

A new method in estimation of total hexavalent chromium in Portland pozzolan cement

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ABSTRACT: Variamine blue was used first time for the detection of hexavalent chromium from cement samples. In present method, cement was treated sequentially with water, sulphate and carbonate buffer to extract soluble, sparingly soluble and insoluble hexavalent chromium respectively. Extracted Cr (VI) was determined using variamine blue as chromogenic reagent. The determination is based on the reaction of hexavalent chromium with potassium iodide in an acid medium to liberate iodine. This oxidizes variamine blue to form a violet coloured species having an absorption to maximum at 556 nm. Energy-dispersive X-ray spectroscopy (EDX) and Infrared Spectroscopy (IR) confirmed the complete extraction of hexavalent chromium by sequential extraction process. SRM 2701 (Reference material from NIST, USA) was used for revalidating the results. The percentage of recovery for proposed and reference method (diphelycarbazine method) varied from 98.5 to 101 and 97.5 to 100.5. Whereas, their relative error percentage varied from -1.5 to 0.33 and -2.5 to 0.5.

Keywords: Portland cement; Estimation; Chromium; Variamine blue; UV-visible; IR; EDX

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RESUMEN: *Un nuevo método en la determinación del cromo hexavalente total en cemento Portland puzolánico.* El azul de variamina se utilizó por primera vez para la detección de cromo hexavalente en muestras de cemento. En el presente método, el cemento se trató secuencialmente con agua, y tampones sulfato y carbonato para extraer el cromo hexavalente soluble, poco soluble e insoluble, respectivamente. El Cr (VI) extraído se determinó utilizando azul de variamina como reactivo cromógeno, por reacción del cromo hexavalente con yoduro de potasio en un medio ácido para liberar yodo. Esto oxida al azul de variamina para formar una especie de color violeta con una absorción máxima a 556 nm. El análisis por energía dispersiva de rayos X (EDX) y la espectroscopía de infrarrojos (IR) confirmaron la extracción completa de cromo hexavalente mediante el proceso de extracción secuencial. Se utilizó SRM 2701 (material de referencia de NIST, EE.UU.) para validar los resultados. El porcentaje de recuperación para el método propuesto frente al de referencia (método de la difenilcarbazida) varió de 98.5 a 101 y 97.5 a 100.5, mientras que su porcentaje de error relativo varió de -1.5 a 0.33 y -2.5 a 0.5.

Palabras claves: Cemento Portland; Estimación; Cromo; Azul de variamina; UV-visible; IR; EDX

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1. INTRODUCTION

Chromium, in its non toxic +3 oxidation state, is present in raw materials (clay, lime or ore) used for cement production. But at high temperature of cement rotary kiln, this trivalent chromium oxidises

into reactive hexavalent form (1). Health of workers in cement industries is at risk due to exposure to this hexavalent chromium. Airborne hexavalent chromium has been proved to be a human respiratory carcinogen and some of its compounds were found to be contact allergens (2–4). Leaching of Cr (VI)

from concrete structures, like water reservoirs and pipes used for water transport can also lead to the contamination of water (5). Thus, the detection of hexavalent chromium in cement sample becomes necessary. Although, the use of cement containing more than 2.0 mg/kg soluble Cr (VI) in hydrated cement, was restricted by European Directives 2003/53/EC (6), yet there is no check on concentration of hexavalent chromium in cement samples used in India. The most common detecting reagent used for Cr (VI) is diphenylcarbazide (DPC) (7, 8). However, the major problem associated with this reagent is interference caused by other metal ions (Fe^{III} , Mo^{IV} , Cu^{II} , Hg^{II} etc.) present in the cement (9). Apart from DPC, many organic molecules were also used for the same. However, the main limitation of these reagent is either their carcinogenic behaviour or less selectivity (10).

Therefore, there is a need of simple and sensitive reagent for estimation of concentration of Cr (VI). Recently, variamine blue had been used for detection of hexavalent chromium in steel, industrial effluents, natural water samples and soil samples (11). Simple reaction conditions, no extraction or heating and high colour stability has made variamine blue a better reagent than others (11). In this paper, variamine blue is used for detection of Cr (VI) in cement samples. Sequential extraction and detection of Cr (VI) (water soluble, sparingly soluble and insoluble chromium (VI)) has been carried out using this reagent.

2. EXPERIMENTAL

2.1. Instrumentation

A HACH Spectrophotometer (Made in USA) with 1 cm quartz cell was used for the absorbance measurements. Residues left after extraction of

water soluble Cr (VI) (extraction 1) and extraction of sparingly soluble Cr (VI) (extraction 2) were dried and ground. Infrared spectra of these powders were then recorded from KBr pellets in the range $4000\text{--}200\text{ cm}^{-1}$ on a SHIMADZU FTIR 8400S spectrophotometer. EDX was performed with a JEOL Model JED – 2300. The cement sample (S1) and its residue left after extraction of insoluble Cr (VI) (extraction 3) was dried and ground. The fine powder, thus obtained, was used to take EDX spectrum.

2.2. Reagents and solution

All the chemicals used were of analytical / GR grade. Variamine blue dye solution (0.05%) was prepared by dissolving 0.05 g in 25 mL absolute alcohol and then the volume was made 100 mL using distilled water. A solution of potassium iodide (2.0%) was prepared by dissolving 2.0 g potassium iodide in water and diluting it up to 100 mL. A solution of sodium acetate (2M) was prepared by dissolving 16.407 g sodium acetate in distilled water and the volume made up to 100 mL in a volumetric flask. Sulfuric acid (1M) was prepared by diluting 6.95 mL of stock H_2SO_4 to the mark in a 250 mL volumetric flask with distilled water. Stock solution of Cr (VI) was prepared by dissolving 0.2829 g, $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water to make the volume 1L. Standard solutions of 0.05, 0.1, 0.2, 0.04, 0.08, 1 ppm were made by dilution of stock solution.

2.3. Materials

Cement samples used are fly ash based Portland Pozzolan Cement of different brands and the %age of pozzolanic material is not less than 10% and not more than 25% (Table 1). The study of chemical composition of PPC samples (Table 2) has been carried out at Shankar Laboratory, New Delhi. Due to

TABLE 1. Sample details

Brand name	ACC	Jaypee	Birla	Prism	Mysem	Reliance
Sample ID	S1	S2	S3	S4	S5	S6
Weak/year of Manufacturing	23/2015	22/2015	21/2015	22/2015	21/2015	21/2015

TABLE 2. Chemical composition of Portland Pozzolan Cement

Sample ID	Constituents %										
	LOI	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	IR	Na ₂ O	K ₂ O	Cl
S1	2.23	31.7	3.3	9.3	41.7	1.9	1.8	8.51	0.28	0.2	0.29
S2	2.41	32	3.4	8.8	40.2	1.4	2.16	10.6	0.21	0.18	0.22
S3	2.42	31.2	3.4	9.5	41	1.7	2.16	9.12	0.37	0.25	0.18
S4	2.33	31	3.21	8.1	42.2	1.5	2.1	8.65	0.45	0.31	0.19
S5	2.11	32	3.4	9.8	40	1.9	2.16	9.65	0.18	0.18	0.21
S6	2.63	32	3.4	10.8	40.1	1.3	1.8	8.3	0.21	0.11	0.19

the unavailability of hexavalent chromium certified reference cement, SRM 2701 Hexavalent Chromium in contaminated Soil from NIST (National Institute of Standards and Technology, USA) was used for revalidating the method accuracy. The certified concentration of Cr (VI) in SRM 2701 is 551.12 ± 34.5 mg/Kg.

2.4. Extraction of water soluble Cr (VI) species (Extraction 1)

The Cr (VI) from cement samples was extracted using five day extraction process (12, 13). In this method, 100 mL distilled water was added to 1.0 g cement sample. The contents were mixed thoroughly with a glass rod. This mixing was repeated for five days to ensure complete leaching of hexavalent chromium. After five days, filtration was done using Whatman 42 filter paper. Two washings were required. Insoluble part was kept for estimation of sparingly soluble and insoluble chromium and filtrate was used for detection of water soluble hexavalent chromium.

2.5. Extraction of sparingly soluble Cr (VI) species (Extraction 2)

Sparingly soluble Cr (VI) is present in cement in the form of strontium chromate (14). For its detection, residue left after extraction 1 was transferred to a 250 mL glass beaker. To this was added, 40 mL of ammonium sulfate buffer (0.05 M ammonium sulfate and 0.05 M ammonium hydroxide) and contents were stirred for 30 min. Filtrate obtained after stirring was used to estimate sparingly soluble chromium and residue was kept for estimation of insoluble chromium (14).

2.6. Extraction of insoluble Cr (VI) species (Extraction 3)

To the residue obtained after extraction 2, was added 40 mL of carbonate buffer (3% (w/v) sodium carbonate and 2% (w/v) sodium hydroxide) in 250 mL glass beaker. The reaction mixture was stirred for 30 minutes and filtered (14). Filtrate was used to estimate the concentration of insoluble chromium.

2.7. Determination method

To the filtrate of extraction 1, 1 mL of 2% potassium iodide was added. Addition of sulphuric acid (1.0 mol/L, 1 mL, the oxidation of iodide to iodine was effective in the pH range 1.0 to 1.5) to the reaction mixture gave appearance of yellow colour indicating the liberation of iodine. To this was added variamine blue (0.05%, 0.5 mL) and 2 mL of 2 mol/L sodium acetate solution (Buffer solution).

The resulting solution was kept for 10–15 minutes to ensure the completion of reaction (appearance of violet colour). The absorbance at 556 nm, of the coloured solutions had a linear relationship to the Cr (VI) concentration. The similar procedure was used for filtrates obtained after extraction 2 and 3. All the solutions were also analyzed for chromium concentration by standard DPC method (15). The concentration of Cr (VI) can be calculated using the following formula: $C_{\text{Cr(VI)}} = C V_1 / M V_2$.

Where $C_{\text{Cr(VI)}}$ is the concentration of hexavalent chromium (ppm), C is the concentration of Cr (VI) in $\mu\text{g/ml}$, V_1 is the volume of water in which the original sample is suspended, V_2 is the volume of filtrate which is transferred to the volumetric flask, cm^3 . M is the mass of the cement sample.

3. RESULTS AND DISCUSSION

Cr (III) is slightly soluble in alkaline medium in the form of $\text{Cr}(\text{OH})_6^{-3}$ and therefore, generally does not interfere in detection of Cr (VI). But if it is in excess, $\text{Cr}(\text{OH})_6^{-3}$ can bind with Cr (III)-DPC complex to give positive interference in detection of Cr (VI) by standered DPC method (11). To overcome this interference by Cr (III), variamine blue is used as chromogenic reagent in detection of Cr (VI) because the mechanism of action in this case is different. In this method iodide ion gets oxidized into iodine on reaction with chromate in an acidic medium. The liberated iodine oxidized variamine blue, in the presence of sodium acetate, (buffer solution, pH 4) is to form a violet-coloured solution (Figure 1). This coloured solution gave maximum absorbance at 556 nm. The reagent blank had a negligible absorbance at this wavelength and was set at zero.

3.1. Analytical Parameters

The calibration graph is linear and can be explained by equation: $y = 0.062x - 0.001$, where y is integrated absorbance and x is analyte concentration (Figure 2). The regression value obtained for the calibration plot is 0.998. The detection limit ($D_L = 3.3\sigma/S$) and quantification limit ($Q_L = 10\sigma/S$) of Cr (VI) were found to be 0.05 and 0.16 $\mu\text{g/ml}$, where σ is the standard deviation of blank samples ($n=5$) and S is slope of calibration curve.

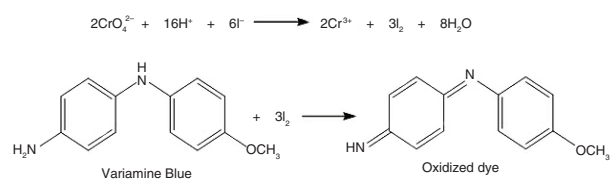


FIGURE 1. Oxidation of Variamine Blue (VB) by liberated Iodine (I₂).

The experimental data to get calibration curve is given in supplementary material.

3.2. Validation of proposed method

“SRM 2701 Hexavalent Cr in contaminated Soil” from NIST (National Institute of Standards and Technology, USA) was used for revalidating the results obtained by the proposed method (Table 3).

3.3. Leaching procedure and verification for Cr (VI) extraction

For complete leaching of water soluble hexavalent chromium, five days extraction procedure was followed. Long stirring in water ensured the extraction of some hexavalent chromium that was present in solid phases of cement. Sparingly soluble Cr (VI) was extracted by treatment of residue of extraction 1 with ammonium sulfate buffer (0.05 M $(\text{NH}_4)_2\text{SO}_4$ -0.05 M NH_4OH). However, the insoluble chromium was extracted using carbonate buffer (3% (w/v) sodium carbonate and 2% (w/v) sodium hydroxide).

3.4. IR spectra

In the IR spectrum (16), bands for CO_3^{2-} ion appeared at 1425, 1497, 875 and 732 cm^{-1} and for chromate ion in the range $850\text{--}950\text{ cm}^{-1}$ (specially for ZnCrO_4 and CaCrO_4) (8, 17, 18). IR spectrum of cement sample S1 show band at 877 and 1430 cm^{-1} (Figure 3). The intensity of these bands decreased after the extraction of water soluble and sparingly soluble Cr (VI) (residue of extraction 1 and 2 respectively). Decrease in intensity of band at 877 cm^{-1} can either be due to leaching of hexavalent chromium in extraction process or reduction in carbonate concentration (due to formation of carboxyaluminates (19, 20). or replacement of carbonate by sulphate ion in Aft (alumina ferric oxide tri-sulfate) and AFm (alumina ferric oxide mono-sulfate) phases) (21, 22).

Since vibrational bands for carbonate and chromate band appeared in the range, $870\text{--}880\text{ cm}^{-1}$, it is difficult to get a distinct information regarding decrease in concentration of chromate ion. Nevertheless, it can be used as supporting data to other techniques like EDX and UV-Vis spectrophotometer.

TABLE 3. Determination of Cr (VI) in standard sample (SRM 2701 from NIST)

	Hexavalent chromium in SRM 2701 (in ppm)				Recovery (%)	RSD (%)	T-test	F-test
	Water soluble	Sparingly soluble	Insoluble	Total				
Certified value	-	-	-	551.12±34.5	-	-	-	-
Proposed method	125±2.74	115.2±8.70	309.2±14.45	549.4±25.89	99.69	4.7	0.93	0.97
Reference method	126±3.67	114.6±2.97	309.2±14.45	550.8±29.58	99.94	5.3		

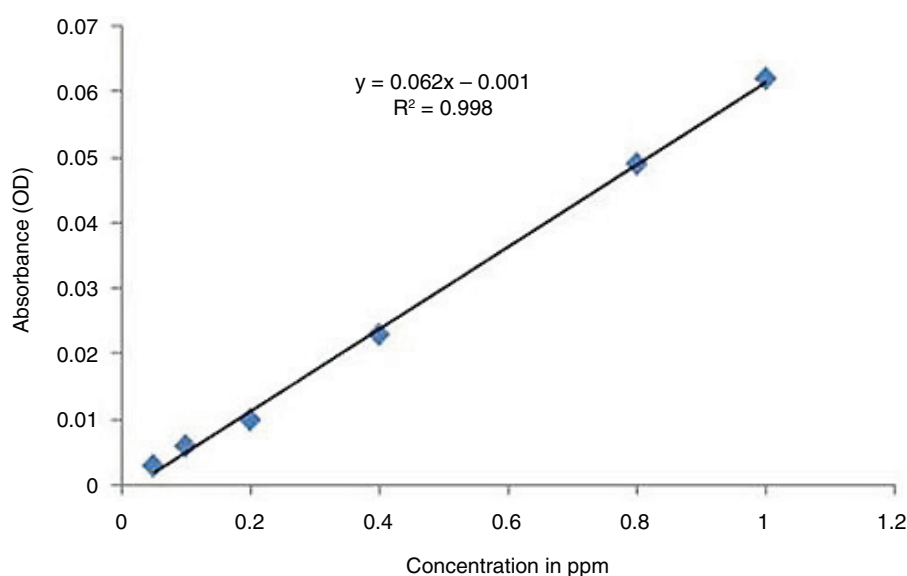


FIGURE 2. Calibration graph.

3.5. EDX spectra

Extraction of hexavalent chromium was also confirmed by EDX spectra of sample S1 and the residues left after extraction 3. Generally chromium gave a peak in range of 5.0 to 6.0 KeV in EDX spectrum (23–26). In sample S1, this peak appeared at 5.2 KeV in its EDX spectrum (Figure 4), however this appeared as very weak peak after extraction 3. (Figure 5)

3.6. Determination of hexavalent chromium in Cement samples

Variamine Blue method was applied to filtrates of extraction 1, 2 and 3 of six different samples of Portland pozzolan cement for estimation of water soluble, sparingly soluble and insoluble hexavalent

chromium. To check the accuracy of proposed method, all the six cement samples were also tested for same using standard DPC methods.

Tables 4–6 gave a comparison of proposed method with standard method in terms of parametric tests (T and F test), percentage of relative standard deviation (RSD) and percentage of recovery. The percentage recoveries in six cement samples (from S1 to S6) were spiked with known concentration of hexavalent chromium. A null hypothesis indicating that both Cr (VI) determination methods adopted in this research relied on each other was evaluated by comparing both the means with parametric test (T and F test). These tests for the comparison of means were calculated. The calculated values were compared with the tabulated value at a proper degree of freedom (27) and results indicate reliability of these methods from 2 to 12 ppm

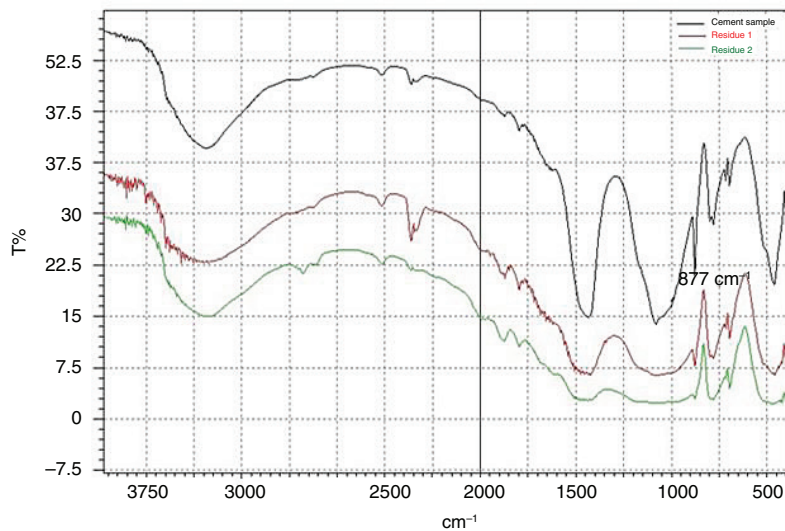


FIGURE 3. Overlay of spectrum of cement sample S1 and its residue after extraction 1 and 2.

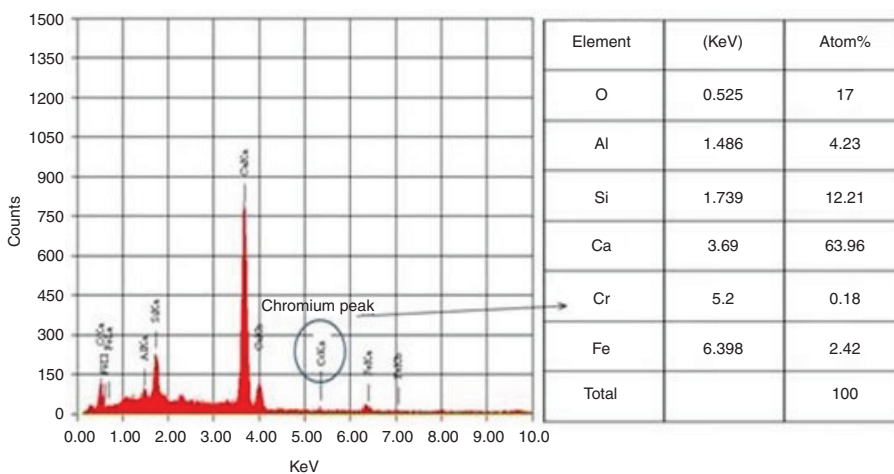


FIGURE 4. EDS spectrum of cement paste before sequential extraction.

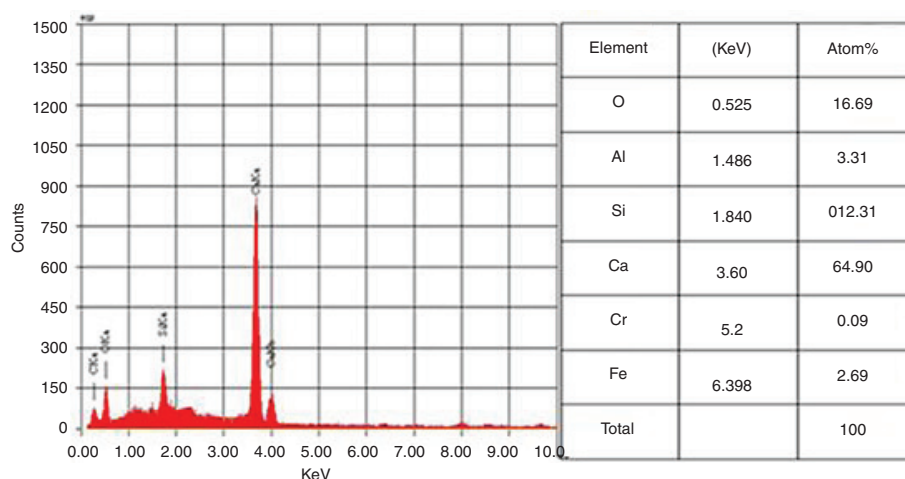


FIGURE 5. EDS spectrum of cement paste after sequential extraction.

TABLE 4. Determination of water soluble Cr (VI) in various Cement samples

Sample ID	Soluble Cr (VI) Added* (ppm)	Proposed method			DPC method			T-test	F-test
		Soluble Cr (VI) Found	RSD (%)	Recovery (%)	Soluble Cr (VI) Found	RSD (%)	Recovery (%)		
S1	-	23±1.58	6.9	-	24±2.12	8.8	-	0.42	0.58
	2	24.7±1.07	4.4	98.64	25.4±1.90	7.1	98.23	0.38	0.33
S2	-	20±1.64	8.3	-	20±1.92	9.5	-	0.84	0.77
	4	23.58±1.57	6.7	98.25	24.3±0.97	4	101.25	0.41	0.38
S3	-	23±2.49	10.8	-	26±1.52	5.9	-	0.07	0.36
	6	28.7±1.11	3.9	99.1	32.2±1.68	5.2	100.63	0.01	0.44
S4	-	26±2.63	10.21	-	29±3.02	10.38	-	0.1	0.79
	8	33.9±2.10	6.2	99.71	36.4±2.42	6.7	98.32	0.12	0.79
S5	-	17±1.92	11.3	-	18±2.17	11.91	-	0.49	0.82
	10	27.1±1.05	3.86	100.44	27.6±1.19	4.33	98.57	0.52	0.81
S6	-	19±1.49	7.83	-	20±2.35	7.22	-	0.47	0.40
	12	31.1±2.25	11.73	100.32	31.8±1.35	4.25	99.38	0.57	0.35

*Added as sodium chromate (Na_2CrO_4), a Mean \pm 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.

concentration (28). At a 95% confidence level, the calculated T- and F-values do not exceed the theoretical values (Table 3–6) indicating no significant difference between the proposed and the reference method. Consequently, the developed method is as accurate and precise as that of reference method (Figure 6).

No insoluble Cr (VI) was detected by both the methods for samples, S1, S3 and S4. Results obtained by proposed method were in good agreement with standard method except for sample S3 and S4, where concentration of water soluble Cr (VI) by proposed method was found to be less than that of obtained by standard method. Concentration of water soluble and sparingly soluble Cr (VI) was found to be maximum in sample S4 and minimum in S5 by both

the methods. It was observed that in Portland pozzolan cement samples, 54–55% of the total hexavalent chromium was water soluble. The percentage of sparingly soluble and insoluble Cr (VI) was found to be 30% and 10% respectively. Although, the industries and researchers are more concerned about water soluble hexavalent chromium, sparingly and insoluble Cr (VI) are also toxic (29). Thus detection of all type of Cr (VI) in cement sample is necessary for the safety of workers.

4. CONCLUSIONS

From the present study, we can conclude that variamine blue can be used as a reagent for detection of Cr (VI) in cement samples as the results

TABLE 5. Determination of Sparingly soluble Cr (VI) in various Cement samples

Sample ID	Sparingly soluble Cr (VI) Added* (ppm)	Proposed method			DPC method			T-test	F-test
		Springle soluble Cr (VI) Found	RSD (%)	Recovery (%)	Springle soluble Cr (VI) Found	RSD (%)	Recovery (%)		
S1	-	10±1.48	14.5	-	11±1.58	14.37	-	0.43	0.20
	2	24.7±1.07	10.3	99	25.4±1.90	11.31	100.77	0.19	0.72
S2	-	15±1.14	7.81	-	15±2.07	14.2	-	1.00	0.27
	4	18.9±0.93	4.89	99.58	18.8±0.84	4.45	98.95	0.84	0.85
S3	-	13±1.19	8.91	-	14±1.92	13.55	-	0.46	0.38
	6	18.8±0.96	5.09	98.73	20.2±1.19	5.92	100.8	0.08	0.68
S4	-	15±1.33	9.01	-	16±1.30	8.05	-	0.12	0.97
	8	22.8±1.04	4.55	99.13	23.7±1.65	6.99	98.7	0.35	0.39
S5	-	11±0.23	2.04	-	11±1.62	14.73	-	0.72	0.00
	10	20.9±0.91	4.37	99.52	21.2±2.59	12.21	100.95	0.82	0.07
S6	-	14±1.92	13.94	-	13±1.48	11.59	-	0.39	0.63
	12	26.1±1.87	7.18	100.31	25±1.87	7.5	99.84	0.37	1.00

*Added as Calcium chromate.

TABLE 6. Determination of Insoluble Cr (VI) in various Cement samples

Sample ID	Insoluble Cr (VI) added (ppm)	Proposed method			DPC method			T-test	F-test
		Insoluble Cr (VI) Found	RSD (%)	Recovery (%)	Insoluble Cr (VI) Found	RSD (%)	Recovery (%)		
S1	-	ND	-	-	ND	-	-	-	-
	2	1.94±0.36	18.8	97	2.08±0.26	12.44	104	0.5	0.52
S2	-	11±1.36	12.49	-	10.5±1.6	14.2	-	0.64	0.74
	4	14.7±1.32	9	98	14.8±1.97	13.3	98.8	0.9	0.45
S3	-	ND	-	-	ND	-	-	-	-
	6	5.94±0.99	16.7	99	6.18±0.81	13.17	103	0.69	0.71
S4	-	ND	-	-	ND	-	-	-	-
	8	8.02±0.93	11.64	100.25	8.1±0.82	10.11	101.25	0.89	0.8
S5	-	8±0.78	9.48	-	10.30±1.10	10.64	-	0.01	0.53
	10	18.4±0.81	4.43	102.4	21.2±2.58	12.2	106	0.07	0.05
S6	-	10±0.74	7.49	-	11.1±1.43	12.9	-	0.15	0.23
	12	21.94.1±1.9	8.5	99.72	23.4±2.12	9.1	101.8	0.28	0.81

*Added as lead chromate (PbCrO₄).

obtained by using variamine blue method are in good agreement with standard DPC method. Concentration of hexavalent chromium by this method is found to be slightly less than standard DPC method. Because this method is free from interference caused by Cr (III). Thus the results are more accurate and reliable than the standard DPC method. Advantage of this method over standard method is the high colour stability of dye formed. Sequential extraction of hexavalent chromium was

confirmed by IR and EDX spectroscopy. It has been observed that in Portland pozzolan cement samples (S1-S6), 54–55% of the total hexavalent chromium was water soluble, 30% sparingly soluble and 10% insoluble Cr (VI). Presence of sparingly and insoluble Cr (VI) cannot be ignored, as these forms can also be toxic if inhaled. Thus, the detection of total hexavalent chromium by a suitable method is necessary for the health of workers in the cement industries.

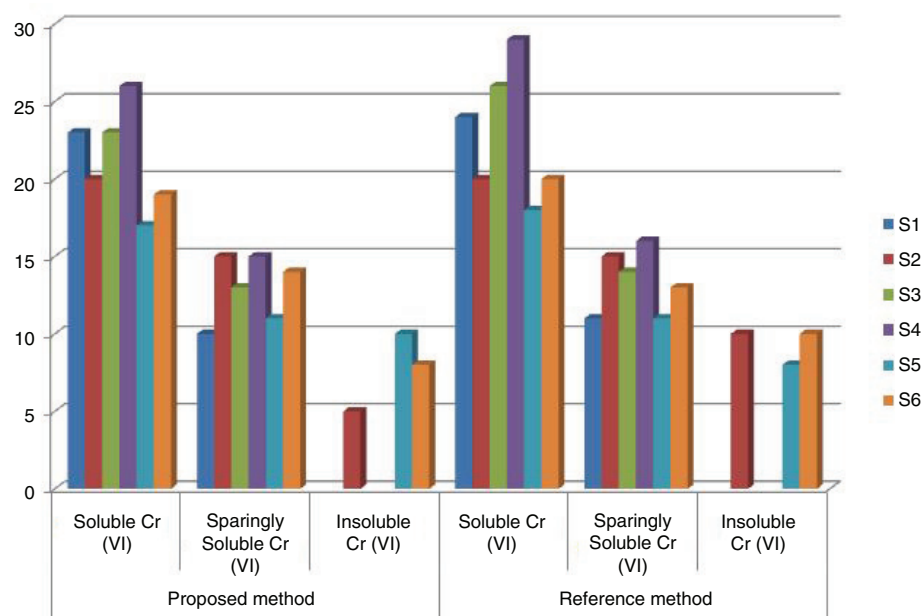


FIGURE 6. Concentration of Cr (VI) found by proposed method and reference method for samples S1-S6.

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SUPPLEMENTARY MATERIAL

Calibration data of proposed method (Varamine Blue method)

DR/2010 User Experiment Report: Hexavalent chromium

High Limit: 12 mg/L of Cr (VI)

Low Limit: 0.05 mg/L of Cr (VI)

Monochromator Wavelength: 556 nm

TABLE 7. Calibration data (Proposed method)

S.No	Standard Concentration	Absorbance (Optical density)
1	0.05	0.003
2	0.1	0.006
3	0.2	0.010
4	0.4	0.023
5	0.8	0.049
6	1	0.062

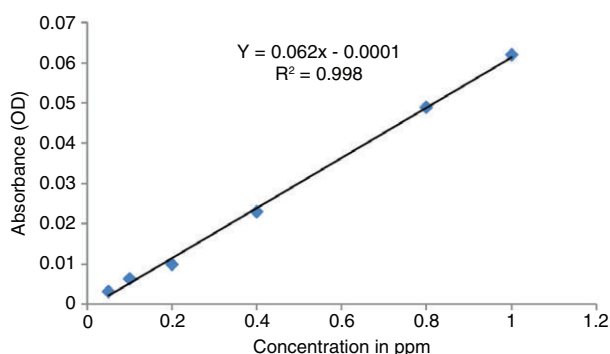


FIGURE 7. Calibration curve (proposed method).

Calibration data of Reference method (Diphenylcarbazide) [given in table 8]

DR/2010 User Experiment Report: Hexavalent chromium

High Limit: 2.0 mg/L of Cr (VI)

Low Limit: 0.001 mg/L of Cr (VI)

Monochromator Wavelength: 540 nm

TABLE 8. Calibration data (Reference method)

S.No	Standard Concentration	Absorbance (Optical density)
1	0.05	0.010
2	0.1	0.041
3	0.2	0.090
4	0.4	0.220
5	0.6	0.290
6	0.8	0.422
7	1	0.520

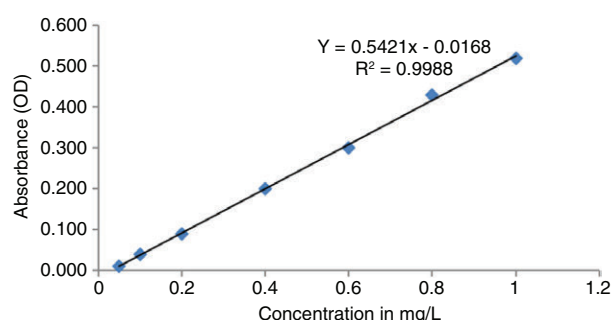


FIGURE 8. Calibration curve (Reference method).