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Iminostilbene As New Spectrophotometric Reagent For Determination Of Chromium(VI) In Soils And Industrial Effluents

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ABSTRACT

New oxidative electrophilic coupling method is developed for spectrophotometric determination of trace amounts of chromium(VI) in soil and industrial effluent samples. The method is based on the reduction of chromium(VI) by an electrophilic coupling reagent, 3-methyl-2-benzothiozoline hydrazone hydrochloride hydrate(MBTH) which subsequently couples with iminostilbene(ISB) in acidic medium to form a green colored product having λ_{max} at 700nm. The color is stable up to 24h and obeyed Beer's law in the concentration range of 0.1-4.0μg ml^{-1}. The optimum reaction conditions and other important analytical parameters are established to enhance the sensitivity of the proposed methods. Interference due to various non-target ions is also investigated. The proposed method can be applied to the analysis of chromium(VI) in selected soils and industrial effluents. The performance of proposed methods can be evaluated in terms of recovery tests by standard addition method and the results indicate the significance of proposed method over reference spectrophotometric method.

KEYWORDS

Spectrophotometry;
Chromium(VI);
Iminostilbene;
Oxidative electrophilic coupling method;
Soils and industrial effluents.

INTRODUCTION

Chromium is found throughout the environment in three major oxidation states. Chromium(0), chromium(III) and chromium(VI). The most stable form, chromium(III), occurs naturally in the environment, while chromium(VI) and chromium(0) are generally produced by industrial processes[1]. The determination of micro quantities of chromium in environmental matrices and industrial effluents is of particular importance in connection with the growing interest in environmental problems. It is known that an increase in the content of this element in soils makes them less fertile and that the toxic effect depends to some extent on the chromium oxidation state. On the other hand, it has also been established that the introduction of chromium salts into soils has some positive effects, such as increase in sugar contents and yield, favorable changes in chemical composition and activation of some biochemical process in plants. Obviously, the concentration and oxidation state of chromium, like those of other micro elements are of great significance for its physiological action. For example, as an essential trace nutrient for humans, chromium(III) is involved in glucose metabolism and/or the mechanism of insulin action. This has been demonstrated in experiments involving one type of impaired glucose tolerance. Of the two oxidation states namely, trivalent and hexavalent the latter is harmful to animals and plants and its micro determination is becoming a subject of importance[2].

The methods proposed for the determination of metals in varied soil and industrial effluent matrices include: electro-analytical[3], radio-analytical[4] and chromatography[5]. However, these methods have proved to be deficient with respect to specificity, sensitivity, simplicity and analysis time. For example, polarography demands extensive selectivity regarding the pH and the supporting electrolytes, otherwise, interference by various metal ions may likely to be encountered. Besides, the ions may cause direct interference if they are polarographically active in the potential range of interest, as well as indirect interferences by co-precipitation of metals with the hydroxides of polyvalent cation formed at medium pH. Radio-analytical methods are reliable for arcane academic purpose, but are seldom used for routine analysis of metals in soil and industrial effluent samples. Chromatographic methods are valuable techniques for speciation studies rather than routine quantitative analysis. Further, the cost of the instrument is relatively high and its maintenance demands sophistication.

Various optical methods such as inductively coupled plasma atomic emission spectrometry, electrothermal atomization atomic absorption spectrometry (ETAAS) and atomic absorption spectrometry (AAS) have been used for detection, quantitation and characterization of these metals. ETAAS presents problems owing to the formation of metal carbide during the ashing and atomization steps, which decrease the sensitivity. Besides, these instruments are highly expensive, their day-to-day maintenance cost is high and are not free from various types of inherent interferences.

Amongst the optical methods visible spectrophotometry seems to be the most appropriate for the determination of toxic metals, as it provides sensitive, precise and accurate measurements of suitable analytes and offers practical and economical advantages over other methods. Besides, visible spectrophotometric detection is much more viable as a useful technique to develop a portable on-line or at-line system.

In this paper we report first-ever use of iminostilbene (ISB) as a spectrophotometric reagent for the determination of chromium(VI) in selected soils and industrial effluents. The chemical reaction involved has been studied and the results showed that the method is simple and sensitive. Besides, ISB along with MBTH offers clear advantages over most of the chromogenic reagents currently used for the purpose and the procedure shows positive features over the existing methods.

MATERIALS AND METHODS

Reagents and apparatus

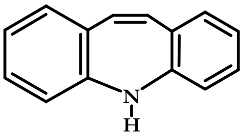
Stock solution of chromium(VI) (1000μg ml^{-1}) was prepared by dissolving known amount of potassium chromate in 100ml of distilled water. Solutions of required strength were prepared by diluting the stock solution with distilled water.

ISB was received as gift sample from max pharma, India and fresh solution(0.1% w/v) was prepared by dissolving in distilled alcohol. Aqueous solution of MBTH(0.05% w/v) was prepared by dissolving in distilled water. The solutions of MBTH and ISB are stable for a week if refrigerated and protected from light. Solutions of diverse ions were prepared by dissolving their corresponding salts. Alcohol was distilled before use. Specord 50 UV-vis spectrophotometer with 1.0-cm silica quartz matched cell was used for recording the absorption spectrum and absorbance measurements.

Procedure

Appropriate volumes of standard solution of chromium(VI), 0.5ml of 5N phosphoric acid, 0.5ml of 0.05% (w/v) MBTH and 1.5ml of 0.1% (w/v) ISB were added to a series of 25-ml calibrated flasks. The contents were mixed thoroughly and kept aside for 15min to allow the reaction to be completed. The resultant green colored solutions in the standard flasks were made up to the volume with distilled alcohol. The absorbance of each solution was measured against the corresponding reagent blank at 700nm. Concentration of chromium in test solution was calculated from the regression equation computed from the Beer's law data as a reference. The concentration of chromium(VI) determined and optical characteristics are presented in TABLE 1.

TABLE 1: Spectral data for the determination of chromium(VI) with ISB using MBTH as an electrophilic coupling reagent

Parameters	 ISB
Color	Green
λ_{max}(nm)	700
Stability(h)	24
Beer's law(μg ml^{-1})	0.1-4.0
Recommended chromium(VI) concentration(μg ml^{-1})	1.2
Molar absorptivity(L mol^{-1}cm^{-1})	1.30×10^4
Sandell's sensitivity(μg cm^{-2})	0.0065
Regression equation^a	
Slope 'a'	0.1290
Intercept 'b'	0.1196
Correlation coefficient 'r'	0.9949

^{a}Regression curve: y=ax+b where x is the concentration of chromium(VI) in μg ml^{-1} and y is the absorbance

RESULTS AND DISCUSSION

ISB belongs to dibenzazepines which are important tricyclic antidepressant drugs. They are commonly used for the treatment of depressive disorders[6] and their efficacy in alleviating depression has been well established. ISB(5H-dibenz[b,f]azepine) is a solid having solubility in alcohol. It is a precursor to opipromol(4-[3-(5H-Dibenz[b,f]azepin-5-yl) propyl]-1-piperazineethanol; 5[γ-[4-β-hydroxyethy) perazisolropyl] dibenzo[b,f] azepine; N-[3-[4-(2-hydroxyethyl)-piperazinolpropyl] iminostilbene) which is extensively commercialized under the trade names; dinsidon, ensidon, insidon, nisidana to mention a few.

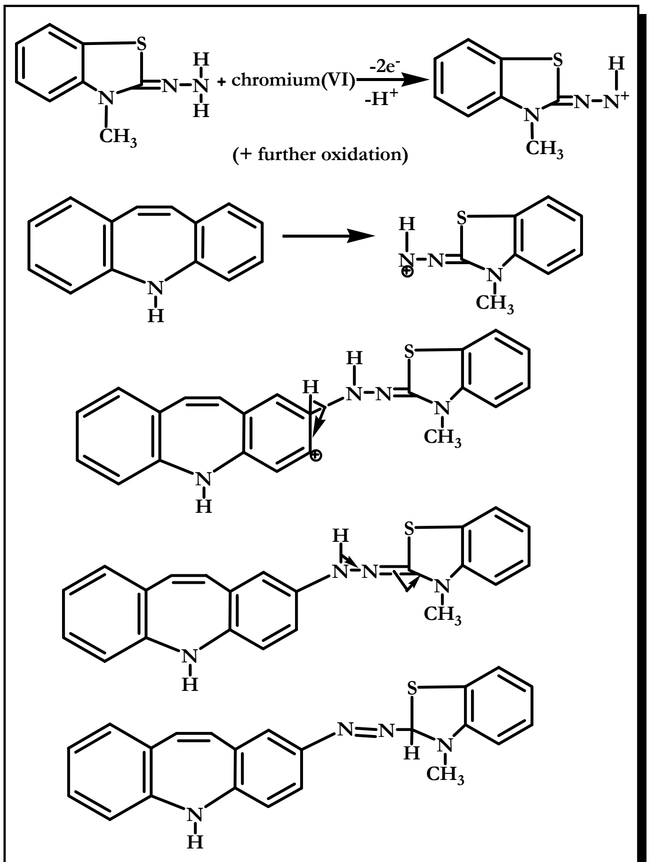
MBTH was first introduced for the determination of aromatic amines and imino heteroatomic compounds and aliphatic aldehydes. Later, it was extended for the determination of a large number of organic compounds such as those containing methylene groups, carbonyl compounds, Schiff's bases, aromatic hydrocarbons, saccharides, steroids, olefins, phenols, furfural and heterocyclic bases[7].

Reaction mechanism and stability

The chemical reaction in the spectrophotometric study involves the reduction of chromium(VI) by MBTH and subsequent coupling with ISB in aqueous acidic medium to form a green colored species and attained maximum absorbance at 700nm. At this wavelength the reagent blank showed practically negligible absorbance. Green colored derivatives under the optimized condition were stable up to 24h. The absorbance varied by ±2% over a period of 24h. and the reaction mechanism is represented in SCHEME 1.

Order of addition of reagents

During the course of study it was observed that the sequence of addition of reagents also influenced



SCHEME 1: Proposed reaction mechanism between MBTH and ISB

to a great extent to the intensity and stability of the color. Less intense and unstable color was observed when we followed the sequence of addition either (i) ISB-acid-substrate-MBTH or (ii) substrate-acid-ISB-MBTH. But, the sequence (iii) substrate-acid-MBTH-ISB and (iv) MBTH-acid-substrate-ISB gave more intense and stable green colored products. This was expected as the reactions (i) and (ii) produce radical cation, while in (iii) and (iv) electrophilic substitution reaction was involved. We selected order (iii) for further spectrophotometric investigations.

Effect of temperature

The color development was independent of temperature in the range of 20-35^{0}C and gave the most useful results at room temperature. At higher temperature the absorbance values decrease and this indicates the dissociation of the color product on prolonged heating. Therefore, the experimental work has been carried out at room temperature.

Effect of reaction time

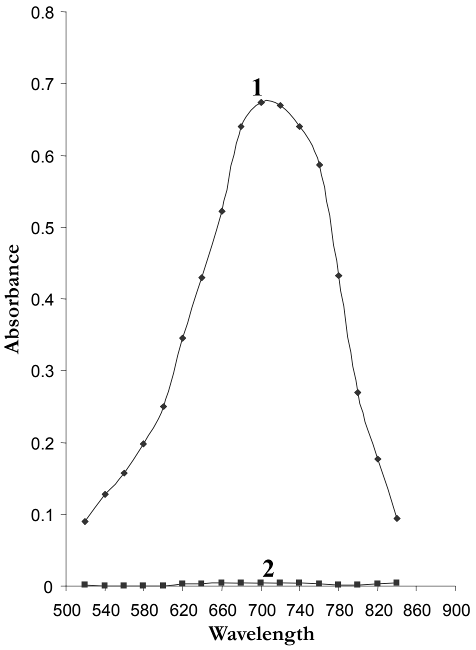


Figure 1: Absorption spectra of the reaction product of (1) Cr^{6+} (1.2μg mL^{-1})+MBTH+ISB, (2) Reagent blank

Experiments were conducted to optimize the reaction time in the determination of chromium(VI). It was found that the green color formed in the reaction was stable after 15min and remained constant up to 24h. Therefore, 15min was reasonable for the absorbance study.

Effect of different acids

The stability and sensitivity of the green colored solution depends on the nature and concentration of the acid medium. The color was less intense in CH_3COOH, HCl and H_2SO_4 medium, but was more intense in H_3PO_4 medium. Therefore, H_3PO_4 was selected as an acidic medium in the reaction study.

Optimization of analytical variables

Effect of phosphoric acid

Effect of different concentration levels of phosphoric acid on the color development was studied by using phosphoric acid in 2-10N range. Maximum absorbance was observed when 5N was used. The effect of different volumes was studied in the volume range of 0.2-2.0ml of 5N phosphoric acid. Maximum absorbance was observed when 0.5ml was used. Relatively less intense color was obtained when less than 0.5ml and more than 0.5ml of phosphoric acid was used. Therefore, 0.5ml of 5N phosphoric acid was used for further study.

Effect of MBTH

Effect of different concentration levels of MBTH was studied in the concentration range of 0.01-0.1% of MBTH. Maximum absorbance was observed when 0.05% of MBTH was used. Effect of different volumes of MBTH was studied in the volume range of 0.2-2.0 ml. Maximum absorbance was noticed in the colored product in which 0.5 ml of 0.5% MBTH present. Therefore, 0.5ml of 0.05% (w/v) MBTH was selected for further study.

Effect of ISB

Effect of different concentration levels of ISB was studied in the concentration range of 0.01-0.1% of ISB. Maximum absorbance was observed when 0.05% of ISB was used. Effect of different volumes of ISB was studied in the volume range of 0.2-3.0ml. Maximum absorbance was noticed when 1.5ml of 0.05% ISB was used. Therefore, 1.5ml of 0.05% (w/v) ISB was selected for further study.

Analytical data

Green colored species obeyed Beer's law in the concentration range of 0.1-4.0μg mL^{-1}. Molar absorptivity and Sandell's sensitivity values were 1.318×10^4L mol^{-1} cm^{-1} and 0.0065μg cm^{-2} respectively. Regression analysis of Beer's law revealed correlation coefficient value 0.9949, intercept value 0.1196 and slope value 0.1290. These are described by a regression equation, Y=ax+b, where Y is the absorbance of a 1-cm layer, a is the slope, b is the intercept and x is the concentration of the chromium (VI) in μg mL^{-1} by the least squares method. The reproducibility was studied by replicate analysis of a standard chromium(VI) solution over a period of 24h. Other important analytical parameters are presented in TABLE 1.

The accuracy and precision of the proposed methods were evaluated by performing recovery tests by standard addition method. These tests were performed by adding known amounts of standard solutions at different concentration levels to a fixed amount of real samples and the mixtures were analyzed by the proposed procedures. Each test was repeated five times.

Effect of diverse ions

In order to establish the analytical potential of proposed method, the effect of some possible interfering ions which often accompany chromium(VI) was examined by carrying out the determination of 1.2μg mL^{-1} of chromium(VI) in presence of number of other ions by the proposed method. An ion was considered to be interfered with the determination if the obtained absorbance values differed by more than 3% from that of chromium(VI) alone. As the developed methods are based on the oxidation of MBTH with chromium(VI), strong oxidizing or reducing agents are expected to interfere by oxidation of MBTH. Metals such as iron(III), vanadium(V) manganese(VII) and cerium(IV), non metals such as bromate, iodate and periodate were found to be interfered severely and caused low recovery of chromium(VI). However, using appropriate masking agents could eliminate the interference from these ions. Masking agents such as EDTA, tartrate and citrate were not interfered in the determination of chromium(VI). The use of a mixture of tartaric acid(50mg) and citric acid(5mg) has been found to have effective masking action on a large number of foreign metal ions. During the interference studies, if a precipitate was formed, it was removed by centrifugation. The maximum tolerable concentrations of different ions(defined as the foreign-ion concentration causing an error smaller than ±3% for determining the analyte of interest) in the determination of chromium(VI) are listed in TABLE 2.

TABLE 2: Effect of diverse species in the determination of 1.2μg ml^{-1} of chromium(VI) by proposed method

Foreign ions	Tolerance limit (μg ml^{-1})
Bi^{3+}, Ba^{2+}, Ti^{4+}, EDTA, Br^-, citrate, tartarate, oxalate	200
Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, K^+ Hg^{2+}, Ni^{2+}, CH_3COO^-	100
NO_3^-, Cl^-, Br^-, SO_4^{2-}, NH_4^+, Co^{2+}, Cu^{2+}	50
Chloramine-T, Chloramine-B, IO_3^-, IO_4^-, BrO_3^-	0.2

Applications

Collection, preparation and determination of soil samples

Soil samples were collected about 0.5 kilometer away from waste treatment plant of a factory, which used chromium extensively in plating baths. The treated industrial effluents(water) from the factory were released into the neighboring fields, which were ultimately used for irrigation purposes. Static sampling procedure was adopted and six soil samples were collected at random from depth of 0-20cm with a distance of about 50m between each sampling site.

Known amount of soil sample(5.0g) was taken in a platinum crucible and then heated it for 3h in a muffle furnace at 550^{0}C. After cooling, the sample was transferred into a platinum basin and added 2.0ml of double distilled water, 1.0ml of concentrated sulphuric acid and 10.0ml of concentrated hydrofluoric acid and heated on a sand-bath until vapors of SO_3 appeared. The residue was dissolved in 5.0ml of double distilled water acidified with hydrochloric acid to pH 3[8]. The pH of the solution was raised to ~10 by the addition of concentrated ammonia solution to precipitate the iron and aluminum. Filtered off the precipitate with a suitable filter paper and washed it with three 3-ml portions of double distilled water. Evaporated the filtrate to ~20ml, cooled, acidified the solution to pH 3 with hydrochloric acid, transferred it into a 25-ml standard flask and diluted up to the mark with distilled water. Iron, which is commonly found in most of the soil samples, interferes and its elimination is necessary. Methods reported in the literature for the elimination of iron(III) interference, include: either precipitation as hydroxide or use of masking agents. The former method is extensively used[9]. We have reported a simple spot test to know the presence of iron(III) in filtrate. This involves the use of KSCN solution which gives red color with iron(III)[10] (1 drop of filtrate+1 drop of 2N H_2SO_4+1 drop of thiocyanate, HCl is avoided as it gives dense fumes of NH_4Cl). Absence of red color is an indication that iron(III) precipitation process is almost complete.

TABLE 3: Determination of chromium(VI) in selected soils

Soil[a]	Proposed method($\mu g ml^{-1}$) ± RSD[b]	Atomic absorption spectrometry($\mu g ml^{-1}$) ± RSD[b]
Leached chernozem	2.36 ± 0.6	2.38 ± 0.5
Podzolized black	2.51 ± 0.5	2.54 ± 0.7
Brown	3.53 ± 0.5	3.54 ± 0.6
Gray forest	3.63 ± 0.6	3.67 ± 0.8

[a] Obtained from mineralogical mnstitute museum, university of mysore
[b] Relative standard deviation, n=5.

About 2.5ml or other suitable aliquot of the above prepared solution was taken and oxidized from chromium(III) to chromium(VI)[11] by adding 3ml of bromine water and boiled for 3min to ensure that all chromium(III) was oxidized to chromium(VI). The solution was cooled and diluted to volume in a 100-ml standard flask. An aliquot of this solution was taken for analysis by the proposed method. The results are presented in TABLE 3.

Waste waters from industries (plating baths)

The solution was obtained from waste chromium baths and was determined by taking 2.5ml of the sample and diluting to 25ml with distilled water. Bromine water(3ml) was added and boiled for 3min to ensure that all chromium(III) was oxidized to chromium(VI). The solution was cooled and made up to 100ml in a standard flask. To enhance the reliability of the method standard addition test was conducted.

Ten aliquots of the above solution were transferred to ten 25-ml standard flasks; 5 of the aliquots were then spiked with 100μl solution and contain-

TABLE 4: Determination of chromium(VI) in plating baths solutions by proposed method

Sample[a]	Cr(VI) found[b] $\mu g ml^{-1}$	Cr(VI) added $\mu g ml^{-1}$	Cr(VI) determined $\mu g ml^{-1}$	Recovery(%)
Plating bath 1	1.0	0.8	1.75	97.2
		1.6	2.55	98.0
		2.0	2.99	99.6
Plating bath 2	1.2	0.8	1.96	98.0
		1.6	2.77	98.9
		2.0	3.10	98.8

[a] Bath 1 and 2 referred to the diluted samples from two different factories
[b] Atomic absorption spectrophotometry method

ing 1.0, 1.2μg ml^{-1} of chromium. Aliquots of this solution were analyzed by proposed methods. The results are presented in TABLE 4.

CONCLUSION

The proposed method, besides being simple, inexpensive, sensitive and precise also has the advantage of determination without the need for extraction or heating. The method does not involve complicated reaction conditions. The proposed oxidative coupling method has significant advantages over other existing methods in terms of simplicity and free from most of the interfering substances. Statistical analysis of the results revealed that the proposed method yield accurate and reproducible values in the determination of chromium(VI) in various soils and industrial effluent matrices. Applications of the method in the determination of chromium(VI) in a variety of real samples have demonstrated their practical utility.

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