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Ultra Trace Spectrophotometric Determination of Chromium In Presence of Cationic Micellar Solution

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Abstract: A very simple, fairy selective, direct and fast spectrophotmetric method is offered for the analysis of chromium(VI) with 1,5-diphenylthiocarbazone (dithizone). Dithizone worked as a new spectrophotometric reagent in fairly acidic (0.003-0.012M H_2SO_4) micellar media with λ_{max} = 520nm. The existence of micelle reduces the cost, avoids the earlier solvent extraction steps and increasing the selectivity, sensitivity. 0.05 – 10 mg L^{-1} was the observed linear calibration graphs for Cr(VI) with the 1:3 (Cr^{VI}: dithizone) stoichiometric composition of the chelate. 20 ng cm^{-2} and 1.2×10^5 L $mol^{-1}cm^{-1}$ were the obtained average Sandell's sensitivity and molar absorption coefficient for Cr(VI), respectively. The effect of more than 50 complexing agents, anions and cations, and has been analyzed at 1 mg L^{-1} of Cr(VI). The developed procedure was productively employed in the measurement of Cr(VI) in numerous complex synthetic mixtures, environmental waters (polluted and potable) and soil samples.

Keywords: Spectrophotometry, Chromium, Micellar Media, Dithizone, Environmental Samples.

2. INTRODUCTION

Chromium largely exist in either trivalent or hexavalent oxidation states, as in other oxidation states it is unstable and short lived Arduini *et al.,* (2006). The toxicity and essentiality of chromium purely depend on the form in which it is supplied and its oxidation states. Chromium in its +3 oxidation state is known as an essential nutrient and is used to control lipid and glucose metabolism in membranes. In addition Cr(VI) because of its high oxidation state is identified as carcinogenic and may cause a series of disease from dermatitis to kidney and lung cancer Barceloux, (1999). In metallurgical industry chromium is very important. The salts of Cr are used in several industrial products and procedure for examples steel production, leather tanning, metal finishing, electroplating, metal corrosion inhibitors, pigment manufacturing, and catalyst application. Consequently they are present in the effluent discharge and in municipal sewage Nath *et al.,* (2005) Venkateswaran *et al.,* (2007) Babel and Opiso, (2007) Zayed & Terry, (2003). The analysis and monitoring of Chromium is extremely important because of its high accumulation in the environment, soil and water Srivastava and Takur, (2006) Kar *et al.,* (2008).

There are numerous instrumental techniques for the determination of chromium, such as inductively coupled plasma-atomic emission spectrometer (Oktor *et al.,* 2008), inductively coupled plasma- mass spectrometer (Hirata *et al.,* 2000), neutron activation analysis Martiez and Bulbulian, (2005), atomic absorption spectrophotometry Adria *et al.,* (2000), and electrochemical analysis Dominguez *et al.,* (2008). On the other hand spectrophotometric methods for the analysis of metal ions have a powerful interest because of their low cost and easiness of operation.

The number of metal ions form water insoluble complex with 1, 5-Diphenylthiocarbazone (dithizone) Marczenko, (1976). These hydrophobic complexes are usually extracted by carcinogenic, time taking and lack selective solvent extraction procedures into carbon tetrachloride or chloroform. Micellar system produced by certain concentration of surfactant molecules known as CMC is the most frequently favored method now days in Analytical Chemistry. They are comparatively non-toxic, easy to use, optically transparent and stable Diaz and Medel, (1986). Micelles due to its dynamic hydrophobic and hydrophilic character are not only using to solubilize the water insoluble complexes but also to improve the sensitivity and precision of the spectrophotometric method Humaira *et al.,* (2007).

The present paper explains a non-extractive determination of chromium^{VI}-dithizone system by spectrophotometer in the presence of inexpensive anionic micellar without the solvent – extraction step. This reported method is more simple, rapid, selective, precise and accurate than all of the accessible spectrophotometric procedures Narayana and Cherian, (2005) Dayananda and Revanasiddappa, (2007) Ahmed and Reazul, (2011) Revanasiddappa and Kumar, (2002) Telepcakova, *et al.,* (2005) Revanasiddappa and Kumar,

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2. EXPERIMENTAL

Apparatus

Absorption spectra were measured on a double-beam UV/VIS spectrophotometer of Perkin Elmer (Germany) (Model: Lambda-2). The acidity of the reaction mixture was recorded using a pH meter of WTW (Weilheim, Germany) which is assembled with glass-Ag/AgCl electrode. A atomic absorption spectrophotometer of Hitachi Ltd. (Model 180-50, S.N.5721-2) with the requisite conditions were used for the determination of chromium.

Reagents and standard solutions

Analytical-grade salts were used for the preparation of standard solutions. A system of Milli-Q purification (PURELAB Prima 7 BP, PURELAB Classic UV) was applied for water in ultrapure level with 0.050 µS cm^{-1} conductivity. Glass vassals were washed by placing in acidic mixture of $K_2Cr_2O_7$ or $KMnO_4$, and then cleaned by 50% solution of nitric acid and finally washed many times with ultrapure water.

Cetyltrimethylammonium bromide (CTAB) standard solution (0.3 M): A54.67 g of pure CTAB (E.Merck Darmstadt, Germany) was dissolved in 250–300 mL ultrapure water to prepared a solution of 500 mL of CTAB. Th solution was then placed for 15 min in sonicator and diluted with ultrapure water when it became transparent.

1,5-Diphenylthiocarbazone (Dithizone) standard solution (1.95 × 10^{-3} M): Prepared by dissolving the required quantity (0.05%) of dithizone (Merck, Darmstadt) in a identified volume of 2-propanol (Fluka, Germany). Dilutions were made as necessary.

Chromium(VI) Standard solution (1.92×10^{-2}): 0.28289 g of $K_2Cr_2O_7$ was dissolved in 100 mL of ultrapure water to prepared a stock solution of amount 1000 mg L^{-1}.

Chromium(III) Standard solution (1.92×10^{-2}): 0.304 g of chromium(III) chloride was dissolved in 100 mL of ultrapure water to prepared a stock solution of amount 1000 mg L^{-1}.

3. ANALYTICAL PROCEDURES

Present Method

A sequence of standard solutions having 0.5–100 µg of chromium (VI) in a 10 mL volumetric flask was added with 61 – 142 fold molar excess of a dithizone (1.0 mL of 1.95 × 10^{-3} M preferably) and 0.3–1.2 mL (1.0 mL preferably) of 0.1 M H_2SO_4 followed by the combination 3 - 5 mL (4mL preferably) of 0.3 M CTAB. The solution was prepared with ultrapure water. At 520 nm the absorbance was calculated in opposition to a reagent blank. The chromium in an unidentified sample was analyzed employing a recent calibration graph. EDTA or thiocyanide were used as masking agent.

Synthetic mixtures for Chromium (VI) determination

The chromium (VI) was determined in a number of synthetic mixtures with different compositions of various ions by applying the present Cr^{VI}-dithizone procedure in micelle. Masking agent, EDTA was used. Accurate recoveries with high reproducibility were attained in the results **(Table, 1- 3).**

Environmental waters samples for Chromium (VI) determination

Samples were taken from different areas of Sindh. A sample was filtered first and then in each 100 mL of sample 10 mL of HNO3 (concentrated) was added. The mixture was placed for evaporation just about to dryness and then to remove the salts heated with 10mL of ultapure water. The cool mixture was neutralized with ammonium hydroxide. Into a 25 mL volumetric flask, filtered neutralized mixture was shifted quantitatively and the solution with ultrapure water.

0.5 – 1 mL of the prepared sample was shifted into a volumetric flask (10 mL), and the $chromium^{VI}$ in the requisite samples were analyzed according to a present method **(Table 4)**. Masking agents, EDTA or thiocyanide were used.

Soil samples for Chromium (VI) determination

15-25 g of dried homogenized soil was digested using a micro-Kjeldahl flask (100 mL) equipped with a reflux condenser. Flasks were placed on digester with 10mL concentrated HNO_3 and glass beads. After the first vigorous cycle was ended, 5 mL of H_2SO_4 (concentrated) was added to the cooled mixture. The excess of potassium permanganate solution (1% w/v) was added to the system and the solution was heated till the white dense fumes came out. The excess of potassium permanganate and manganese oxides were eliminated by addition of 2.5% w/v solution of sodium azide. The filtered solution was neutralized by using

dilute solution of ammonium hydroxide. 0.5 – 1 mL of 0.01% w/v EDTA was added to the system. Into a 25 mL volumetric flask, filtered neutralized mixture was shifted quantitatively and the solution with ultrapure water.

0.5 – 1 mL of the prepared sample was shifted into a volumetric flask (10 mL), and the chromium^{VI} in the requisite samples were analyzed according to a present method **(Table 5**). Masking agents, thiocyanide was used. The outcomes of these samples by the proposed procedure were observed in good agreement with AAS results.

4. RESULTS AND DISCUSSION

Optimum conditions for the color reaction

The Absorption spectra of chromium (VI)-dithizone in micelle media were measured by a spectrophotometer. A symmetric curve with the maximum absorbance at 520 nm was observed **(Fig. 1).** In all instance, absorbances were calculated at 520 nm in opposition to a reagent blank.

In a number of surfactans (anionic, cationic and nonionic) CTAB was observed to be the best surfactant for the analysis of Cr^{VI}. 1 – 7 mL of 0.3 M CTAB were analyzed and it was found that 3 - 5 mL of 0.3 M CTAB resulted a maximum and stable absorbance of the Cr^{VI}- chelate **(Fig. 2).** 4 mL of 0.3 M CTAB was used for all analyses,. H_2SO_4 was observed to be the best acids for the system in a number of acids (hydrochloric, sulfuric, phosphoric and nitric). 0.3 – 1.2 mL of 0.1 M H_2SO_4 (or pH 1.3 – 2.5) was observed to result a maximum and stable absorbance of the Cr^{VI}-chelate **(Fig. 3).** 1 mL of 0.1 M H_2SO_4 (or pH 3.19) was used for all analyses,.

The reaction is instantaneous, and stayed unchanged for 24 h. The absorbance was resulted to be firmly unchanged all through the temperature range of 5 - 45^oC. Room temperature (25±5^oC) was used throughout the studies.

Various ratios of dithizone were studied to a fixed amount of Cr(VI). Dithizone molar ratios 1:61 to 1:142 were found to resulted maximum and constant absorbance to 0.1 mg L^{-1} Cr^{VI} metal ion **(Fig. 4).** Similar results were observed for the reagent molar ratios with respect to 1 mg L^{-1} of Cr^{VI} metal. 1 mL of 1.95×10^{-3} M dithizone reagent was used for all analyses.

The effect of metal concentration was observed in the range of 0.01 – 100 mg L^{-1}, divided in three sets of dissimilar concentrations (0.01 - 0.1, 0.1 - 1, 1 – 10 mg L^{-1}) for ease of the calculation. The linear absorbance was observed for 0.05 – 10 mg L^{-1} of chromium(VI) at 520 nm. The Sandell's sensitivity (Sandell, 1965) (quantity for 0.001 unit absorbance) was observed to be 20 ng cm^{-2}. The average molar absorption coefficient (1.2×10^5 L mol^{-1} cm^{-1}) was calculated from the slope of the calibration graph. One of the three calibration graphs is showing the limit of detection **(Fig. 5).** All optimized parameters are shown **(Table 1).**

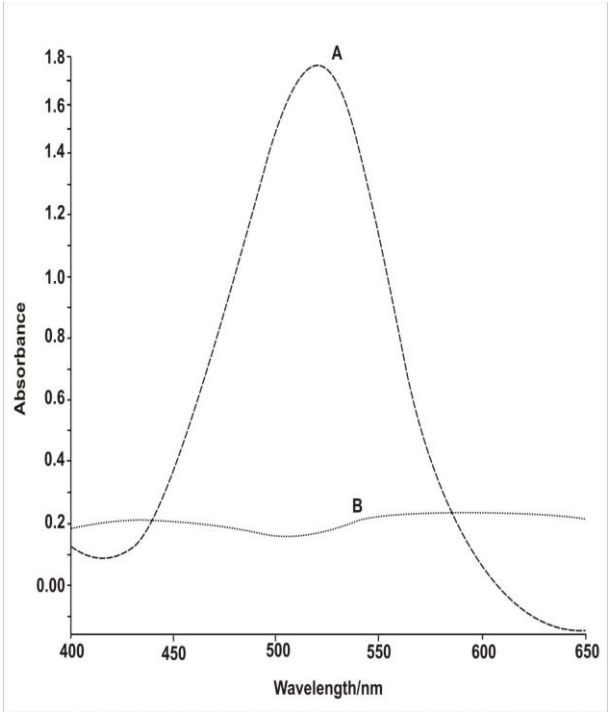


Fig. 1. A and B absorption spectra of Cr^{VI}-dithizone system and the reagent blank (λ_{max}=520 nm) in cationic micellar media of cetyltrimethylammoniumbromide (CTAB).

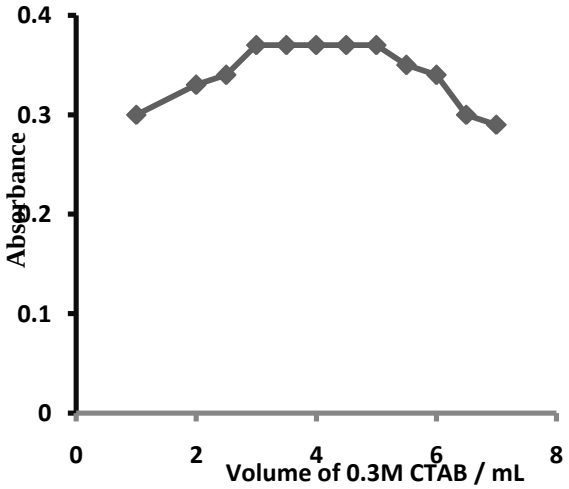


Fig. 2. Effect of surfactant on the absorbance of Cr^{VI}-dithizone system

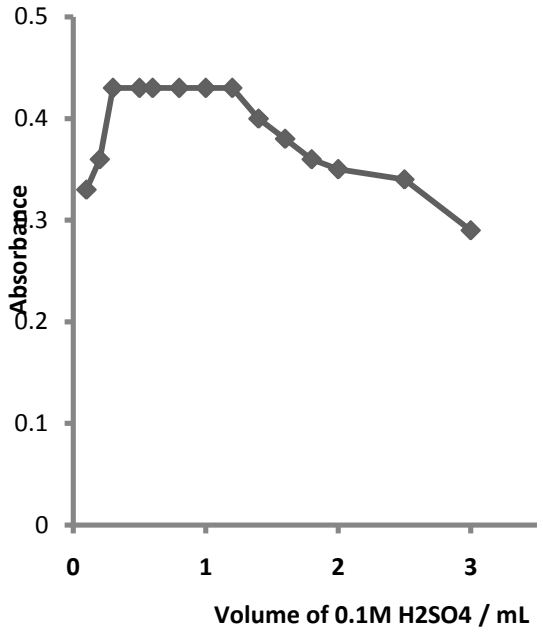


Fig. 3. Effect of the acidity on the absorbance of Cr^{VI}-dithizone system

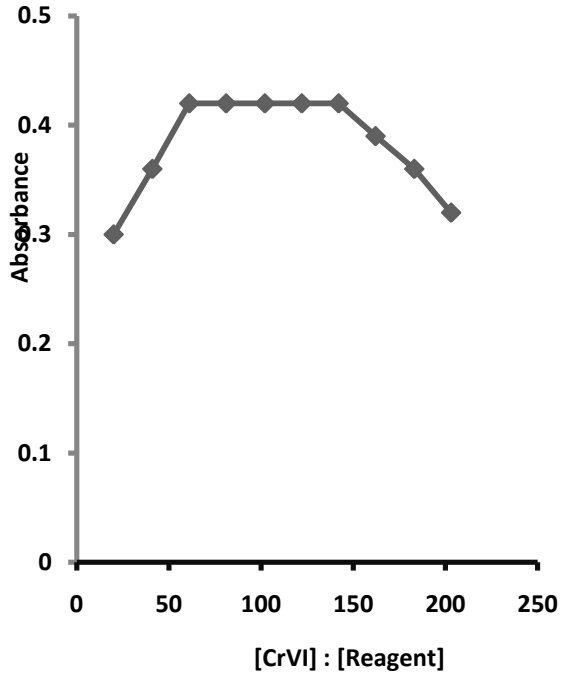


Fig. 4. Effect of reagent [Dithizone:Cr^{VI} molar concentration ratio] on the absorbance of Cr^{VI}-dithizone system (1mgL-1)

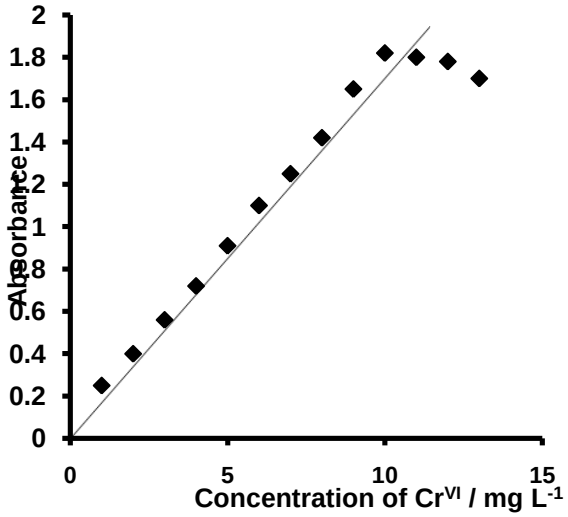


Fig. 5. Calibration graph: B, 1-10 mgL^{-1} of Cr(VI)

The interference of over 50 complexing agents, anions and cations, and on the analysis of 1 mg L^{-1} of Cr^{VI} was calculated. The principle of effect Ojeda *et al.*, (1987) was the 5% difference in the value of absorbance of Cr^{VI} alone. 1000-fold amount of thiocyanide or bromide; a 500-fold amount of fluoride; a 200-fold amount of ascorbic acid, acetate or tartrate; 100-fold amount of azide, citrate, EDTA, iodide, carbonate, phosphate or azide were resulted no effect. EDTA prevented the interference of 50-fold of Mo^{VI}, 25-fold of In^{III}, 10-fold of Pb^{II}, 10-fold of Ce^{IV} or 10-fold of Co. EDTA and thiocyanide removed the interference of 10-fold of Cd^{II}, 10-fold of Fe^{II}, 10-fold of Ni^{II} or 10-fold of Zn^{II}. Thiocyanide and ascorbic acid could be masked 10-fold of Cu^{II}, 10-fold of V^{V} or 5-fold of Hg^{II}. When the precipitate was produced during the measurements of interference, it was eleminated by centrifugation. Interference studies are summarized in **(Table 2).**

Stoichiometric composition of the complex was calculated by Job's method Job (1928) which was found to be 1:3 for Cr^{VI}-dithizone complex.

Evaluation of the Method

The different quantities of chromium were determined (each determined five times) to assess the precision of the current method. 2 - 0% for 0.5 – 100 µg of Cr^{VI} in 10 mL was the relative standard deviation (n = 5), showing that current method is very reproducible and precise. The Sandell's sensitivity (Sandell, 1965) (quantity for 0.001 unit absorbance) and detection limit (3s of the blank) for chromium(VI) were oberved to be 20 ng cm^{-2} and 2 µg L^{-1}, respectively. The consistency of this method was evaluated by recovery measurements. The spiked environmental samples with

Cr^{VI} were resulted excellent recovery by the present method (Table 4). The method was in addition assessed by measuring a number of synthetic mixtures containing chromium(VI) and various ions. The measurements of soil samples by the current procedure were in good approach with the results observed by AAS (Table 5). Therefore, the accuracy and precision of the current study were admirable.

5. APPLICATIONS

The current procedure was fruitfully implemented to the measurement of chromium(VI) in a number of synthetic mixtures of different addition **(Table 3).** The current method was as well implemented for the calculation of Cr^{VI} in several environmental and soil. In reason of the unidentified composition of environmental water samples, the equal amount of each sample were calculated for chromium(VI); the recoveries in both the spiked and the unspiked samples are in excellent approach **(Table 4).** The outcomes of soil samples determined by the current study were resulted to be in good approach with those observed by AAS **(Table 5).**

Table 1 Selected analytical parameters obtained with optimization experiments

Parameter	Studied range	Selected value
Wavelength, λ/nm	200 – 800	520
Acidity / M H_2SO_4	0.001 – 0.03	0.003 – 0.012 (preferably 0.01 M)
pH	3.3 – 0.82	1.3 – 2.5 (preferably 1.08)
Surfactant / M Cetyltrimethylammoniumbromide (CTAB)	0 - 0.21	0.09 – 0.15 (preferably 0.12)
Time / h	0 – 24	1 min – 24 h (preferably 5min)
Temperature / °C	0 – 70	10 – 40 (preferably 25 ± 5)
Reagent (fold molar excess, M:R)	1:1 – 1:203	1:61 - 1:142 (preferably 1:102)
Linear range / mg L^{-1}	0.001- 100	0.05 – 10
Molar extinction coefficient / L mol^{-1} cm^{-1}	1×10^4 - 5.0 $\times 10^5$	1.2 x 10^5
Sandell's Sensitivity / ng cm^{-2}	1-100	20
Detection limit /µg L^{-1}	1 – 100	2
Reproducibility (% R SD)	0 – 5	0 – 2
Regression Coefficient	0.996-0.999	0.998

Table 2. Table of tolerance limits of foreign ions*, Tolerance ratio, [Species (x)] / Cr^{VI} (w/w).

Species, x	Tolerance ratio, x/Cr^{VI}	Species, x	Tolerance ratio, x/ Cr^{VI}
Ammonium(I)	100	Iron (II)	10^{a+b}
Arsenic (III)	100	Iodide	100
Arsenic (V)	100	Lead (II)	10^{a}
Ascorbic acid	1000	Manganese (II)	100
Azide	100	Magnesium	100
Acetate	200	Mercury (II)	5^{b+c}
Antimony	100	Molybdenum (VI)	50^{a}
Bismuth (III)	25^{a}	Nickel (II)	10^{a+b}
Bromide	200	Nitrate	100
Barium	100	Palladium	100
Beryllium	50	Phosphate	100
Cadmium	10^{a+b}	Potassium	100
Calcium	100	Selemium (VI)	100
Cesium	50	Selenium (IV)	100
Cerium (IV)	10^{a}	Sodium	100
Citrate	100	Sulfate	100
Carbonate	100	Sulfide	100
Chloride	50	Tartrate	500
Chromium (III)	100	Thiocyanite	200
Cobalt	10^{a}	Thallium (I)	100
Copper	10^{b+c}	Tin (II)	100
EDTA	100	Tungsten (VI)	100
Fluoride	500	Vandadium (V)	10^{b+c}
Indium (III)	25^{a}	Zinc	10^{a+b}

*Tolerance limit was defined as ratio that causes less than 5 percent interference

[a]With 10 mg L^{-1} EDTA, [b]With 10 mg L^{-1} thiocyanide, [c]With 10 mg L^{-1} ascorbic acid,

Table 3 Determination of chromium(VI) in some synthetic mixtures

Sample	**Composition of mixtures / mg L^{-1}**	**Chromium(VI) / mgL^{-1}**		***Recovery* ± *s* (%)**
		Added	***Found****	
A	Cr^{6+}	0.50 1.00	0.51 1.00	102 ± 0.6 100 ± 0.0
B	As in A + Ca (20) + Na (20) + K (20)	0.50 1.00	0.50 0.99	100 ± 0.0 99 ± 0.8
C	As in B + Cr^{3+} (20) + As^{3+} (20) + NO_3^- (20)	0.50 1.00	0.49 0.99	98 ± 0.7 99 ± 0.8
D	As in C + Mg (20) + Mn^{2+} (20) + Sn^{2+} (20)	0.50 1.00	0.53 1.05	106 ± 1.3 105 ± 1.4
E	As in D + Ba (20) + Se^{4+} (20) + Azide (100)	0.50 1.00	0.54 1.08	108 ± 1.7 108 ± 1.6

*Average of five analyses of each sample.

Table 4 Determination of chromium in some environmental water samples

Sample	Chromium/μgL^{-1}		Recevery ± s (%)	s_r (%)
	Added	Found[a]		
Tap water	0 100 500	12 111 514	 99.1 ± 0.4 100.4 ± 0.3	 0.25 0.32
Well water	0 100 500	14 114 513	 100 ± 0.0 99.8 ± 0.4	 0.00 0.26
River water (Indus river)	0 100 500	16 117 516	 100.9 ± 0.6 100 ± 0.0	 0.24 0.00
Sea Water (Arabian sea)	0 100 500	9.25 110 511	 100.7 ± 0.4 100.3 ± 0.3	 0.23 0.16
[c]Drain water (Pulp & paper industry)	0 100 500	48 147 549	 99.3 ± 0.6 100.2 ± 0.4	 0.25 0.15
[d]Lake Water	0 100 500	32 134 533	 101.5 ± 0.6 100.2 ± 0.7	 0.18 0.34

[a]Average of five determinations
[b]The measure precision is the relative standard derivation (s_r)
[c]Pulp and paper Industry, Karachi
[d]The Manchar Lake, Dadu, Sindh

Table 5 Determination of chromium(VI) in some surface soil samples

Serial No.	[a]Chromium(VI) / mg kg^{-1}		Samples Source
	AAS	Proposed method[b]	
S1	2.1	2.2 ± 1.2[b]	Traffic soil (Hyderabad bus terminal)
S2	0.7	0.68 ± 1.5	Roadside soil (Hyderabad – Karachi highway)
S3	0.18	0.20 ± 1.0	Marine soil (Sand of Arabian Sea)
S4	4.66	4.62 ± 1.8	Industrial Soil (Pharmaceutical Company)
S5	0.3	0.28 ± 0.3	Agricultural soil (Sindh University Campus)

[a]Average of five analyses of each sample
[b]The measure of precision is the standard deviation, ± s

6. CONCLUSIONS

In this research work, a rapid, purely selective, ultra sensitive and environmental friendly micellar procedure with the Cr^{VI}-dithizone complex was developed for the ultra trace analysis of Cr(VI) in environmental and soil samples. The existence of micelle provides the environmental friendly media and removes all the tedious solvent extraction procedure and decrease the cost and toxicity even as improving the sensitivity, selectivity and molar absorption coefficient. The molar absorptivity of the Cr^{VI}-dithizone in the system of micelle (cationic CTAB) are approximately ten-times 1.2 x 10^5 L mol^{-1} cm^{-1} the result obtained in the standard procedur and the absorption maxima is also shifted bathochromically when compared with standard method, consequential in an enhance in the sensitivity of the method. Hence, the current method will be productively implemented to the examining of trace quantity of Cr(VI) metal ion in samples of environmental and soil.

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