

Indirect Extraction-Spectrophotometric Determination of Chromium

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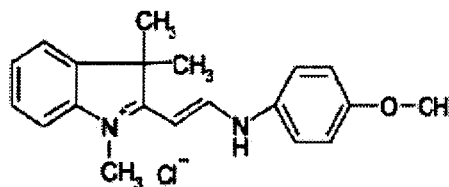
An analytical procedure for the indirect spectrophotometric determination of trace amounts of hexavalent chromium in a model sample of water has been developed. Chromium in its hexavalent state is reduced to its trivalent state in the presence of an excess of iodide ion in an acidic medium. The liberated triiodide ion forms with a cationic dye ion associate which is extracted into toluene. The extraction of chromium(VI) is the highest from a 0.08 mol dm⁻³ sulfuric acid medium. The intensively coloured complex absorbs at $\lambda = 430$ nm. The system obeys Beer's law in the concentration range up to 2 mg dm⁻³. Corresponding limit of detection (based on 3 σ) is 0.234 mg dm⁻³ Cr(VI).

Chromium compounds are widely used in chemical manufacture, in leather, textile, and in other industries. The determination of chromium is important because of the contrasting biological effect of its two common oxidation states, chromium(III) and chromium(VI). The former is an essential element, while the latter is toxic [1].

Spectrophotometry still represents an attractive technique for the determination of metal in aqueous media because of its simplicity and being inexpensive. Most of these methods require control of temperature and long reaction time. In addition, the stability of the coloured products is not satisfactory. Hence, a new determination method for chromium(VI) is necessary. The spectrophotometric determination of chromium(VI) using diphenylcarbazide is still most commonly used [2]. The diphenylcarbazide method is sensitive but involves the interference of many metal ions, e.g. Fe(III), Mo(VI), V(V), etc. [3]. Some papers describing techniques used for the indirect spectrophotometric determination of chromium were published. *Mehra et al.* [4] followed the method for the indirect spectrophotometric determination of chromium in aqueous samples with a Chromogen Ferene-TM. In this investigation the chromium in its hexavalent state is reduced to its trivalent state in the presence of a known excess of iron(II) and then measured as its tris complex with the reagent Ferene-TM. Similarly *Balasubramanian and Maheswari* [5]

have reported indirect spectrophotometric determination of chromium by using generated nitrite to diazotize *p*-nitroaniline and coupling the formed diazonium salt with *N*-(1-naphthyl)ethylenediammonium dichloride to form an azo dye. *Abdullah and Hassan* [6] and *Bet-Pera and Jaselskis* [7] have suggested an indirect spectrophotometric approach for chromium determination using tiron and the ferrozine complexes of iron(II), respectively. These procedures are either time-consuming or require strictly controlled experimental conditions.

In the present work we suggest a simple and rapid method for indirect determination of hexavalent chromium. The method is based on the reduction of chromium(VI) with KI in an H₂SO₄ medium by means of the formation of triiodide ion then measured as its complex with the dye reagent in toluene. Cationic Yellow 42 (CY42)



was examined as a new reagent.

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EXPERIMENTAL

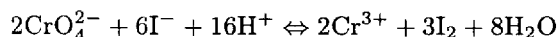
All chemicals used were of anal. grade. Distilled water was used for preparing reagent solutions. A stock solution containing 10^{-3} mol dm^{-3} chromium(VI) was prepared by dissolving 2.9418 g $\text{K}_2\text{Cr}_2\text{O}_7$ in 100 cm^3 of water. Appropriate volume of this solution was diluted to obtain the working solution. A 10^{-3} mol dm^{-3} aqueous solution of dye was prepared by dissolving the precise amount of this reagent. The required concentration of iodide ions was reached with the addition of 3 mol dm^{-3} solution of KI and the required acidity of the medium by means of 1 mol dm^{-3} solution of H_2SO_4 . Solutions of diverse ions for interference studies were prepared by dissolving the amount of each compound of needed 0.1 mol dm^{-3} concentration of the ion of interest. Absorbance measurements were made by a Zeiss 11 spectrophotometer with 0.2 cm glass cells at $\lambda = 430$ nm.

Procedure

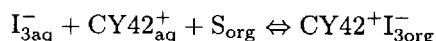
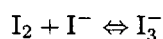
The appropriate volumes of 1 mol dm^{-3} sulfuric acid, 3 mol dm^{-3} iodide ions, and 10^{-3} mol dm^{-3} CY42 were pipetted to 0.6 cm^3 of 10^{-4} mol dm^{-3} $\text{K}_2\text{Cr}_2\text{O}_7$. This was diluted with water until the volume of the solution was 5 cm^3 . After adding each reagent, it was mixed thoroughly and then left to stand in the dark for 3 min. Then the formed ion associate was extracted in a test tube at room temperature by 5 cm^3 of toluene for 30 s. After equilibrium was established, the organic phase was separated and absorbance of the organic phase was measured at 430 nm against toluene. A reagent blank is prepared similarly but without chromium.

RESULTS AND DISCUSSION

The analytical approach for determination of chromium is dependent on two reactions which must be quantitative. First, chromium in hexavalent state must oxidize an equivalent amount of iodide ions. It is known that Cr(VI) and iodide ion react quantitatively in an acid medium as follows [8]



In the presence of an excess of iodide ion, the liberated iodine forms triiodide ion, which combines with a cationic dye ion associate extracted into organic phase formed by solvent (S_{org})



In order to find the optimum conditions for the formation and extraction of ion associate, the effects of

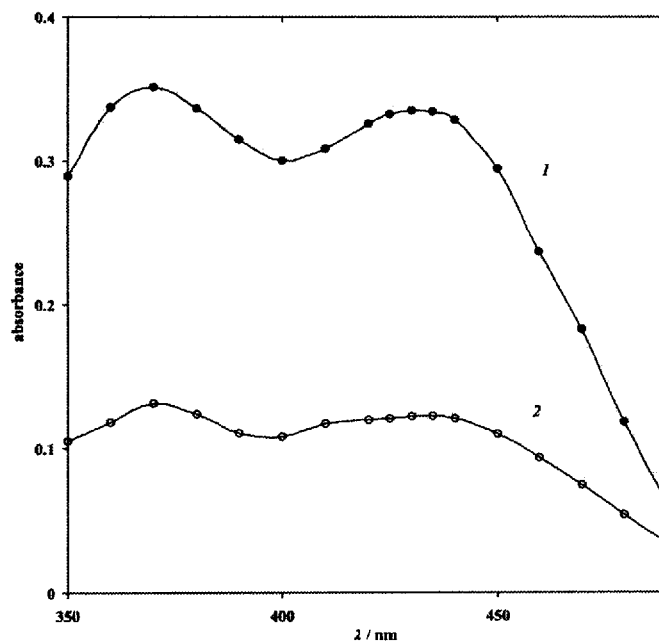


Fig. 1. Absorption spectra of ion associate $\text{CY42}^+\text{I}_3^-$ (1) and blank test (2). 0.08 mol dm^{-3} H_2SO_4 , 0.12 mol dm^{-3} KI, 2×10^{-4} mol dm^{-3} CY42.

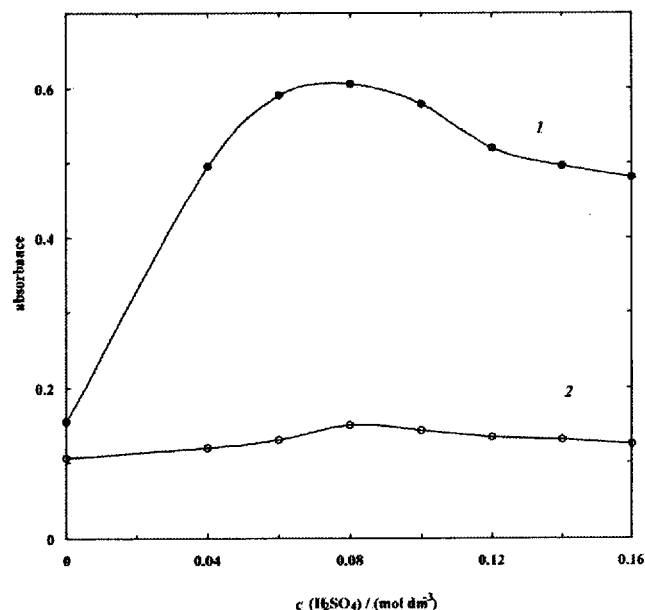


Fig. 2. Effect of acidity on the extraction of ion associate with CY42 by toluene. 1.25 mg dm^{-3} of Cr(VI), 0.12 mol dm^{-3} of KI, 2×10^{-4} mol dm^{-3} of CY42; 1. ion associate, 2. blank test.

the medium acidity, concentration of iodide ions, as well as dye reagent on the absorbance of the coloured extracts were investigated.

The absorption spectra of the ion associate formed by triiodide ion with cationic dye CY42, as well as reagent blank, are shown in Fig. 1. The absorption

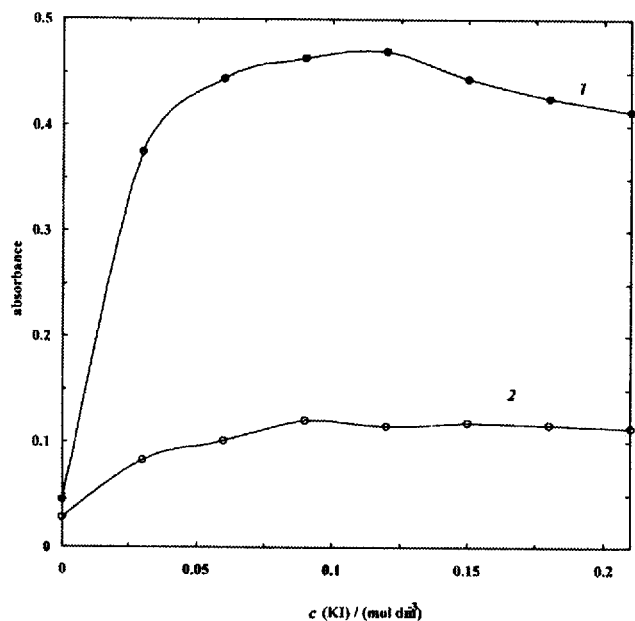


Fig. 3. Influence of the concentration of iodide ions on the extraction of ion associate by toluene, 1.25 mg dm^{-3} of Cr(VI), 0.08 mol dm^{-3} of H_2SO_4 , $2 \times 10^{-4} \text{ mol dm}^{-3}$ of CY42; 1. ion associate, 2. blank test.

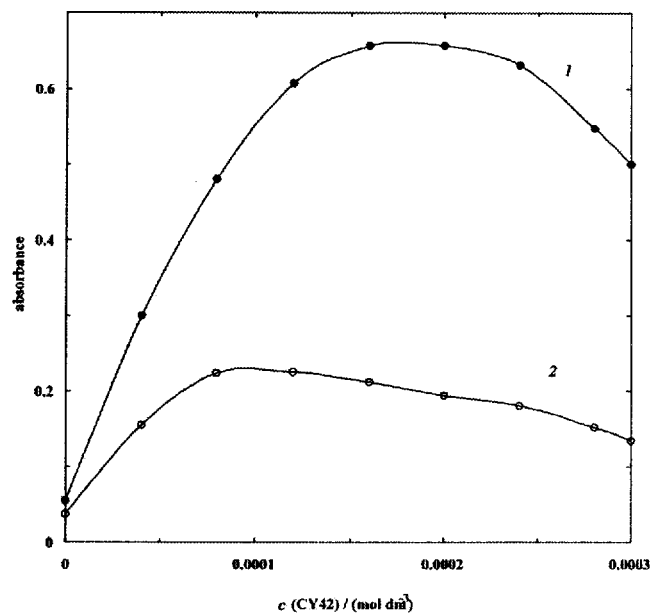


Fig. 4. Influence of the concentration of CY42 on the extraction of ion associate by toluene, 1.25 mg dm^{-3} of Cr(VI), 0.08 mol dm^{-3} of H_2SO_4 , 0.12 mol dm^{-3} of KI; 1. ion associate, 2. blank test.

maximum of the ion associate in organic solvent is 430 nm . All further absorbance measurements were made at this wavelength.

The effect of acidity on the redox reaction between chromium(VI) and iodide ion was examined. A series of experiments were carried out with 1.25 mg dm^{-3} Cr(VI) at various concentrations of H_2SO_4 ; the results are shown in Fig. 2. The extraction of the system is the highest during extraction from the sulfuric acid medium in the optimum range from 0.07 to 0.09 mol dm^{-3} H_2SO_4 . All further experiments were carried out at 0.08 mol dm^{-3} H_2SO_4 .

The effect of the concentration of iodide ions on the extraction of the ion associate was studied (Fig. 3). As can be seen, the absorbance of the extract of ion associate was the highest with a concentration of 0.06 – 0.12 mol dm^{-3} of KI. Therefore, this concentration was recommended for subsequent measurements.

Fig. 4 shows the effect of the CY42 concentration on the absorbance of coloured ion associate. Absorbance increased with the increasing concentration of the reagent and became constant in the range 1.2 –

$2 \times 10^{-4} \text{ mol dm}^{-3}$ of solution of CY42. Then, with the increasing concentration of CY42 absorbance decreased.

A solution containing a known amount of chromium(VI) and varying amounts of diverse ions was prepared and the influence of some selected cations and anions on the system was investigated at a fixed chromium(VI) concentration (1.25 mg dm^{-3}) under optimum reaction conditions. The tolerance limit of interfering ions was $\pm 5 \%$ in absorbance. Ni(II), Co(II), Zn(II), Cd(II), Mo(VI), CH_3COO^- , NH_4^+ up to $200:1$ φ_r ratio, Mn(II), Cu(II), V(V), HPO_4^{2-} , SO_4^{2-} ($\varphi_r = 100:1$) were without significant effect (less than $\pm 3 \%$ change of absorbance). Ions such as Al(III), Cr(III), Pb(II), Fe(III), Ag(I) are tolerated in the ratio $1:10$. Fe(II) and Hg(II) were the ions which interfered significantly ($> 20 \%$ at a ratio $1:1$).

Based on the obtained results, an indirect spectrophotometric procedure for chromium determination was developed. It was found that the system obeys Beer's law over the concentration range up to 2 mg dm^{-3} of chromium(VI). According to the pro-

Table 1. Determination of Chromium(VI) in Water Doped by Cr(VI) ($n = 4$, average)

| Sample | Concentration of Cr(VI)/(mg dm^{-3}) | | Recovery | RSD/% |
|--------|---|-------|----------|-------|
| | Determined | Known | | |
| 1 | 0.41 ± 0.08 | 0.41 | 106.6 | 7.8 |
| 2 | 0.80 ± 0.05 | 0.83 | 105.1 | 4.1 |

cedure recommended, the regression equation in this concentration range of Cr(VI) is $A = 0.164c - 0.014$, with a correlation coefficient $R^2 = 0.991$. The molar absorptivity of the colour system is $3.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$. Corresponding limit of detection (based on 3σ) is 0.234 mg dm^{-3} Cr(VI). The method was tested for the indirect determination of Cr(VI) in samples of drinking water doped with chromium(VI). Table 1 shows the analytical results of the samples to which known amounts of chromium(VI) were added. The advantage of the proposed method is the greater colour stability (5 h) compared with the diphenylcarbazide method (30 min) and as for water analysis, it is applicable to waters containing large amounts of molybdenum or vanadium relative to chromium, in contrast to diphenylcarbazide method, where these elements interfere.

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