

Spectrophotometric Determination of Chromium (III) with Isatin in the Presence of Surfactant

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Abstract

A spectrophotometric determination of chromium (III) carried out with isatin as a complexing agent in the presence of hexadecyltrimethylammonium bromide (HTAB) as a surfactant for increasing the sensitivity of the system. The complex between chromium (III) and isatin formed at pH 3.0. Beer's Law was obeyed for chromium (III) over the range $0.45 - 8.50 \mu\text{g L}^{-1}$ with molar absorptivity $1.69 \times 10^4 \text{ L. mol}^{-1} \cdot \text{cm}^{-1}$ and Sandell's sensitivity was $4.7 \times 10^{-3} \mu\text{g cm}^{-2}$. The proposed method has been successfully applied to the determination of chromium (III) in igneous rock from Snam hill in Iraq , and no other method investigated chromium (III) in same rock in order to compare with proposed method.

الخلاصة :

تم تقدير الكروم الثلاثي عن طريق تكوينه معقدًا مع الإيساتين وبوجود هكساديكاييل تري ميثايل أمونيوم برومايد (HTAB) كعامل يزيد من المساحة السطحية لتكوين المعقد وبالتالي يزيد من الحساسية للنظام. يتكون معقد الإيساتين مع الكروم الثلاثي عند دالة حامضية تبلغ 3.0 ، وأن المعقد يخضع لقانون بير عند مدى من تركيز الكروم الثلاثي يبلغ $0.45 - 8.50$ مايكروغرام . لتر⁻¹ عند أمتصاصية مولارية تبلغ 1.69×10^4 لتر . مول⁻¹ . سم⁻¹ كما تبلغ قيمة حساسية ساندل 4.7×10^{-3} مايكروغرام . سم⁻² . تم استخدام هذه الطريقة الطيفية لتقدير أيون الكروم الثلاثي في الصخور النارية في جبل سنام الموجود في العراق ، ولم يتم تقدير الكروم الثلاثي في هذا النوع من الصخور بطريقة تحليلية أخرى لغرض مقارنة النتائج.

Introduction

Chromium occurs naturally as heavy metal in the earth's crust, it is contribute with other heavy metals to increase the hardness of earth's crust [1,2]. Chromium is found throughout the environment in three major oxidation states : chromium (0) , chromium (III) and chromium (VI). The most stable form, chromium (III) , while chromium (VI) and chromium (0) are generally produced by industrial processes [3].

Various techniques such as NAA [4, 5], UV-visible [6], ICP-MS [7-9] and AAS [10] and kinetic method [11] with high sensitivity for the determination of chromium reported, so far need complicated and expensive equipment. Moreover, such techniques are usually not available in most laboratories. Very few methods for chromium determination are based on the complex formation with Cr (III) in aqueous solution [12].

The analytical chemists have to be aware of the influence of surfactant assemblies on the chemical equilibrium , and can exploit their unique properties for improving analytical methodologies and for the development of entirely new concepts in analytical chemistry [13].

Isatin (1H – indole – 2,3 – dione) is synthetically versatile substrates , where they can be used for the synthesis of large variety of heterocyclic compounds, such as indoles and quinolines, and as raw material for drug synthesis [14].

In this paper , a facial , sensitive and selective method has been reported for the determination of chromium (III) using isatin as spectrophotometric reagent in presence of hexadecyltrimethylammonium bromide (HTAB) as surfactant. The method was used for the determination of chromium in ultra igneous rock from Snam hill in Iraq.

Experimental Section

Reagents: All chemicals in this experiment were analytical reagent grade and double – distilled water was used. Chromium stock solution (1×10^{-2} mol L⁻¹). Prepared by dissolving 0.400 g of chromium nitrate nonahydrate (obtained from Aldrich Co.) in 99.5% ethanol and diluting to volume with ethanol in 100 mL volumetric flask. Isatin stock solution (1×10^{-3} mol L⁻¹). Prepared by dissolving 0.015 g of isatin(98.0%,Aldrich)in 99.5%ethanol and diluting with ethanol to 100 mL. Hexadecyltrimethylammonium bromide (HTAB, 95.0%, Merck) , Sodium dodecylbenzene-sulfonate (SDBS, Merck), Sodium dodecylsulfate (SDS, Merck) and Triton X114 (polyoxyethylene-t-octylphenol) from (BDH Co.) were used without additional purification.

The (HTAB) solution (1×10^{-3} mol L⁻¹) prepared by dissolving 0.036 g of HTAB in 100 mL of deionized water. Buffer solution (pH 3 ± 0.2) prepared by adding 15 mL of 0.2 mol L⁻¹ acetic acid to 35 mL of 0.2 mol L⁻¹ sodium acetate. Other standard solutions of different metals used to study the effect of diverse ions were prepared by dissolving weighed quantities of their salts in deionized water or in diluted sulphuric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in water. All the chemicals used were of analytical reagent grade.

The absorbance measured by SpectroScan 80D UV-Vis. Spectrophotometer / UK.and the pH was measured by MoLab pH Level 1 from WTW / Germany.

Procedure

A portion of Cr (III) standard solution transferred to 25 mL volumetric flask ; 3.0 mL of the 1×10^{-3} mol L⁻¹ isatin solution; 1.5 mL of buffer solution were added. Then 5.0 mL of 1×10^{-3} mol L⁻¹ Hexadecyltrimethylammonium bromide (HTAB) solution was added, perchloric acid and ammonia were added in amounts to achieve the media acidity (pH=3) , and the volume was made up to 25mL.

The absorbance of the solution at 355 nm measured in 1 cm cell against reagent blank prepared in the same way but without chromium.

Results and discussion

Characteristics of Chromium ion complex

The absorption spectra of Cr (III) – isatin complex and Cr (III) – isatin – HTAB complex against blank are shown in Fig. 1. The Cr (III) complex with isatin was green in color with absorption maximum 355 nm ; the use of surfactant (HTAB) increase of absorption maximum to 404 nm with an increasing in absorbance signal and as a result the determination sensitivity of Cr (III) is increase.

Optimum Conditions for determination of Chromium

The pH effect on the chromium (III) – isatin – HTAB system carried out over the pH range 2.0 – 4.0 at 404 nm against the reagent blank. The acidity was adjusted with perchloric acid and ammonia. Maximum absorbance was obtained at pH 3.4 , in more or less than this range the absorbance decrease, this may be attributed to decomposition of the complex.

When the effect of amount of HTAB studied the result showed that HTAB must be present in the system in a minimum concentration of (2×10^{-3} mole L⁻¹) because the absorbance signal is maximal and constant at this concentration of surfactant. Therefore, (2×10^{-3} mole L⁻¹) of HTAB was selected for further investigation.

The effect of different surfactants (cationic, anionic and non-ionic) on the Cr (III) complex was studies. The result showed that the cationic surfactant (HTAB) promoted an increase in the absorbance signal and as a result the determination sensitivity increased , but no mentioned effect to anionic surfactant (SDS and SDBS) or nonionic surfactant (Triton X114) as shown in Table 1.

Chromium complex composition

The composition of chromium (III) – isatin complex under experimental condition was determined by continuous variations [15-17]. A series of solutions which contain varying amount of Cr^{3+} and varying amount of isatin with keeping constant concentration of complex, 2ml of acetate buffer at pH 3.0 were taken and the absorbance measured in 1cm cells, after standing at room temperature for one hour, at 404nm, using ethanol (95.5%) as a blank. Fig. 2. shows a plot of absorbance versus mole fraction of the metal ion indicating a maximum which corresponds to 1:2 (M:L) ratio in the complex.

Analytical Parameter

Under the optimum conditions described above, calibration graphs for Cr (III) – isatin complex was constructed by plotting absorbance values as a function of the analyte concentration. The calibration graphs was linear in the range $0.45 - 8.50 \mu\text{g L}^{-1}$ of Cr (III). The molar absorptivity was $1.69 \times 10^4 \text{ L. mol}^{-1} \cdot \text{cm}^{-1}$, and the corresponding Sandell's sensitivity was $4.7 \times 10^{-3} \mu\text{g cm}^{-2}$.

Effect of Divers Ions

The effect of many foreign ions on the determination of Cr (III) was studies. The tolerance limits of interfering species were established at those concentrations that do not cause more than 2% error in absorbance values of chromium (III) at $2.0 \mu\text{g L}^{-1}$ (Table 2). As can be seen, most ions were tolerated at high concentrations and the results indicated that Al (III) and Fe (III) interfere severely which eliminated by the addition of urea, as given in the procedure for the analysis of igneous rock.

Real Sample analysis

The method was applied to the determination of chromium (III) in certified values in igneous rock from Snam Hill in Iraq. The matrix elements, such as Fe (III), Al (III) and other rare earths coexist in basic igneous rock. A 0.5 gm sample was dissolved with 1:3 HCl + HNO_3 and the residue was dissolved in 10 ml of 1M HCl, diluted with 10 ml of distilled water and filtered if needed. Finally, the solution was taken up to 50 ml with distilled water in volumetric flask. An aliquot of solution (10 ml) was taken individually and analyzed by the proposed procedure after masking Al (III) with $1 \times 10\text{M}$ urea solution. Generally urea is used as a precipitate of Al (III), Ga (III), Th (IV), Bi (III), Fe (III). Recovery tests (Table 3) were satisfactory (about 97.3% - 98.0%) with relative standard deviation of 2.4% - 4.3%.

Conclusion

The method using isatin as spectrophotometric reagent to determine chromium (III) in the presence of HTAB is selective, rapid and simple. The Cr (III) – isatin complex is stable and determination sensitivity is comparable to other analytical methods. The method involves less sophisticated instrumentation, no extraction step is required and hence the use of organic solvents, which are generally toxic pollutants, is avoided.

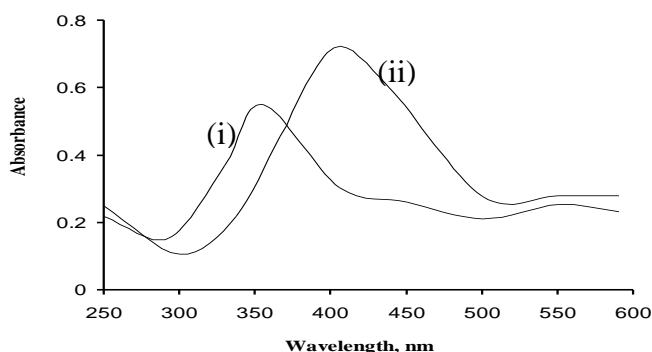


Fig. 1. (i) Spectra of Cr (III) – Isatin complex. (ii) Spectra of Cr (III) – Isatin – HTAB complex at (pH = 3.4).

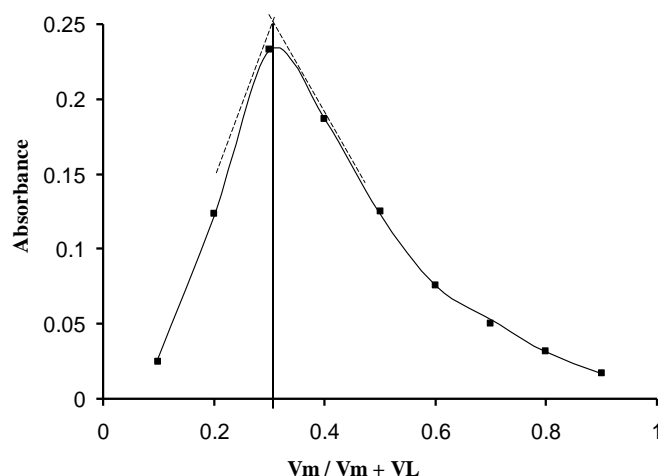


Fig. 2. Determination of ligand to metal ratio (Job Plots).

Table 1. Absorption characteristics of Cr (III) – isatin complex in the different surfactant.

Surfactant	λ_{max} (nm)	Abs.
None	355	0.120
Hexadecyltrimethylammonium bromide (HTAB)	404	0.338
Sodium dodecylsulfate (SDS)	351	0.117
Sodium dodecylbenzene-sulfonate (SDBS)	348	0.136
polyoxyethylene-t-octylphenol (Titron X114)	358	0.107

Table 2. Effect of foreign ions on the determination of chromium (III).

Foreign ion	Tolerance limit (ppm)
Ba^{2+} , Cu^{2+}	100
NH_4^+ , K^+ , Na^+ , PO_4^{3-} , CH_3COO^-	50
Ni^{2+} , Fe^{2+} , Co^{2+}	75
Mg^{2+} , Zn^{2+} , Mn^{2+} , SO_4^{2-} , Cl^-	100
Al^{3+}	10
Fe^{3+}	15

Table 3. Recovery test for chromium (III) determination in Igneous rock sample.

Sample	Chromium (III) concentration, $\mu\text{g L}^{-1}$		Relative Standard Deviation, %	Recovery, %
	Added	(mean \pm stand deviation) (n=3)		
Igneous rock	-	16.3 ± 0.6	3.7	-
	10.0	21.1 ± 0.5	2.4	98.0
	20.0	30.0 ± 1.29	4.3	97.3

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