

Simple spectrophotometric determination of chromium in industrial effluents and water samples

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ABSTRACT

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of chromium in industrial effluents and natural water samples. The method is based on the reaction of chromium(VI) with potassium iodide in acid medium to liberate iodine. This liberated iodine bleaches the violet color of the thionin. The decrease in absorbance at 600nm is directly proportional to the chromium(VI) concentration and obeys Beer's law in the range 2-14 $\mu\text{g mL}^{-1}$ for chromium(VI). The molar absorptivity, Sandell's sensitivity, detection limit and quantitation limit of the method were found to be $0.967 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $1.08 \times 10^{-2} \mu\text{g cm}^{-2}$, $0.034 \mu\text{g mL}^{-1}$ and $0.105 \mu\text{g mL}^{-1}$ respectively. The optimum reaction conditions and other analytical conditions were evaluated. The effect of interfering ion on the determination is described. The chromium(III) can be determined after oxidation to chromium(VI). The developed method has been successfully applied to the analysis of the chromium in industrial effluents and natural water samples.

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KEYWORDS

Chromium determination;
Spectrophotometry;
Thionin.

INTRODUCTION

Chromium is one of the most widely distributed heavy metals in the earth's crust. It is normally found in two oxidation state ie Cr(III) and Cr(VI). 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 chromium oxidation state. 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 ion associates^[7] have the disadvantage of producing 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 includes 4-(2-

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pyridylazo)resorcinol^[12], phenylarsenazo^[13], gallacetophenone oxime^[14], citrazinic acid^[15], trifluoroperazine hydrochloride^[16], leuco xylene cynol FF^[17], variamine blue^[18] and azure-B^[19]. Of these reagent, some have been reported to be carcinogenic, while few others are less selective. The need for a sensitive simple reliable method for the determination of chromium in industrial effluents and natural water samples 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 thionin. Chromium(III) is determined after it is oxidized to chromium(VI) by bromine water. The proposed method has been used to determine chromium in industrial effluents and natural water samples.

EXPERIMENTAL

Apparatus

A secmam 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 ($1000\mu\text{g mL}^{-1}$) was prepared by dissolving 0.2829g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 100mL of water. The stock solution was further diluted as needed. Standard chromium(III) stock solution ($1000\mu\text{g mL}^{-1}$) was prepared by dissolving 0.2829g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 50mL of water, adding 1mL saturated sodium sulfite solution, acidifying with 1mL of 2.5mol L^{-1} sulfuric acid, and then boiling for 2 min to remove excess SO_2 and diluting with water to 100mL. Suitable volume of this solution was diluted to obtain the working standard. HCl 2mol L^{-1} , KI 2%, acetic acid 2mol L^{-1} and saturated aqueous bromine were used. A 0.1% solution of thionin was prepared by dissolving 0.1g of thionin in water containing HCl (2mol L^{-1} , 1mL) and made up to 100 ml with distilled water. Methyl isobutyl ketone was used for the extraction of iron.

PROCEDURE

Determination of chromium(VI)

An aliquot of a sample solution containing $2-14\mu\text{g mL}^{-1}$ of chromium(VI) was transferred into a series of 10mL calibrated flasks. Potassium iodide (2%, 1mL) and hydrochloric acid (2mol L^{-1} , 1mL) were added and mixture was gently shaken until the appearance of yellow color indicating the liberation of iodine. Thionin (0.1%, 0.5mL) was then added and the reaction mixture was shaken for 2 min, for maintaining pH 4, 2mL of acetate buffer was added. The contents were diluted to 10mL with distilled water and mixed well. The absorbance of the resulting solution was measured at 600nm against reagent blank.

Determination of chromium(III)

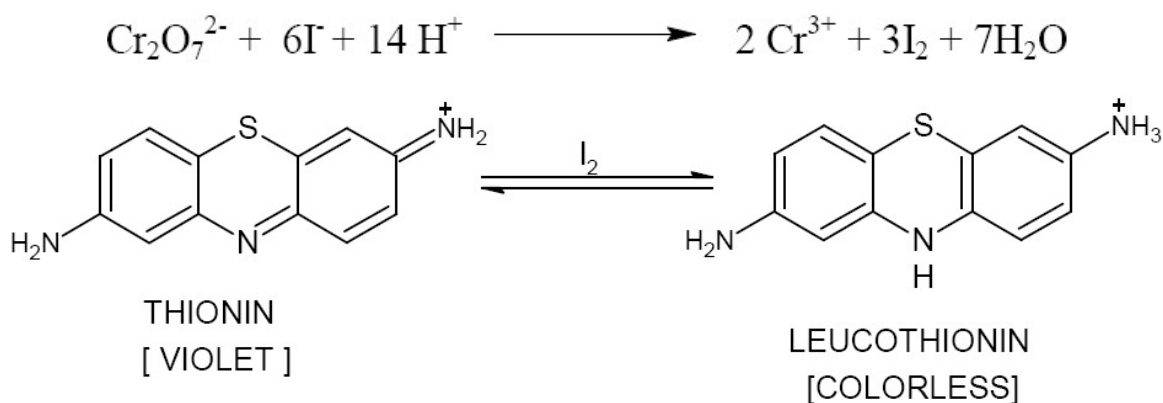
An aliquot of a sample solution containing $2-14\mu\text{g mL}^{-1}$ of chromium (III) was transferred in to a series of 10mL calibrated flasks. A volume of 0.5mL saturated bromine water and 0.5mL of 4mol L^{-1} KOH solution were added to each flask and allowed to stand for 5 minutes. Then 0.5ml of 2.5mol L^{-1} sulphuric acid and 0.5mL of 5% sulphosalicylic were added and then above procedure for chromium(VI) was followed. The absorbance of the resulting solution was measured at 600nm against reagent blank.

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

Analyse separately, an aliquot ($2\mu\text{g mL}^{-1}$) of a mixture according to the procedure for chromium(VI) and established the concentration of chromium(VI), Analyse another aliquot ($2\mu\text{g mL}^{-1}$) 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.

Analysis of industrial effluents

Tannery effluent was diluted 10 times and chromium plating effluent was diluted to 50 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 $12\ \mu\text{g mL}^{-1}$ chromium was treated with 0.5 mL of 1 mol L^{-1} NaOH and 0.5 mL of 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 by the above method.

RESULTS AND DISCUSSION

Effect of iodide concentration and acidity

The effect of iodide concentration and acidity on the

decolorization was studied with $5\ \mu\text{g mL}^{-1}$ of chromium solution. 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 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 0.1% thionin was used for subsequent decolorization.

Effect of pH

The variation of absorbance of known concentra-

TABLE 1 : Determination of chromium in natural water samples

sample	Proposed method						Reference method ⁸					
	Cr(III) in $\mu\text{g mL}^{-1}$ added	Cr(III) $\mu\text{g mL}^{-1}$ found	Relative error	Std deviation	^b t-test	^c F-test	Cr(III) $\mu\text{g mL}^{-1}$ found	Relative error	Std deviation	^a t-test	^b F-test	
Natural water samples	4.00	3.99	-0.25	0.019	1.17	1.90	4.01	0.30	0.02	1.12	1.67	
	6.00	6.01	0.21	0.03	0.74	2.00	6.02	0.33	0.05	1.96	1.66	
	8.00	8.02	0.25	0.027	1.65	1.35	8.03	0.37	0.025	1.78	2.08	

^aTabulated t-value for four degree of freedom at P (0.95) is 2.78; ^bTabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39

TABLE 2 : Determination of chromium in industrial effluents

Samples	Chromium found in $\mu\text{g mL}^{-1}$											
	Proposed method						Reference method ⁸					
	Cr(III) ^a	Cr(VI)	^b t-test		^c F-test		Cr(III)	Cr(VI)	^b t-test		^c F-test	
			Cr(III)	Cr(VI)	Cr(III)	Cr(VI)			Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tannery Effluent ^e	318.22 \pm 0.02	ND ^d	1.12	ND ^d	1.70	--	318.42 \pm 0.03	--	1.49	--	2.0	--
Chromium Plating effluent ^f	31.2 \pm 0.15	69.32 \pm 0.19	1.49	1.41	1.50	1.58	31.74 \pm 0.16	69.64 \pm 0.25	0.56	1.2	1.33	2.08

^a. Mean \pm standard deviation; ^b Tabulated 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; ^d ND ,not detected

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tion of the chromium with pH of the medium was studied. A series of buffer solutions differing by pH 1 was prepared, and using each of these buffers, system was studied. The maximum absorbance value was found at pH 4. Hence, the solution was maintained at pH 4 throughout the study using acetate buffer (pH 4).

Choice of oxidising agent.

Chromium(III) was determined after it was oxidized to chromium (VI). Various oxidizing agents¹⁹ 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 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 2-14 $\mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's sensitivity for the colored system was found to be $0.967 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $1.08 \times 10^{-2} \mu\text{g cm}^{-2}$ respectively. The detection limit ($D_L = 3.3\sigma/S$) and quantitation limit ($Q_L = 10\sigma/S$) (where σ 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 0.034

$\mu\text{g mL}^{-1}$ and 0.105 $\mu\text{g mL}^{-1}$ respectively.

Effect of interfering ions

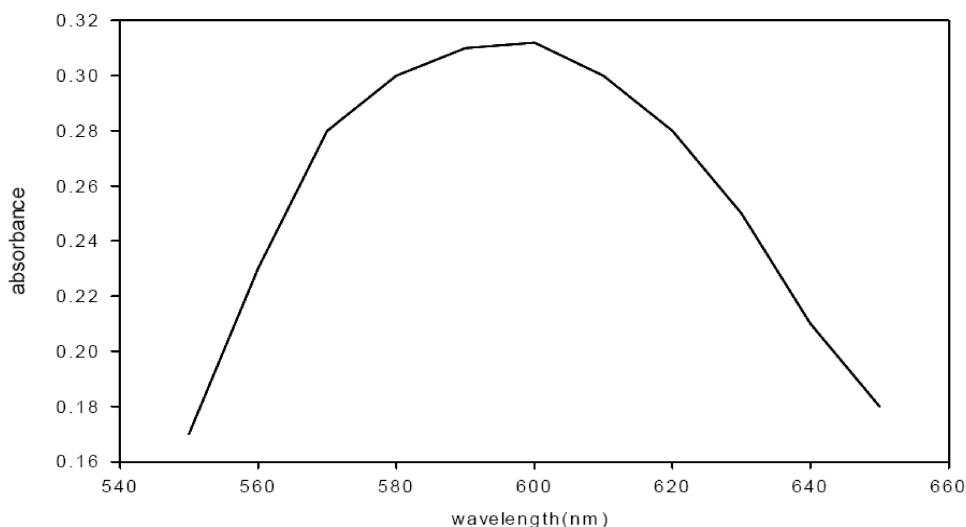
The effect of various ions at $\mu\text{g mL}^{-1}$ levels on the determination of chromium(VI) was examined. The tolerance limits of interfering species were established at those concentrations that do not cause more than 2.0% error in absorbance values of chromium(VI) at 5 $\mu\text{g mL}^{-1}$ (TABLE 3). 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.

Applications

The proposed method was applied to the quantita-

TABLE 4 : Effect of interfering ions on the determinations of 5 $\mu\text{g mL}^{-1}$ Chromium(VI)

Ions	Tolerance limit $\mu\text{g mL}^{-1}$	Ions	Tolerance limit $\mu\text{g mL}^{-1}$
Fe ³⁺	10	Ce ⁴⁺	20
Na ⁺	1000	MoO ₄ ²⁻	750
Ni ²⁺	75	F ⁻	1000
Cu ²⁺	10	CO ₃ ²⁻	1000
Cd ²⁺	500	PO ₄ ³⁻	1000
Hg ²⁺	100	Citrate	1000
Ba ²⁺	1000	Tartarate	1500
Bi ³⁺	1500	Oxalate	1000
Mn ²⁺	500	Sulfate	1000
Al ³⁺	500	Chloride	1000
Ca ²⁺	50	Nitrate	750
Co ²⁺	75	Acetate	1000
		EDTA	2500



tive determination of chromium in industrial effluents samples and water samples, the results are presented in TABLES 1&2 respectively. Statistical analysis of the results by F and t-tests showed no significant difference in accuracy and precision of the proposed and reference method⁸. 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 bleached color stability (5hr) compared to the standard diphenylcarbazide method (30min). The method 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 steel, industrial effluents and water samples.

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