Determination of Total Chromium in Workplace Atmospheres

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The determination of chromium in most samples is extremely difficult because of very low levels present. The only widely available analytical method with sufficient sensitivity is graphite furnace atomic absorption spectrometry (GFAAS), yet values reported in the early literature were divergent. This paper describes a new analytical method to estimate occupational exposure levels of total chromium in workplace atmospheres by atomic absorption spectrometry with a background correction using a cellulosic membrane for sample and solubilization through wet mineralization with nitric acid. The atomisation temperature used was 2500°C and a cleaning step for graphite furnace after each samples serie was realized. The validation of GFAAS method was made in concordance with International Conference on Harmonization (ICH). Standard calibration solutions were used for the range 10 - 100µg/L and they were used in calculating the performance parameters for this method. The performance characteristics established during the "in-house" validation of the method indicate that it gives good information about mobility of total chromium in workplace atmospheres and it was validated. Determinations were undertaken over a three-year period in different points of a chroming room and led to different results for the total chromium concentration, ranging between 0.0018-0.051 mg/m^3.

Keywords: total chromium, GFAAS, "in-house" validation, workplace atmospheres

Trace heavy metals are the major pollutants in the environment. It has been widely recognized that the impact of detrimental heavy metals on the ecological system, biological organisms as well as on human health does not only depend on the total amount of the element, it also depends significantly on its chemical forms [1].

Chromium is a metallic element that can be found primarily in the mineral chromate, which is present in soil, waters, rocks, fauna and gases. Chromium is a major pollutant for environment, usually as a result of some industrial pollution including tanning factories, steel works, industrial electroplating, wood preservation and artificial fertilizers [2].

Chromium species exist mainly in two different oxidation states in the environment, Cr (III) and Cr (VI). Cr (III) is known to be an essential trace nutrient involved in the mechanism of the pancreatic hormone insulin and/or glucose metabolism [3]. On the other hand, Cr (VI) is toxic to biological systems especially to humans. Chromium (VI) is water soluble and extremely irritating and toxic to the human body tissue due to its potential and permeability of biological membranes [4]. The major toxic effects of Cr (VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and local effects in lungs [5]. Occupational exposure to total chromium can be determined by means of workplace atmospheres measurements and biological monitoring (in urine) [6].

This paper aims to present a new determination method for total chromium in workplace atmospheres using graphite furnace atomic absorption spectrometry (GFAAS) with a background correction.

Experimental part

Instrumentation

A GBC AVANTA PM atomic absorption spectrophotometer with a deuterium background correction and a GF PAL 3000 graphite furnace atomizer system was used. A chromium hollow cathode lamp was used as radiation source at 357.9 nm. There were trials using different working parameters, to reach optimum conditions. These are indicated in table 1.

Table 1
OPERATING PARAMETERS FOR GFAAS

Parameters	
Lamp current (mA)	6.0
Wavelength (nm)	357.9
Slit (nm)	0.2
Air flow rate (L/min)	6 (stopped during atomizing)
Sample volume (µL)	10
Temperature program	
Drying	110^0 C (Ramp 10 s, Hold 20 s)
Ashing	1110^0 C (Ramp 10 s, Hold 20 s)
Atomizing	2500^0 C (Ramp 0.8 s, Hold 2 s)
Cleaning	2600^0 C (Ramp 1 s, Hold 2 s)

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Personal sampling pump, 1 to 3 L/min with flexible connecting tubing was used for samples.

Standard solution and reagents

Calibration chromium stock solution 1mg/mL (Carlo Erba) and nitric acid 1/10(V/V) of analytical purity have been used.

To determine the performance parameters for the method (linearity, accuracy, precision and robustness) standard calibration solutions were used in the concentration range 10 - 100 µg/L [7,8].

The detection and quantification limits were established according to ICH (International Conference on Harmonization) recommendations [9,10].

Accurately known flow rate between 1 and 3 L/min was established for a sample size of 10 to 1000 L. It was not exceeding a filter loading of cca. 2 mg total dust.

The following were used: calibration stock solution 1mg/mL (Carlo Erba); nitric acid; cellulose ester membrane filter, 0.8 µm pore size and 37 mm diameter, in cassette filter holder.

Open the cassette filter holders and transfer the sample to clean beakers. Add 3 mL conc. HNO_3 and heat. Repeat using 1mL conc. HNO_3. Add 0.5 mL conc. HNO_3 and 5 mL distilled water and heat until the volume is reduced to ca. 3 mL, then dilute with distilled water to 10 mL.

Clean all glassware with acid and rinse thoroughly with distilled or unionized water before use.

Results and discussions

Calibration curve

A calibration curve is obtained (fig. 1) with the equation (1):

$$A_{357.9} = 0.09562 + 0.01044 \cdot [C] \qquad (1)$$

where [C] is the Cr concentration expressed as µg/mL, with a correlation coefficient of R = 0.9969 and an average standard deviation of the line of 3.23317 for probability p = 0.0001 (table 2).

Table 2
PARAMETERS VALUES OBTAINED FROM THE CALIBRATION CURVE

Parameter	Value	Error	
A	0.09562	0.00977	
B	0.01044	3.36042×10^{-4}	
R	SD	N	p
0.9969	3.23317	8	1×10^{-4}

where: A = ordinate at origin; B = slope; R = correlation coefficient; SD = standard deviation of experimental points from the regression line; N = number of points; p = probability that points do not observe the regression line generated.

The line was obtained using the least squares method and weights given by the individual errors of each of the N = 8 points for which determinations were performed.

Method validation

The values of the performance characteristics have been estimated through statistical calculation using the *Microcal Origin 6.0* software and are centralized in table 3.

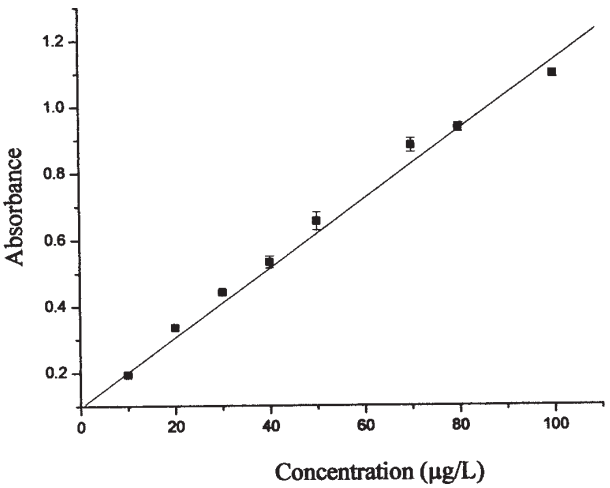

Fig. 1 The calibration curve obtained at 357.9 nm

Table 3
PERFORMANCE PARAMETERS OF THE METHOD

Parameter	Value
Detection limit	3.08 µg/L
Quantification limit	9.35 µg/L
Working range	10 -100 µg/L
Retrieval coefficient	100.4
Repeatability, RSD (%)	1.92
Reproducibility, RSD (%)	2.01

In order to asses the robustness of the analysis method the stability in time of the sample solutions was tested.

To study the stability in time of the sample solutions, they were stored in the refrigerator for a week and the absorbance was read. Then the related graphic was drawn (fig. 2). The working range is linear during the 10 - 100 µg/L intervals, which allows for the analysis of a wide spectrum of concentrations.

It was proven that the method is a specific one and measurements were performed at the wavelength of 357.9 nm. There are no elements known to interfere.

The retrieval coefficient calculated according to the formula should be between 99 and 101%. Our values of 100.4 were found to be within this interval, thus the method is accurate.

RSD was found to be lower than 2%, thus the method is repeatable and reproducible.

With regards to robustness, we found that the solutions are not stable in time, even when stored in a refrigerator in the dark.

Application to real samples

The validated method was applied on samples taken from chromium - plating room, using bars of various diameters. The samples were taken from several points of the room: from the chromium - plating platform – big diameter bars, from the chromium - plating platform – small diameter bars and from a 20 m distance from installations. All determinations were made during winter, over a three-year period. The results are presented in table 4. The mandatory limit value at national level is 0.05 mg/m^3, in accordance with 1218/06.09.2006 Government Decision.

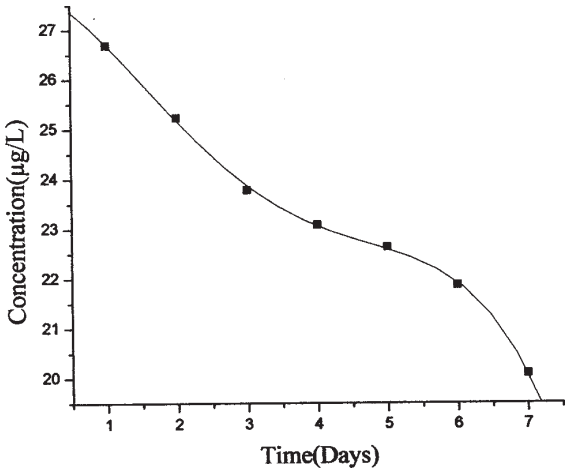

Fig. 2 Stability in time of the sample solutions

Year	Area: platform chromium-plating installation big diameter bars (mg/m^3)	Area: 20 m from the chromium-plating installation big diameter bars (mg/m^3)	Area: platform chromium-plating installation small diameter bars (mg/m^3)	Area: 20 m from the chromium-plating installation small diameter bars (mg/m^3)
2002	0.0042	0.0018	0.0510	0.0145
2003	0.0030	0.0080	0.0151	Below detection limit for the method presented
2004	0.0061	0.0018	0.0111	0.0018

Table 4
RESULTS OF TOTAL CHROMIUM DETERMINATIONS OVER A THREE-YEAR PERIOD

Conclusions

A method for the determination of total chromium in workplace atmospheres through atomic absorption (GFAAS) la 357.9 nm was developed. The method is specific, is linear within the range of 10 – 100 µg/L, having a detection limit of 3.08 µg/L and a quantification limit of 9.35 µg/L. The method is accurate, repeatable and reproducible. Based on the results related to the method robustness, we may reach the conclusion that solutions used for determinations should be fresh.

The validated method was successfully applied in determinations undertaken in a chromium-plating room on bars of various diameters. Following the results obtained in 2002, steps have been taken to reduce the total chromium level in that chromium-plating room and to improve the working conditions for the manufacturing staff. The total chromium values obtained in 2003 and 2004 were below the limit imposed by the legislation in force, which means that the measures taken in 2002 proved effective.

Research shall continue for the summer season, to study the influence of temperature on the total chromium determinations. The results will be published in a future paper.

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