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Spectrophotometric Determination of Hexavalent Chromium Content in Commercial Cement – an Assessment of the Optimal Conditions for the Analysis of Chromium (VI)

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Abstract

Throughout the world the content of hexavalent chromium in cement is under control. In Europe, the new restrictions on the amount of this substance prohibit the use of cement having concentration more than 2 ppm. However, hexavalent chromium contents in cements above 2 mg kg^{-1} are still found frequently. The study represents a contribution to the establishing of possible limitations of this compound. The analyses showed that 7 of 10 cements analyzed by us satisfy the requirements for limit value of 2 ppm for water-soluble chromium (VI) in cement available in our market. Chromium (VI) was analyzed using the reference diphenylcarbazide spectrophotometric method from TRGS 613.The results for the absorbance spectra showed that maximum absorbance peak of the hexavalent chromium complex was at 538.7 nm. It was recorded in the range 25-200μg Cr(VI) L^{-1}) using Varian Cary 50 reader system. Parameters such extraction time in dependence of the rotary of the stirring and wavelength variation were optimized and the results obtained were satisfying. In the present work a cement sample from the Devnya manufacturer was tested and it was found that this cement satisfies the European standard requirements. Finally, this application describes a simple and rapid, cost-effective analysis to measure low levels of hexavalent chromium.

Keywords:

Hexavalent chromium in cement; spectrophotometric determination

1. Introduction

Hexavalent chromium is one of the most widespread toxic environmental pollutants, which is inevitably present in building materials such as cement and concrete [1]. Hexavalent chromium is highly toxic and known human carcinogen and mutagen [2, 5-8]. Cement producers are required to control the content of chromium (VI) in various types of production. From January 17th, 2005 in Europe new restrictions on the amount of chromium (VI) in cement came into force by the Directive 2003/53/EC [9]. Water soluble chromium in cement is limited to 2 mg/kg in European standards and the restriction is applied to a wide range of products such as mortars, grouts, tile adhesives etc. [2-4]. The construction trade cooperative, health agencies, and cement industries adopted the “Low chromate cement and formulations” trade regulation.

1.1. Hexavalent chromium in cement

Chromium is a naturally occurring element in the natural environment in rocks, animal and plant species, soil, volcanic dust and gases. High levels of chromium are found in

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minerals such as chromite. Elevated concentrations of chromium (VI) in the environment are the result of industrial pollution.

Trace element chromium exists as raw materials mainly used for cement production. Its content is mainly in the form of chromium (III), which is inert and insoluble, but during the course of treatment, chromium (III) can be partially oxidized to Cr (VI). Chromium(VI) compounds are powerful oxidants, and, except the hexafluoride, contain oxygen as a ligand, such as the chromate anion (CrO_4^{2-}) and chromyl chloride (CrO_2Cl_2) [8]. Chromium compounds have never been deliberately added to cement, except in China to save time, hence the cost of production [10].

1.2. European legislative requirements

Recently, the European Parliament and the Council published a Directive (2003/53/EC) relating to restrictions on the marketing and strict limitations on the use of cement containing more than 2 mg kg^{-1} of soluble chromium (VI) [9]. In the early 2005 this Directive was registered as a national regulation of all EU members. At the same time CEN/TC51 Technical Committee has prepared a draft European standard (PrEN 196-10: 2004) for the determination of water soluble chromium (VI) in cement [11].

Cr(VI) cannot be removed from the raw cement economically, but must be reduced to Cr(III). In order to fulfill the strict Directive limitations of 2 ppm water soluble chromium (VI) the cement producers are obliged to add reducing agents such as ferrous sulfate, ammonium ferrous sulfate, manganese sulfate etc. Furthermore, the producers must provide information on safe shelf life [12]. Due to the manner and form chosen by most cement producers for adding reducing agents, the monitoring of chromium (VI) led to different analytic results; the 2 ppm limit value for chromium (VI) is often exceeded.

For the reasons mentioned above, the monitoring of hexavalent chromium is of great importance in order to preserve the human health and to ensure minimal environmental impact.

Several analytical instrument techniques can be employed for the determination of this hazardous substance such as spectrophotometry [13,14], ion chromatography [15], pulse chromatography [16], by the use of HPLC-ICP-MS, FPLC-ETAAS and selective extraction techniques [14], but the most applied in routine analysis is determination by UV-Vis spectrophotometry [13,14].

According to the literature it is fact that there is currently no approved method for measuring Cr(VI) in cement and no uniform extraction procedure proposed. It was found that the leachability of for the soil stabilized by cement was high in some cases, and the amount of Cr(VI) leached was larger than could be accounted for by the "soluble Cr(VI)" in the cement as determined by the standard method [8].

The new Guidance on the application of this European standard ((PrEN 196-10: 2006, Annex B) claims that occasionally the method can be applied without modification but in many other cases it will be necessary to modify the extraction and/or filtration procedure [11].

In this article, various sample preparation procedures, are evaluated for the determination of Cr (VI) in cement by UV-Vis absorption spectroscopy based on the German TRGS 613 [12].

For the estimation of the optimal time of extraction different extraction times were applied. In order to reduce the time of the analysis and hence the cost of the analysis, the optimal extraction time was found.

2. Experimental

2.1. Reagents and solutions

All chemicals (Sigma Aldrich) were of analytical-reagent grade and employed without further purification. Distilled water was used in the preparation of the various solutions.

All solutions were prepared according to the German TRGS 613-standard method [12]. Thus, the stock $K_2Cr_2O_7$ solution of 1 g L^{-1} was prepared by dissolving 2.829 g of dried potassium bichromate in 1000 cm^3 of distilled water. The standard solution of 5 mg L^{-1} Cr (VI) was prepared as 5 cm^3 of the stock solution were pipetted into a volumetric flask and diluted with distilled water to 1000 cm^3.

Diphenylcarbazide solution was prepared by dissolving 1 g of 1,5-diphenylcarbazide (DPC), $CO(NHNHC_6H_5)_2$, in 100 cm^3 acetone and acidified with a drop of acetic acid. Hydrochloric acid solution was prepared by mixing of concentrated HCl with water in a ratio 1:1.

2.2. Instrumentation

UV-Vis spectrophotometer (Carry 50 Scan, Varian) equipped with a 10mm short path length cell was used for absorbance measurements. The spectrophotometer is controlled by Cary WinUV software.

2.3. Sample preparation

The cement samples were prepared using paste extraction method based on TRGS 613. 10.0 g of cement sample was accurately weighted (±0.01 g), then 40 cm^3 of water were added and the mixtures were stirred for 15 min (stirred bar 40 mm, 300 rpm). The suspensions were filtered through 0.45 μm filters. Finally 20 cm^3 were pipetted from the filtrate and were treated for the final preparation.

2.4. Analytical procedure

The construction of the calibration curve is achieved by measuring the absorption of six standard solutions against blank. Briefly, standard solutions containing 2.5 to 20.0 mg L^{-1} chromium (VI) were prepared as consequently 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 cm^3 of chromium standard solution were pipetted into 100 cm^3 volumetric flasks. The solutions were diluted with approximately 40 cm^3 of water. Then to each flask, both 2 cm^3 of hydrochloric acid and 2.0 cm^3 of the diphenylcarbazide indicator solution were added and diluted to the corresponding volume. The reagents were mixed thoroughly by swirling and the flasks were mixed once again and left for 15 minutes to allow color development. The cement filtrates are treated as to each flask 2 cm^3 of hydrochloric acid was added, and then 2.0 cm^3 of the diphenylcarbazide indicator solution were added. The pH of the solutions should be 1 to 2; if no it should be adjusted with hydrochloric acid and diluted to the volume of 100 cm^3. The absorbance of the solution was measured after 15 – 30 minutes. The above procedure was applied to the leachate solutions.

The absorbance of the colored solutions has a linear relationship to the chromium (VI) concentration and it is measured at wavelength 540 nm against the blank.

2.5. Evaluation of the concentration

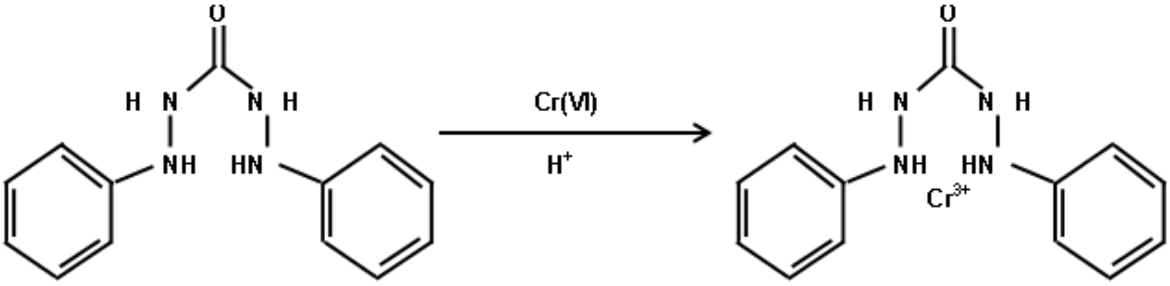
The following equation was use for the calculation of the Cr (VI) concentration:

$Cr(VI)_{soluble} = C\ V_1/M\ V_2$, g

where $Cr(VI)_{soluble}$ is the concentration of water soluble hexavalent chromium (ppm), C is the concentration of Cr (VI) in mg in 100 cm^3 volumetric flask, V_1 is the volume of water in which the original sample is suspended, cm^3, V_2 is the volume of filtrate which is transferred in the volumetric flask, cm^3, M is the mass of the cement sample, g.

3. Results and discussion

Various cement samples from the Bulgarian market were analyzed. The analyses are carried out without oxidation process. The performance of the extraction of the hexavalent chromium was achieved by the procedure of TRGS 13. The analytical procedure involves forming a complex that is purple-red in color (Cr(VI) oxidizes 1,5 diphenylcarbazide to 1,5 diphenylcarbazone).



It is necessary to remember that this complex forms and is stable only in an acidic environment and for that reason it is envisaged the acidification of the solution containing chromate extracted from the cement. The maximum absorption is at l=540 nm. The change in spectras over the range 190-1100 nm (Figure2) were recorded in two separate experiments using the WinUV Scan.

Spectrophotometric measurement should be made at least 15 but not more than 30 minutes after the addition of reagent to the sample. The amount of radiation absorbed is compared with a previously obtained calibration plot and is related to the metal concentration by the calibration data. Accuracy depends on the promptness of the analysis. According to the literature detection limit of the method is 3 µg L^{-1}, interfering substances - iron, vanadium, and mercury may interfere [17].

Results for the unknown Cr(VI) in cement extracts determined from using the standards are summarized in Table 1. The precision (RSD) and relative error is good and the time required to analyze the sample is minimal.

Table 1 Spectrophotometric analyses of cement samples

Cement sample No	Concentration of Cr (VI), $\bar{x} \pm tS/\sqrt{n}$, (mg kg^{-1})	RSD $S_r = (S/\bar{x})\,100$, (%)
I	2.5 ± 0.2	12.8
II	1.2 ± 0.1	9.2
III	1.1 ± 0.1	4.0
IV	1.3 ± 0.1	4.8
V	0.9 ± 0.1	8.1
VI	3.0 ± 0.1	1.1
VII	2.3 ± 0.1	2.2
VIII	1.8 ± 0.2	6.5
IX	2.0 ± 0.1	3.2
X	1.6 ± 0.1	6.1

Number of determination *n, 5; t*, Students *t*-value at 95% probability; *S*, standard deviation; $\bar{x}$, an average

It should be noted that according to the current regulations, the maximum level allowed for content of Cr (VI) in cement are higher for sample I, VI and VII. However, the levels of hexavalent chromium present in the next seven samples satisfy the European standards.

In this study a sample of the cement manufacturer Devnya was tested because of its meeting the European standard requirements.We accepted the results obtained by the paste extraction method from TRGS 613 as an example (the mixture is agitated at 300 rpm for 15min.) and compared them against the concentration of hexavalent chromium in the extracts obtained as follows: 1) at constant speed of stirring and time of extraction 5, 10, 15 and 20 minutes respectively, and 2) at speeds of 500, 400, 300 rpm and time of extraction 10, 12.5 and 15 minutes respectively.

Table 2. Determination of Cr(VI) of the filtered extracts using different extraction time

Cement sample No	Concentration of Cr (VI), $\bar{x} \pm tS / \sqrt{n}$, (mg kg^{-1})	RSD $S_r = (S/ \bar{x})\ 100$, (%)	Recovery (%)
I. 5 min, 300rpm	0.584± 0.009	2.86	78.92
II. 10 min, 300rpm	0.616 ± 0.039	11.79	83.24
III. 15 min, 300rpm	0.74 ± 0.013	3.31	100
IV. 20 min, 300rpm	0.748 ± 0.012	3.05	101.08

Number of determination *n, 5; t*, Students *t*-value at 95% probability; *S*, standard deviation; $\bar{x}$, an average

As it can be seen from the Table 2 the cement extracts of samples I and II showed poor recovery, especially for I sample. The accuracy for sample II was poor but the precision and repeatability were good.

The results in Table 2 and Fig.3 indicate that the amount of Cr(VI) extracted strongly depends on the extraction time at constant speed of the rotary. In order to reduce the time for the analysis it was carried out research on the procedure for the extraction of chromium (VI). The curve of Fig.4 shows that the amount of the Cr(VI) in the extracts increases with the period of extraction.

Table 2 shows that the recovery was lower with lower time of extraction at 300 rpm but the recoveries of sample II and sample III in Table 3 are very good. Therefore the procedures of chromium (VI) extraction at 12.5 min and 400 rpm and 10 min, 500 rpm can be applied.

Table 3. Determination of Cr(VI) of the filtered extracts using different extraction time and revolutions per minute

Cement sample No	Concentration of Cr (VI), $\bar{x} \pm tS / \sqrt{n}$, (mg kg^{-1})	RSD $S_r = (S/ \bar{x})\ 100$, (%)	Recovery, (%)
I. 15 min, 300 rpm	0.688 ± 0.012	3.29	100
II. extraction 12.5 min, 400 rpm	0.692 ± 0.041	10.99	100.58
III. extraction 10 min, 500 rpm	0.704 ± 0.009	2.25	102.33

Number of determination *n, 5; t*, Students *t*-value at 95% probability; *S*, standard deviation; $\bar{x}$, an average

The determination of the analyte is carried out by the absorption of radiation at a fixed value of wavelength (540 nm). The kinetic curve of formation of chromium dyphenilcarbazide complex was registered. The analysis is started after the components are mixed. The kinetic curve shown in Fig.5 determines the reaction rate.

The calibration curve (Fig.6a) demonstrate an excellent linearity and reproductively. Figure 6 b shows an overall scan of the standards prepared in the concentration range 25-200 mg L^{-1}. The scan of chromium (VI) standards solutions (Fig.6b) showed that maximum absorption is not 540 nm as it is in the standard method. Thus l_{max} for the standard 6, standard 5 and standard 4 having concentrations 200, 150 and 100 mg Cr(VI) L^{-1}), respectively, is at 538.7 nm. l_{max} for the standard 3 is at 538 nm and l_{max} for standards 2 and l_{max} for standards 1 are moved toward the shorter wavelengths. Therefore, wavelength maximum l_{max} is shifted to shorter wavelengths with a decrease in standard solutions concentration.

The innovative Cary WinUV software gives the final results without acquiring additional calculations. The results presented in this work demonstrate an excellent linearity and reproductively for rapid and sensitive measurements of low levels of hexavalent chromium in cement. This simple and cost-effective methodology has a potential for cost saving and increasing sample throughput in comparison with other approach such as HPLC-ICP-MS, FPLC-ETAAS and selective extraction techniques in the screening of Cr(VI).

4. Conclusion

Since the European Community has established rules for implementing the restrictions on the amount of toxic metals such as hexavalent chromium, thus monitoring of chromium (VI) is of great importance for the preservation of human health and to ensure minimal environmental impact.

In the present work 3 out of 10 kinds of cements analyzed did not satisfy the European standard requirements. In this study it was found that the amount of the Cr(VI) in the extracts increases with the period of extraction. The concentration of Cr (VI) is dependant from the speed of the rotary. Therefore, in order to reduce the time of the analysis the procedures of chromium (VI) extraction at 12.5 min and 400 rpm and 10 min, 500 rpm can be applied.

It was found that the wavelength maximum l_{max} is shifted to shorter wavelengths with a decrease in standard solutions concentration. Thus, the maximum absorbance value at 538.7 nm was recorded in the range 100-200mg Cr(VI) L^{-1}) using Varian Cary 50 reader system. Therefore, for spectrophotometric determination of hexavalent chromium content in cement by the reference method from TRGS 613, the optimal l_{max} is 538.7 nm.

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