Analytical methods for the determination of Cr^{6+} from fixed source emissions

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Abstract
This study aimed to develop two analytical methods for the determination of Cr^{6+} from fixed source emissions, such as the molecular absorption spectrophotometric method (UV-VIS) and the graphite furnace atomization absorption spectrometry method (GTAAS). The first stage in the development of analytical methods involves establishing the optimal operating conditions for, taking air samples, treating them for analysis, and the proceeding for analysis, followed by validating the method by determining performance parameters. For both methods is highly recommended, the use of isokinetic sampling with a sampling probe by the heated glass, quartz, or PTFE. The limit of detection and the limit of quantification were concluded to be 12.38µg/m^3 and 40µg/m^3, respectively for the UV-VIS method and the GTAAS method 0.12 µg/m^3 and 0.54 µg/m^3 respectively.

Keywords: *isokinetic sampling, fixed source emissions, UV-Vis, GTAAS*

INTRODUCTION

Given the toxicity of the Cr^{6+} compounds in recent years, several studies have been developed to identify and quantify them in the environment. Given its carcinogenic, mutagenic character, with particularly strong effects on the human body, there is a tendency to identify substitutes of Cr^{6+} compounds in technological processes, where possible, or, where they cannot be replaced, conditions are imposed such us strict emission monitoring and emission limit values as low as possible. Exposure to hexavalent chromium compounds can cause skin allergies, dermatitis, and ulcers, perforation of the nasal septum, and bronchial carcinomas [1-3].

In a few situations Cr^{6+} is found only in this form in environmental factors, most of the time in the matrix we have met a mixture of chromium compounds in the oxidation state III and VI. The determination of Cr^{6+} from environmental factors, therefore, suppose, first of all, a species of the two forms of chromium, Cr^{6+} and Cr^{3+} [4-6]. The best-known method of species is based on the reaction of Cr^{6+} with 1,5-diphenylcarbazide (DPC) in a strongly acidic environment (Fig.1) with the formation of a complex combination of Cr^{3+} with 1,5-diphenylcarbazone of red-purple colour whose intensity that is directly proportional to the Cr^{6+} concentration [7].

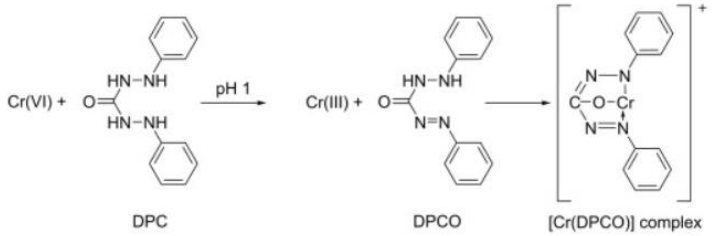


Fig. 1. The reaction of 1,5-diphenylcarbazide (DPC) with Cr^{6+}

In the main, the methods for determining hexavalent chromium are divided into two categories [8-10]:

- *chromatographic methods* are based on liquid chromatography coupled with specific detectors. They have the advantage that they require a simple pre-treatment of the sample,

they are fast but they need high-performance equipment that will be not always available.

- *non-chromatographic methods* that first involve a sample separation procedure, such as solid-phase extraction or liquid-liquid extraction. The most commonly used techniques are Spectrometric techniques. These methods are more time spending but are less expensive and easy to apply in a routine lab activity.

The development of one method for the determination of Cr^{6+} from the emissions of fixed sources implies the establishment of the optimal sampling conditions, sample preparation, and analytical quantification but also the validation of the method by determining the performance parameters and verifying the adequacy for the purpose. A variety of spectrophotometric and colorimetric techniques has been designed to determine Cr^{6+} [11-14]. The most common colorimetric method uses the selective reaction of Cr^{6+} with 1,5-diphenylcarbazone complex. Compared to the trivalent form, hexavalent chromium is considered an extremely dangerous metal due to its oxidizing, mutagenic, and carcinogenic properties. Cr^{6+} compounds are approximately 1,000 times more cytotoxic and mutagenic than Cr^{3+} [15-17].

This study aimed to develop two analytical methods for the determination of Cr^{6+} from fixed source emissions, respectively the molecular absorption spectrophotometric method (UV-VIS) and the graphite furnace atomization absorption spectrometry method (GTAAS).

For both methods is highly recommended, the use of isokinetic sampling with a sampling probe by the heated glass, quartz, or PTFE.

MATERIALS AND METHODS

Equipment

The experiments for establishing the optimal conditions for the analysis of hexavalent chromium by UV-VIS technique were performed using a CINTRA 5 UV-VIS spectrophotometer by GBC Scientific Equipment Pty Ltd. Cintra 5 UV-VIS spectrophotometer with double beam covering a wide spectral range, from 190-1100 nm. For pH measurement, we used Multiparameter model Seven Excellence, METLLER TOLEDO AG SWITZERLAND with pH electrode InLab Expert Pro-ISM. The experiments for establishing the optimal conditions for the analysis of hexavalent chromium by GTAAS technique were performed using an AAS FS 280 spectrometer, by-VARIAN equipped with graphite oven type GTA 120 and autosampler-dispenser PSD 120.

Reagents

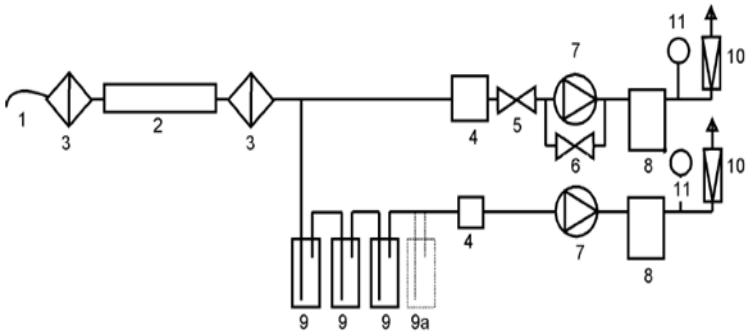
Reagents and chemicals used in this study were of analytical grade. All glassware used was decontaminated by soaking it in 10% (v/v) HNO_3 solution for 24 hours and rinsed with ultrapure water. Ultra Clear TWF UV water purification system, Manufacturer SIEMENS (SG WATER) -Germany was used to obtain ultrapure water. Sodium hydroxide (97%, Sigma Aldrich), 0.1M NaOH absorbent solution; 1,5-diphenylcarbazide reagent (≥98,0%, Sigma Aldrich), 0.5% solution (w/v) DPC was dissolved in acetone (freshly prepared); Sulfuric acid (96%, ultrapure, ChemLab), 5M H_2SO_4 solution; Sodium chloride, saturated solution, 300 g/L NaCl, (99.99%, Merck); Isoamyl alcohol (≥ 99.0%, Sigma Aldrich); A standard solution of 1000mg/L Cr^{6+} (Sigma-Aldrich) was used to calibrate the method.

Sampling

For both methods, the sampling conditions were the same: isokinetic sampling with heated glass, quartz or teflon sampling probe, and retaining Cr^{6+} in an absorbent solution containing a 0.1M NaOH.

In figure 2 it is the sampling system [18] that it was used for UV-VIS and GTAAS verification methods of real samples. In the time of sampling, it was paid attention in maintaining and

verification of pH absorbent solution, more than 8.5 for the reason of reduction of Cr^{6+} to Cr^{3+}, a case that invalidated the samples.



1 nozzle
2 probe
3 filter (either behind or in front of the probe)
4 dryer
5 main-stream valve
6 by-pass valve
7 pump
8 gas volume meter
9 absorber
9a safety bottle (optional)
10 gas flow meter
11 temperature and pressure measurement

Fig. 2. Schematic of an isokinetic system for air sampling on the filter and absorbent solutions

The exposed absorbent solutions, after the pH checking, were taken quantitatively together with the washing solutions of the sampling system into a uniquely identified container (solution P1) and the filter is transported in a Petri dish in the laboratory extraction.

The sample preparation for analysis involves the same steps for both methods in the first phase of Cr^{6+} recovery from absorbent and filter solutions: extraction of water-soluble Cr^{6+} from the filter in P1 solution by stirring in the ultrasonic bath for 30 minutes, followed by filtration to remove any suspended particles and potential traces of precipitated Cr^{3+} and makeup to the mark with the absorbent solution (solution P2) in a dimensioned flask.

RESULT AND DISCUSSION

Determination of Cr^{6+} with UV-Vis spectrometry

The determination of Cr^{6+} with UV-Vis spectrometry involved pipetting 35 mL of absorbent solution exposed into a 100 ml beaker, adjusting the pH to 1.0 ± 0.2 with 6N sulfuric acid followed by a quantitative collection of the solution into a 50 mL volumetric flask. It was added 1.0 mL of 1.5% diphenylcarbazide solution 0.5% in water, mixed and left to stand for 10 minutes untill developed colour. The absorbance was measured at a wavelength of 540 nm from the control sample using tanks with an optical path of 50 mm.

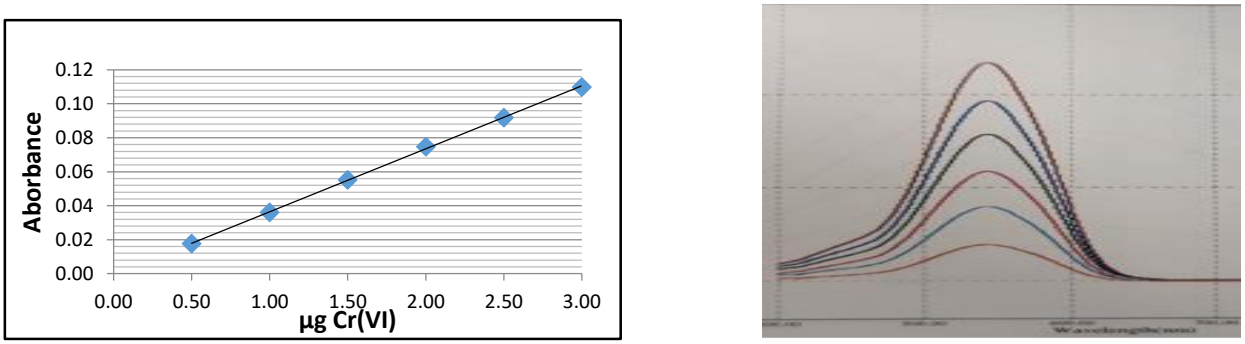
The analytical parameters of the optimized method were: 1) the optimal wavelength, 2) the volume of 1,5-diphenylcarbazide 0.5%, and 3) the stability of the coloured complex. The results of the optimization tests are presented in Table 1.

Table 1. Test results to establish optimal operating conditions.

Optimized parameter	Tests performed	The optimal value
Wavelength	Was drawn the spectrum for a series of solutions with concentrations from 0.5 to 3μg Cr^{6+}/volumetric flask, noting that the wavelength corresponding to the maximum absorbance was 540 nm.	540 nm
DPC volume 0.5%	The volume of 1,5-diphenylcarbazide solution was varied: 0.5 ml; 0.75ml, 1ml; 1.5ml, and 2ml keeping the other reagents constant, and absorbance was measured for Cr^{6+} concentrations between 0.5 - 3μg/volumetric flask. It was observed that starting with 0.75ml of soil. DPC 0.5% absorbance remains approximately constant.	1mL
Stability of the complex	The time variation of the absorbance of the solutions of 1 and 3μg Cr^{6+}/volumetric flask was registered; maximum absorbance is obtained after 10 minutes and remains constant for 2 h.	2 h measurement

The working range for plotting the calibration curve was established by applying the F homogeneity test of concentration dispersions located at the extremes of the proposed working range (0.5-3µg/volumetric flask) and the test results showed the lack of significant differences in dispersions at the working range, so the concentration range was 0.5-3 µg/volumetric flask Cr^{6+} meets the requirements of the statistical test and can be used as a working range for the tested method.

Once the working range was established, the calibration curve was drawn in 6 points: 0.5; 1; 1.5 2; 2.5 and 3µg Cr^{6+}/ volumetric flask inscribing on the ordinance of the absorbents and the abscissa the concentrations of the standards, in µg (Fig. 3). Calibration curve parameters validate the accuracy and precision of the method calibration (Table 2).



a b

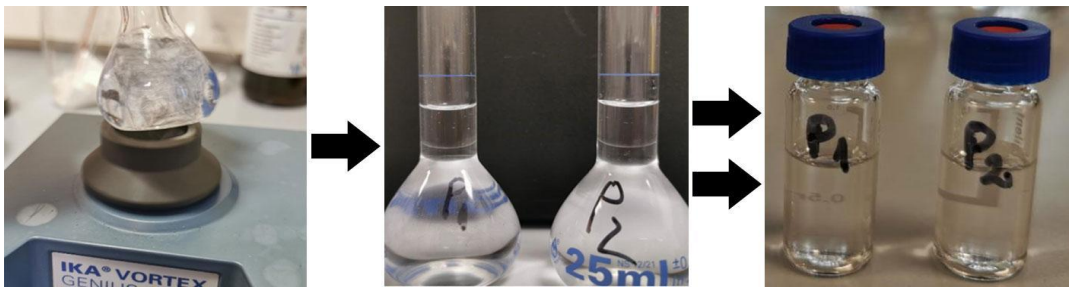
Fig. 3. a) Calibration curve on the range of 0.5-3 µg Cr^{6+}/volumetric flask, b) Overlapping the spectral profiles of Cr^{6+} standard solutions obtained by the UV-VIS method

Table 2. Hexavalent chromium calibration data for the range 0.5-3 µg Cr^{6+}/volumetric flask

Calibration Curve Parameters	x_i (µg/L)	0.5	1	1.5	2	3
	$y_i(H_{peak})$	0.0176	0.0361	0.0553	0.0747	0.1099
	y = -0.0006+0.0370x					
	a = 0.00431		b = 0.01853		R = 0.9996	
	S_y = 0.0008		S_{x0} = 0.0204		V_{x0} = 1.17%	

Determination of Cr^{6+} with electrothermal atomization (graphite furnace) - GTAAS method

25 mL of the exposed sample was transferred in a 50 mL volumetric flask, adding 0.25 mL of 5M H_2SO_4 solution and 1.00 mL of DPC 0.5% solution. The mixture was vortexed for 10 minutes to complete the reaction chain. Afterward, was added 20 mL of NaCl solution (300 g/L) and 2.5 mL of isoamyl alcohol. The mixture was stirred for 5 minutes, followed by the liquid-liquid extraction. The organic solvent was transferred to the vial of the PSD 120 carousel and an amount of 10 µL was injected into the graphite furnace. The pre-concentration factor of the method was 10. Figure 4 shows the steps taken to determine hexavalent chromium by the GTAAS method.



a) b) c)

Fig. 4. The steps are taken to determine hexavalent chromium by the GTAAS method: a) crom-1,5-difenilcarbazona complex formation; b) isoamyl alcohol liquid-liquid extraction; c) extracts of Cr^{6+}

Temperature program optimization. To obtain the best analytical results in graphite furnace atomic absorption spectrometry (GFAAS), it is necessary to optimize the furnace temperature program. This ensures the reduction of interferences due to the sample matrix without loss of the analyte. A temperature program for the graphite furnace analysis contains at least three basic steps: *drying, calcination, and atomization*. By selecting the optimum temperature and time, we obtain the highest analyte absorption signal and the lowest background noise signal. Spectral interferences that occur in the presence of anions or cations of iron or aluminum are associated with the optimization temperature [19, 20]. Therefore, the optimization of the chromium temperature program is very important to eliminate or minimize both analytical losses and possible interferences. The highest signal was obtained when the atomization temperature was set at 2400°C. The optimum drying, calcination, and atomization temperatures were 150°C, 1100°C, and 2400°C, respectively. The graphite tube was cleaned at a temperature of 2600°C. The optimal flow rate of argon was 0.3 L/min for the drying, calcination, and cleaning stages. Because the recommended wavelength for determining chromium is 357.9 nm, it was not necessary to activate the background correction, this being used in the case of wavelengths with values lower than 350nm. It was also not necessary to use matrix modifiers because it was found that they do not bring any improvement to the method. To increase the signal-to-analyte to background-signal ratio, a graphite tube with a pyrolytic platform was used, recommended in the case of loaded matrices. Pyrolytic graphite has an additional advantage because the contamination from the sample is greatly reduced for most of the elements [21]. The tests for optimizing the temperature program and establishing the modifiers were performed with a solution of 6 μg/L Cr^{6+} in isoamyl alcohol. The setting for the GTAAS analysis is shown in Table 3.

Table 3. GFAAS instrumental parameters for the quantification of hexavalent chromium

Parameters				
Calibration Mode			Concentration / (μL^{-1})	
Measurement Mode			Peak Height	
Replicates			2	
Wavelength			357.9 nm	
Slit Width			0.2 nm	
Lamp Current,			7.0 mA	
Background Correction			BC Off	
Calibration Algorithm			Linear	
Graphite tube type			platform tubes, pyrolytic coated	
Sample Volume			20 μL	
Step	Temperature (^{0}C)	Time (s)	Flow (L/min)	Gas Type
1	45	20	0.3	Normal
2	90	25	0.3	Normal
3	120	10	0.3	Normal
4	150	5	0.3	Normal
5	1000	10	0.3	Normal
6	1000	5	0.3	Normal
7	1100	0.7	0.0	Normal
8	2400	0.8	0.0	Normal
9	2400	2.5	0.0	Normal
10	2600	2	0.3	Normal
11	400	9.7	0.3	Normal

Taking into account the special features of the matrix in which the analyte is found, isoamyl alcohol, as seen in Table 3, the increase in temperature on the drying stage was slower, increasing the time overtime to prevent losses due to rapid evaporation of alcohol and avoid ignition of its vapors.

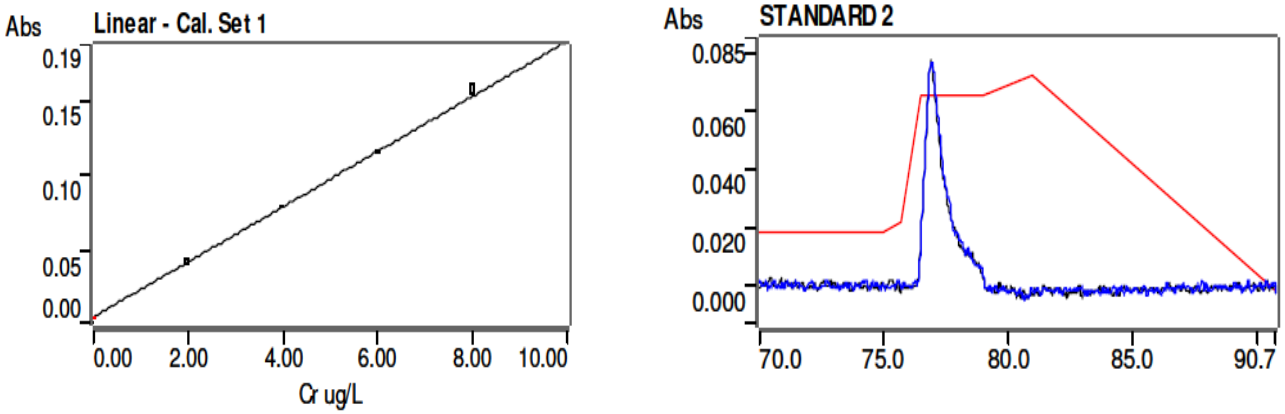
Calibration range. For the graphite furnace technique, it is necessary to prepare a bulk solution of known concentration, from which, with the help of the dispenser - autosampler system, the standard solutions are automatically prepared and injected to draw the calibration curve. For the method for determining hexavalent chromium, a calibration range consisting of five points was chosen, respectively 2 µg/L, 4 µg/L, 6 µg/L, 8 µg/L, and 10 µg/L Cr^{6+}. The bulk was prepared at a concentration of 10 µg/L Cr^{6+}.

Using the pairs of values of hexavalent chromium concentration (X_i) and absorbance (Y_i) presented in Table 4, the calibration line was drawn by inscribing on the ordinance the absorbents of the standard samples, and on the abscissa the corresponding hexavalent chromium concentrations, in µg / LCr^{6+}.

Table 4. Hexavalent chromium calibration data for the range 2-10 µg / L Cr^{6+}

Calibration Curve Parameters	x_i (µg/L)	2	4	6	8	10
	$y_i(H_{peak})$	0.0415	0.0768	0.1144	0.1561	0.1880
	y = 0,00431 + 0,01853x					
	a = 0.00431		b = 0.01853		R = 0.9996	
	S_y = 0.0025		S_{x0} = 0.13406		V_{x0} = 2.23%	

Using the SpectrAA software of the used equipment, the calibration curve for the hexavalent chromium presented in figure 5 was drawn, writing on the ordinance the absorbents of the standard samples, and on the abscissa the corresponding concentrations of hexavalent chromium, in µg/LCr^{6+}. Calibration curve parameters validate the accuracy and precision of the method calibration (Fig. 5).



a) b)

Fig. 5. a) Calibration curve in the range 2 -10 µg/L Cr^{6+}; b) the spectrum profile,4 µg/L Cr^{6+}

In-house methods validation for determining a Cr^{6+} source from fixed sourced emissions. The validation of the method is defined by a certain analytical requirement and the confirmation that the considered method should be capable of executing the required/imposed application [22, 23]. The objective of validating an analytical method is to demonstrate that it is suitable for the desired purpose. Both methods were subjected to validation and the values of the following performance and methodology parameters were determined: calibration range, linearity, Limit of Detection (LOD) and Limit of Quantification (LOQ), recovery accuracy, bias, repeatability, and measurement uncertainty. Table 5 shows the comparative parameters of the performance values for both methods.

The calculation of the performance parameters related to the volume of gaseous effluent sampled, in µg m^3, was performed in the following conditions: volume of gaseous effluent sampled: 60 l; solution volume P2: 200 ml.

Table 5. Parameter performance values of the determination methods of Cr^{6+} emissions

Parameters	Method UV-Vis	Method GTAAS
Calibration range	0.5; 1; 1,5; 2; 2.5; 3 µg Cr^{6+}	2; 4; 6; 8; 10 µg/L Cr^{6+}
Limit of Detection, LOD, (µg/m^3)	12.38	0.12
Limit of Quantification , LOQ,(µg/m^3)	40	0.54
Repeatability, %	1.78	9.22
Bias, %	5.3	-16.84
Recovery, %	105.3	83.16
Measurement uncertainty, %	4.0	17.3

CONCLUSIONS

The analytical methods developed in its study allow us to determine the hexavalent chromium in the gaseous effluent from various industries. In the case of high hexavalent chromium emissions related to Electroplating and Anodizing industry, we recommend using the method of molecular absorption spectrophotometric method (UV-VIS).

In the case of glass factories or incinerators, we recommend the method of graphite furnace atomization absorption spectrometry method (GTAAS) whose sensitivity is much better.

Following the validation, the performance parameters of both methods fall within the acceptability criteria specific to the techniques used.

Based on the tests performed for the development and validation of the methods, we appreciate that both methods can be used to determine the Cr^{6+} concentration from the emissions of fixed sources.

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