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Estimation of Toxic Hexavalent Chromium (Cr^{6+}) in Metal Components Present in Electronic and Electrical Materials with or without using Coordinating Ligands

G. Swarnabala [a*], K. Suresh [a,b], B. Divya [a,c] and Anahita Bharadwaj [a,d*]

[a] Swaram Biochem, Secunderabad – 500011, India.
[b] BITS, Hyderabad, India.
[c] Department of Chemistry, Institute of Aeronautical Engineering, Dundigal, Hyderabad-500043, India.
[d] Department of Agricultural & Biological Engineering, Penn State College, Pennsylvania, USA.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The aqueous solutions of toxic hexavalent chromium have been analyzed using diphenyl carbazide (DPC) dissolved in organic solvents as a coordinating ligand since early nineteen hundreds. The chemistry is not clear due to the formation of an unstable, suggested organometallic complex, which is only An intermediary. The structure of the same could not be determined or is hypothetical even today with a further suggested, molecular structure in which instead of pi bonded

**Corresponding author: E-mail: swarnabalaganti@gmail.com, anahita.b02@gmail.com;*

delocalization of benzene rings expected to be as in sandwich compounds, electron empty d-orbital of hexavalent chromium facilitating the electron transfer and giving the observed color of the obtained complex as in inner field coordinating complexes. The electrical and electronic equipment requires the estimation of hexavalent chromium up to ~0.2 % (~2000 ppm) present in high chromium containing solid matrix, with DPC using standard International Electro-technical Commission (IEC) method.

However, the visible yellow color can be directly measured on UV-Vis spectrophotometer with the hexavalent chromium stripped or leached out into acidic aqueous solutions from these materials using the known IEC method for leaching. The presence of interfering ions is ruled out with the leaching procedure given in it. Therefore, the stability of these aqueous acidic solutions containing hexavalent chromium was checked for 16 days. So that direct measurement can be done without DPC.

Screws, Fork Pivot Bore and Rat Trap Box containing hexavalent chromium were analyzed and compared with and without DPC. It is noted that the analysis of these materials can satisfactorily be achieved easily or simply without adding DPC on UV-Vis spectrophotometer or any other organic ligands or using high-end equipment such as Ion Chromatography (IC).

Keywords: Hexavalent chromium; electronic and electrical materials; diphenylcarbazide; UV-Visible spectrophotometer; IEC 62321:2008.

1. INTRODUCTION

The latest review on analysis of hexavalent chromium involves electroanalytical methods [1] using different electrode platforms such as solid or screen-printed electrode – SPE, and various functional materials. Carbon nanomaterials, metal and metal oxide nanomaterials form the reference for electroanalytical testing procedure for the method validation and development as sensors detect the trivalent and hexavalent chromium ions systematically.

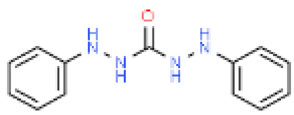
Several Environmental Projects were taken up for study around the year 2009, and some older ones were revised for developing the method for analysis of hexavalent chromium in electrical and electronic equipment [2-6]. Materials like metal parts coated with hexavalent chromium which are placed anywhere in the appliances and individual components such as screws, rivets, bolts, frames, chassis, electrical switches, fuses, wire, cables, cabinets, plugs, terminators, spacers, bars, antennae, and accessories, etc., which are chrome plated or coated are likely candidates [7-8].

The presence of hexavalent chromium using DPC reagent by spectrophotometry in water samples [9-13], its theory on use, utility [13-18] including an interesting discussion on the formation of colored complex, and the speciation is described in depth [19-32]. The same DPC reagent by spectrophotometry method was used for Nacogdoches wastewater treatment plant from East Texas, USA [33-34] along with ion chromatography (IC) for comparison. Same method of analysis on spectrophotometry for Portland cement is also available [35].

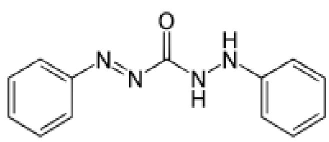
Some trials were carried out a) to simplify the procedure adopted by this method and to get more accurate results, b) the speciation of trivalent and hexavalent chromium stability. One of the trials involves addition of hypochlorite agent for the complex formed by hexavalent chromium and diphenyl carbazide [36-38]. The salient features of the discussion in literature [19-30,39-40] about this colored complex gives an understanding as follows:

$$2CrO_4^{2-} + 3C_{13}H_{14}N_4O + 8H^+ \rightarrow [Cr^{3+}(C_{13}H_{12}N_4O)_2]^+$$

Chromate ion   Diphenyl carbazide   Cr(III)diphenyl carbazone



Diphenyl carbazide (DPC)



Diphenylcarbazone (DPCA)

a) Cr^{2+} does not react with DPC;
b) color does not develop under any circumstances;
c) pure DPC does not react with Cr^{6+};
d) little oxidation of red orange DPC to the colorless DPCA takes place;
e) red violet solutions are obtained on reaction of DPCA with Cr^{3+} ion in DM;
f) DPC in acidic medium with Cr^{6+} reddish violet color complex formation occurs;
g) DPC reduces Cr^{6+} to Cr^{3+}, DPC to DPCA and hence, Cr^{3+} DPCA is reddish violet and can be measured at 530nm on UV-Vis spectrophotometer.
h) Cazeneuve [22] proposed intense colour may be due to organometallic compound formation;
i) $Cr^{2+}(DPCA)_2$ molecular structure with magnetic moment for four electrons in Bohr Magnetons (BM) is 4.9 (4.8 BM expected), is proposed by Bose [39] for the redox reaction, which on enolation gives carbazide complex [40], which maybe $3d^4$ high spin, no magnetic moment, possibly octahedral

Cr(II) $(DPC)_2$ structure is proposed [41]. Vosburgh and Cooper method [42] suggests that in the case of a mixture of several coloured complexes, the absorption spectra of solutions containing the reactants reacting in different molar proportions, would not show a constant wavelength of maximum absorption, thus confirming formation of a single complex. Job's Variation method [43] confirmed 1:2 structure $(CrO_4)^{2-}$:DPC, while this was suggested by Mole Ratio method [31] using K_2CrO_4. Stability Constant was determined as 2.8 x 10^{-12} l mol^{2-}, confirming the coloured complex stability. In another study, the thesis [44] discusses the oxidation product of Cr(III) and DPC, confirming the presence of hexavalent chromium by the colored chelate complex formation [45-47].

$Cr^{2+}(DPCA)(H_2O)_4$ complex was isolated [48] and structure evaluated confirming the no contribution for magnetic moment for $3d^4$ complex with UV-Vis spectrum of Cr(II) for $^3t_{2g}\, e_g^1$ configuration, showing ligand-field spectrum for the splitting of the ^5D ground state term. The experimental spectrum shows a very high intensity charge transfer metal to ligand band at 540nm [27], and a shoulder with low intensity at about 750nm. So, unlike the organometallic compound in which ligand pi-orbitals are delocalized like a sandwich-like structure, the structure was assumed to be six coordinated tetragonal structure.

Considering the solution chemistry of hexavalent chromium, it has been quite well-known fact [32, 49-67] that Cr^{6+} is toxic and in <10^{-3} M (0.002 M or <10 mg level) concentration easily gets converted to non-toxic Cr^{3+} in aqueous or dilute acidic solutions. It forms several species such as CrO_4^{2-}, $HCrO^{4-}$, $Cr_2O_7^{2-}$ etc, depending on the pH of the solution. Around pH = 1-6, the $HCrO^{4-}$ dominates in <10^{-3} M solution of Cr^{6+}, increasing the rate of reduction to Cr^{3+} species [49]. However, at >10^{-3} M concentration of Cr^{6+}, in the same pH range, a more stable $Cr_2O_7^{2-}$ species is found to dominate as $H_2Cr_2O_7$ [49]. Soil and waste sludge samples were extracted and analysed [62] using DPC for hexavalent chromium and were validated as per European standard.

The literature [32, 49-67] given above can be summarized to two conditions:

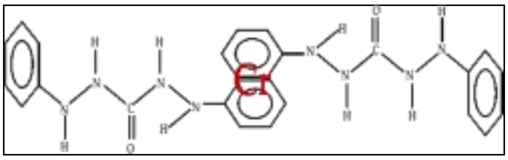
a) aqueous or acidic (pH = 1 - 6) Cr^{6+}<10^{-3}M solutions and
b) aqueous or acidic (pH = 1 – 6) Cr^{6+} >10^{-3} M solutions.

The former lead to a higher rate of reduction compared to the latter and as the Cr^{3+} ions predominate, the analysis of available Cr^{6+} ions become very difficult to the analyst. So, researchers have stabilized the available Cr^{6+} by acidification or by using liquid-liquid ion-association method in which large cationic compounds in organic solvents are precipitated by DPC solutions [68-69]. The acidic or ion-associated Cr^{6+}, thus formed, is analyzed on UV-Vis spectrophotometer and quantified giving the chromium content in the sample.

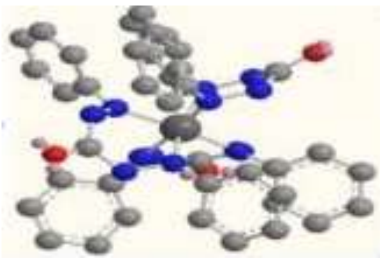
In the present context, where the analysis of electronic, electrical equipment (EEE) is considered, the Restriction on Hazardous Substances (RoHS) regulations requires, that the amount of toxic hexavalent chromium (Cr^{6+}) should be <1000 mg/kg (~0.2 %) in the given sample [70-71] and does not restrict the quantity of Cr^{3+} in the final product.

Generally, in these materials, maximum amount of Cr^{3+} is used while Cr^{6+} is used during passivation or as a surface coating. Therefore, an analyst is expected to give the toxic Cr^{6+} content accurately. IEC 62321:2008 [4,72-75] and other available methods of analysis using different analytical tools [32, 49-67] normally, analyze Cr^{6+} in the given product measured as DPC complex on UV-Vis spectrophotometer or on Ion chromatography (IC) or as total Cr using instruments like Atomic Absorption Spectrometer (AAS) or Inductively Coupled Plasma (ICP) Absorption or Emission or Mass Spectrometer.

It may be deduced that (a) due to the uncertainty in the organometallic resonance stabilized cationic final product formation with DPC, wherein the isolation and characterization was not possible. Two structures are proposed with $Cr^{2+}(DPC)_2$ and $Cr^{2+}(DPC)_2(H_2O)_4$ complex formation. The first one, is the hexavalent chromium forming octahedral complex with the ligands. A molecular structure given below is obtained with the ligand positioned around the suitable six branched chromium. The second structure is a proposed hexavalent chromium being 'sandwiched' between the delocalized rings, like bis(benzene)chromium [76-77]. It is proposed because of the use of x-ray diffraction. The apparent conflict between the two theories for the structure is due to use of molecular model and the use of x-ray diffraction techniques [18,75].



Structure 1. X-ray Diffraction of DPC-Cr^{6+} complex



Structure 2. Molecular model of DPC-Cr^{6+} complex

The colour of the compound could be a result of electron transfer, rather than the d-orbital shifts between the delocalized rings. Since chromium has the outer electron configuration of $3d^5 4s^1$, Cr^{6+} will have the d^0 configuration; presence of empty d-orbital assisting electron transfer.

Another paper also discusses analysis of Cr^{6+} up to ~100 mg/L in solutions by UV-Vis spectrophotometer using DPC ligand. It does not predict the amount of toxic Cr^{6+} accurately, and so cannot give the toxicity levels of the sample as per the requirement, (b) if the other instruments such as AAS or ICP are used, total chromium is analysed, and many laboratories give this value as per the requirement of standard, this again, is not true because it implies that the EEE material is non-toxic (since what is analyzed is not exactly Cr^{6+} but non-toxic Cr^{3+}), (c) IC used for lower concentrations, is tedious, needs expertise, this and the AAS or ICP are expensive and (d) the reported value for chromium is being kept at RoHS requirement range, which need not be followed. The manufacturer can be left to use trivalent chromium amount to his free will. Hence, an analyst is expected to prove his/her skill to analyze the amount of Cr^{6+} alone separately.

In this context, the following points have motivated us to think of trying to analyze the total amount of Cr^{6+} in the given solution of the product.

(a) In the case of $>10^{-3}$ M solutions, as there are a greater number of available stable Cr^{6+} ions, even if there is small amount of reduction, it is practically not quantifiable or is slower and so negligible. Though, these also have been analyzed by precipitating with DPC, there is a possibility to analyze them directly without the addition of organic ligands as the EEE materials are likely to fall more into this category. (b) An analogous situation is discussed in Vogel's textbook [78] discussing Analysis of British Chemical Standard BCS-CRM No: 225/2, Ni-Cr-Mo steel for simultaneous Cr & Mn analysis on UV-Vis spectrophotometer in which it is in hexavalent state and low quantities as compared to manganese. (c) Suitable use of different wavelengths for all the three situations - UV-Vis spectrophotometer at 440 nm for bright yellow Cr^{6+} in acidic solution, 350 nm for green Cr^{3+} solution and 540 nm for purple after addition of DPC to Cr^{6+} solution. (d) Proposed organometallic ligand coordination, is expected to form a classical, stable coordinated complex of metal to ligand (1:3), however it was suggested that two ligands were delocalizing onto the metal atom with the primary benzene rings, indicated by X-ray diffraction [41,67,76-77,79-82], thus allowing a gross ambiguity in the said analysis (not strong d- d transitions but electron charge transfer transitions).

In addition, the present authors have also observed that a stoichiometric addition of ligand solution does not give stable absorbance values as the purple color of the solution changes with every drop of ligand added before it can be put into the instrument for analysis. This probably occurred as there is fast reduction to Cr^{3+}, which does not coordinate with DPC, due to the predicted resonating structures making the analysis very difficult, for those Cr^{6+} solutions which are below the 5% level as observed by other authors too [39-41].

So the analysis without organic ligands for near quantitative observation is attempted (with at least a minimum of 95% of Cr^{6+} measurement). In this paper, details of stability of pure Cr^{6+} solutions in acidic medium over a period of two weeks are presented. The analysis mentioned below gives some clue to the extent of toxicity due to the sample in hand and rationale on to the extent it can be restricted, which is likely be useful during manufacturing of the products in which hexavalent chromium is used and also in the prediction of the amount of hexavalent present in the finished products. A quick assessment can be made, in the absence of reagent, in the aqueous acidic solutions that are obtained after extraction immediately, before the process of redox starts in them.

Experimental Section Reagents: Triply-distilled and deionized water (Milli-Q) was used for all procedures. For the acid reduction, the 98% sulfuric acid, 98% phosphoric acid and analytical grade reagents $K_2Cr_2O_7$, from M/s MERCK, were used. 1,5-Diphenylcarbazide purchased from Sigma-Aldrich was used. 1M sulfuric acid was prepared by taking 5.6 ml of standard 18M sulfuric acid was made up to 100 ml in a volumetric flask. 0.7M H_3PO_4 acid was prepared by taking 6.9 ml of standard 13.7 M phosphoric acid and made up to 100 ml in a volumetric flask.

Apparatus used: The UV-Visible spectrophotometer (UV-2450, Shimadzu) at 200 nm to 600 nm with optical quartz cells of 1 mm path length taking precautions of cleaning the surface and rinsing three times before filling were used. Calibrated weighing balance (1 mg ±MU), thermometer (100 ^oC) 10, 20, 50, 100 ml volumetric flasks (A grade) were used. Assorted calibrated Eppendorf auto pipettes, 0.45 μ filter cellulose membranes were used.

Samples analyzed: Cr^{6+} coated Screws; Fork Pivot Bore and Rat Trap Box, as shown in Fig. 1 were used for analysis. The comparative results obtained from the standard method [49], the modified new method (modified [49]) and the IEC specified method for steel samples [44-48], are given in Table 5.

Standard solutions for measurement on UV – Vis spectrophotometer: 2000 mg, 1500 mg, 1000 mg, 750 mg, 500 mg, 250 mg, 100 mg, 50 mg, 25 mg, 10 mg hexavalent chromium solutions were prepared by weighing appropriate amount of $K_2Cr_2O_7$ dried at 105 ^oC in DI water and adding 5 ml of each 1M H_2SO_4 and 0.7M H_3PO_4 and made up to in a 100 ml volumetric flask. To obtain linearity they were diluted such that the absorbance remains measurable on the instrument at optimum. 2000 mg, 1500 mg, 1000 mg, 750 mg solutions 3 times, 500 mg, 250 mg, 100 mg solutions 2 times and 50 mg, 25 mg, 10 mg solutions were used for direct measured, (Tables 1-4, Graphs 1-3).

Standard solutions for linearity on UV-Vis spectrophotometer: (Table 5, Fig. 1)

(i) For measurement at 540 nm, the normally used 1.0, 2.5, 5.0 and 7.5 ppm standard solutions.
(ii) For the IC with UV detector – the routine 10, 20, 30 and 40 ppm standard solutions and
(iii) For yellow acidic solutions 100, 250, 500 and 750 ppm solutions were used [9-13].

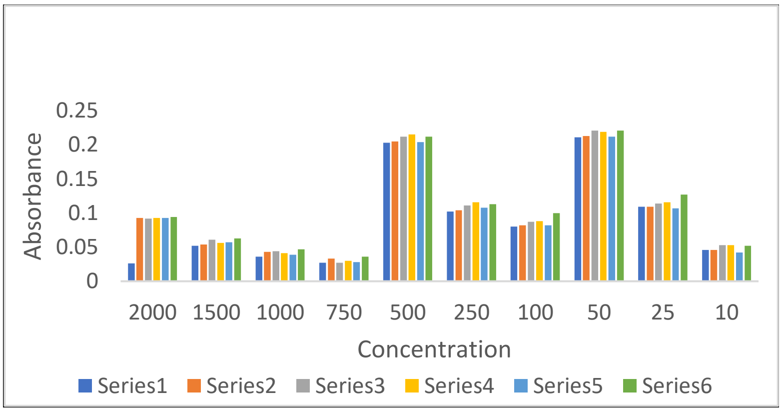
2. RESULTS AND DISCUSSION

To check the stability of acidic Cr^{6+} solutions, the following experiment was conducted and was used for logical deduction to go ahead with the process. Pure $K_2Cr_2O_7$ salt was weighed and dissolved in acidic solutions as described in the Experimental section. These solutions were left outside and monitored for two weeks by scanning between 200 to 600 nm. A broad band around 434 to 440 nm and two sharper peaks around 349 to 350 nm and 256 to 257 nm was monitored. The broad 440 nm band corresponding to Cr^{6+} [49] and the other two peaks due to probable Cr^{3+} and Cr^{2+} are [49] in the solution. If the disintegration of Cr^{6+} to the other two species is rapid, the absorbance values of the broader band should reduce considerably, and the other two peaks must increase substantially. The trend observed does not seem so, from the data for absorbance in Tables 1-3 with the corresponding Graphs 1, 2, 3, indicating that there is no or significant disintegration of hexavalent chromium.

Table 1. Trends in absorbance for 1st, 2nd, 5th, 6th, 8th, & 16th days of the concentration of Cr^{6+} for 2000, 1500, 1000, 750, 500, 250, 100, 60 and 20 mg between 434-440 nm

Wavelength nm	2000	1500	1000	750	500	250	100	50	25	10
Absorbance 1st day	0.026	0.052	0.036	0.027	0.203	0.102	0.08	0.211	0.109	0.046
Absorbance 2nd day	0.093	0.054	0.043	0.033	0.205	0.104	0.082	0.213	0.109	0.046
Absorbance 5th day	0.092	0.061	0.044	0.027	0.212	0.111	0.087	0.221	0.114	0.053
Absorbance 6th day	0.093	0.056	0.041	0.03	0.215	0.116	0.088	0.219	0.116	0.053
Absorbance 8th day	0.093	0.057	0.039	0.028	0.204	0.108	0.082	0.212	0.107	0.042
Absorbance 16th day	0.094	0.063	0.047	0.036	0.212	0.113	0.1	0.221	0.127	0.052

As can be seen in the Trends graph, the observed absorbance values are same or are in very close range and not too different

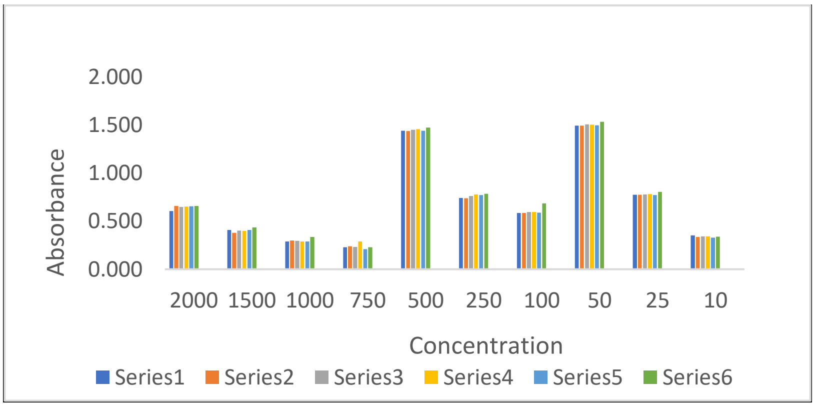


Graph 1. Trends in absorbance for 1st, 2nd, 5th, 6th, 8th, & 16th days of the concentration of Cr^{6+} for 2000, 1500, 1000, 750, 500, 250, 100, 60 and 20 mg between 434-440 nm

Table 2. Trends in absorbance for 1st, 2nd, 5th, 6th, 8th, & 16th days of the concentration of Cr^{6+} for 2000, 1500, 1000, 750, 500, 250, 100, 60 and 20 mg between 349 - 350 nm

Wavelength nm	2000	1500	1000	750	500	250	100	50	25	10
Absorbance 1st day	0.605	0.410	0.290	0.230	1.439	0.741	0.586	1.494	0.774	0.352
Absorbance 2nd day	0.658	0.380	0.300	0.240	1.437	0.739	0.586	1.493	0.774	0.334
Absorbance 5th day	0.649	0.403	0.295	0.231	1.450	0.762	0.596	1.506	0.779	0.343
Absorbance 6th day	0.652	0.399	0.290	0.290	1.456	0.777	0.596	1.504	0.782	0.342
Absorbance 8th day	0.654	0.410	0.289	0.210	1.441	0.771	0.588	1.496	0.770	0.330
Absorbance 16th day	0.658	0.434	0.335	0.230	1.472	0.783	0.684	1.533	0.805	0.339

As can be seen in the Trends graph, the observed absorbance values are same or are in very close range and not too different

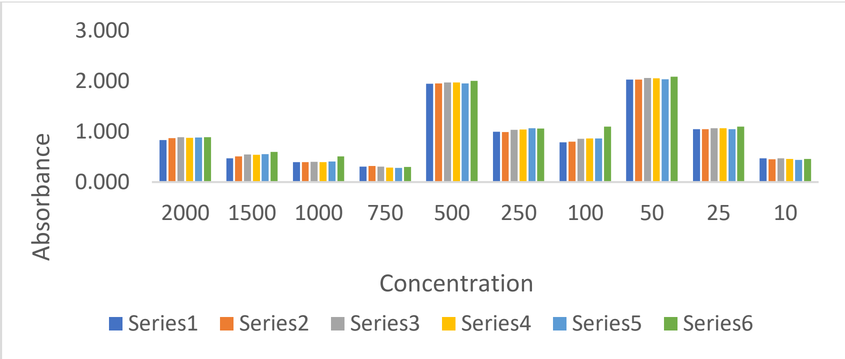


Graph 2. Trends in absorbance for 1st, 2nd, 5th, 6th, 8th, & 16th days of the concentration of Cr^{6+} for 2000, 1500, 1000, 750, 500, 250, 100, 60 and 20 mg between 349 to 350 nm

Table 3. Trends in absorbance for 1st, 2nd, 5th, 6th, 8th, & 16th days of the concentration of Cr^{6+} for 2000, 1500, 1000, 750, 500, 250, 100, 60 and 20 mg between 256-257nm

Wavelength nm	2000	1500	1000	750	500	250	100	50	25	10
Absorbance 1st day	0.833	0.470	0.396	0.310	1.950	0.997	0.788	2.036	1.051	0.470
Absorbance 2nd day	0.873	0.510	0.396	0.320	1.957	0.995	0.802	2.034	1.051	0.450
Absorbance 5th day	0.892	0.551	0.400	0.310	1.975	1.036	0.858	2.062	1.066	0.470
Absorbance 6th day	0.880	0.539	0.396	0.290	1.979	1.043	0.868	2.057	1.067	0.460
Absorbance 8th day	0.884	0.557	0.406	0.280	1.954	1.069	0.867	2.041	1.048	0.440
Absorbance 16th day	0.890	0.598	0.512	0.300	2.006	1.064	1.102	2.093	1.103	0.460

As can be seen in the Trends graph, the observed absorbance values are same or are in very close range and not too different

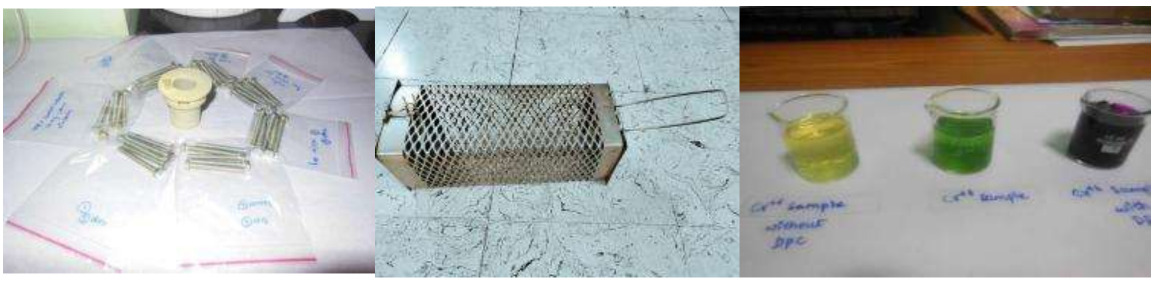


Graph 3. Trends in absorbance for 1st, 2nd, 5th, 6th, 8th, & 16th days of the concentration of Cr^{6+} for 2000, 1500, 1000, 750, 500, 250, 100, 60 and 20 mg between 256 to 257nm

Table 4. The absorbance values of hexavalent chromium (Cr^{6+}) >10^{-3} M acidic solutions kept for two weeks. Average absorbance on 1st, 2nd, 5th, 6th, 8th and 16th days for at different wavelengths to show their stability for over 15 days

S.No	Concentration mg/L	Absorbance values at 434 - 440 nm	Absorbance values at 349 - 350 nm	Absorbance values at 256 - 257 nm
1	2000	0.09	0.65	0.88
2	1500	0.06	0.40	0.54 - 0.59
3	1000	0.04	0.34	0.40 - 0.51
4	750	0.03	0.12	0.31
5	500	0.21	1.44 - 1.47	1.95 - 2.0
6	250	0.11	0.74 - 0.78	0.94 - 1.07
7	100	0.085 - 0.10	0.59 - 0.68	0.85 - 1.10
8	50	0.21 - 0.22	1.50 - 1.53	2.04 - 2.09
9	25	0.11 - 0.13	0.77 - 0.81	1.05 - 1.1
10	10	0.047 - 0.052	0.34	0.47

The observed absorbance values are same or are in very close range and not too different



(a) Screws and Fork Pivot Bore (b)Rat Trap Box (c) Cr^{6+} without/with DPC & Cr^{3+} samples

Fig. 1. (a) Screws and Fork Pivot Bore (b) Rat Trap Box samples and (c) Cr^{6+} without/with DPC & Cr^{3+} samples

Table 5. Analysis of hexavalent chromium in Screw, fork pivot bore and rat trap box, comparative study on UV-Vis at 440 nm, 540 nm and on Ion chromatography (IC) at 540 nm. Samples - absorbance, concentration, and amount of Cr^{6+} in mg/Kg

S No	UV-Vis 440 nm	UV-Vis 540 nm	IC- 540 nm
		Standards used for linearity – ppm	
1	100	1.0	10
2	250	2.5	20
3	500	5.0	30
4	750	7.5	40

Sample	UV-Vis 440 nm			UV-Vis 540 nm			IC- 540 nm	
	Abs in duplicate	Conc	Amount mg/Kg	Abs in duplicate	Conc	Amount mg/Kg	Conc	Amount mg/Kg
Screw	0.092 0.092	20.993	**105.00**	0.958 0.957	19.07	**95.35**	19.76	**88.00**
Fork Pivot Bore	0.030 0.029	7.782	**40.40**	2.17 2.17	7.892	**40.98**	8.01	**38.50**
Rat Trap Box	0.029 0.029	7.80	**43.00**	2.75 2.74	7.16	**44.00**	7.98	**42.75**

Abs: Absorbance; Conc: Concentration

The amount of hexavalent chromium in UV-Vis at 440 nm obtained for the yellow solutions is comparable and accurate with the amount obtained using diphenylcarbazide, measured on UV-Vis at 540 nm and on IC at 540 nm. In Fig. 1, it is also shown that the recovery of the spiked standard has resulted in the confirmation of the accurate concentration mentioned for the samples in this table.

The experiment was carried out from 2000 mg/kg to 10 mg/kg level on UV-Vis spectrophotometer without reduction or adding ligand for precipitation as:

1. Cr^{6+} in H_3PO_4/H_2SO_4 (0.7 M/1 M) gives bright orange color and can be measured on UV-Vis spectrophotometer at 440 nm wavelength [49].
2. The above-mentioned solutions were measured for 16 days by scanning between 200 to 600 nm. The broad band at 440 nm for Cr^{6+} and sharp peaks at 350 nm and 256 nm correspond to probably Cr^{3+} and Cr^{2+} species in the solutions.
3. From Table 4, it is evident that the measured average absorbance values at 440 nm, 350 nm and 250 nm are almost constant over a period of 16 days and so it suggests that the degradation or disintegration to reduced species is NOT very significant. This trend is followed for Cr^{6+} from 2000 mg - 750 mg perfectly. It was observed that from 750 mg to 100 mg level the variation is also quantifiable, albeit with a reservation. Below 100 mg until 10 mg, there is slightly more disintegration and is less quantifiable. However, judging from the absorbance values, more than 85-90%, the toxic Cr^{6+} analysis can be obtained with easy and quick assessment. Substantial variation in absorbance values is observed once it reaches about 10 mg/kg level i.e., 0.01% or 10^{-2} M or 10 ppm solution, in comparison to the other higher concentrations.
4. So, it appears that there is no need to reduce Cr^{6+} and then coordinate with DPC to measure it. Instead, in the presence of excess of Cr^{3+} we can still measure Cr^{6+} in UV- Vis spectrophotometer, up to 2000 mg/kg.

Table 5 gives details of the analysis done for the three samples selected for the study – Screws coated with Cr^{6+}, Fork Pivot Bore submitted by a client as a sample which has Cr^{6+} coating and the Rat Trap Box coated with Cr^{6+}. The samples were stripped off their Cr^{6+} coating by dipping in water and boiling for an hour as given in the IEC standard (44-48). The analysis on UV-Vis at 440 nm for the yellow solution and at 540 nm using DPC to obtain purple solution as per the standard method result in very similar results suggesting the latter procedure is warranted (Fig. 2). The analysis of these materials on Ion chromatography (IC) also found to be closer. In fact, some of the screw sample solutions were spiked for 20 ppm and 40 ppm of Cr^{6+} and were recovered; suggesting no necessity to add

organic ligands and adjust the pH, wait for the purple color to form, and measure. The structural ambiguity of the purple color obtained also need not be addressed or considered [18, 75].
Hence, it may be deduced, from Table 5, that the hexavalent chromium need not be measured using organic ligands, as it gives similar results without the organic ligand and can be measured at 440 nm on UV-Vis spectrophotometer, as the extracted solutions of the material in testing are stable for the next two weeks.

Photometric Method Report

Wavelengths
Wavelength Name: WL440.0
Wavelength: 440.00 nm

Calibration Curve
Column for Cal. Curve: WL440.0
Cal.Curve Type: Multi Point
Cal.Curve Unit: mg/l
Selected Wavelength WL440.0
Calibration Equation Abs = K1*(Conc) + K0
Zero Interception Not Selected

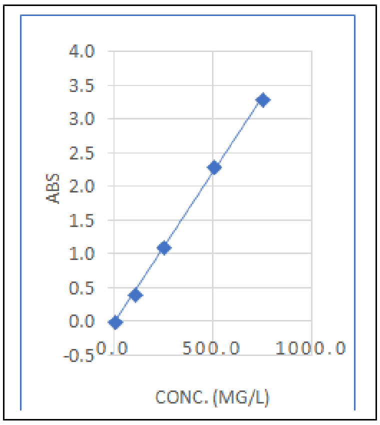


Fig. 2. UV-Vis Spectrophotometer analysis of the sample at 440 nm for hexavalent chromium obtained from the instrument

List 1. Standard table

	Sample ID	Type	Ex	Conc	WL440.0	W_{gt}. Factor	Comments
1	blank	Standard		0.0	-0.0	1.0	
2	std 1	Standard		100.0	0.4	1.0	
3	std 2	Standard		250.0	1.1	1.0	
4	std 3	Standard		500.0	2.3	1.0	
5	std 4	Standard		750.0	3.3	1.0	

List 2. Sample table

	Sample ID	Type	Ex	Conc	WL440.0	Comments
1	sample 1	Unknown		20.993	0.092	
2	sample 1	Unknown		20.993	0.092	
3	sample 2	Unknown		7.782	0.03	
4	sample 2	Unknown		7.780	0.029	
5	sample 3	Unknown		7.80	0.029	
6	sample 3	Unknown		7.80	0.029	
7	sample 1	Unknown		41.090	0.182	20 ppm spike
8	sample 1	Unknown		42.086	0.186	20 ppm spike
9	sample 1	Unknown		39.874	0.176	20 ppm spike
10	sample 1	Unknown		59.271	0.360	40 ppm spike
11	sample 1	Unknown		58.843	0.388	40 ppm spike
12	sample 1	Unknown		57.326	0.342	40 ppm spike

20 ppm and 40 ppm spikes has been done in the Screw sample to show that there is 90-110% recovery of the standard and there is no ambiguity in the experimental values obtained for the samples. Average value of sample concentration for 20 ppm is also same as sample concentration obtained individually for the sample in duplicate

3. CONCLUSION

The acidified aqueous solutions of Cr^{6+} kept at room temperature were monitored for two weeks for any change in absorbance for the broad band at 440 nm corresponding to Cr^{6+}. It was found to have stable absorbance and did not show signs of disintegration. The analysis of screw samples at 440 nm, after simple aqueous extraction, using dichromate solutions as standards, resulted in the similar amount as that measured by all three methods - standard method of analysis using IEC standards, measurement on Ion Chromatography (IC) with UV detector and on UV-Vis spectrophotometer at 540 nm with DPC ligand as reagent.

For other samples – Screw, Fork Pivot Bore and a Rat Trap Box, the analysis in both methods resulted in a similar amount. The sample values obtained with and without ligand are reported. They are found to be closer to that of the values obtained by passing through Ion chromatography (IC) column too, thus proving that one can conduct the experiment without adding any ligand and get the estimation accurately.

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DEDICATION

Dedicated to my research guide and mentor, Prof. M. V. Rajasekharan, School of Chemistry, University of Hyderabad, on his 70th birthday celebration

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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be analysed different protocols are adopted, such as extraction of chromium by variety of methods. After analysis by UV-Vis spectrophotometer, and the amount of chromium hexavalent present in samples, concentration is expressed as a function of a unit area of the sample; 2006.

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