===== **ARTICLES** =====

Spectrophotometric Determination of Chromium(III) with 2-Hydroxybenzaldiminoglycine[1]

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Received January 21; in final form March 30, 2005

Abstract—A spectrophotometric method employing 2-hydroxybenzaldiminoglycine (HBIG) is proposed for the determination of chromium(III). The results of the determinations are compared with the standard diphenyl carbazide method. The presently developed method is direct, simple, rapid, selective, sensitive and precise.

INTRODUCTION

Most of the effects of chromium have been studied in relation to its occupational hazards. The increase in the discharge of industrial effluents and sewages is a cause of concern. The contamination of chromium in groundwater makes it improper for drinking. In view of such an environmental problem, constant monitoring and analysis of chromium becomes a necessity. In a continuation of the development of suitable methods for the determination of metals, especially in natural samples [1–2], a sensitive and selective method has been developed for the determination of chromium(III) in its pure form, natural samples, industrial effluents, and alloys. Though a number of spectrophotometric methods have been reported for the determination of chromium(VI) [3–5], only a limited number of methods are available for chromium(III) [6, 7]. However, no reagent exhibits outstanding performance for direct spectrophotometric determination of chromium(III) in aqueous medium. The use of 2-hydroxybenzaldiminoglycine (HBIG) as a reagent for the sensitive and selective determination of chromium(III) is investigated in the present work.
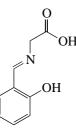
EXPERIMENTAL

Apparatus

A Shimadzu UV–visible double beam spectrophotometer equipped with quartz cells of 1-cm optical path was used for all absorbance measurements. A systronics digital pH meter (model 3335) was used for pH study.

Reagents

2-hydroxybenzaldiminoglycine. The reagent was prepared as reported in [8] by dissolving an aqueous solution of glycine (0.01 mol) with potassium hydroxide (0.56 g/50 mL) and stirred for about an hour on a water bath (50–60°) until a clear solution was obtained. To the solution, salicylaldehyde (1.22 g) in ethanol (20 mL) was added and the mixture was again heated on a water bath (50–60°) for about 2–3 hours, until a clear solution is obtained. This solution was used as the reagent. The reagent is slightly alkaline with a pH of 8 and shows no absorption in the studied wavelength region. The structure of the synthesized reagent may be represented as follows.

Chromium(III) *solution* was prepared by dissolving chromium chloride (1.66 g) in distilled water and diluting the solution to a known volume (250 mL).

Buffer solution (pH 7.5) was prepared by mixing disodium hydrogen orthophosphate (0.01 M) and sodium hydrogen orthophosphate (0.01 M).

Diverse ion solutions were prepared in suitable concentrations using analytical grade chemicals.

General Procedure

Sample solutions containing buffer solution (2 mL), chromium(III) solution (0.14–0.77 mg mL), and reagent (HBIG) solution (2 mL) were mixed in 25-mL volumetric flasks. The solutions were quantitatively diluted, and the absorbances were measured at 565 nm against a reagent blank. A calibration graph was also prepared under similar conditions.

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[1] This text was submitted by the authors in English.

Table 1. Determination of chromium(III)

Sl. No.	HBIG method				Diphenyl carbazide method		
	Cr(III) taken (μg/mL)	Cr(III) found (μg/mL)	recovery (%)	error (%)	Cr(III) found (μg/mL)	recovery (%)	error (%)
1.	5.17	5.19	100.4	0.4	5.15	99.6	0.4
2.	10.34	10.39	100.5	0.5	10.30	99.6	0.4
3.	15.52	15.48	99.7	0.3	15.62	100.6	0.6
4.	20.69	20.68	99.9	0.1	20.88	100.9	0.9
5.	25.87	25.89	100.1	0.1	25.98	100.4	0.4
6.	31.04	30.97	99.8	0.2	31.25	100.7	0.7

Table 2. Statistical Comparison

Sl. No.	Method	Av. error* (%)	S.D*	C.V* (%)
1.	2-hydroxybenzaldiminoglycine (HBIG)	0.27	0.33	0.33
2.	Diphenylcarbazide method (DPC)	0.57	0.56	0.56

* 6 replicates.

Standard Method (Diphenyl Carbazide Method)

The sample solution was heated with sulfuric acid–nitric acid mixture, then oxidized to convert chromium(III) to chromium(VI) with potassium permanganate and then spectrophotometrically analyzed using diphenyl carbazide at 540 nm by the standard method [9].

RESULTS AND DISCUSSION

Spectral Characteristics

The absorption spectra of chromium(III)–HBIG complex in disodium hydrogen orthophosphate and sodium hydrogen orthophosphate buffer (pH 7.5) solution were recorded against water and reagent blank, respectively. The complex shows an absorption maximum at 565 nm. Hence, all the measurements were made at 565 nm.

Calibration Graph and Precision

The system obeys Beer's law over the concentration range 2–39 μg mL of chromium(III). The determinations of chromium(III) were carried out in the concentration range of 5–31 μg mL, and the results of the determinations are presented in Tables 1 and 2. The apparent molar absorptivity was found to be 0.401×10^3 L mol cm. The standard deviation and coefficient of variation calculated for six replicate measurements are in good agreement with that of the standard method.

Effect of pH

The complexation reaction between chromium(III) and HBIG was studied over the pH range 1.0–10.0. The absorbance remained constant and maximum in the pH range 7.0–8.0. Therefore, determinations were carried out at pH 7.5 by use of disodium hydrogen orthophosphate buffer solution.

Table 3. Effect of diverse ions on the determination of chromium(III). Amount of chromium(III) taken is 15.5 μg/mL

Diverse ions	Tolerance limit (μg/mL)
Sodium(I) , nitrate, phosphate, chloride, molybdate and barium(II)	800
Acetate and hydroxide	600
Bromide, bicarbonate, thiosulphate, nickel(II), magnesium(II), calcium(II) and zinc(II)	350
EDTA, vanadate, oxychloride, carbonate, zirconium(II), ammonium(I) and iron(III)[a]	200
Iodide, tartarate, citrate, nitrite, sulphate, manganese(II), potassium(I), mercury(II) and bismuth(II)	150
Tetraborate, thiocyanate, borate, oxalate, tin(II), cadmium(II), lead(II), cobalt(II) and strontium(III)	100
Aluminium(III), titanium(II), lithium(I) and copper(II)	40

[a] Masked with NaF (5 mL, 1% w/v)

Table 4. Determination of Chromium(III) in natural water sample

Sl. No.	Cr(III) added (μg/mL)	Cr(III) found (μg/mL)	Recovery (%)
1.	5.17	5.19	100.3
2.	10.34	10.45	101.0
3.	15.52	15.75	101.4
4.	20.69	20.87	100.8
5.	25.87	25.93	100.2
6.	31.04	31.12	100.3

Stability of the Complex

The formation of chromium(III)–HBIG complex is instantaneous and the absorbance of the complex remains constant for not less than five hours.

Effect of Diverse Ions

In order to assess the possible application of this method, the effect of some ions on the determinations were studied. In this study, various amounts of ionic species were added to 15.5 μg mL of chromium(III) in buffer solution taken in a 25-mL standard flask and color was developed as outlined for general procedure. The tolerance limits are shown in Table 3. The tolerance was taken as the amount of foreign ions required to cause a ±2% error in absorbance. The main interference was shown by iron(III), which was effectively masked with sodium fluoride (5 mL, 1% w/v) solution. The results on closer examination show that all the studied anions and most of the cations do not interfere with the determination of chromium(III).

APPLICATIONS

Determination of Chromium(III) in Environmental Sample

The presently developed method was applied to the determination of chromium(III) in a natural water sample, and the results are given in Table 4. The recoveries reveal that the method can be applied successfully for the determination of chromium(III) in natural water samples.

Table 5. Determination of Chromium(III) in effluent samples (Tannery and Dyeing unit)

Sl. No.	Cr(III) added (μg/mL)	Tannery		Dyeing Unit	
		Cr(III) found (μg/mL)	recovery (%)	Cr(III) found (μg/mL)	recovery (%)
1.	5.17	5.20	100.5	5.20	100.5
2.	10.34	10.45	101.0	10.47	101.2
3.	15.52	15.74	101.4	15.77	101.6
4.	20.69	20.84	100.7	20.84	100.7
5.	25.87	25.94	100.2	25.96	100.3
6.	31.04	31.14	100.3	31.15	100.3

Table 6. Determination of chromium(III) in alloys

Sample composition (%)	Sl. No.	Alloy taken (μg/mL)	Amount of Cr(III) found (μg/mL)	Amount of Cr(III) found (%)	Average of Cr(III) found (%)	S.D C.V (%)
Stainless Steel (Cr – 11–13, Ni – 10, C – 0.1–0.4, Fe – 77)	1.	40.0	4.36	10.90		
	2.	80.0	8.77	10.96		
	3.	120.0	13.26	11.05	11.01 ± 0.084	0.767
	4.	160.0	17.80	11.12		
	5.	200.0	21.84	10.92		
	6.	240.0	26.62	11.09		
Ferrochrome (Cr – 65, Fe – 35)	1.	4.00	2.42	60.50		
	2.	5.60	3.45	61.61		
	3.	7.20	4.39	60.97	63.34 ± 2.35	3.72
	4.	8.80	5.83	66.25		
	5.	10.40	6.80	65.38		
	6.	12.00	7.84	65.33		

Determination of Chromium(III) in Industrial Effluents

The method was applied to the determination of chromium(III) in two effluent samples taken from two industries, and the recoveries are given in Table 5. The results show that the method is highly accurate in estimating chromium in effluent samples.

Determination of Chromium(III) in Alloys

The method was applied to the determination of chromium(III) in two alloys, stainless steel and ferrochrome type steel. In both cases, iron is masked by using sodium fluoride solution. The results are summarized in Table 6. The results are in good agreement with the certified values, and, hence, the presently developed method is effective in the determination of chromium in alloy samples.

CONCLUSIONS

From the above discussion, it can be concluded that HBIG is a potential reagent for the spectrophotometric determination of chromium(III). The most favorable characteristic of HBIG is its high sensitivity toward chromium. The presently developed method has the advantages of being one-step, simple, rapid, and selective without a need for heating or extraction. Regarding accuracy and precision, the method is quite comparable with the standard methods. The method is free from interference from different ions and hence can be used for routine analysis of chromium(III) in alloys, water, and effluent samples.

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