

Spectrophotometric Determination of Chromium (VI)

Using a new Organic Reagent 4 – (6 – Nitro – 2 – Benzothiazolylazo)
– Resorcinol

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Abstract

This work include the preparation of a new organic reagent 4 – (6 – Nitro – 2 – benzothiazolylazo) – resorcinol (6 – NO₂BTAR) and its use spectrophotometric method for determination of microamounts of chromium . (6–NO₂BTAR) reacts with chromium (VI) to form a stable orange 1 : 2 (metal : ligand) complex at 460 nm at pH 7.2 . The molar absorptivity of the complex is 3423 L . mol⁻¹ . cm⁻¹ . Beer's law is obeyed in the rang (0.5 – 25) µg . ml⁻¹ with a detection limit of 0.31 µg . ml⁻¹ and the stability constant was found to be 9.2059 × 10⁹ L² . mol⁻² . The relative standard deviation , recovery and relative error values of method were found to be R.S.D%=1.05%,Re%=99%,Erel=-1% . The most important interference were du to Ag⁺,Cd²⁺,Cu²⁺,Ni²⁺,Fe²⁺,Co²⁺,Fe³⁺, and MoO₄²⁻ and suitable masking agents were used . The method was applied successfully for determination of chromium in clay river of AL – Hilla .

Introduction :-

Thiazolyl azo compounds have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents . These dyes have been useful in the spectrophotometric determination due is good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify . (1,2)

Chromium is most commonly found in the trivalent state in nature . Hexavalent chromium compounds are also found in small quantities (3) , but the biological effects of the metal in the two oxidation states are markedly different . Cr (III) is relatively non – toxic and is regarded as an essential trace element , whilst Cr (VI) is of relatively high toxicity and has been shown to be a carcinogen in animal studies (4) . Chromium (VI) probably exists at lower levels in natural water samples , and must therefore be preconcentrated prior to using the various methods , which are usually not sensitive enough to directly detect trace Cr (VI) . Only a few extraction and preconcentration methods , including ion – exchange , supercritical fluid extraction , ion pair RP – HPLC , coprecipitation , soluble membrane filter , solid – phase extraction and solvent extraction , have been reported for the determination and speciation of low levels of individual Cr species , even with the most sensitive techniq , such as spectrophotometric (5,6,7) .

A spectrophotometric determination of Chromium (VI) and Vanadium (V) is based on the reaction of these ions with perphenazine , 4 [3 – (2 – chloro – 10 H – phenothiazin – 10 – yl) propyl] – 1 – piperazine – ethanol hydrochloride

, to give a red – colored product showing a maximum absorbance at 526 nm , with molar absorptivities is $1.87 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for Chromium (VI) and Sandell sensitivity of $2.8 \text{ ng} \cdot \text{cm}^{-2}$ (8) .

The present paper describes the preparation of 4 – (6 – Nitro – 2 – Benzo – thiazolyazo) – Resorcinol , is a sensitive and selective reagent for the spectro photometric determination of micrograms quantities of Chromium (VI) without need for a preliminary steps .

Experimental

Instruments

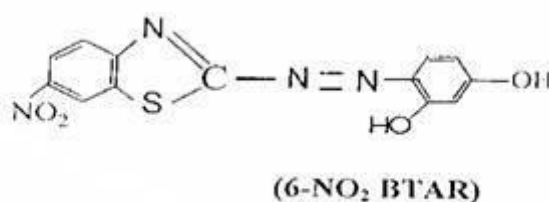
Absorption spectra were recorded with Cintra 5 – GBC scientific Equipment , while absorption measurements were obtained with PyeUnicam UV – Visible SP8 – 100 double – wave length spectrophotometer both with matched 1cm quartz cells . pH of the solution was measured using a Philips PW 9421 pH meter ($\text{pH} \pm 0.001$) , IR 9025 Pye Unicam was used .

Reagent

All chemicals were used of analytical – reagent grade unless stated otherwise . All solutions were prepared with de – ionized water .

Preparation of Reagent

2 – Amino – 6 – nitrobenzo thiazol (1.9519 gm) was dissolved in 10 ml of concentrated sulphuric acide and 40 ml of water . Sodium nitrite solution (prepared from 10 % NaNO_2 in 35 ml of water) was added dropwise with cooling to 0°C and stirring . Then the resulting diazonium salt solution was added dropwise , with cooling to the solution of the resorcinol (prepared by dissolving 1.1 gm of resorcinol in 50 ml ethanol) . A red product was obtained and left to stand overnight , then filtered , and dried . The structure of the synthesized reagent is given below .



6 – NO₂B TAR – solution (1×10^{-3}) M was prepared by dissolving (0.0790) gm of pure reagent in 250 ml of absolute ethanol .

Standard chromium (VI) solution

A solution of Chromium (VI) ($1 \text{ mg} \cdot \text{ml}^{-1}$) was made by dissolving (1.8673) gm of K_2CrO_4 (BDH) in 500 ml of water .

Procedure

1 ml of sample solution containing $30 \mu\text{g} \cdot \text{ml}^{-1}$ of chromium (VI) was transferred to a 10 ml volumetric flask and adjust the pH to 7.2 with 0.1 M sodium hydroxide , add 3 ml of 1×10^{-4} M ethanolic (6 – NO₂BTAR) solution

and diluted to the mark with distilled water . Measure the absorbance of the resultant solution after 15 min , at 460 nm and 25 °c against blank solution prepared the same procedure .

Results and Discussion

Physical and chemical properties of 6 - NO₂BTAR

The reagent is a deep red powder melting at (205 – 207) °c , and is hardly soluble in water but soluble in organic solvents . The solution is yellow , (maximum wavelength = 440 nm) . The reagent was identified using elemental analysis and IR are given in Table 1 .

Table 1 Elemental Analysis and I.R of the reagent

	% C	% N	% H
Theoretical	49.36	17.71	2.54
Found	48.99	17.25	2.23

Group	O – H	C – H	C = N	C = C	C – S	N = N	–NO ₂
V / cm ⁻¹	3100 – 3600	2860 - 2940	1650	1480	1210	1510 – 1400	1340

Color reaction of 6 – NO₂BTAR with metal ions

The test of 6 – NO₂BTAR with 25 metal ions and method oxides was carried out by adding 3 ml of 1×10^4 M reagent solution to the metal ion solution (1 ml of 100 µg . ml⁻¹), pH (ranged from 1 – 10 against reference of 6 – NO₂BTAR solution at same pH) and temperature (at room temperature and 70 °C) as a reaction conditions . The metal ions that gave a color with reagent are CrO₄²⁻, MoO₄²⁻, Ag⁺, Ni²⁺, Pb²⁺, Cu²⁺, Sn²⁺, Co²⁺, Fe²⁺, Sr²⁺, Cd²⁺, Hg²⁺, Bi²⁺, Fe³⁺, As³⁺, Ti⁴⁺ and VO₃⁻.

Absorption spectra and characteristics of the complex

Chromium (VI) ions and 6 – NO₂BTAR form an orange complex with an absorption maximum at 460 nm in aqueous medium . The absorption spectra of 6 – NO₂BTAR and its chromium complex under the conditions used are shown in Fig . 1

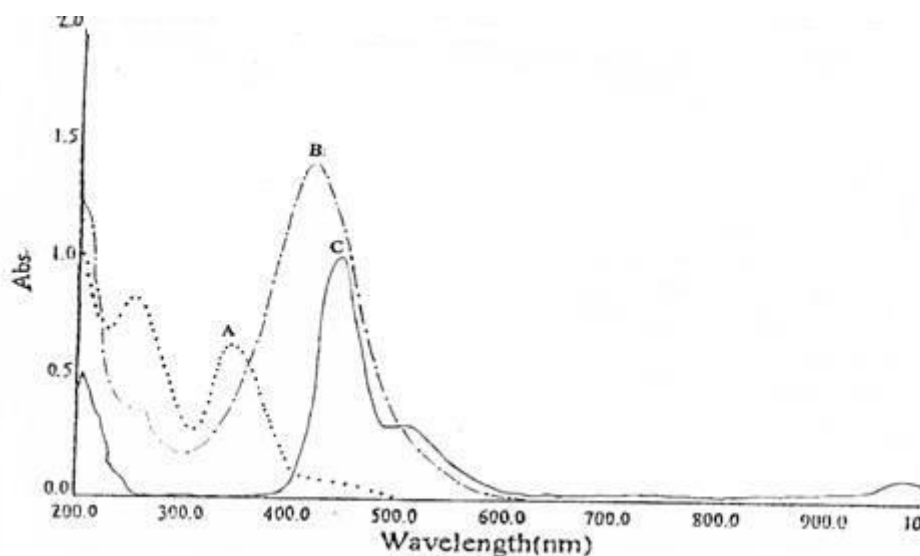


Fig . 1 : Absorption spectra of (A) Cr (VI) , (B) 6 – NO₂BTAR , (C) Cr (VI) 6 – NO₂BTAR complex at pH = 7.2 .

The optimum analytical condition on the formation of the complex , where found the absorbance reached its maximum within 15 min and remained stable , for at least 24 h . The temperature was varied between 20 and 30 °c which was regarded as proper temperature of the complex formation .

Effect of Reagent amount

The reagent amount sufficed to complete the reaction was found 3 ml of 1×10^{-4} M (6 – NO₂BTAR) solution added to $30 \mu\text{g} \cdot \text{ml}^{-1}$ of chromium (VI) .

Effect of pH

The pH effect on the chromium (VI) – (6 – NO₂BTAR) complex was studied over the range 2 – 9 , and the results are shown in Fig 2 . The best pH range was observed between (7 – 8.2) . At pH < 7 a decreases in absorbance was absorbed due to competition between the hydrogen ion and the chromium (VI) cation . With the increase of the hydrogen ion concentration , the competition leads to a less favorable complex formation . Therefore , the optimum pH was 7.2 , where the absorbance was maximum and stable .

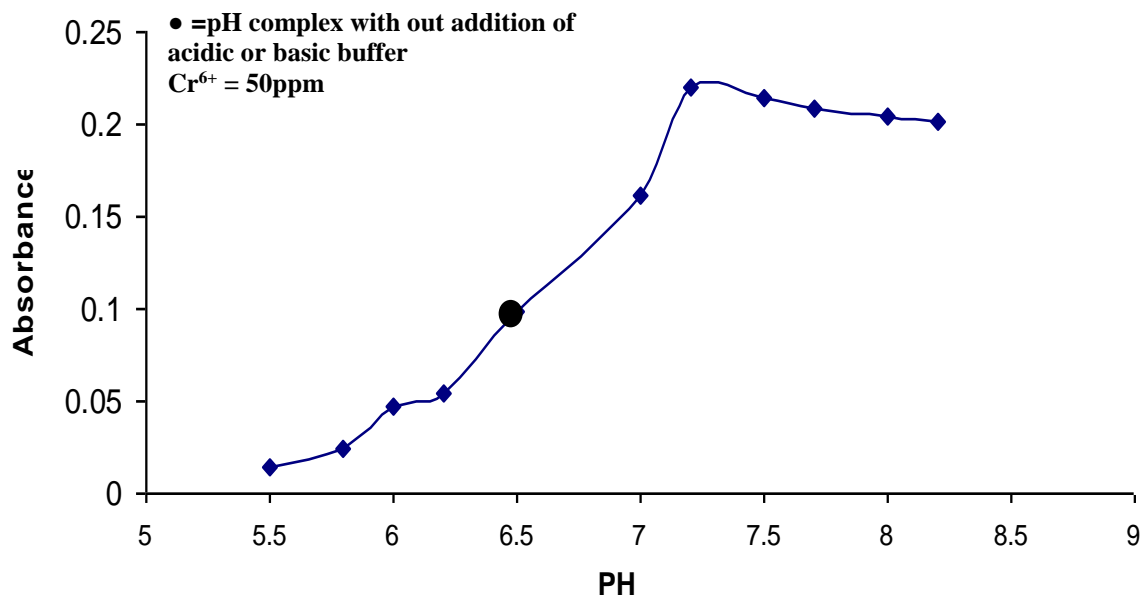
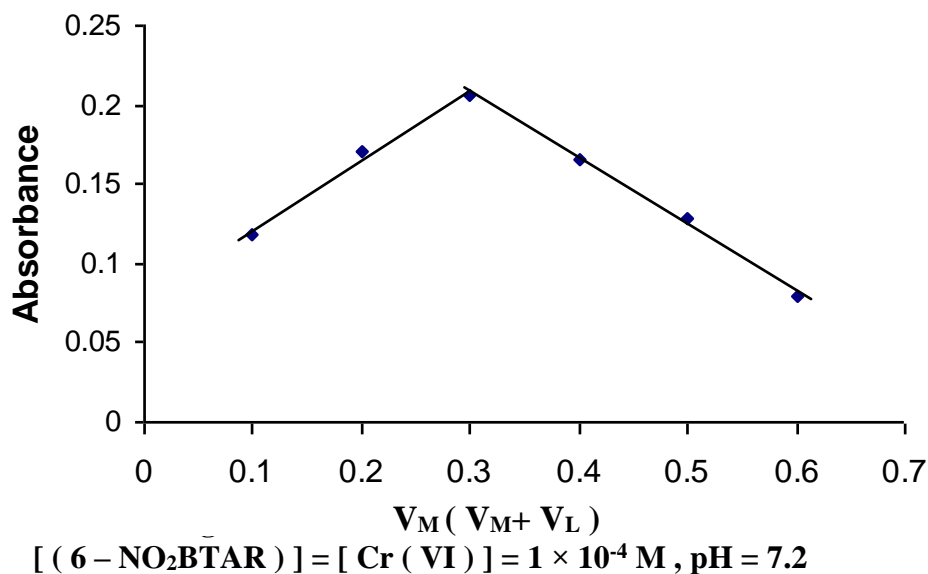
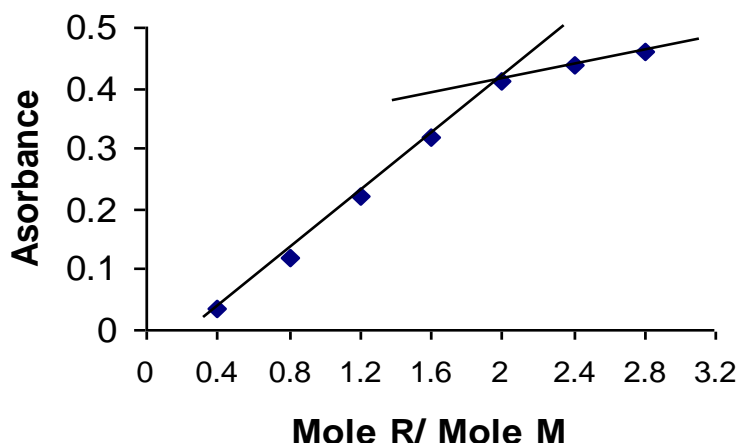


Fig . 2 : Effect of pH on the absorbance of chromium complex , Cr (VI) = 50 $\mu\text{g} \cdot \text{ml}^{-1}$.

Composition of the Cr (VI) – (6 – NO₂BTAR)

The complex composition was determined by of continuous variations ⁽⁹⁾ and the mole ratio ⁽¹⁰⁾ methods (Fig 3 , 4) . Both methods indicated that the complex has a molar ratio of 1 : 2 [Cr (VI) : 6 – NO₂BTAR] at pH 7.2 . The stability constant was found to be $9.2059 \times 10^9 \text{ L}^2 \cdot \text{mol}^{-2}$.





Calibration graph and Sensitivity

The present studies indicate that Beer's Law is obeyed for chromium (VI) over the concentration range (0.5 – 25) $\mu\text{g} \cdot \text{ml}^{-1}$, with a correlation coefficient $r=0.9996$. The molar absorptivity of the complex is calculated as $3423 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and the Sandal's sensitivity⁽¹¹⁾ was $0.0015 \mu\text{g} \cdot \text{cm}^{-2}$ of chromium (VI).

Precision and Accuracy

To assess the precision and accuracy of the method , determinations are carried out for a set of seven measurements of $10 \mu\text{g} \cdot \text{ml}^{-1}$ of chromium (VI), the R.S.D % was 1.05 % . The recovery and Erel % for the complex solution were found to be 99 % , and -1 % respectively . These values indicate that this method has the highly accuracy and precision .

Interference studies

To study the effect of various metal on the determination of chromium (VI) with (6 – NO₂BTAR) , the selectivity various masking agents are examined . These are oxalic acid , citric acid , tarataric acid , 5 – sulphosalicylic acid , 1 , 10 – phenanthroline , sodium fluoride , and ascorbic acid . The results are shown in Table 2 .

Table 2 : Effect masking agents

Cr ⁶⁺ ($\mu\text{g} \cdot \text{ml}^{-1}$)	Masking agent (2) ml , [0.01] M	Absorbance
10	Complex without any addition	0.186
10	Oxalic acid	0.187
10	Citric acid	0.144
10	Tarataric acid	0.192
10	5 – sulphosalicylic acid	0.196
10	1 , 10 – phenanthroline	0.101
10	Sodium fluoride	0.183
10	Ascorbic acid	0.189

The results indicate that citric acid and 1 , 10 – phenanthroline caused masking for chromium , while other masking agents have no or little effects on

the absorbance . Therefor these use as masking agents suitable for eliminating the effect of the interfering ions are given in Table 3 .

**Table 3 : Effect of foreign ions , concentration of
Cr (VI) = 10 ppm**

Foreign ion	Form added	Amount added / ppm	Error %
Ag ⁺	AgNO ₃	25	0.1
Cd ²⁺	CdCl ₂ . H ₂ O	20	- 0.2
Cu ²⁺	CuSO ₄	15	0.5
Ni ²⁺	NiCl ₂ . 6H ₂ O	15	- 0.5
Fe ²⁺	FeSO ₄	20	0.3
Co ²⁺	CO (NO ₃) ₂ . 6H ₂ O	20	0.4
Fe ³⁺	FeCl ₃	10	0.8
MoO ₄ ²⁻	(NH ₄) ₂ MoO ₄	10	0.1

Application

As a test of the method , sample of clay river of Al – Hilla was analysed according to the method which is described below ⁽¹²⁾ .

A sufficient amount of wet clay was dried at 105 c^o for 48 h . One gram of the dried and powdered clay was weighted accurately . This weight , largely , dissolved in concentrated nitric acid (20 – 30 ml) , after that little deionized distilled water added an the solution was filtered using whatman– 1 filter paper . The filtered solution was completed in 50 ml volumetric flask .

In order to confirm the detected results obtained by the recommended method was found be 143 µg / g of dried clay , and compared by atomic absorption spectrometry (AAS) (standard addition method) was found to be 158 µg / g of dried clay . The results obtained by the two methods are shown a good agreement for the determination of chromium (VI) in different samples .

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التعین الطیف لایون کروم (VI) باستخدام الكاشف الجدید 4 [(6- نایترو - 2
بنزو ثیازولیل] ازد زیزورسینول
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الخلاصة

تضمن البحث تحضير كاشف عضوي جديد 4 - (6 - نایترو - 2 - بنزو ثیازولیل أزو) - ریزورسینول واستخدام في تقدير كميات مايكروغرامية من ايون الكروم (VI) باستخدام الاشعة فوق البنفسجية والطول الموجي للامتصاص الاعظم للمعقد المتكون من تفاعل الكاشف (NO₂BTAR - 6) مع ايون الكروم (VI) هو 460 نانومتر عند pH = 7.2 وبنسبة 1 : 2 من الايون الفلزي إلى الكاشف . وبلغت قيمة معامل الامتصاص المولاري 3423 لتر . مول⁻¹ . سم⁻¹ ووجدت مدى التراكيز التي تطاوع قانون بير تقع ضمن (0.5 - 25) مايكروغرام كروم (VI) مليلتر⁻¹ ووجد كشف 0.31 مايكروغرام . مليلتر⁻¹ اما قيمة ثابت الاستقرار مساوية إلى 9.2059×10^9 لتر² . مول⁻² ، وحدد دقة وضبط الطريقة التحليلية المتبعة باستخدام محلول قياسي من أيون الكروم (VI) ذي التركيز 10 مايكروغرام مليلتر⁻¹ فكانت قيمة % Erel , % R.S.D هي 1.05 , % 99 , % -1 على التوالي . كذلك تم دراسة تأثير ايونات Ag⁺ , Cd²⁺ باستخدام محلول قياسي من أيون الكروم (VI) ذي التركيز 10 مايكروغرام مليلتر⁻¹ فكانت قيمة % Erel , % R.S.D هي 1.05 , % 99 , % -1 على التوالي . كذلك تم دراسة تأثير ايونات Ag⁺ , Cd²⁺ , Cu²⁺ , Ni²⁺ , Fe²⁺ , Co²⁺ , Fe³⁺ و MoO₄²⁻ . وهذه الطريقة طبقت لتقدير الكروم في مياه شط الحلة .