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GFAAS method for determination of total chromium in urine

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Abstract Chromium in urine can be regarded as a marker of internal chromium exposure. More frequent effects are observed to the skin, respiratory and renal systems. Occupational exposure to total chromium can be determined by means of workplace atmospheres measurements and biological monitoring (in urine). Because very small quantity is excreted, considerable analytical sensitivity is required for urinary total chromium determinations. This paper describes a new determination method for total chromium in urine using graphite furnace atomic absorption spectrometry (GFAAS) with a background correction. The atomisation temperature used was 2400^{o}C and a cleaning step for graphite furnace after each samples series was realized. The validation of GFAAS method was made in concordance with International Conference on Harmonization (ICH). To determine the performance parameters for the method (linearity, accuracy and precision) standard calibration solutions were used in the concentration range of 10 - 100 µg/L. After validation, total chromium determinations in urine were made to involved personal in pigments obtaining process. The measured values of total chromium are situated between 0.01 – 29.67 µgCr/g Creatinine (under the maximum accepted limit - 30µgCr/g Creatinine).

Keywords: total chromium, urine, GFAAS, validation

1. Introduction

Chromium is an essential micronutrient for humans and is involved in glucose metabolism and in the mechanism of action of insulin. Chromium is an essential element for human life, in quantities of 0.05-0.2 mg/day [1,2].

Occupational exposure to total chromium can be determined by means of workplace atmospheres measurements and biological monitoring (in urine) [3]. The diagnosis of chromium intoxication is determined based on:

- professional exposure to chromium, chromium compounds and alloys. For determining the level of this exposure the following elements are used: professional anamnesis, as well as the results of total chromium determination in the workplace air;
- clinical picture;
- laboratory exams: exposure indicators.

The major toxic effects of chromium are chronic ulcers, dermatitis and corrosive reaction in nasal septum and local effects in lungs.

This paper aims to present a new determination method for total chromium in urine using graphite furnace atomic absorption spectrometry (GFAAS) with a background correction. The proposed method was applied to appreciate workers involved in pigments obtaining process' exposure.

2. Experimental

2.1. 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. The optimum operating parameters for GFAAS are indicated in Table 1.

2.2. Standard solution and reagents

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

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To determine the performance parameters for the method (linearity, accuracy and precision) standard calibration solutions were used in the concentration range 10 - 100 μg/L [4].

The detection and quantification limits were established according to ICH recommendations [5, 6].

2.3. Application to real samples

In the pigment manufacturing department considered in the study determinations were performed to identify the total chromium levels in urine of exposed workers. The department includes a number of 10 workers (operators, mechanics and electricians), all male, aged 22-46, with the same employment record at the workplace.

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
Ashing	900^0 C
Atomizing	2400^0 C
Cleaning	2700^0 C

Urine samples were collected into clean glassware (treated with nitric acid and rinsed thoroughly with distilled water). The analysis of total chromium in urine was realised on spot sample.

Urinary creatinine was determined with the Jaffé method [7]. The total chromium/creatinine rapport was calculated according with legislation.

3. Results and Discussions

3.1. Calibration curve

A calibration curve was obtained (Fig. 1) with the equation (1):

$$A_{357.9} = 0.6983 + 0.01198[A] \quad (1)$$

where [A] is the Cr concentration expressed as μg/mL, with a correlation coefficient of R = 0.99691 and an average standard deviation of the line of 2.13436 for probability p = 0.0001 (Table 2).

Table 2. Parameters values obtained from the calibration curve

Parameter	Value	Error	
A	0.6983	0.00898	
B	0.01198	3.85416×10^{-4}	
R	SD	N	P
0.99691	2.13436	8	1×10^{-4}

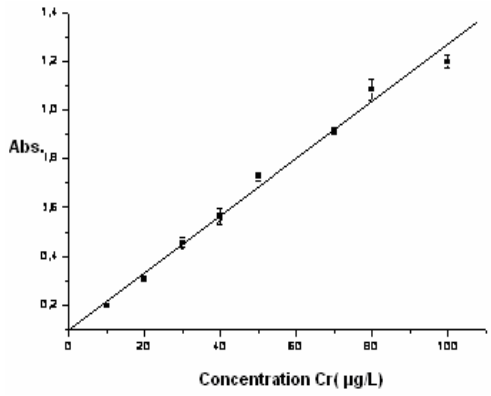

Fig. 1 The calibration curve obtained at 357.9 nm

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

3.*2. 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.

The working range was linear in the 10 - 100 μg/L interval, 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 100.25 was found to be within this interval, thus the method is accurate.

Table 3. Performance parameters of the method

Parameter	Value
Detection limit	2.47 µg/L
Quantification limit	7.49 µg/L
Working range	10 -100 µg/L
Retrieval coefficient	100.25
Repeatability, RSD (%)	1.61
Reproducibility, RSD (%)	1.37

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

The highest values for urinary total chromium 11.85 - 29.67 µg/g Creatinine were found for operators (5 persons); for the other studied categories of workers such as mechanics (4 persons) and electrician (1 person), the values ranged from 0.01 to 4.42µg/g Creatinine (Table 4).

The mandatory limit value at national level is 30 µg/g Creatinine in accordance with 1218/06.09.2006 Government Decision.

Table 4. Measured values of urinary total chromium and creatinine

Exposed workers	Total chromium (µg/L)	Creatinine (g/L)	Total chromium (µg/g Creatinine)
Operator 1	13.51	1.14	11.85
Operator 2	13.96	1.09	12.80
Operator 3	27.44	1.07	25.64
Operator 4	30.87	1.07	28.85
Operator 5	29.07	0.98	29.67
Mechanic 1	0.01	1.15	0.01
Mechanic 2	1.64	1.10	1.49
Mechanic 3	3.13	1.00	3.13
Mechanic 4	4.07	0.92	4.42
Electrician	0.99	0.90	1.10

It is obvious that the operators are highly exposed as compared to equipment maintenance staff (mechanics, electricians), who enter occasionally the work environment.

4. Conclusions

A method for the determination of total chromium in urine through atomic absorption (GFAAS) la 357.9 nm was developed. The method is specific, linear within the range of 10 – 100 µg/L having a detection limit of 2.47 µg/L and a quantification limit of 7.49 µg/L. The method is accurate, repeatable and reproducible.

The validated method was successfully applied in a pigment manufacturing department. We suggest strict observance of individual health and safety and hygiene norms. Medical examinations before employment and then regularly are highly useful for monitoring workers' health.

The study continues with analysing possible differences between smokers and non-smokers.

5. References

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