture was gently shaken until the appearance of yellow color indicating the liberation of iodine. Then variamine blue (0.05% , 0.5 mL) was added to it, followed by the addition of 2 mL of 2 mol L^{-1} sodium acetate solution. The contents were diluted to the mark with distilled water and mixed well. The absorbance of the colored species was measured at 556 nm against the corresponding reagent blank.

Determination of chromium(III)

An aliquot of a sample solution containing 2-12 μg mL^{-1} of chromium(III) was transferred in to a series of 10 mL calibrated flasks. A volume of 0.5 mL saturated bromine water and 0.5 mL of 4.5 mol L^{-1} KOH solution were added to each flask and allowed 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 then above procedure for chromium(VI) was followed. The absorbance of the resulting solution was measured at 556 nm against reagent blank.

Analysis of mixture containing chromium(III) and chromium(VI)

Separately, an aliquot (2 μg mL^{-1}) of a mixture according to the procedure for chromium(VI) and established the concentration of chromium(VI), was analysed. Another aliquot (2 μg mL^{-1}) according to the procedure described for chromium(III) to establish the concentration of total chromium[Cr(III) + Cr(VI)], was analysed. The difference between the two values is the concentration of chromium(III) in the mixture.

Analysis of chromium steels

Alloy steels were dissolved in approximately 8 mL of aqua regia. It was evaporated nearly to dryness on a sand bath , sulfuric acid (1-2 mL, 1:1) was added and evaporated until salts crystallized, to this 10 mL of water was added. The solution was warmed, filtered and treated with 10 mL of HCl and 10 mL of methyl isobutyl ketone to extract iron.[1,18] The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of sample solutions were analysed according to the procedure for chromium(III).

Analysis of industrial effluents

Tannery effluent was diluted 50 times and chromium plating effluent was diluted to 10 times before analysis. Suitable aliquot of sample solutions were analyzed according to the procedure for determining chromium(III) and chromium (VI). Solutions were also analysed according to the standard diphenylcarbazide method.

Determination of chromium in natural water samples

An aliquot of the natural water samples containing not more than 12 μg mL^{-1} chromium was treated with 0.5 mL, 1 mol L^{-1} NaOH and 0.5 mL 0.2 mol L^{-1} EDTA. Any precipitate formed was centrifuged off. The solution was transferred into a 10 mL standard flask and the chromium content determined as per the method discussed above (Table 1). Solution were also analysed according to the standard diphenylcarbazide method.

Determination of chromium in soil samples

A known amount of (1g) air dried homogenized soil samples, spiked with known amounts of chromium(VI) was taken and then fused with 5g anhydrous sodium carbonate in a nickel crucible and evaporated to dryness after the addition of 25 mL of water. The dried material was dissolved in water, filtered through whatman No. 40 filter paper in to 25 mL calibrated flask and neutralized with dilute ammonia. It was then diluted to a known volume with water. An aliquot of this sample solution was analysed for chromium(VI). Solution were also analysed according to the standard diphenylcarbazide method.

Results and Discussion

This method involves the liberation of iodine by the reaction of chromium with potassium iodide in an acidic medium. The liberated iodine selectively oxidizes variamine blue in the presence of sodium acetate to form a violet colored species, which shows a maximum absorbance at 556nm. The reagent blank had negligible absorbance at this wavelength. The absorbance spectra of the colored species are presented in Figure 1, and the reaction system is represented in Scheme 1.

Effect of iodide concentration and acidity

The oxidation of iodide to iodine was effective in the pH range 1.0 to 1.5, which could be maintained by adding 1 mL of 2 mol L^{-1} HCl in a final volume of 10 mL. The liberation of iodine from KI in an acid medium was quantitative. The appearance of yellow color indicates the liberation of iodine. Although any excess of iodine in the solution will not interfere. It was found that 1 mL of each 2% KI and 2 mol L^{-1} HCl were sufficient for the liberation of iodine from iodide by chromium(VI) and 0.5 mL of 0.05 % variamine blue was used for subsequent oxidation of variamine blue for the full color development.

Effect of the reagent concentration

Constant and maximum absorbance values were obtained in the pH range 4.0-5.0. This could be achieved by the addition of 2 mL of 1 mol L^{-1} sodium acetate solution in a total volume of 10 mL. An increase in the pH above 5 affected the stability of the colored species, whereas color development did not take place below pH 3, The optimum concentration of variamine blue leading to maximum color stability was found to be 0.5 mL of 0.05 % reagent per 10 mL of reaction mixture. A 2 mL portion of 1 mol L^{-1} sodium acetate solution was found to be sufficient for complete and maximum color development. The maximum absorbance was obtained instantaneously and required no heating under reaction conditions. Under the optimum reaction conditions, the color system was stable for a period of 4hr.

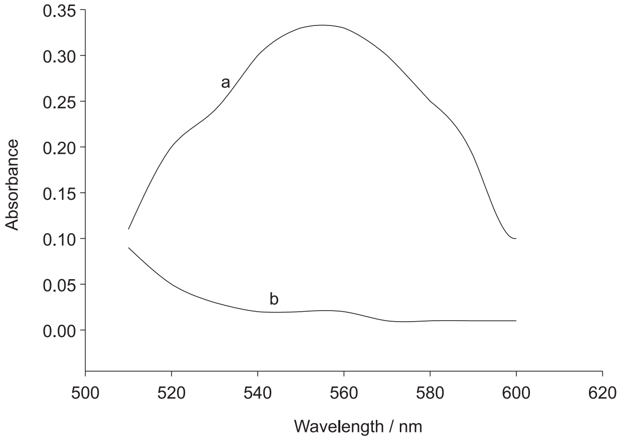
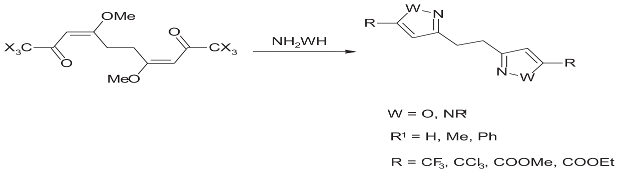


Figure 1. Absorption spectra of colored species (Cr, 1 mg mL^{-1}) *vs.* reagent blank (a) and reagent blank *vs.* distilled water(b).



Scheme 1.

Choice of oxidizing agent

Chromium(III) was determined after it was oxidized to chromium (VI). Various oxidizing agents[19] were used, persulfate in the presence of a silver ion as the catalyst in an acid solution, permanganate in an acid medium, and hydrogen peroxide and bromine in an alkaline medium. For all these methods, excess oxidizing agent must be destroyed before the determination of Cr(VI) to avoid the interference with the determination. Usually, excess persulfate and peroxide were removed by boiling, and permanganate was destroyed by adding sodium azide. In the present investigation, bromine water in an alkaline

Table 1.Determination of chromium in natural water and soil samples

Sample	Cr in μg mL^{-1} added^a	Proposed method Cr μg mL^{-1} found	Relative error in %	Std deviation	^{b}t-test	^{c}F-test	Reference method Cr mg mL^{-1} found	Relative error in %	Std deviation	^{b}t-test	^{c}F-test
Naturalwater	4.00	4.01	0.25	0.02	1.12	1.67	4.02	0.50	0.02	1.12	1.54
samples	6.00	5.99	-0.17	0.02	1.11	1.82	6.02	0.50	0.03	1.49	1.87
Soil	4.00	3.99	-0.25	0.02	1.57	2.00	4.01	0.15	0.03	1.49	1.76
samples	6.00	6.02	0.33	0.05	0.89	1.92	6.03	0.83	0.04	1.12	2.10

[a] Chromium concentration expressed in μg mL^{-1} ;[b] Tabulalated t-value for four degree of freedom at P 0.95) is 2.78; [c] Tabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39.

Table 2. Determination of chromium in alloy steels

Samples	Chromium certified in %	Amount of Chromium found in %	Standard deviation	% of recovery	t-test^d	F-test^e
GKW Steel,India(0.05g/100ml);C 0.54, Mn 0.89, S 0.018,P 0.034,Si 0.33, V 0.13^a	1.02	1.013	0.01	99.30	0.67	1.90
Stainless steel no.394(0.05g/100ml); Ni 8.12,Fe 70-71^b	18.0	17.94	0.03	99.70	0.75	1.50
FerrochromeCr 65,Fe 35	65.0	64.54	0.04	99.30	1.27	1.40

[a] Diluted to 10 times before analysis; [b] Diluted to 20 times before analysis; [c] diluted to 40 times before analysis;[d] .Tabulated t-value for four degree of freedom at P (0.95) is 2.78; [e]. Tabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39.

Table 3.Determination of chromium in industrial effluents

Samples	Chromium found in mg mL^{-1}											
	Proposed method						Reference method					
	Cr(III)^a	Cr(VI)	t-test^e		F-test^f		Cr(III)^a	Cr(VI)	t-test^e		F-test^f	
			Cr(III)	Cr(VI)	Cr(III))	Cr(VI)			Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tannery Effluent^c	318.56 ±0.20	ND^b	1.78	ND^b	1.82	—	317.74 ± 0.21	—	1.49	—	1.62	—
Chromium Plating effluent^d	32.22 ±0.35	69.22 ±0.14	1.41	1.90	1.94	1.40	32.54 ±0.31	69.40 ±0.16	1.73	1.39	1.94	1.33

[a]. Mean ± standard deviation; [b] ND ,not detected;[c] Solution diluted 50 times before analysis; [d] Solution diluted 10 times before analysis; [e]. Tabulated t-value for four degree of freedom at P (0.95) is 2.78; [f]. Tabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39.

medium was used to oxidize Cr(III) to Cr(VI) and the excess oxidizer was removed by the addition of sulfosalicylic acid (5 %).

Analytical data

Beer's law was obeyed in the range of 2-12 μg mL$^{-1.}$ The molar absorptivity and Sandell's sensitivity for the colored system was found to be 0.911×10^4 L mol^{-1}cm^{-1}, 1.14 ×10^{-2}μg cm^{-2} respectively. The detection limit(D_L =3.3 s/S) and quantitation limit (Q_L=10 σ/S) (where s is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration curve) for the chromium determination were found to be 0.02 μg mL^{-1} and 0.07 μg mL^{-1} respectively.

Effect of interfering ions

The effect of various ions at ¼g mL^{-1} levels on the determination of chromium(VI) was examined. The tolerance limits of interfering species were established at those concentrations that do not cause more than 2% error in absorbance values of chromium(VI) at 2 μg mL^{-1} (Table 4). The results indicated that Cu(II), Fe(III), Ce(IV) interfere severely. However, the tolerance level for these ions may be increased by the addition of 1 mL of 1% EDTA.

Application

The proposed method was applied to the quantitative determination of chromium in natural water samples, soil

Table 4 .Effect of interfering ions on the determinations of 2 μg mL^{-1} Chromium(VI)

Ions	Tolerance limit (μg mL^{-1})	Ions	Tolerance limit (μg mL^{-1})
Fe^{3+}	10	Ce^{4+}	20
Na^{+}	1000	MoO_4^{2-}	750
Pb^{2+}	500	F^{-}	1000
Ni^{2+}	75	CO_3^{2-}	1500
Cu^{2+}	10	PO_4^{3-}	1000
Cd^{2+}	500	AsO_3^{3-}	750
Hg^{2+}	100	Citrate	1000
Ba^{2+}	1000	Tartarate	1500
Bi^{3+}	1500	Oxalate	1500
Mn^{2+}	500	Sulfate	1000
Al^{3+}	500	Chloride	1000
Ca^{2+}	100	Nitrate	750
Co^{2+}	75	Acetate	1000
		EDTA	1500

samples, standard alloy steels and industrial effluents samples, the results are presented in Table 1, 2 and 3 respectively. Statistical analysis of the results by F and t-tests showed no significant difference in accuracy and precision of the proposed and reference method.[8] The precision of the proposed was evaluated by replicate analysis of samples containing chromium at three different concentrations.

Conclusions

The proposed method for determining chromium(VI) is facile, rapid, sensitive and has a wide analytical range without the need for extraction or heating. The developed method does not involve any stringent reaction conditions and offers the advantages of high color stability (4 hr) compared to the standard diphenylcarbazide method (30 min). The methods has the added advantage of determining individual amounts of Cr(VI) and Cr(III). The proposed method has been successfully applied to the determination of trace amounts of chromium in alloy steels ,industrial effluents, natural water samples and soil samples.

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