



Use of Variamine Blue Dye in Spectrophotometric Determination of Water Soluble Cr(VI) in Portland Cement

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ABSTRACT

Variamine blue dye as chromogenic reagent was used for Portland cement samples in determination of soluble hexavalent chromium. This method was based on the reaction of Cr(VI) with potassium iodide in acidic medium to liberate iodine, which oxidized variamine blue to form a violet colored species having an absorption maximum 556 nm. The extraction of soluble Cr(VI) for quantification in cement was done according to European method. The validity of this method was thoroughly examined by comparing with standard DPC method as well as the accuracy of the method was checked using a standard reference material of National Institute of Standards & Technology (NIST), USA.

Key words: Water soluble Cr (VI), Portland cement, Variamine blue, Spectrophotometer

INTRODUCTION

Chromium was present in raw materials used for the production of cement. In its +3 oxidation state, it is not harmful, but during production of cement, at high temperature this harmless form gets converted into toxic hexavalent form¹. Hexavalent chromium is water soluble and leached out during hydration of cement. Leaching of Cr(VI) becomes a health hazard for the workers at construction field because it can cause cancer, mutations and skin dermatitis²⁻⁵. Contact dermatitis is one of the major problems reported in the workers at construction

sites, who worked with cement⁶⁻⁹. To control the toxicity of Cr(VI), European government has limited the chromium content to 2.0 ppm relative to the mass of cement¹⁰. Number of research showed that in India chromium level was found in between 12 to 33 ppm¹¹. Keeping the toxicity of cement in mind, it becomes necessary to estimate the chromium content in cement used¹². Several methods for determination of hexavalent chromium in cement samples are available in literature. Spectrographic method for the determination of hexavalent chromium using diphenylcarbazide (DPC) method¹³⁻¹⁵, where extracted solution from cement

was adjusted to final volume and acidified (pH 2.1 to 2.5). Then 0.25% solution of DPC was added. DPC causes reduction of Cr(VI) to Cr(III) by itself undergoing oxidation. Thus oxidized DPC and Cr(III) formed a magenta-colored complex. This concentration of complex was measured by the spectrophotometer with a maximum absorption at 540 nm. However, the matrix of cement-related materials is complicated and contains a variety of interacting cations such as Mn^{+2} , Fe^{+2} , Fe^{+3} , and Ca^{+2} that may cause problems with the accurate determination of Cr(VI) using DPC methods¹⁶. Therefore, the estimation of Cr (VI) species in cement-related materials requires an additional effort.

An oxidizing agent ($Na_2S_2O_8$) was implemented to remove the interfering effect of reducing agent (ferrous ion) and ortho phosphoric acid was used for the removal of interfering species (ferric ion) during detection by standard DPC method. These implementations had been taken in standard method, known as EN196-10¹⁷. Some author proposed hyper technique and developed methods to determine chromium species in cement through HPLC-ICP-MS, FPLC-ETAAS, Wavelength-Dispersive X-ray Fluorescence Spectrometry, direct spectrophotometric determination of Cr(VI) in 1, 2, 5, 8 Tetrahydroxyanthraquinone (Quinalizarin), Catalytic adsorptive stripping voltammetry with DTPA and nitrate¹⁸⁻²². Although these advanced techniques can detect chromium in very low concentration with high accuracy, precision, and selectivity, but the cost is very high. On industrial level application of these techniques is not possible. Thus spectroscopic methods are still the most used techniques for the determination of Cr(VI) in cement extracts²³⁻²⁵.

The most widely used method for determination of hexavalent chromium from cement extract is DPC, but it suffers serious interference from ions present in aqueous cement extract, high blank value and also formed complex (Cr^{+3} coordinated with diphenylcarbazone (DPCA)) is stable for 30 minutes¹⁰. Keeping these drawbacks in mind, in present work a facile, sensitive, accurate and reliable method for the determination of trace amounts of the chromium is used.

EXPERIMENTAL

Apparatus

A HACH Spectrophotometer (Made in USA) with 1 cm quartz cell was used for the absorbance measurements. A pH meter and conductometer was used to monitor the pH of the equilibrating solutions and conductivity of double distilled water. The pH meter was standardized using pH 4, 7, and 10 buffer solutions. A digital balance was used for weighing all the reagents.

Chemicals and Solutions

All chemicals used were of analytical reagent grade and doubly distilled water, were used for the preparation of aqueous solutions. All reagents used were of analytical reagent grade (A.R. grade). Variamine blue dye solution (0.05%) was prepared by dissolving 0.05 gram in 25 mL absolute alcohol and diluted to 100 mL with double distilled water. The 0.25% diphenylcarbazide (DPC) solution was prepared as per the procedure followed by 1.0 gram of diphenylcarbazide (DPC) was dissolved in 75 mL ethanol. To this was added 5 gram phthalic anhydride and 6 drops of concentrated H_2SO_4 and made up to 100 mL with ethanol. Standard Cr(VI) stock solution (1000 ppm) was prepared by dissolving 0.2829 gram of $K_2Cr_2O_7$ in 100 mL of water. This stock solution was used for the preparation of working solutions. Sulfuric acid (1 M) was prepared by diluting 6.95 mL of stock H_2SO_4 to the mark in a 250 mL volumetric flask with water. A solution of potassium iodide (2.0%) was prepared by dissolving 2.0 gram potassium iodide in water and diluting it up to 100 mL. A solution of sodium acetate (2M) was prepared by dissolving 16.407 gram sodium acetate in water and diluting the solution to 100 mL in a volumetric flask.

Cement Samples

The Ordinary Portland Cement (OPC, 43-Grade of ACC brand) used for this work, samples of ordinary Portland cement (OPC) were supplied by Oriental Structural Engineers Pvt. Ltd. Chemical composition of OPC has been carried out and data obtained are presented in Table 1.0, respectively.

Determination of water soluble Cr(VI) in cement samples

Aqueous cement extracts were prepared

according to the European standard method (EN196-10)¹⁷, weigh accurately 25.0 g of the cement sample in mixer with 25.0 mL of distilled water, mixing the mixture for 15 ± 1 minute intensively at 300 rpm. Immediately filter the suspension with vacuum filtration. A known amount of aliquot of cement sample was spiked with known amount of Cr(VI). Thus the determination of water soluble Cr(VI) in cement extract as well as in spiked cement extract samples by variamine blue (proposed method) as well as analyzed according to the standard diphenylcarbazide method (reference method).

Variamine Blue method (proposed method)

An aliquot of cement samples solution with and without added Cr(VI) were taken in volumetric flasks. Potassium iodide (2%, 1 mL), sulphuric acid (2M, 1 mL) were added and mixture was gently shaken until the appearance of yellow color (iodine liberated). Then variamine blue (0.05% 0.5 mL) was added to it, follow by the addition of sodium acetate solution (2M, 2 mL). The contents were mixed well; the absorbance of the colored species was measured at 556 nm against the corresponding reagent blank (Scheme 1).

Diphenyl carbazide method (Reference method)

To cement samples, 2.5 mL of 1, 5 dipenyl carbazide solutions and sulfuric acid (1:4) was

added. The solution was then made upto 100 mL with double distilled water. DPC causes reduction of Cr(VI) to Cr(III) by itself undergoing oxidation. Thus DPCA and Cr(III) formed a magenta-colored complex (Scheme 2). Absorbance of all the solutions against blank was recorded at wavelength of 540 nm

RESULT AND DISCUSSION

Analytical data

The quantitative determination of soluble Cr(VI) in aqueous solutions was done by constructing a calibration plot. For the calibration curve, solution of concentration varying from 2-12 ppm with addition of all chemicals and reagents required for detection were made and their absorbance values were recorded. The plot of absorbance versus concentration was found to be linear till 12 ppm of soluble Cr(VI). A linear relationship between absorbance values and amount of soluble Cr(VI) suggests the use of the present method for quantitative determination of Cr(VI) in aqueous samples. The detection limits, quantification limit, slope and regression value are given in Table 2.

Validation of method

The percentage of recovery of various Cr(VI)-spiked solutions as well as their relative

Table 1: Chemical composition of ordinary Portland cement (OPC-43 grade)

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	LOI	Others
%(w/w)	63.5	21.70	5.84	3.50	2.00	1.10	0.35	0.10	0.5	0.30

Table 2: Analytical parameters

Analytical parameters	Proposed method (VB)	Reference method (DPC)
Detection limit (DL)	0.05	0.04
Quantification limit (QL)	0.18	0.13
Slope	0.029	0.518
regression value	0.998	0.996
Range (for linearity)	2-12	0.05-1.0
Sensitivity	Low	High

DL = 3 s/S, QL= 10 s/S where s is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration curve

Table 3: Validation test

Sample	Proposed Method (VB)				Reference method (DPC)						
	Cr(VI) added (ppm)	Cr(VI) found (ppm)	RSD* (%)	Relative error (%)	Recovery (%)	Cr(VI) found (ppm)	RSD (%)	Relative error (%)	Recovery (%)	T ^a test	F ^b Test
OPC NIST	5	4.55± 1.2	9.87	-9	91	4.93± 1.2	14.59	-1.4	98.6	0.13	0.33
	10	9.78± 0.5	8.87	-2.2	97.8	10.0± 0.9	10.59	0.2	100.2	0.39	0.64
	15	15.01± 1.1	4.43	0.07	100.06	15.05± 1.4	10.65	0.33	100.33	0.85	0.10

*Relative standard deviation, Mean ± standard deviation (n = 5). ^a Tabulated t-value for 8 degrees of freedom at 5% level of significance is 2.306. ^b Tabulated F-value for (4,4) degrees of freedom at P (0.95) is 6.39.

standard deviation, relative error and parametric test (t and f test) were also calculated to express the validation of proposed methods (results are given in table 3). Results were compared statistically for the validity of the proposed method. All the experiment were performed at least five times, and student's t test and f test methodology were used for comparison between two different Cr(VI) determination method. The calculated t and f values were compared with test value at a proper degree of freedom, the results showed that both methods are reliable up to 15 mg/L solution.

Determination of Soluble Cr(VI) in Cement samples

The proposed method was applied to the quantitative determination of water soluble Cr(VI) in cement samples, the results are presented in Table 4. A variation in results was obtained in detection by standard method and present method (Figure 1). High concentration of Cr(VI) by DPC method may be due to presence of many interfering ions, because it was already mentioned in literature that DPC reagent was very sensitive to produce color¹⁶.

Effects of Ions on the Variamine Blue Spectroscopic method

An additional effort was made to investigate the effect of various common ions on spectroscopic determination of 5 ppm soluble Cr(VI) from variamine blue method. For cations like Na⁺ and K⁺, no significant effects were observed up to

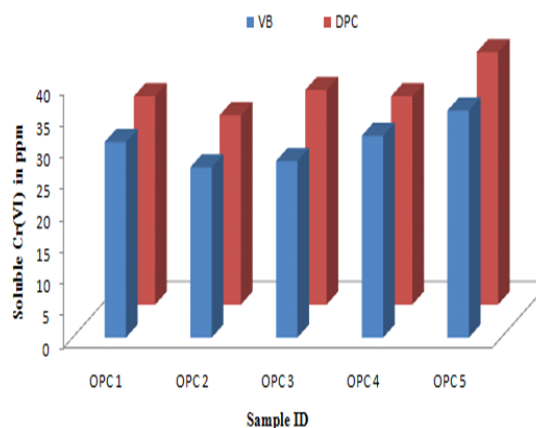
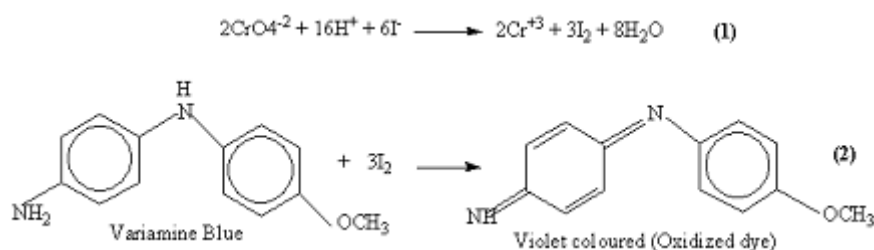


Fig. 1: Variation in soluble Cr(VI) results by both method

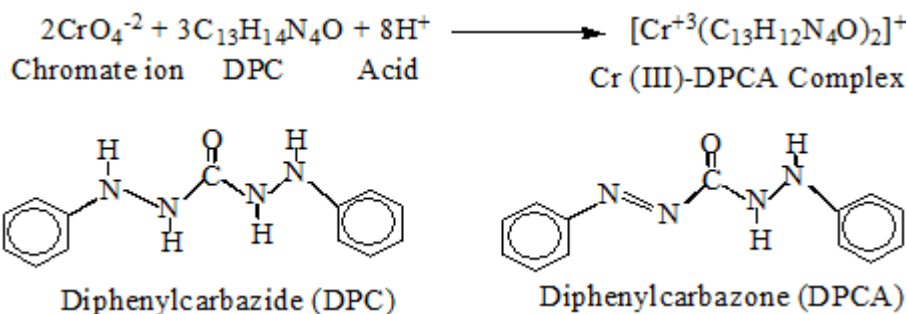
Table 4: Water soluble Cr(VI) in Ordinary Portland cement samples

S. No	Sample ID	Date of manufacturing Weak No./Year	Soluble hexavalent chromium(ppm) Average (n=5 replicate) ± Standard deviation			
			VB	RSD	DPC	RSD
1	OPC NIST	-	0.98±0.03	3.06	1.09±0.02	1.8
2	OPC 1	40/2014	31±0.5	1.6	33±1.5	4.5
3	OPC 2	42/2014	27±0.9	3.3	30±1.9	6.3
4	OPC 3	01/2015	28±0.7	2.5	34±2.5	7.4
5	OPC 4	04/2015	32±0.5	1.6	33±2.0	6.06
6	OPC 5	05/2015	36±0.8	2.2	40±1.2	3.0

RSD: Relative standard deviation



Scheme 1:



Scheme 2:

1,000 mg/L of each ion. Aluminum (Al^{3+}) and magnesium ions (Mg^{2+}) may interfere with the Cr(VI) determination when the concentration is higher than 500 mg/L. Common anions, such as nitrate (NO_3^-) and chloride (Cl^-), did not affect up to 750 mg/L, and no effects were observed for sulfate (SO_4^{2-}) and carbonate (CO_3^{2-}) up to 1200 mg/L. Effect of ferric ion (25 ppm) may be considerable, but can be minimized by addition of 5.0 mL of orthophosphoric acid.

CONCLUSIONS

The chromium concentration estimated by DPC method was found to be more than variamine blue method. Comparatively high concentration of chromium in DPC method may be attributed to interference caused by various ions because of high colour sensitivity of DPC. Since, the interference by other ions is less in present method, this method

can be used for accurate detection of Cr(VI) in cement sample. High colour stability of Variamine blue dye added an additional feature to this reagent.

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