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Spectrophotometric Determination of Chromiumin(III) in Water Using Sodium Bismuthate as an Oxidizing Reagent

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***Abstract**: A simple, sensitive, inexpensive and rapid spectrophotometric method for the determination of trace amounts of chromium (III) in water through oxidation using sodium bismuthate ($NaBiO_3$) is described. $NaBiO_3$ is found to be an effective oxidizing agent for aforesaid oxidation and carries advantages such as easy handling, non-toxic and eco-friendly. Chromium (VI) forms a pink/purple colored complex with diphenyl carbazide (DPC) having λ_{max} 540 nm. Major cations and anions did not show any interference. Beer's law is applicable under concentration range 20.8 – 104.0 µg/l of chromium. The method is highly reproducible and has been tested for chromium estimation in synthetic water samples. The correlation coefficient R^2 is greater than 0.999.*
***Key words:** Spectrophotometric determination; Chromium(III); Sodium bismuthate; Diphenyl carbazide*

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I. Introduction

Chromium compounds have numerous applications in industry; however their discharge into ground water is of great concern due to their hazardous effect. Chromium is an essential nutritional supplement for humans and animals. It plays an important role in glucose metabolism[1,2]In nature, chromium is found usually in trivalent and hexavalent states. Chromium (III) is toxic in aquatic life when its concentration in water is more than 5 mg/l while Chromium (VI) is more toxic and maximum permissible limit in toxic water is 0.05 mg/l[3].

Determination of Cr(VI) in micro-quantities is of increasing interest to analytical chemists. Although atomic absorption spectrometry (AAS) is the sensitive, successful and commonly used method for chromium determination[4], AAS has the disadvantage of being unable to differentiate between the oxidation states of chromium. Other sensitive methods described for chromium (VI) determination includes ion chromatography (IC)[5], electrophoresis[6], neutron activation[7] and ICP-MS[8]. These methods are quite sensitive and selective but very expensive and complex. With growing concerns for safeguarding our environment, there is need to determine the chromium content in water by a method which is sensitive and selective and at the same time is simple and cost effective too. Spectrophotometric methods are generally used for analysis of chromium in water[9-11]. The oxidation of Cr(III) is reported by various oxidizing agents such as $KMnO_4$[12], H_2O_2[13], MnO_2[14], etc. but use of sodium bismuthate in the oxidation of Cr(III) is not explored. In the present work, we report a sensitive, selective and simplified approach for determination of Cr(III) in the water. Herein, a small quantity of chromium is readily determined spectrophotometrically by the oxidation of Cr(III) to Cr(VI) which was further characterized by diphenylcarbazide (DPC) method[15]. Sodium bismuthate has been reported earlier for the oxidation of organic compounds[16,17]. Herein, Sodium bismuthate is found to be an effective oxidizing agent for oxidation of Cr (III) to Cr(VI). Sodium bismuthate has many advantages like not expensive, easy to handle and non-toxic. Cr(III) was oxidized to Cr(VI) which in acidic medium develops a pink color with DPC and the species so formed absorbs at 540 nm

II. Experimental

2.1 Apparatus: A Lab India UV-VIS 3200 double beam spectrophotometer equipped with quartz cuvette of 1 cm optical path was used for all the absorbance measurements. ELICO pH meter (LI 120) was used for pH measurements.

2.2. Reagents: Chromium(III) nitrate nonohydrate ($Cr(NO_3)_3.9H_2O$, Sigma Aldrich) was used to prepare the stock solution of Cr(III). All other reagents used were of analytical grade.

Stock solution of Chromium(III) (1mg/ml) was prepared by dissolving $Cr(NO_3)_3.9H_2O$ (0.7698 g) in 2 N sulfuric acid and diluted to 100 ml with deionized water.

DPC solution was prepared by dissolving 0.01 g of diphenylcarbazide in 10 ml acetone.

2.3. Oxidation of Chromium(III) into Chromium(VI): Aliquots of 0.001 mg/ml of Cr(III) solution (0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, 1.0 ml) were mixed with 1 ml of 2 N H_2SO_4 in a corning glass test tube. 0.02 g of $NaBiO_3$ was added to this mixture and boiled for30 min in a water bath until effervescence ceases. The solution was allowed to cool and centrifuged at 7000 rpm for 10 min.

2.4. Determination of Chromium(VI): The supernatant liquid of Cr(VI) in each case was collected and transferred to volumetric flask, 1 ml DPC reagent was added and the solution was diluted to 10 ml. The absorbance was measured at 540 nm against reagent blank. Cr(III) was estimated as Cr(VI) using calibration graph of standard $K_2Cr_2O_7$ solution.

2.5. Analysis of mixture containing Chromium(III) and Chromium(VI): An aliquot mixture of chromium was analyzed separately for Cr(III) and Cr(VI). The amount of Cr(III) was estimated as:

The amount of Cr(III) =Total amount of Cr(III)+Cr(VI) –Amount of Cr(VI)

III. Results and discussion

3.1 Oxidation of Cr(III) into Cr(VI): Cr(III) was oxidized to Cr(VI) using $NaBiO_3$ in acidic medium. It was observed thatduring oxidation process the color of the solution changes from light blue (Cr(III)) to Pale yellow (Cr(VI)). Reaction mechanism of oxidation of Cr(III) by sodium bismuthate is given below.

$2Cr^{3+} + 5NaBiO_3 + 14H^+ = Cr_2O_7^{2-} + 5\,Bi^{3+} + 8H_2O$

3.2. Absorption spectrum: The yellow color solution was collected and to this solution, 1ml H_2SO_4 (2 N) and 1 ml DPC solution was added, immediately pink color appeared. The intensity of color varied and increases with increase in the concentration of Cr(VI). Appearance of pink color on addition of DPC reagent confirms that Cr(III) species have been oxidized to Cr(VI) species. It is well known that Cr(VI) develops pink/purple color with DPC in acidic medium [15]. The absorption spectrum obtained exhibits λ_{max} at 540 nm and is typical for the λ_{max}value of Cr(VI) species with DPC (Fig. 1) .

3.3. Calibration graph and precision: The determination of chromium was carried out in the given concentration range and the results are depicted in Table 1. Standard Calibration graph for determination of Cr(VI) was obtained for different series of 10^{-5} M standard solution of $K_2Cr_2O_7$.1 ml of H_2SO_4 (2 N) and 1 ml of DPC was added to 0.2, 0.4, 0.6, 0.8 and 1.0 ml of $K_2Cr_2O_7$ solution and the final volume was made 10 ml (Fig. 2). The absorbance of prepared series (as depicted in Table 2) was carried out at 540 nm. The system obeys Beer Lambert law over the concentration range 20.8-104.0 µg/l of chromium. The absorbance of each solution of the series (Table1) was extrapolated to the standard curve of Cr(VI) and its concentration was determined. The standard deviation calculated for five replicate measurements are found to be in good agreement. The percentage recovery of chromium varied from 99.5% to 100.3% for different series of the samples. The average error (%) for different series of Cr(III) solution is found to have a significantly low value of 0.28.Calibration curve for chromium(VI) gave the correlation coefficient, R^2 >0.999 this indicates strong correlation between absorbance and concentration.

3.4. Tolerance of foreign species: Tolerance of various foreign species at mg/l level has been examined in the determination of Cr(VI) (Table 3). Tolerance levels of foreign species were investigated up to those concentrations which did not cause more than ±2 % error in absorbance value of Chromium (VI) at 100 µg/l concentration.

It should be noticed that oxidation of Cr(III) has been reported earlier with potassium permanganate [10], a strong and effective oxidizing agent. However potassium permanganate is itself dark purple in color and if present in slight excess may interfere in the analysis of Cr(III), while with sodium bismuthate such problem does not occur. So, the qualitative as well as quantitative analysis of Cr(III) by $NaBiO_3$ as oxidizing agent is more reliable and easy to perform.

IV. Conclusion

Spectrophotometric determination of Cr(III) in water samples was carried out using sodium bismuthate. Sodium bismuthate is found to be an effective oxidizing agent to convert Cr(III) into Cr(VI), which was then determined by DPC method. The percentage recovery of chromium in different series of prepared water sample varied from 99.5% to 100.3%. The average error in determination of chromium was found significantly low with a value of 0.28%. Overall, the method is reliable, reproducible, sensitive, effective, fast and easy to perform.

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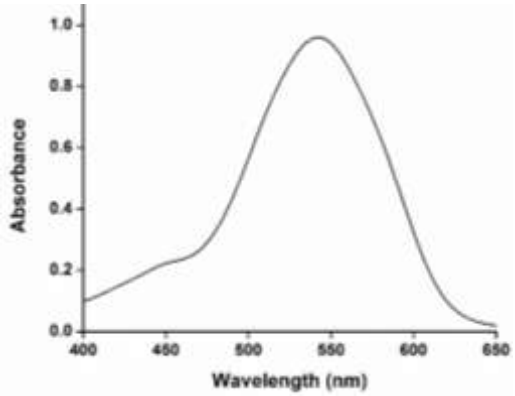

Fig. 1. Absorption spectrum of Cr(VI) with DPC.

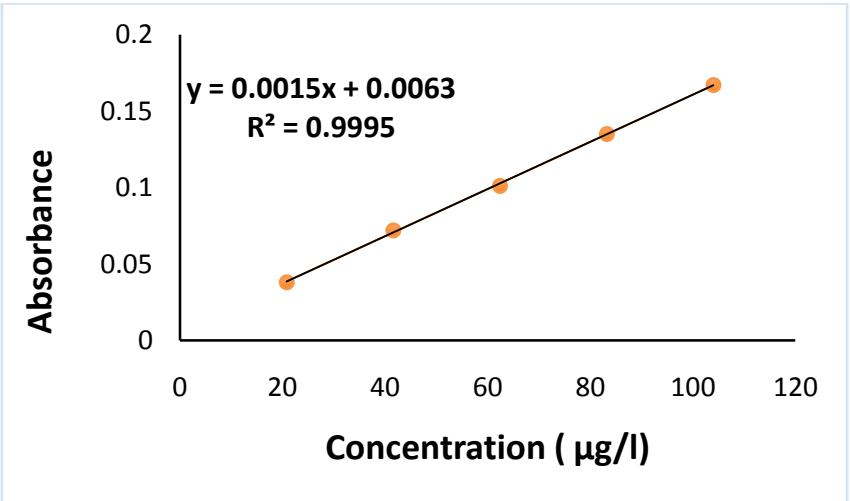

Fig. 2. Calibration graph of Chromium(VI).

Table1. Analytical results of chromium determination in synthetic water samples.

Cr(III) taken (µg/l)	Cr(VI) added ((µg/l))	Cr* Found (Diphenyl carbazide method) (µg/l)	Recovery (%)	Error (%)
20.8	-	20.7	99.5	0.5
41.6	-	41.5	99.7	0.3
62.4	-	62.5	100.1	0.1
83.2	-	83.1	99.8	0.2
104.0	-	103.9	99.9	0.1
20.8	10.4	31.1	99.7	0.3
20.8	20.8	41.4	99.5	0.5
20.8	31.2	52.2	100.3	0.3
20.8	41.6	62.5	99.8	0.2

*Cr(III) was oxidized using sodium bismuthate
Average Error (%) = 0.28, S.D. (%, n=5) = 0.25

Table 2. Standard series of chromium(VI)

Sl.No.	Volume of standard $K_2Cr_2O_7$ taken (ml)	Final volume (ml)	Concentration of Cr (µg/l)
1	0.2	10	20.8
2	0.4	10	41.6
3	0.6	10	62.4
4	0.8	10	83.2
5	1.0	10	104.0

Table 3. Tolerance of foreign species in the determination of Cr(VI) (100 µg/l)

Ion	Tolerance limit (mg/l)	Ion	Tolerance limit (mg/l)
Ca^{2+}	100	CO_3^{2-}	100
Na^{+}	100	CH_3COO^{-}	50
Pb^{2+}	50	Cl^{-}	100
Fe^{2+}	5	NO_3^{-}	100
Cd^{2+}	50	F^{-}	50
Bi^{3+}	50	SO_4^{2-}	100
Cu^{2+}	5	Br^{-}	50
K^{+}	100	Zn^{2+}	50
Mg^{2+}	50	Al^{3+}	50

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