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Rapid Determination of Chromium (III) in Natural Water and Industrial Effluents Using Kinetic Spectrophntometric Method

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ABSTRACT

A new simple and rapid catalytic kinetic method for determinatioo of trace amounts of chromium (III) is described. The method is based on the catalytic effect of chromium (III) on the reduction of Methylene blue by nscorbic acid in acidic media. The reaction monitored spectrophotometrieally by measuring the decrease of absorbance at 664 nm at 25° C. The fixed-time method was used for the first 300 s. Under the optimum conditions, the amount of Cr(III) in tbe eoncentration range of 0.5 - 520.0 ¤g mL^{-1} (III) can be determined with a limit of detection of 0.09 ¤g mL^{-1} of chromium (III). The relative standard deviations of six repliente measurements are 2.8 and 2.1% for 50.0 and 500.0 ¤g mL^{-1} of chromium (III), respectively. The effect of certain foreign species upon the reaetion rate was investigated for the assessment of the selectivity of the method. The proposed method was successfully applied to the determination of chromium (III) in real samples with satisfactory results. The new developed method was found to have fairly good selectivity, sensitivity, rapidity, reproduceability and simplicity

Keywords: Methylene blue; Chromium(III); Ascorbic acid; Kinetic method; Spectrophotometry

INTRODUCTION

Chromium (III) is one of the most important components of endocrine gland *in vivo*, which can catalyze the process of glucose and cholesterin metabolism. Lack of chromium (III) will result in turbulence in the metabolism of glucose and cholesterin, even atheroma On the other hand, too much chromium (III) in environment will endanger soil, jeopardize plants and human kind [1].

The most common techniques used for direct determination of tracc levels of chromium are atomic absorption spectrometry (AAS) employing flame or electrothermal atomization [2-7] iaductively coupled plasma mass spectroraetry (ICP-MS) [8-11], inductively coupled plasma atomic emission spectrometery (ICP-AES) [12-15], inductively coupled plasma optical emission spectrometery (ICP-OES) [16,17], ion chromatography [18-20] and X - ray fluorescence [21]. All these analytical techniques can only yield informatioo on the total concentrations of chromium. There is a need for isolation and preconcentration of chromium, when the above mentioned techniques are used for determination of chromium in real samples. Solvent extraction methods [22] are lengthy, needs large volumes of toxic and expensive organic solvents, time consuming and lacks sensitivity due to much interference. It would be more interesting and significant to search for development of a new type uf spectrophtometric methnd for selective detection of chromium (III).

A wide variety of reagents have been proposed for ihe spectrophotmetric determination of chromium. Some spectrophotometric methods based on the oxidation of organic compounds [23-37]. The catalytic methods are widely used because they have excellent sensitivity and

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sufficient accuracy without using expensive or special equipment. It is believed that this method somehow is the most suitable for determination of trace elements in biological samples [38. 39].

In the present work, a kinetic spectrophotometric method for determination of trace amounts of chromium (III) is proposed. This method is based oo the catalytic effect of chromium (III) on the reduction of Methylene blue (MB) by ascorbic acid (AA) in acidic media. The reaction was followed spectrophotometrically by monitoring the decrease of absorbance of MB at 664 nm with a fixed time between 0.5-5.0 minutes. It was found that in acidic solution, chromium (III) catalyzed reduction of MB. Thus, we developed a simple, sensitive and selective method for the kinetic determinaion of chromium (III). The resulting method, which has a detection limit of 0.09 ∞g mL^{-1}, has been successfully applied to the determination of chromium (III) in real samples.

EXPERIMENTAL

Reagents and chemicals

All chemicals were of analytical reagent grade obtained from Merck, and were used without further purification. Double distilled water (conductivity about 0.6 μSi) was used throughout the experiment. Chromium (III) standard stock solution with concentratioo of 1000 0 μg mL^{-1} was prepared by dissolviog 0.5120 g of $CrCl_3.6H_2O$ in 100 mL of water. Working solutioos were prepared by appropriate dilution of the stock solution with water daily.

Ascorbic acid solution of 2.0×10^{-2} M was prepared daily by dissolving 0.2048 g of ascorbic acid in 100 mL of water.

MB (with empirical formula $C_{16}H_{18}ClN_3S$) solutioo (2.0×10^{-4} M) was prepared by dissolving ll.0178 g of MB in an appropriate amount of water and was diluted to 250 mL in a volumetric flask. It was stored in the dark at 4°C and was replaced every month.

Sulfuric acid solution (3.0 M) was prepared by careful dissolving 40.75 mL of concentrated sulfuric acid (a = 98 %, d = 1.84 kg/l) in 250 mL of water.

Apparatus

A Shimadzu spectrophotometer 160-A with 1ll mm glass cell was used for absorbance measurements at a fixed wavelength.

Recommended procedure

To a series of 10 mL volumetric flasks, 0.5mL of 3.0 M sulfuric acid, 1 mL of 2.0×10^{-4} M MB solution and 2 mL of 10.0 ∞g mL^{-1} of chromium (III) were added. Then 0.2 mL of 2.0×10^{-2} M ascorbic acid solution was added and the solution diluted to the mark with double distillated water. After shaking, the solution was transferred into a 1.0 cm cell of the spectrophotometer. The start of the reaction (t=0) was taken as the moment at which the last drop of ascorbic acid solution had been added. The variation of the absorbance of the dye was measured every 30 s from the time of addition of ascorbic acid during 300s. It was indicated that the absorbance is reduced constantly. The measured parameter was "net absorbance versus time", the difference between sample and blank absorbance ($\Delta A = \Delta A_s - \Delta A_b$) versus time, where ΔA_s and ΔA_b are the variation of the absorbances of sample and blank respectively.

Procedure for real sample preparation

For analysis of industrial effluents including chromium-plating effluent , tannery effluent and cement effluent, after filtering, chromium-plating effluent was diluted 20 times , tannery effluent was diluted 50 times and cement effluent analyzed without dilution. Suitable aliquots of sample solutions were analyzed, after neutralizing them with dilute ammonia according to the procedure for determination of chromium (III).

Natural water analysis was performed by filtering environmental water sample and analyzed for chromium (III) There were no sign of chromium existence in the water samples. To these samples, knowo amounts of chromium (III) were spiked and analyzed by the pmposed procedure.

For soil analysis, 2.0 g of air dried and homogenized soil sample, spiked with known amounts of chromium (III) was taken and fused with 10 g of anhydrous sodium carbonate in a silica crucible. The residue was dissolved in 25mL of water and evaporated to dryness. The residue was dissnlved again in water, filtered through Whatman No. 40 filter paper into a 50 mL volumetric flask and neutralized with dilute ammonia. An aliquot of this solution was

analyzed for chromium (III) according to the general procedure. All real samples were also analyzed according to the method explained in reference [40], for comparison of the results.

RESULTS AND DISCUSSION

MB is a well known redox indicator and is susceptible to reduction irreversibly by ascorbic acid in acidic media leading to the formation of a colorless product

In order to find the optimum conditions, the influence of reagents concentrations and temperature on the reaction rate was studied based on fixed time method. The optimum conditions were chosen to obtain minimum absorbance variations for blank and maximum variations for the sample solutions. In the mean time, extended linearity, and short measuring time were considered in adjustments. Calibration graph was obtained under optimum conditions by plotting net absorbance "ΔA" versus chromium (III) concentration.

Reagents Concentrations Optimiazation

Effect of sulfuric acid concentration

The effect of various acid types with the same concentration such as sulfuric acid, hydrochloric acid and phosphoric acid was studied. The results show that sulfuric acid gives greater sensitivity. The effect of sulfuric acid concentration on obtaining maximum sensitivity was investigated while, the concentration of MB was 2.0×10^{-5} M, and that of AA was 4.0×10^{-4} M for catalyzed and uncatalyzed reaction (Fig.1). The results show that by increasing the acid concentration up to 0.3 M, the sensitivity increased. On the other hand, higher acid concentration, cause a small decrease of the sensitivity (ΔAs −ΔAb). This maybe attributed to protonation of MB at higher acid concentrations. Therefore, 0.3 M of sulfuric acid was used as the optimum concentration.

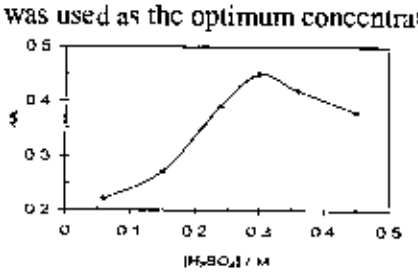

Fig. 1.Optimization of acid concentration. MB, 1.0 mL (2.0×10^{-4} mol L^{-1}); Cr^{3+}, 2 mL (10.0 μg mL^{-1}); Ascorbic acid, 0.2 mL (2.0×10^{-2} mol L^{-1}); 25 °C, 5.0 min.

Effect of Methylene Blue Concentration

The effect of MB concentration on the reaction rate was studied with 0.3 M sulfuric acid and 4.0×10^{-4} M ascorbic acid. The results show that by increasing the MB concentration up to 1.0×10^{-5} M, the sensitivity increases. Thus, 1.0×10^{-5} M of MB was selected as optimum concentration of MB (Fig. 2).

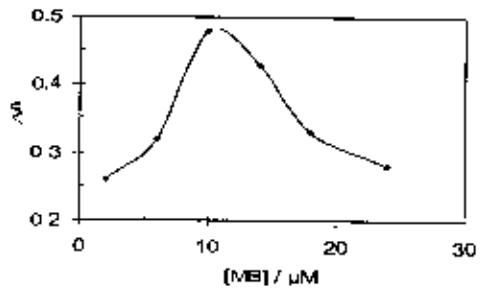

Fig. 2.Optimization of MB concentration. H_2SO_4, 1.0 mL (3.0 mol L^{-1}); Cr^{3+}, 2 mL (10.0 μg mL^{-1}); Ascorbic acid, 0.2 mL (2.0×10^{-2} mol L^{-1}), 25 °C; 5.0 min.

Effect of Ascorbic Acid Concentration

The influence of AA concentration on the reaction rate was studied in the range of 4.0×10^{-4} to 2.8×10^{-3} M under optimum conditions (Fig. 3). The results show that by increasing the ascorbic acid concentration up to 1.2×10^{-3} M, the sensitivity increased. Therefore, 1.2×10^{-3} M of ascorbic acid concentration was selected for further studies.

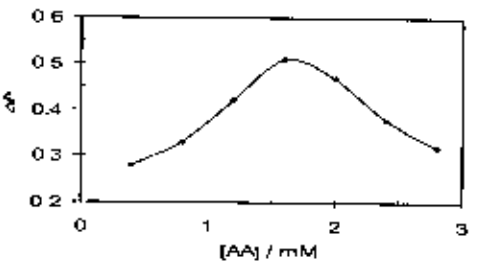

Fig. 3. Optimization of Ascorbic acid concentration. H_2SO_4, 1.0 mL (3.0 mol L^{-1}); MB, 0.5 mL (2.0×10^{-5} mol L^{-1}); Cr^{3+}, 2 mL (10.0 μg mL^{-1}); Ascorbic acid, 0.6 mL (2.0×10^{-2} mol L^{-1}); 25 °C and5.0 min.

Effect of Ionic Strength

The effect of ionic strength was studied by using 3.0 M KNO_3 solution under optimum reagents concentrations With increasing KNO_3 concentration, the change in absorbance decreased. It maybe attributed to interaction between ions (K^+ and NO_3^-) and catalyst or MB. Thus, we continued our study in the absence of KNO_3.

Effect of Temperature

The influence of temperature on the sensitivity was studied in the range of 15 - 35 °C with the optimum reagent concentrations. The results show that with increasing temperature up to 25 °C, the net absorbance increased and hence it was selected as optimum temperature for the rest of the work.

Effect of Time

Time effect was studied by measuring the absorbance and its changes during 0.5 - 5 min. The reaction rate increased up to 120 s. At still higher time, the change in absorbance was almost constant. Thus, 120 s was selected as optimum. The results are shown in (Fig.4).

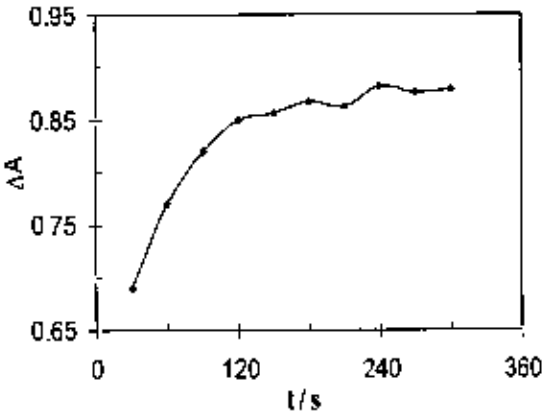

Fig. 4.Optimization of time. H_2SO_4, 1.0 mL (3.0 mol L^{-1}); MB, 0.5 mL (2.0×10^{-4} mol L^{-1}); Cr^{3+}. 2 mL (10.0 μg mL^{-1}); Ascorbic acid. 0 6 mL (2.0×10^{-2} mol L^{-1}), 25 °C .and5.0 min

Calibration Graph and Detection Limit

A calibration graph (Fig. 5) was obtained by applying the fixed time method under the optimum conditions and in the concentration range of 0.5 – 520.0 ∝g mL^{-1} of chromium (III). The maximum absorbance wavelength of MB was at 664 nm. According to our investigations, there was no interference by other ions at this wavelength, even for Cr (III). The linear regression equation, is given in Eq. (1).

$$\Delta A = 0.003\,[Cr^{3+}] + 0.0562 \quad (R^2 = 0.9995, n = 6) \quad (1)$$

The experimental detection limit is 0.09 ∝g mL^{-1} (defined as three times the standard deviation of the blank divided by the slope of the calibration graph, $3S_b/m$). The relative standard deviations (R.S.D. %) for the determination of 50.0 and 500.0 ∝g mL^{-1} (n = 6) are 2.8 and 2.1%, respectively.

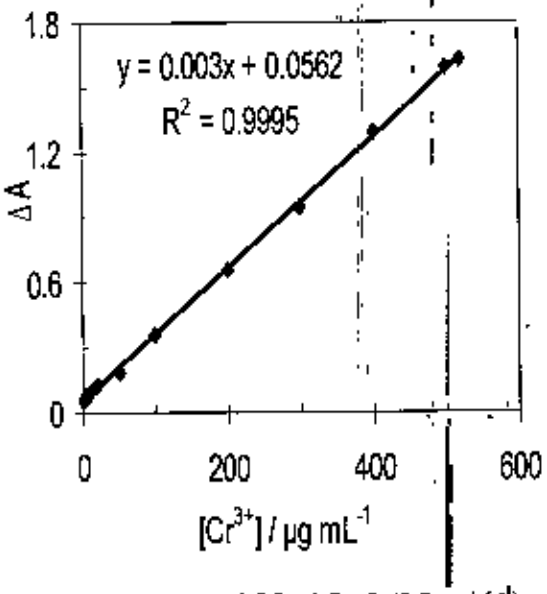

Fig. 5. Calibration curve. H_2SO_4, 1.0 mL (3.0 mol L^{-1}); MB, 0.5 mL (2.0×10^{-4} mol L^{-1}); Ascorbic acid, 0.6 mL (2.0×10^{-2} mol L^{-1}). 25 °C and 120 s.

Effect of Interfering Ions

In order to investigate the analytical applicability i.e. selectivity of the method, the effects of several foreign ions were examined by carrying out the determination of 50.0 ∝g mL^{-1} chromium (III). The results are listed in Table 1. As it can be seen, most of cations even chromium (VI) and anions do not interfere in determination of chromium (III) by the present method.

APPLICATION

The chromium (III) contents of industrial effluents, natural water and soil determined by the proposed method, are shown in Tables 2 and 3, respectively. Statistical test (F test) was used for confirming the precision of proposed method. As it can be seen, results of statistical test have noticeable difference in critical value

Table 1. Tolerance limit of foreign ions on the determination of 50.0 ∞g mL^{-1} of Cr^{3+}

Foreign species	Tolerated limit of foreign ions to chromium(III)
Li^+, Na^+, K^+, NH_4^+, Ba^{2+}, Ca^{2+}, Mg^{2+}	1000
Al^{3+},Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+},Sn^{4+}, As^{5+}, Cr^{VI}	1000
CO_3^{2-}, $CH_3CO_2^-$, HPO_4^{2-}, $H_2PO_4^-$, PO_4^{3-}	1000
NO_3^-, SO_4^{2-}, SO_3^{2-}, F^-, Cl^-, Br^-, I^-, NO_2^- *	1000
Hg^{+2}, Ag^+	800
Hg^+	500
Mn^{2+}, Tl^+	100
V(V), Mo(VI)	80
Fe^{3+}	25
$C_2O_4^{2-}$, SCN^-	300
ClO_3^-, ClO_4^-	0.1

* After masking with 3mL of 5% sulfamic acid.

Table 2. Determination of chromium in industrial effluents

Sample	Cr^{+3} (∞g mL^{-1}) [a]		Statistical test
	Proposed method	Ref. method [40]	F test [b]
Chromium plating effluent [c]	29.3±0.4	29.6±0 3	1.8
Cement industry effluent	35.7± 0.5	36.1±0.7	1 9
Tannery effluent [d]	486.1±0.6	486.4±0.5	1.4

[a] Mean±standard deviatiou (n=6).
[b] Tabulated F-value for (5,5) degrees of freedom at P(0 95) is 5.05.
[c] Solurion diluted 20 times before analysis.
[d] Solution diluted 50 times before analysis.

Table 3. Chromium determination in soil and water samples

Sample	Cr^{+3} (∞g mL^{-1}) [a]						Statistieal test
	Proposed method			Ref. method [40]			F test [b]
	Add	Found	Recovery%	Add	Found	Recovery%	
Soil	10.0	9.9 ± 0.4	99 0	10.0	10.1±0.3	101.0	1.8
	50 0	50.1 ± 0 3	100.2	50.0	50.0±0.2	100 0	2.2
Mineral water	20 0	20.2 ± 0.3	101.0	20 0	20.1±0.2	100.5	2 2
	200 0	200.2 ± 0 2	100.1	200.0	200 3±0.4	100.2	4.0

[a] Mean±standard deviation (n=6).
[b] Tabulated F-value for (5,5) degrees of freedom at P(0 95) is 5.05.

Table 4. Most relevnnt spectrophotometrie method for chromium(III) determination

Analyte	Dynamie range (μgmL^{-1})	Dynamic range (μgmL^{-1})	Matrix	Ref.
Cr^{3+}, Cr^{6+}	0.03 - 1 2, 0.003 - 4	0.01, 0.001	Natural water	41
Cr^{3+}, Cr^{6+}	Ox , 0.007.5 - 0.35	0.0075	Natural water	42
Cr^{3+}, Cr^{6+}	Ox., 1 - 50	0.01	Electroplating wastewater	44
Cr^{3+}, Cr^{6+}	0 85 - 25, 0.16 - 20	0.024, 0.023	Pharmaceutical	24
Cr^{3+}, Cr^{6+}	0.005 – 0.400, Red.	0.002	Automotive Indostry	34
Cr^{3+}	2 - 39	-	Natural water	43
Cr^{3+}	0.010 – 0.027	0.001	Pharmaceutical	45
Cr^{3+}	0 5 - 520	0.09	Natural water, industoal effluent	This work

Ox.: Cr^{3+} must be oxidized and calculated from total chromium
Red.: Cr^{6+} must be reduced and calculated from total chromium.

CONCLUSION

Most of the spectrophotometric methods for determination of chromium (III) ion have small linear dynamic range and/or low sensitivity (Table 4). In order to cope with these difficulties, the present method was proposed which has advantages such as wide linear dynamic range, reproducibility, sensitivity and high tolerance limit of common ions. It is a powerful tool for rapid and sensitive determination of chromium (III) ion in various samples. The low R.S.D% of real sample analysis is an indication of method versatility for real samples analysis.

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