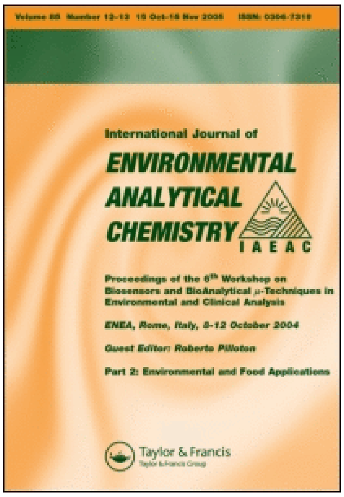

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Spectrophotometric determination of Chromium(VI) using cyclam as a reagent

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A simple, rapid, sensitive, and inexpensive method for spectrophotometric determination of chromium(VI), based on the absorbance of its complex with 1,4,8,11-tetraazacyclotetradecane (cyclam) is presented. The complex showed a molar absorbtivity of $1.5 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ at 379 nm. Under optimum experimental conditions, a pH of 4.5 and $1.960 \times 10^3\,\mathrm{mg\,L^{-1}}$ cyclam were selected, and all measurements were performed 10 min after mixing. Major cations and anions did not show any interference; Beer's law was applicable in the concentration range 0.2–20 $\mathrm{mg\,L^{-1}}$ with a detection limit of 0.001 $\mathrm{mg\,L^{-1}}$. The standard deviation in the determination is $\pm 0.5\,\mathrm{mg\,L^{-1}}$ for a 15.0 $\mathrm{mg\,L^{-1}}$ solution ($n = 7$). The described method provides a simple and reliable means for determination of Cr(VI) in real samples.

Keywords: Spectrophotometry; Cyclam; Chromium(VI)

1. Introduction

Chromium exists primarily in trivalent or hexavalent oxidation states. Chromium(VI) exists as the chromate ion in basic solutions and as hydrogen chromate or dichromate in acidic solutions. Chromium(VI) is a notorious environmental pollutant because it is a strong oxidant and much more toxic than chromium(III). Chromium(VI) ion along and many of its compounds are known to be highly toxic. Chromium compounds that are inhaled have been linked with lung cancer, while those ingested can cause kidney and liver damage [1, 2]. Other studies have indicated that Cr(VI) can cause genetic mutations and modifications to the structure of DNA [3, 4]. Concern over the toxicity of Cr(VI) has led the Fedral Water Pollution Prevention to identify it as a priority pollutant and the United States Environmental Protection Agency to limit atmospheric emissions to 5 ppm. In some European countries and in Japan, water districts impose even lower limits, creating a need for more sensitive methods of detection [5].

Determination of Cr(VI) micro-quantities is of increasing interest to analytical chemists, particularly environmental scientists. Although atomic absorption

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spectrometry (AAS) is the most common method of chromium detection, AAS has the disadvantage of being unable to differentiate between the chromium oxidation states. Besides AAS, numerous other methods have been described for Cr(VI) determination; ion chromatography (IC), electrophoresis, ICP and ICP-MS work perfectly well and are hard to beat in terms of selectivity and sensitivity [6–17].

Because of the high cost of the above instruments, colorimetric and complexometric determination of various metal ions in solution are still the method of choice for many researchers [18–22]. Several papers describe the determination of Cr(VI) in small quantities using complexometric titration or colorimetric procedures. Feigl and Anger [23], Sandell [24], and Snell and Snell [25] reviewed the earlier work on the detection and determination of chromium(VI). Micro amounts of chromium(VI) also have been determined spectrophotometrically with diphenylcarbohydrazides, malachite green, crystal violet, cesium iodide, varamine blue, alizarine, 3, 3′-diaminobenzidine, pyridine-2, 4, 6-tricarboxylic acid, triethylenetetraminehexaacetic acid, *O*-toluidine, α-naphythyl, and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. Indirect determination of chromium(VI) was achieved by using iron(III) and ferrozine [2, 26–31]. Thiazolyl blue was proposed as a reagent for extraction photometric determination of trace amounts of Cr(VI) [32]. Klaus *et al.* [22] described strip spot tests to determine Cr(VI) in aqueous samples. El-Shahat *et al.* [18] proposed a method for the direct determination of Cr(VI) and/or V(V); the method is based on the reaction of these ions with perphenazine to give a red-coloured product showing a maximum absorbance at 526 nm. Balogh *et al.* [33] described the solvent extraction of Cr(VI) ion associates with cyanine dyes including the heterocyclic radicals of 1,3,3-trimethyl-3*N*-indoline, benzooxazol, benzothiazol, and quinoline. The associates in acidic medium in the presence of Cl^- are extractable by aromatic hydrocarbons and esters of acetic acid. Andruch *et al.* [34] showed the procedure for Cr(VI) extraction and spectrophotometric determination of Cr(VI) using the dye 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium chloride. Perclay *et al.* [35] compared the results of the two polymers Chelex-100 and poly(chloromethyl)vinyl benzene to which cyclam was attached. The polymer supported cyclam provided >95% extraction of copper and zinc. The resin was used as a solid sample for electro-thermal atomic absorption spectrometry, or the metal was back-extracted with nitric acid.

In this article, a new method for the spectrophotometric determination of Cr(VI) using cyclam (structure 1) is proposed. A complex that showed a maximum absorbance at 379 nm was immediately formed by the addition of cyclam to a sample containing Cr(VI). The best conditions under which cyclam binds Cr(VI) were carefully selected; the effects of coexisting ions on the determination of Cr(VI) are included. This method is new, rapid, sensitive, and inexpensive, and is superior to most of the reported methods in simplicity. The suggested method has been applied for the determination of Cr(VI) in natural water and chromium-plating electrolyte waste without prior separation.

Structure 1.

2. Experimental

2.1. *Apparatus*

A Milton Roy (Spectronic Genesys 5) spectrophotometer was used. The spectra were recorded in the visible region using 1 cm quartz cuvettes. A 523 WTW pH meter with a WTW pH glass electrode was used for all pH measurements. Calibration of the pH meter was performed at regular intervals.

2.2. *Reagents*

Analytical grade reagents and deionized, ultrafiltered water were used throughout. 1,4,8,11-Tetraazacyclotetradecane (cyclam) solutions were prepared from an Across sample which was used without further purification.

Stock solution (2941 mg L^{-1} of Cr(VI)) was prepared by dissolving 99+% Aldrich potassium dichromate in deionized water. The remaining solutions were prepared by appropriate dilutions of the standard. Cr(VI) solutions were stored in dark plastic containers for one week, after which new solutions were prepared.

The 1,4,8,11-tetraazacyclotetradecane solutions of concentrations 25, 50, 100, and 200 mg per 0.100 L of water were prepared and kept in volumetric flasks. The standard solutions of Cr(VI) in the concentration range of 0.05–200 mg L^{-1} were prepared by appropriate dilutions of the stock.

2.3. *Procedure for determination of Cr(VI)*

One millilitre of each standard sample was placed in a test tube; the pH was adjusted to 4.5 by the addition of 0.4 M HCl. Two millilitres of 25 mg L^{-1} cyclam solution was added to all standard samples. The test tubes were shaken to mix the contents well, the mixture was then transferred to the cuvettes, and the absorbance was measured over the range 350–700 nm against a reagent blank (water or cyclam). The operation was repeated with all solutions of the reagent.

3. Results and discussion

3.1. *General discussion*

The spectrophotometric method for determining micro-quantities of Cr(VI) was based on a complex formation with cyclam. It was based on the following observations: cyclam is transparent above 350 nm (i.e. it does not absorb in the visible region), while the dichromate ion exhibits a spectrum that extends from 250 to 650 nm with characteristic peaks around 256 and 350 nm (reported elsewhere [36]). The addition of small amounts of Cr(VI) to cyclam resulted in the formation of a complex that showed a pronounced absorption maximum at 379 nm.

3.2. *Absorption spectra*

The absorption spectra in the 350–700 nm range for the dichromate ion alone and in the presence of cyclam are displayed in figure 1a and b, respectively. The formation

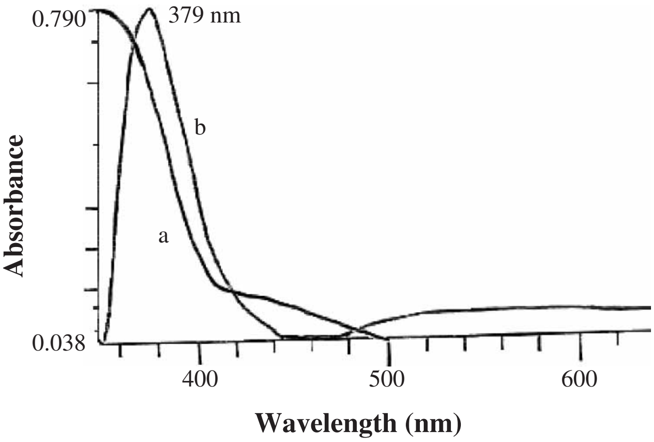

Figure 1. (A) 2.0 mL water + 1.0 mL of 5.4×10^{-5} mol L^{-1} $K_2Cr_2O_7$ (blank is water). (B) 2.0 mL cyclam (1×10^{-2} M) + 1.0 mL of 5.4×10^{-5} mol L^{-1} $K_2Cr_2O_7$ (blank is 1×10^{-2} M cyclam).

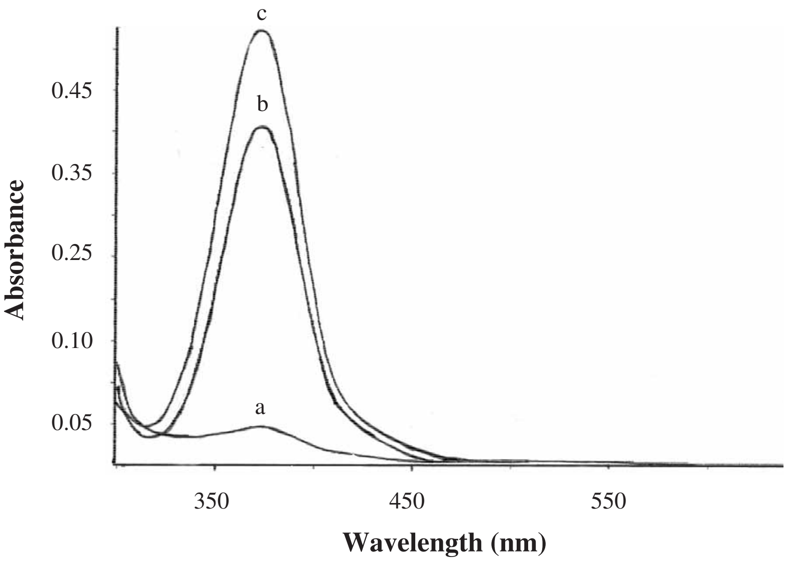

Figure 2. (a) 2.0 mL cyclam (1×10^{-2} M) + 1.0 mL of 3.4×10^{-6} mol L^{-1} $K_2Cr_2O_7$ (the blank is 1×10^{-2} M cyclam). (b) 2.0 mL cyclam (1×10^{-2} M) + 1.0 mL of 2.7×10^{-5} mol L^{-1} $K_2Cr_2O_7$ (the blank is 1×10^{-2} M cyclam). (c) 2.0 mL cyclam (1×10^{-2} M) + 1.0 mL of 3.4×10^{-5} $K_2Cr_2O_7$ (the blank is 1×10^{-2} M cyclam).

of the 379 nm band in figure 1b must be connected with ionic association or chelate formation between Cr(VI) and cyclam.

Relative to the 350 nm band for the dichromate ion, the formation of the complex was accompanied by a new band at 379 nm and, as a result, a blue shift of 29 nm. Although the shift is not large, the form of the curves allows a suitable wavelength for the spectrophotometric determination of Cr(VI) to be chosen.

The behaviour of cyclam after exposure to three different concentrations of Cr(VI) (1, 8, and 10 mg L^{-1}) is presented in figure 2. Clearly, the 379 nm chelate absorbance peak increases by increasing concentration of Cr(VI), indicating the sensitivity of the method.

It appeared that cyclam and dichromate reacted without destroying the ring structure of the reagent. The most probable mechanism for the reaction was that the cyclam nitrogens were protonated partially or fully then the dichromate anion approached to form the complex (scheme 1). The proposed mechanism for the colorimetric reaction between Cr(VI) and cyclam is as follows:

$$\text{Cyclam}(R_4N) + nH^+ \rightarrow R_4NH_n^+$$

$$R_4NH_n^+ + Cr_2O_7^{2-} \rightarrow R_4NH_n^+ : Cr_2O_7^{2-} \text{ (coloured complex)}$$

3.3. *Effect of pH*

The effect of pH on the absorption of the chromium complex was studied at 379 nm with solutions containing 15.8 mg L^{-1} $Cr_2O_7^{2-}$ and 1.960×10^3 mg L^{-1} cyclam. The spectrum of the cyclam-dichromate solution was strongly dependent on the pH of the solution (figure 3). Our experiments showed that the complex did not form at a low pH ($pH < 2$) and a high pH ($pH > 7$). The optimum working pH was found to be $pH = 4.5$.

3.4. *Calibration curves*

Under the optimum experimental conditions described above, a linear calibration graph was obtained in the concentration range 0.2–20 mg L^{-1}, the regression equation

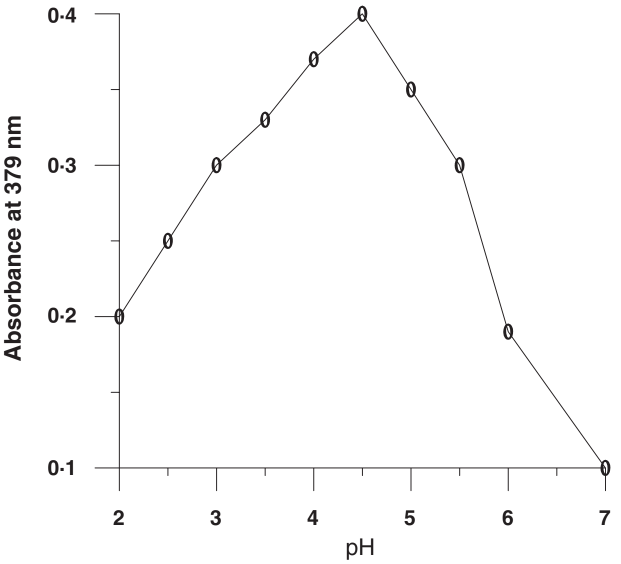

Figure 3. Effect of pH on the complexation. Conditions: 5.4×10^{-5} M Cr(VI), 1×10^{-2} M cyclam, standing time 10 min.

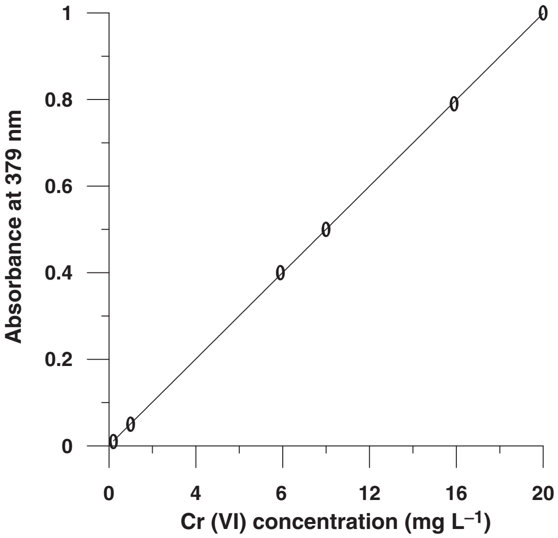

Figure 4. Calibration graph for the determination of Cr(VI). 1×10^{-2} M cyclam, pH = 4.5, and 10 min standing time.

$A = 14\,676.4C_{cr} + 7.2 \times 10^{-4}$ (where A is the absorbance of the complex, and C_{cr} is the molar concentration of Cr(VI)), and a correlation coefficient of 0.99971 was obtained; the results are shown in figure 4. The limit of detection was found to be 0.001 mg L^{-1}. The standard deviation (seven replicates) was ±0.5 mg L^{-1} for a 15.0 mg L^{-1} solution. In the absence of determinate error, the true value fell within 1.44×10^{-2} to 1.53×10^{-2} mg with a confidence interval of 95%.

3.5. *Effect of time and reagent concentration*

The stability of the complex was studied by measuring the absorbance at 379 nm as a function of time (regular time intervals); the complex formed immediately just after mixing, and we noticed no degradation of the complex over several hours (figure 5). All measurements made in our experiments were made 10 min after preparation of the solutions.

The influence of excess reagent concentration on the absorbance of the complex was studied. The absorbance of 15.9 mg L^{-1} dichromate ion after the addition of varying concentrations of cyclam ranging from 245 to 1960 mg L^{-1} at pH = 4.5 was monitored at 379 nm; the reaction of Cr(VI) with cyclam solution increased in sensitivity with increasing solution concentration (figure 6).

3.6. *Effect of other ions on Cr(VI) determination*

Under the optimum experimental conditions for Cr(VI) determination, the effect of diverse ions on the determination of 15 mg L^{-1} Cr(VI) was investigated. The tolerance limits were determined as the maximum concentration that produced a 5% change in the respective absorbance values; the results are summarized in table 1.

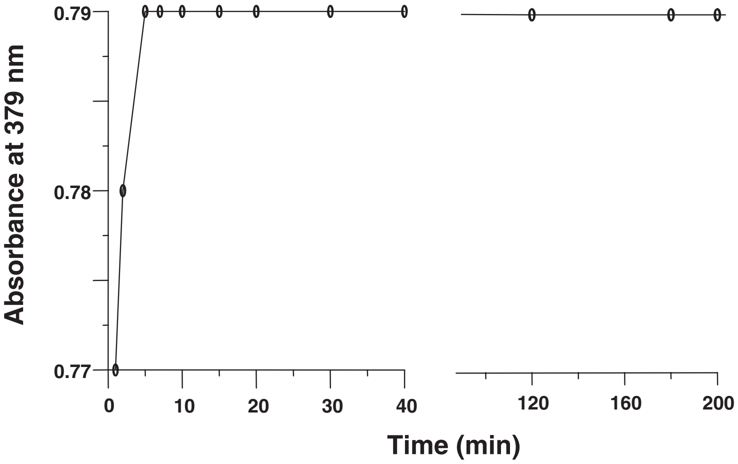

Figure 5. Absorbance change for the complex with the passage of time. 5.4×10^{-5} M Cr(VI), 1×10^{-2} M cyclam, and pH = 4.5.

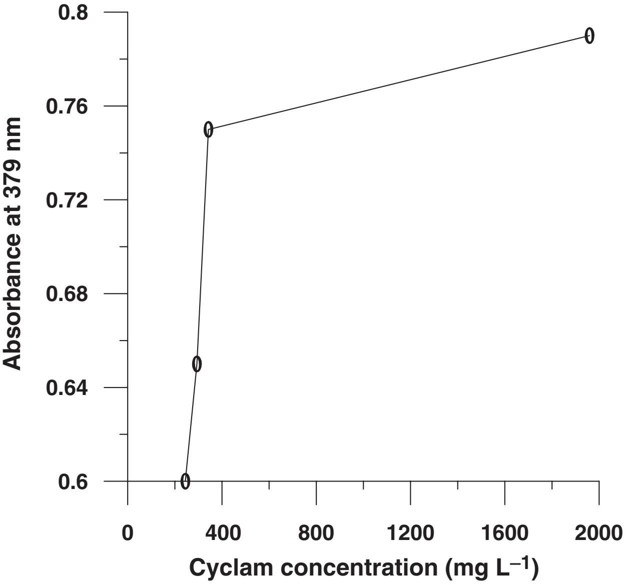

Figure 6. Effect of reagent concentration on complexation, 5.4×10^{-5} M Cr(VI), pH = 4.5, standing time = 10 min.

3.7. *Advantage of the present method*

This method is rapid, sensitive, selective, precise, and accurate. It offers certain advantages over several other methods. In the method recommended by El-Shahat [18], total chromium and vanadium were determined first; then, V was determined after addition of As(III) to reduce Cr(VI) that was calculated by difference, and a detection limit of 0.003 mg L^{-1} was obtained. The colour reaction with malachite green needed 10 min to develop; the detection limit was reported as 0.004 mg L^{-1} [1]. The colour reaction

Table 1. Tolerance limits in the determination of 15 μg mL^{-1} Cr(VI).

Interfering ion	Tolerance limit (mg L^{-1})
Li$^+$, K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}, V^{5+}, Al^{3+}, Cd^{2+}	2500
Fe^{3+}, Co^{2+}, Mn^{2+}, Ce^{+4}, Ni^{2+}, NH$_4^+$, Sr^{2+}, Cr^{3+}, Hg^{2+}	2000
Cl$^-$, NO$_2^-$, PO$_4^3$, MnO$_4^-$, citrate, acetate	1500
Cu^{2+}, Zn^{2+}, SO$_4^{2-}$, S$_2$O$_3^{2-}$	1000

Table 2. Spectrophotometric determination of Cr(VI) in real samples.

	Chromium(VI) (mg L^{-1})			
		Found[a]		
Sample	Added	Present method	I.C. method[b]	Recovery
Natural water[c]	3.0	2.99 ± 0.1	3.0 ± 0.1	99.7
	6.0	6.01 ± 0.2	6.0 ± 0.2	100.2
Polluted water	–	20.25 ± 0.3	20.5 ± 0.3	
	15	35.24 ± 0.1	36.5 ± 0.4	99.9
Chromium plating	–	70.9 ± 0.4	71.1 ± 0.2	
	50	118.7 ± 0.5	121.1 ± 0.5	98.2

[a] Mean ± standard deviation ($n = 7$).
[b] Certified reference calibration standard EMPA/BAM (1000 mg L^{-1} K$_2$CrO$_4$), ion chromatography standard solution from Fluka, Catalogue number 27072.
[c] Volume of the sample taken, 3 mL.

of Cr(VI) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol required heating of the reactants in a boiling water bath for 45 min; the detection limit was 1 mg L^{-1} [28], whereas the reaction was complete immediately after mixing in the present case. In the method of Bet-Pera and Jaselskis [29], permanganate and Fe(III) interfered, and low results were obtained in the presence of Co(II) and Ni(II) because these ions formed ferrozine complexes; there are no such difficulties with the present procedure. The procedure suggested by Malik *et al.* [30] also required 2 h for complete colour reaction. Various oxidants such as permanganate, Ce(IV), V(V), and Fe(III) interfered in the method proposed by Cheng and Goydish [31], but these oxidants did not interfere in the present studies. The present procedure was suitable for detection and determination of Cr(VI) in real samples (natural water and chromium plating electrolyte waste without prior separation). Results for the determination of wastewater samples are summarized in table 2. As can be seen, there is a satisfactory agreement between the results of the proposed method and the ion-chromatographic method for Cr(VI) determination.

4. Conclusion

The present article described a selective, sensitive, and simple method for the direct determination of Cr(VI). This method was based on the reaction of this ion with cyclam to give a coloured complex showing a maximum absorbance at 379 nm.

The colour developed instantaneously upon mixing the reagents and was stable for several hours.

A 1960 mg L^{-1} cyclam, pH of 4.5, and a standing time of 10 min were selected as the optimum experimental conditions most suitable for complexation. This method has been successfully applied for the determination of Cr(VI) in real samples (natural water and chromium plating electrolyte waste) without prior separation.

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