# Indirect Spectrophotometric Method For The Determination Of Chromium

**H.D.Revanasiddappa**
**Department of Chemistry,**
**University of Mysore,**
**Manasagangothri, Mysore 570 006 (INDIA)**
E-mail: hdrevanasiddappa@yahoo.com

**B.P.Dayananda**
Department of Chemistry,
University of Mysore,
Manasagangothri, Mysore 570 006 (INDIA)

## ABSTRACT

An indirect spectrophotometric method for the determination of chromium is presented. The method is based on the oxidation of hydroxylamine hydrochloride to nitrite by chromium(VI) in an acetate buffer of pH $4.0 \pm 0.5$ followed by diazotization of the nitrite produced with p-nitroaniline under acidic condition and subsequent coupling of the diazonium salt with citrazinic acid in an alkaline medium. The formed azo dye has an absorption maximum at 515 nm. Beer's law is valid over the concentration range of $0.2 - 1.8$ $\mu$g ml$^{-1}$ of chromium(VI). The molar absorptivity and Sandell's sensitivity of the color system are $2.1 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ and 2.5 ng cm$^{-2}$, respectively. The detection limit of chromium(VI) is 50 ng ml$^{-1}$. Chromium(III) can be determined after it is oxidized with bromine water in an alkaline medium to chromium(VI). The developed method has been applied successfully to determine chromium in alloy steels, environmental and pharmaceutical samples.
© 2006 Trade Science Inc. - INDIA

## INTRODUCTION

The determination of trace amounts of chromium is of considerable importance owing to its wide use in steel, leather, chrome-plating, textile, paints, chemical manufacture, pharmaceutical, fertilizer and in many other industries produce large amount of chromium wastes. Thus, contamination of water and soil is of major concern[1]. Chromium may exist in water supplies in both the hexavalent and trivalent state, although the trivalent form rarely occurs in potable water[2]. Chromium(III) is an essential nutrient for maintaining normal physiological function[3], whereas chromium(VI) is toxic[4]. Until about forty years ago, interest in chromium was mainly confined to its toxic effects. However, today the element [chromium(III)] is considered to be essential for maintaining the normal glucose metabolism and glucose

# Full Paper

tolerance in human beings. The toxic chromium(VI) causes dermatitis, gastrointestinal ulcers, lung cancer, liver and kidney damage and it may be carcinogenic. In this regard, the determination of trace amounts of chromium is essential in studies of biological and for industrial purposes.

Various chromogenic reagents proposed for the spectrophotometric determination of chromium have been reviewed[5,6], including the most widely used reagent diphenylcarbazide. The standard diphenyl carbazide method suffers serious interferences from Fe(III), Mo(VI), Cu(II) and Hg(II), and also the formed complex is stable for 30 min. Azo based reagents[7,8] and other chelating organic reagents[9] have been developed for the spectrophotometric determination of chromium. Most of these methods are not sufficiently selective, and some of them require close control of temperature and long reaction times. In addition, the stability of the colored products is not satisfactory. Some spectrophotometric methods based on the oxidation of organic reagents[10-12] by chromium(VI) are highly susceptible to the other redox species and the methods based on the formation of ion associates[13] have the disadvantage of high blank value and these methods are lengthy, time consuming, lacks sensitivity due to interference and most of the solvents used in these extraction procedures are generally toxic or carcinogenic. In recent years flow-injection[14] and sequential-injection[15] spectrophotometric methods have been developed for the determination of chromium using the diphenylcarbazide as a reagent, which are automated techniques require expensive experimental set-up and not affordable in most of the laboratories for routine chemical analysis. In view of the above, the present paper deals a sensitive, simple, rapid and cost effective method for the determination of trace amounts of chromium in different matrices.

## EXPERIMENTAL

### Instrument

ANALYTIK JENA AG (model SPECORD-50) and ELICO (model SL-177) spectrophotometers with 1 cm matched glass cells were used for all absor-

bance measurements. The pH measurements were made with an Elico (Model LI-610) digital pH meter.

### Reagents

All of the chemicals used were of analytical reagent grade; distilled water was used for diluting the reagents and samples.

### Standard chromium(VI) solution (1000 μg ml⁻¹)

Prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 100 ml distilled water. The stock solution was further diluted as needed.

### Standard chromium(III) solution(1000 μg ml⁻¹)

Prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 50 ml distilled water, adding 1 ml of saturated sodium sulfite solution, acidifying with 1 ml 2.5 M sulfuric acid, and then boiling for 2 min to remove excess $SO_2$ and diluting with water to 100 ml. A suitable volume of this solution was diluted to obtain the working standard.

### Acetate buffer (pH 4.0)

Prepared by dissolving 13.6g of sodium acetate trihydrate in 80 ml water. Solution pH was adjusted to 4.0 with acetic acid, and the mixture was diluted to 100 ml with water.

### p-Nitroaniline (0.05%)

Prepared by dissolving 0.125 g p-nitroaniline in 55.3 ml concentrated hydrochloric acid and diluting to 250 ml with water.

### Citrazinic acid (CZA )(0.1%)

Prepared by dissolving 0.1 g of citrazinic acid in 2 ml of 4 M NaOH and diluting to 100 ml with water.

### Others

Hydroxylamine hydrochloride (0.1%), bromine water (saturated), sulfosalicylic acid (5%), KOH (4.5M), sulfuric acid (0.5M and 2.5M), HCl (5M), NaOH (4M) and methyl isobutyl ketone(MIBK).

### Standard procedures

### Determination of chromium(VI)

An aliquot of a sample containing 2-18 μg of chromium(VI) was transferred to a series of 10 ml of calibrated flasks. Then, volumes of 0.5 ml each

of the acetate buffer with pH 4.0 and 0.1% hydroxy-lamine hydrochloride solution were added. After 2 min, volumes of 0.5 ml of 0.05% p-nitroaniline and 0.5 ml of 2.5 M HCl were added, and allowed the mixture to stand for two min. Then, volumes of 2 ml each of the 0.1% citrazinic acid and 4 M sodium hydroxide were added, and the mixture was diluted to 10 ml with distilled water and mixed well. After 5 min, the absorbance of the colored azo dye was measured at 515 nm against a reagent blank prepared in the same manner but containing no chromium(VI).
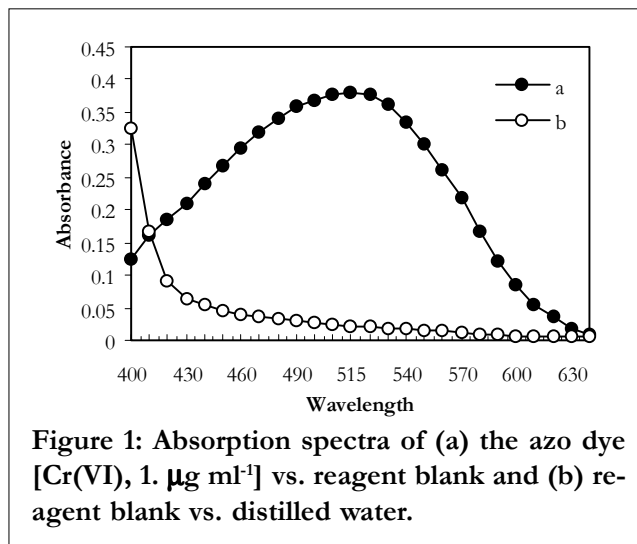
### Determination of chromium(III)

Different aliquots of the sample solution containing 2-18 $\mu$g of chromium(III) were transferred into a series of 10 ml calibrated flasks. To each, a volume of 0.5 ml of saturated bromine water and 0.5 ml of 4.5 M KOH solution were added, and allowed the mixture to stand for 5 min. Then, 0.5 ml each of the 2.5 M sulfuric acid and 5% sulfosalicylic acid were added and developed an azo dye by following the above procedure [chromium(VI)]. The absorbance of each of the colored azo dye was recorded at 515 nm against a reagent blank, omitting chromium(III).

### Determination of chromium in the mixture containing chromium(III) and chromium(VI)

Analyzed separately, an aliquot (18 $\mu$g) of mixture according to the procedure for chromium(VI) to determine the concentration of chromium(VI) and another aliquot (18 $\mu$g) according to the procedure described for chromium(III) to establish the concentration of total chromium [Cr(III) + Cr(VI)]. The difference between the two values is the concentration of chromium(III) in the mixture.

### RESULTS AND DISCUSSION

In the preliminary investigation, an amount of 10 $\mu$g chromium(VI) and 0.1% hydroxylamine hydrochloride were used. The nitrite generated by oxidation of hydroxylamine with chromium(VI) was used to diazotize p-nitroaniline (PNA). The diazonium salt formed was coupled with citrazinic acid (CZA) [2,6-dihydroxyisonicotinic acid] in an alkaline medium to give a red-colored azo dye, which



**Figure 1: Absorption spectra of (a) the azo dye [Cr(VI), 1. $\mu$g ml$^{-1}$] vs. reagent blank and (b) reagent blank vs. distilled water.**

showed a maximum absorbance at 515 nm. The absorption spectra of this red azo dye and reagent blank are shown in figure 1.

The oxidation of hydroxylamine to nitrite by chromium(VI) was completed within 2 min and was effective in the pH range 3.5 – 4.5, which could be maintained by adding 0.5 ml acetate buffer. This reaction is similar to oxidation of hydroxylamine to nitrite by iodine[16,17]. The reaction scheme shows that 10 $\mu$g chromium(VI) reacts with hydroxylamine to generate 6.6 $\mu$g nitrite. Quantitative oxidation of hydroxylamine to nitrite by chromium(VI) was confirmed by performing the diazo coupling reaction with standard nitrite solution, using CZA as the coupling agent. Ten micrograms of chromium(VI), on treatment with hydroxylamine and after the diazo-coupling reaction in total volume of 10 ml gives an absorbance of 0.40 ± 0.01 A, at 515 nm, comparable with 0.40A, the absorbance at 515 nm from the diazo-coupling reaction of 6.6 $\mu$g of standard nitrite solution in a total aqueous volume of 10 ml. The nitrite generated was determined by treating it with 0.5 ml of 0.05%. p-nitroaniline in 2.5 M HCl to form p-nitrophenyldiazonium chloride. The formation of diazonium chloride was completed within 2 min at room temperature. Then, the diazonium chloride was coupled with 2 ml of 0.1% CZA with 2 ml of 4 M NaOH in a total volume of 10 ml. The color system was stable for 4 h.

### Effects of the acid concentration and temperature on diazotization

# Full Paper



SCHEME 1: Proposed reaction pathway
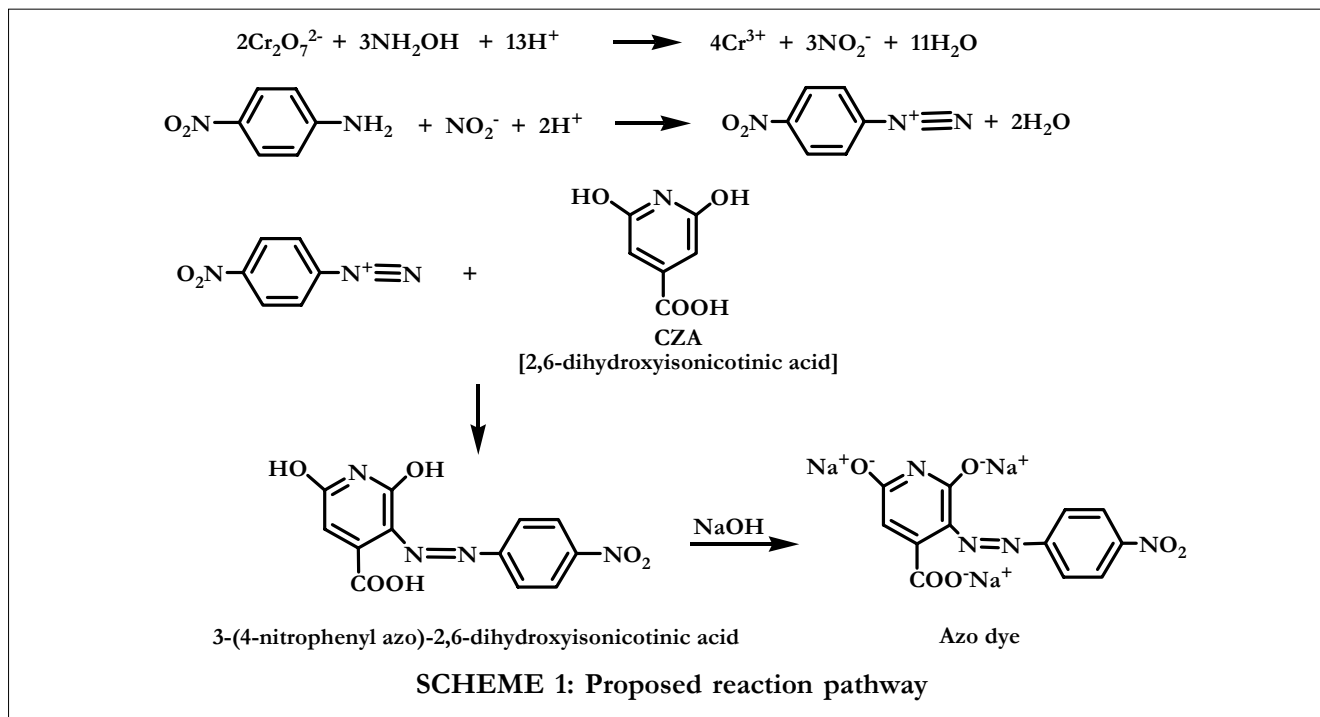
The effect of acidity on the diazotization reaction was studied in the range 0.5-2.5 M hydrochloric acid, and constant absorbance was observed in this range. A decrease in the absorbance was noticed above or below this range. The optimum acidity for the diazotization, as evident from the maximum absorbance and stability of the formed azo dye, was fixed to 0.5 ml of 2.5 M HCl in a total volume of 10 ml. Absorbance found to be constant at higher concentrations, while at lower concentrations the absorbance was decreased. The diazotization and the color development were found to be independent of temperature over the range 10-40$^0$C.

## Effects of reagents concentration

The effects of PNA and CZA concentration on the diazotization and coupling reactions, respectively were studied by adding different aliquots to a fixed amount of chromium(VI) [1$\mu$g ml$^{-1}$]. A volume of 0.5 ml of 0.05% PNA and 2 ml of 0.1% CZA were found to be sufficient for diazotization and coupling reactions, respectively, in a final volume of 10 ml. In both the cases, there was a decrease in absorbance at higher and lower concentrations. Under the optimum reaction condition, a volume of 2 ml of 4 M NaOH in a total volume of 10 ml was selected. At higher NaOH concentrations no change in absor-

bance value observed, whereas absorbance value decreased at lower concentrations.

## Choice of oxidizing agent

Chromium(III) was determined after it was oxidized to chromium(VI). Various oxidizing agents[18], like persulfate with silver ion as catalyst in acid solution, permanganate in an acid medium, hydrogen peroxide and bromine in an alkaline medium, were used. For all these methods, excess oxidizing agent must be removed before the determination of chromium(VI) because oxidizers interfere in the determination. Excess persulfate and peroxide were removed by boiling, and permanganate was removed by adding sodium azide. In the present work, bromine water in an alkaline medium was used to oxidize Cr(III) to Cr(VI), and the excess oxidizer was removed by the addition of 0.5 ml of 5% sulfosalicylic acid.

## Proposed reaction scheme

Chromium(VI), on treatment with hydroxylamine in an acetate buffer of pH 4.0 ± 0.5, generates nitrite, which diazotizes p-nitroaniline in HCl medium to form p-nitrophenyldiazonium chloride. The diazonium chloride is then coupled with citrazinic acid in an alkaline medium to form an azo dye. The proposed reaction pathway is given in SCHEME 1.

⊃ **Full Paper**

**TABLE 1: Effect of interfering ions on the determination of chromium(VI) [1 μg ml⁻¹]**

| Interferents | Tolerance limit ($\mu g\ ml^{-1}$) |
|---|---|
| $Na^+$, $F^-$, $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$, $CH_3COO^-$, EDTA | $\geq 3000$ |
| $Mg^{2+}$, $IO_3^-$, $AsO_3^{3-}$, $PO_4^{3-}$, oxalate, Tartrate | $\geq 2000$ |
| $Ba^{2+}$, $Bi^{3+}$, $MoO_4^{2-}$, Citrate | $\leq 1500$ |
| $Al^{3+}$, $Pb^{2+}$, $Cd^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Sn^{4+}$ | $\leq 500$ |
| $Ca^{2+}$, $Ni^{2+}$, $Ag^+$, $Hg^{2+}$, $Ce^{4+}$, $Ge^{4+}$, $Sb^{3+}$, $Sn^{2+}$, $MnO_4^-$, $WO_4^{2-}$ | $\leq 100$ |
| $Fe^{3+}$, $Fe^{2+}$, $Cu^{2+}$, $Co^{2+}$, $VO_3^-$ | $\leq 10$ |

**Analytical data**

A linear calibration graph was obtained for 2-18 μg of chromium(VI) in a final volume of 10 ml. The slope and intercept were 0.4004 and 0.0015, respectively. The calibration graph has a correlation coefficient of 0.999. The detection limit (DL = 3.3 $\sigma$/S) and quantitation limit (QL = 10 $\sigma$/S), [where '$\sigma$' is the standard deviation of reagent blank (n=10) and 'S' is the slope of calibration curve] of chromium determination were found to be 50 and 150 ng ml⁻¹, respectively. The molar absorptivity ($\varepsilon$) and Sandell's sensitivity (S) of the proposed method were 2.1 × 10⁴ l mol⁻¹ cm⁻¹ and 2.5 ng cm⁻², respectively. The reproducibility of the method was established by an analysis of standard solutions of 2, 6 and 10 μg of chromium in a final volume of 10 ml. Ten replicate determinations of each concentration gave relative standard deviations (RSD) of 1.3, 0.9 and 0.6%, respectively.

**Effect of diverse ions**

In order to evaluate the suitability of the proposed method, the effect of various ions which are likely to interfere in the determination of chromium (VI) was studied by adding a known amount of diverse ions to 1 μg ml⁻¹ chromium(VI) solution. The tolerance limits of interfering species were established at those concentrations that do not cause more than ±2% error in absorbance values. Ce(IV), Cu(II), Mn(VII), Ge(IV), Fe(II), Sn(II), Sb(III), V(V) and W(VI) caused negative interference. Fe(III) showed positive interference. The results indicate that Cu(II), Fe(II), Fe(III) and Co(II) is highly susceptible in the determination of Cr(VI). The interference of Cu(II), Fe(III) and Co(II) can be masked by addition of 1 ml of 1% EDTA. The interference of V(V), Mn(VII) and Ce(IV) can be overcome by extraction of

chromium(VI) as chromyl chloride in 5 ml MIBK after addition of 5 M HCl to provide an overall acidity of 0.3-0.5 M [19]. Chromium(VI) in the organic layer can be stripped by equilibration with 5 ml of water for determination. The interference of other foreign ions can be obviated by using appropriate masking agents in the analysis of samples. The tolerance limits of foreign ions are listed in TABLE 1.

**Applications of the Method**

The proposed method is applied to the determination of chromium in alloy steels, industrial effluents, pharmaceutical samples, water and soil samples.

**Determination of chromium in alloy steels**

Alloy steels were dissolved in approximately 8 ml of aqua regia. It was evaporated nearly to dryness on a sand bath, sulfuric acid (1-2 ml, 1:1) was added and evaporated until salts crystallized, to this 10 ml of water was added. The solution was warmed, filtered and treated with 10 ml of 5 M HCl and 10 ml of MIBK to extract iron[20]. The aqueous layer was separated and diluted to a known volume with water. Suitable aliquots of sample solutions were analyzed according to the procedure for chromium (III). The results obtained are given in TABLE 2.

**Determination of chromium in industrial effluents**

The chromium plating effluent was diluted 10 times, and the tannery effluent was diluted 40 times before analysis. Suitable aliquot of sample solutions were analyzed according to the procedure for determining chromium(III) and chromium(VI). Solutions were also analyzed according to the standard diphenylcarbazide method. The results obtained are shown in TABLE 3.

**Determination of chromium in pharmaceutical**

# Full Paper

## TABLE 2: Determination of chromium in alloy steels

| Sample (w/v) | Certified chromium (%) | Volume of solution (ml) | Chromium found (%) [a] | Recovery (%) | RSD (%) | t-test [b] |
|---|---|---|---|---|---|---|
| GKW steel, India (0.05 g/100 ml) [C 0.54%, Mn 0.89%, S 0.018%, P 0.034%, Si 0.33%, V 0.13%] | 1.02 | 1.0 | 1.000± 0.02 | 98.0 | 2.0 | 2.2 |
| | | 1.5 | 1.010± 0.01 | 99.0 | 1.0 | 2.2 |
| | | 2.0 | 1.012± 0.01 | 99.2 | 1.0 | 1.8 |
| Stainless Steel No. 304 (0.05 g/ 100 ml) [c] [Ni 8.12%, Fe (70-71%)] | 18.0 | 1.0. | 17.80±0.18 | 98.9 | 0.67 | 2.48 |
| | | 1.5 | 17.90±0.15 | 99.4 | 0.61 | 1.49 |
| | | 2.0 | 17.91±0.14 | 99.5 | 0.56 | 1.44 |

[a]Mean ± standard deviation (n = 5)
[b]Tabulated t-value for 4 degrees of freedom at *P* (0.95) is 2.776
[c]Solution diluted 20 times before determination

## TABLE 3: Determination of chromium in industrial effluents

| Sample | Chromium found ($\mu$g ml$^{-1}$) [a] | | | | F-test [b] | | t-test [c] | |
|---|---|---|---|---|---|---|---|---|
| | Proposed method | | Reference method[2] | | | | | |
| | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) |
| Chromium plating effluent [d] | 27.8±0.6 | 63.7±0.4 | 27.9±0.7 | 63.8±0.5 | 1.36 | 1.56 | 0.24 | 0.35 |
| Tannery effluent [e] | 257.5±0.5 | ND[f] | 257.7±0.6 | ND[f] | 1.44 | - | 0.57 | - |

[a]Mean ± standard deviation (n = 5)
[b]Tabulated F-value for (4,4) degrees of freedom at *P* (0.95) is 6.39
[c]Tabulated t-value for 8 degrees of freedom at *P* (0.95) is 2.306
[d]Solution diluted 10 times before determination
[e]Solution diluted 40 times before determination
[f]ND, Not detected

## TABLE 4: Determination of chromium in pharmaceutical preparations

| Sample (w/v) | Certified value of chromium (mg/tablet) | Volume taken (ml) | Chromium found (mg/tablet) [a] | Recovery (%) | RSD (%) | t- test[b] |
|---|---|---|---|---|---|---|
| Winofit [Wockhardt Ltd., India] (0.500 g/25 ml) | 0.100 | 1.0 | 0.0988±0.002 | 98.8 | 2.0 | 1.3 |
| | | 1.5 | 0.0991±0.002 | 99.1 | 2.0 | 1.0 |
| | | 2.0 | 0.0994±0.001 | 99.4 | 1.0 | 1.3 |
| Fourts B [Fourts Laboratories Pvt. Ltd., India] (0.650 g/50 ml) | 0.150 | 1.0 | 0.1485±0.003 | 99.0 | 2.0 | 1.1 |
| | | 1.5 | 0.1489±0.002 | 99.3 | 1.3 | 1.2 |
| | | 2.0 | 0.1491±0.001 | 99.4 | 0.7 | 2.0 |
| Chromoplex [Aristo Phar maceuticals Ltd., India] (0.550 g/50 ml) | 0.200 | 1.0 | 0.1977±0.004 | 98.9 | 2.0 | 1.3 |
| | | 1.5 | 0.1985±0.003 | 99.3 | 1.5 | 1.1 |
| | | 2.0 | 0.1990±0.002 | 99.5 | 1.0 | 1.1 |

[a]Mean ± standard deviation (n = 5)
[b]Tabulated t-value for 4 degrees of freedom at *P* (0.95) is 2.776
**Composition of tablet (w/tablet):**
**Winofit [Wockhardt Ltd., India]: Vitamin E, 200 mg; eicosapentaenoic acid, 90 mg; docosal hexaneoic acid, 60 mg; zinc sulfate, 7.5 mg; folic acid, 2.5 mg; manganese sulfate, 2 mg; vitamin A, 2500 IU; vitamin B$_6$, 1 mg; selenium 40 $\mu$g (0.500 g).**
**Fourts B [Fourts Laboratories Pvt. Ltd., India]: Thiamine mononitrate, 10 mg; riboflavin, 10 mg; pyridoxine hydrochloride, 3 mg; vitamin C, 150 mg; zinc sulfate 80 mg; selenium, 100 mg (0.650 g).**
**Chromoplex [Aristo Phar maceuticals Ltd., India]: Zinc sulfate monohydrate, 27.5 mg; vitamin B$_1$, 10 mg; vitamin B$_{12}$, 15 mg; nicotinamide, 50 mg; calcium pantothenate, 12 mg; folic acid, 1 mg; vitamin C, 150 mg (0.550 g).**

### samples

Samples of finely ground antioxidant multivitamin-multimineral tablets containing chromium(III) were treated with 5 ml of nitric acid, and the mixture was evaporated to dryness. The residue was leached with 5 ml of 0.5 M $H_2SO_4$. The solution was treated with 5 ml HCl and 10 ml MIBK to extract iron. The aqueous layer was separated and diluted

**TABLE 5: Determination of chromium in water and soil samples**

| Sample | Chromium taken ($\mu$g/10 ml) | Proposed method | | | Reference method[2] | | | F-test [b] | t- test [c] |
|---|---|---|---|---|---|---|---|---|---|
| | | Chromium found ($\mu$g/10 ml) [a] | Recovery (%) | RSD (%) | Chromium found ($\mu$g/10 ml) [a] | Recovery (%) | RSD (%) | | |
| River water | 4.0 | 3.97±0.05 | 99.3 | 1.3 | 3.98±0.06 | 99.5 | 1.5 | 1.4 | 0.3 |
| | 8.0 | 7.96±0.03 | 99.5 | 0.4 | 7.97±0.04 | 99.6 | 0.5 | 1.8 | 0.5 |
| Lake water | 4.0 | 3.96±0.06 | 99.0 | 1.5 | 3.97±0.07 | 99.3 | 1.8 | 1.4 | 0.2 |
| | 8.0 | 7.95±0.04 | 99.4 | 0.5 | 7.96±0.06 | 99.5 | 0.8 | 2.3 | 0.3 |
| Soil (2g/ 100ml) | ($\mu$g g$^{-1}$) --- | ($\mu$g g$^{-1}$) 183.5±0.7 | --- | 0.38 | ($\mu$g g$^{-1}$) 183.2±0.8 | --- | 0.44 | 1.3 | 0.6 |
| | 30 | 213.4±0.6 | 99.9 | 0.28 | 213.0±0.6 | 99.9 | 0.28 | 1.0 | 1.1 |

[a]Mean ± standard deviation (n = 5)
[b]Tabulated F-value for (4,4) degrees of freedom at *P* (0.95) is 6.39
[c]Tabulated t-value for 8 degrees of freedom at *P* (0.95) is 2.306

to a known volume with water, after neutralized with dilute ammonia. Suitable aliquots of sample solution were analyzed according to the procedure for chromium(III). The results obtained are presented in TABLE 4.

### Determination of chromium in water

Each filtered environmental water sample (100 ml) was analyzed for chromium. They tested negative. To these samples known amounts of chromium (VI) (400 $\mu$g) were spiked and analyzed for chromium by the proposed method and by the standard diphenylcarbazide method in order to check the validity of the developed method. The results obtained

are shown in TABLE 5.

### Determination of chromium in soil

A known amount of (2 g) air dried homogenized soil sample was fused with anhydrous sodium carbonate[21] in a silica crucible and evaporated to dryness after the addition of 25 ml water. The dried material was dissolved in water, filtered through Whatman No. 40 filter paper. The filtrate was diluted to a known volume with water (100 ml), after neutralized with dilute ammonia. An aliquot of this sample solution was analyzed for chromium according to general procedure for chromium(III). The method is validated by standard addition (30 $\mu$g g$^{-1}$).

**TABLE 6: Comparison of the proposed method with other spectrophotometric methods**

| Reagents | Ref | $\lambda_{max}$ (nm) | Beer's law range (ppm) | $\varepsilon$ (l mol$^{-1}$ cm$^{-1}$) | Remarks |
|---|---|---|---|---|---|
| Pentamethylene bis (triphenylphosphonium) cation | 22 | 365 | 0.0 - 100 | $1.38\times10^3$ | Less sensitive,extractive (1,2-dichloroethane), Mn(VII), Mo(VI) and W(VI) interfere. |
| 4-(2-Thiazolylazo)- resorcinol | 23 | 525 | 0.06 - 1.1 | $4.98 \times 10^4$ | Required heating for 45 min,Fe(III) and Co(II) strongly interfere. |
| N-methylpiperazine -4- carbodithioate | 24 | 410 | 6.5 - 65 | $5.24 \times 10^3$ | Less sensitive, extractive (molten naphthalene), required heating at 60$^0$C for 5 min, EDTA, Fe(III), Co(II) and Cu(II) interfere severely. |
| Rhodamine 6G | 25 | 535 | 0.0 - 8.0 | $2.0 \times 10^4$ | Extractive (toluene), Fe(III), Fe(II) and Mn(VII) interfere. |
| Chlorpromazine-HCl | 26 | 526 | 0.0 - 0.33 | $3.28 \times 10^4$ | Less selective, highly susceptible to other redox specieses. |
| Leuco xylene cyanol FF | 12 | 615 | 0.05 - 0.45 | $8.23 \times 10^4$ | Sensitive, required heating at 90$^0$C for 15 min, Fe(III), Ce(IV) and V(V) interfere severely. |
| Citrazinic acid | This work | 515 | 0.2 - 1.8 | $2.1 \times 10^4$ | Simple, sensitive, no extraction or heating is required and less interference. |

# Full Paper

Sample solutions were also analyzed according to the standard diphenylcarbazide method. The results obtained are given in TABLE 5.

## CONCLUSIONS

The sensitivity, simplicity, temperature independence, stability of the azo dye formed (4 h), wide range of chromium determination and high tolerance towards a large number of foreign ions are the advantages of the proposed method. Since no extraction step is required, the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed method is favorably compared with other reported methods (TABLE 6) in the literature. The method has the added advantage of determining individual amounts of chromium(VI) and Chromium (III). The method is validated by the parallel determinations with standard diphenylcarbazide method. The statistical analysis showed that, there is no significant difference between the proposed and the standard methods. The method developed can serve as an alternative method for determining chromium in various samples.

## ACKNOWLEDGEMENTS

## REFERENCES

[1] A.K.De; 'Environmental Chemistry', 4th ed., New Age International, New Delhi, 229 **(2000)**.

[2] American Public Health Association; 'Standard Methods for the Examination of Water and Wastewater', 18th ed., Washington D.C., 3-59, 3-60 **(1992)**.

[3] J.Versiek, R.Cornelis; Anal.Chim.Acta, **116**, 217 **(1980)**.

[4] J.M.Eckert, R.J.Juddi, P.A.Lay, A.D.Symons; Anal. Chim.Acta, **255**, 31 **(1991)**.

[5] Z.Marczenko; 'Separation and Spectrophotometric Determination of Elements', 2nd ed., Ellis Harwood Limited, Chichester, England, 236 **(1986)**.

[6] S.Ressalan, R.S.Chaun, A.K.Goswami, D.N.Purohit; Rev.Anal.Chem., **16**, 69 **(1997)**.

[7] W.B.Ferng, G.A.Parker; Anal.Chem., **304**, 382 **(1980)**.

[8] G.Z.Fang, C.Y.Miao; Analyst, London, **110**, 65 **(1985)**.

[9] W.B.Qi, L.Z.Zhu; Talanta, **33**, 694 **(1986)**.

[10] J.B.Raj, H.Sanke Gowda; Analyst, London, **120**, 1815 **(1995)**.

[11] A.A.Mohammed, M.F.El-Shahat; Anal.Sci., **16**, 151 **(2000)**.

[12] H.D.Revanasiddappa, T.N.Kiran Kumar; Talanta, **60**, 1 **(2003)**.

[13] M.Kamburova; Talanta, **40**, 707 **(1993)**.

[14] S.Matsuoka, Y.Tennichi, K.Takehara, K.Yoshimura; Analyst, London, **124**, 787 **(1999)**.

[15] Y.Luo, S.Nakano, D.A.Holman, J.Ruzika, G.D.Christian; Talanta, **44**, 1563 **(1997)**.

[16] P.Verma, V.K.Gupta; Talanta, **31**, 1013 **(1984)**.

[17] D.Utley; Analyst, London, **115**, 1239 **(1990)**.

[18] H.Onishi; 'Photometric Determination of Traces of Metals', Part II A, Individual Metals, John Wiley and Sons, New York, 415 **(1986)**.

[19] P.D.Blundy; Analyst, London, **83**, 555 **(1958)**.

[20] F.D.Snell; 'Photometric and Fluorimetric Methods of Analysis', New York, Wiley, 1 **(1978)**.

[21] M.Kolthoff, E.B.Sandell; 'Text Book of Quantitative Inorganic Analysis', 3rd ed., The Macmillan Company, New York, 248 **(1952)**.

[22] D.T.Burns, D.Chimpalee, P.F.Hagan; Anal.Chim.Acta, **198**, 293 **(1987)**.

[23] S.Subramanyam, M.C.Eshwar; Mikrochim Acta, Wein, **II**, 579 **(1976)**.

[24] S.K.Jain, B.K.Puri, A.L.Singla, A.L.J.Rao; Mikrochem. J., **37(2)**, 167 **(1988)**.

[25] V.Maheswari, N.Balasubramanian; Chem.Anal., Warsaw, **41(4)**, 569 **(1996)**.

[26] A.A.A.Mohamed; Bull.Chem.Soc.Jpn, **74(12)**, 2373 **(2001)**.