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Determination of Chromium (III) and Chromium (VI) Using Flow Injection Coupled with Flame Atomic Absorption Spectrometry and Direct Current Plasma Technique

I. S. Bushina*, H. M.Kut*, Seham. S. Elmahmudi*

تحديد Cr^{+3} وCr^{+6} بواسطة جهاز لهب طيف الامتصاص الذري وجهاز التيار المباشر باستخدام طريقة الحقن على العمود المصغر

إسماعيل بشينة و حسن كت، و سهام المحمودي

لقد استخدم عمود مصغر للألومينا المنشطة والمتصل بوحدة الحقن المستمر لجهاز لهب طيف الامتصاص الذري وجهاز بلازما التيار المباشر لطيافية الإصدار الذري DCPAES وذلك من أجل تحديد عنصر الكروم Cr^{+3} وCr^{+6} لعينات مختارة من المياه الجوفية وأخرى من غبار المدارس الابتدائية التي تم تجميعها من منطقة غرب طرابلس. تم تسجيل إشارات الامتصاص الذري بطريقة FIFAAS لكل من Cr^{+3} و Cr^{+6} منفصلة تماماً مع حدود الكشف الأدنى (D.L) تقدر ب 0.03 ميكروجرام/مل بينما عند استخدام DCPAES كانت حدود الكشف الأدنى 0.003 ميكروجرام/مل و 0.002 ميكروجرام/مل لكل من Cr^{+3} وCr^{+6} على التوالي. تشير النتائج أن عينات المياه قد تحتوي على تركيز أقل من حدود الكشف الأدنى لكلا الجهازين لكل من Cr^{+3} وCr^{+6}. أما عينات غبار المدارس فإنها تحتوي على تركيز يتراوح ما بين 0.9-1.5 ميكروجرام/مل بالنسبة Cr^{+3} بينما كان تركيز Cr^{+6} أقل من 0.05 ميكروجرام/مل عند استخدام DCPAES كما توضح هذه الدراسة أن عينات المياه التي تم تجميعها من المصدر خالية من عنصر الكروم أي أقل من الحد المسموح به لغرض الشرب.

Abstract: *Micro column of activated alumina was used in Flow Injection coupled with Flame Atomic Absorption and Direct Current Plasma Atomic Emission Spectrometry (DCPAES), for the determination of* Cr^{+3} *and* Cr^{+6} *in samples of groundwater used for drinking purposes, from different localities, and dust samples from elementary schools of west of Tripoli area. Atomic signals for both species* Cr^{+3} *and* Cr^{+6} *were analyzed by (FIFAAS) with limited detection of 0.03 µg/ml, while in DCPAES it was 0.003 µg/ml and 0.002 µg/ml for* Cr^{+3} *and* Cr^{+6} *respectively. Concentration data obtained for potable water for* Cr^{+3} *and* Cr^{+6} *were found less than the detection limit of both instruments, and concentration data of dust samples for* Cr^{+3} *was in the range of 0.9 to 1.5 µg/ml whereas* Cr^{+6} *was less than 0.05 µg/ml when analyses by DCPAES were used. The results obtained provided evidence that water samples collected from the above mentioned sources were free from any presence of chromium metal.*

INTRODUCTION

The presence of some toxic elements in natural water has been studied by many workers (Hallam, *et al*, 1985) due to their toxicity properties. Particulate matter, such as dust produced by

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*Petroleum Research Centre, P.O. Box. 6431 Tripoli, Libya.

human activity, leads to the distribution of those elements and pollutes the environment. These particulate matters are toxic and cause serious damage to the breathing system. Pollution of the environment by chromium metal is usually generated from different sources such as electroplating, heat exchanger system and metallurgical foundries. Metal speculation became a major interest of researchers and, therefore, it has expanded to the areas of clinical (Cornelis, *et al*, 1993) and environmental (Byrdy and Carusa, 1994) fields. Metal speculation of these fields plays a role for toxicity and some degree of mobility. The toxicity of metals actually depends upon the oxidation state of these metals being present.

In a solution, chromium primarily exists in either the Cr^{+3} or Cr^{+6} oxidation state and the toxicity of chromium metal actually depends upon the oxidation state of this element. Cr^{+3} is acidic and non toxic if it does not exceed the limit, and is even considered to be an essential nutrient for most mammals, whereas Cr^{+6} is a basic and powerful oxidizing agent and quite toxic. Thus for this reason, the determination of the element speciation is necessary. There are many methods that are sensitive and selective for the determination of Cr^{+3} and Cr^{+6} such as liquid chromatography (Schwedt, 1979), ion exchange (Pankow and Janauer, 1974 & Battistoni, *et al, 1983*) and chelating resins (Leyden, *et al 1972*, Miyazaki and Barnes, 198*1*). These procedures are time consuming and prolong sample manipulation, and may disturb the natural chromium speciation state. However, atomic spectroscopic methods have some limitation of which only total metal content could be determined, thus, when metal speciation is an interest then other method must be incorporated (Cox, *et al, 1985*). The flow injection method demonstrated an advantage over conventional direct nebulization, (Bushina, *et al, 1997*) in that it allows the identification and analyzation of a micro sample and prevents the nebulizer from blockage.

In this study, an on-line pre concentration of a micro column of activated alumina was incorporated with Flame Atomic Absorption and Direct Current Plasma Atomic Emission Spectrometer used for a sequential determination of Cr^{+3} and Cr^{+6} in eight groundwater samples (Bushina, *et al, 1997*) and dust. The latter samples were collected from 9 schools in the Abu Isa and Surman towns. The selected areas of the sample source have not been studied before.

EXPERIMENTAL

Methods of Sample Collection

Water samples collected at the source were immediately acidified with (0.5 ml/l) a concentrated nitric acid (sp.gr. about 1.42) and kept in polyethylene containers before the analysis was performed.

Dust samples (mixed with soil) A & B were collected from inside classrooms and elementary school play ground areas during the period of 28–12–1996 to 26–3–1997. Plastic brushes were used for sample collections. All samples were collected in plastic containers and dried in an oven for 24h at 105 °C, and then sieved through 150 μm stainless steel sieve. Table 1, summarizes a typical example of %wt of dust in the samples.

Materials and Reagents

Unless stated otherwise, all chemicals used were of high purity analytical grade. Nitric acid and ammonia solutions were obtained from BDH chemicals, Pool, England. Working standard solutions were prepared daily by serial dilution in nitric acid to give a final acid concentration 0.01M from stock standard solution supplied by VHG lab. Activated acidic, aluminum oxide, (Aldrich Chemicals Co. Ltd.), and further activation

Table 1. Typical examples of %wt of dust in the samples

Sample no.	Total wt (g)	Dust wt (g)	Dust wt (%)
$2A_2$	200	151.8	75.90
$3A_2$	200	154.2	77.10
$3A_3$	370	216.8	58.59
$4A_3$	200	182.2	91.10
$5A_3$	200	185.8	84.45
$6A_3$	110	87.0	79.09
$9A_3$	200	138.5	69.25
$10A_3$	200	144.7	72.35
10B	290	224.05	77.73

(Perrin, *et al. 1980*) was performed before it was used for packing the column. The PTFE (2.5 cm long, 3 mm i.d.) mini column was packed with the activated alumina (140 mesh). Water of high purity was used throughout the experimental work. A buffer solution of pH = 4 (ingold, Besell. Nr. 9863) was used for calibration of pH meter. All the glassware used was immersed in a dilute nitric acid (2M) for 24h, followed by washing in high purity distilled water

Instrumentation and Apparatus

The determination of Cr^{+3} and Cr^{+6} was carried out with the SOLAR 959 automatic atomic absorption spectrometer with direct control via external PC data station and software. The instrument has facilities of graphite furnace GF90 coupled with auto sampler, automatic flame auto sampler and Epson parallel Dot Matrix printer. The experimental conditions are summarized in Table 2. Direct Current Plasma (DCP) Spectrospan (V) Beckman, model V-DUAL, Cat No. 487105 was used. The instrument is coupled with printer Epson and chart recorder, and also has the facilities of Inductive Coupled Plasma (ICP). The operating conditions are depicted in Table 3.

The solutions were adjusted at pH = 2 by Knick Digital pH Meter 646. This was conducted by adding a suitable volume of nitric acid and ammonia solutions. PTFE syringes were used to inject the solutions.

Methods of Digestion of Dust Samples

10 g of each sample were placed in a round bottom flask, then 20 ml of concentrated nitric acid (65%) was added. The samples were then refluxed for 2h. The contents were cooled and filtered, and the residue was washed with 0.1M HNO$_3$ and diluted with distilled water to a volume of 100 ml in a volumetric flask

Table 2. Experimental conditions for flame atomic absorption

	Cr^{+3}	Cr^{+6}
Conc. range (µg/ml)	0.05 – 0.8	0.05 – 0.8
Absorbance	0.005 – 0.076	0.038 – 0.459
Wavelength (nm)	357.9	357.9
Background	Off	Off
Sample loop (ml)	1.0	1.0
Flow rate (ml/min.)	3.0	3.0
Detec.limit (µg/ml)	0.03	0.03
Sensitivity (µg/ml)	< 0.04	< 0.007

Table. 3. Operating condition for DCPAES

	Cr^{+3}	Cr^{+6}
Conc. range (µg/ml)	0.01– 0.1	0.01– 0.1
PMT voltage	4.0	4.0
Wavelength (nm)	357.9	357.9
Sample uptake rate (ml/min.)	3.0	3.0
Nebulizer pressure (psi)	23.0	23.0
Sleeve pressure (psi)	50.0	50.0
Detc. limit (µg/ml)	0.003	0.002
Sample loop (ml)	1.0	1.0
Sample injected (ml)	1.0	1.0

Analytical Procedure

The flow injection manifold consists of a pristatic pump, rotary injections valve and a micro column of activated alumina, which were connected to the nebulizer of the used instrument as shown in Figure 1. An acid carrier stream (0.01M HNO$_3$) passes through the column to maintain its acidity. For the mixture to be eluted, the standard solutions were loaded into the injection valve manifold by syringe and then injected to the carrier stream. This was done since Cr^{+3} is acidic and does not deposit on the column. Ammonia solution (2M) was injected to elute Cr^{+6}.

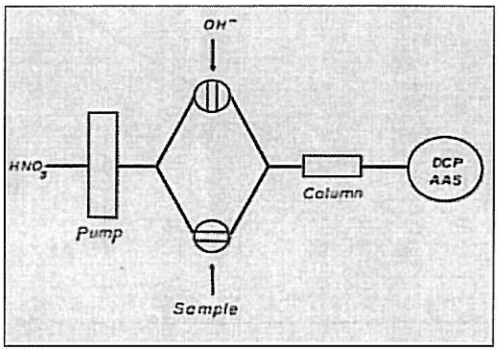

Fig. 1. Flow injection system for determination of Cr^{+3} and Cr^{+6}.

RESULTS AND DISCUSSION

Allumina displays amphoteric properties. The activated allumina, under acidic conditions, has an affinity for ionic species. In contrast, under basic solution, it will have an affinity to cationic species. Thus when using 2M HNO_3 as an eluent for the determination of chromium speciation, Cr^{+3} is eluted, whereas Cr+6 is retained, and upon injection of OH^- the Cr^{+6} is also eluted. Results for the determination of Cr^{+3} and Cr^{+6} using Flow Injection Flame Atomic Absorption Spectrometry (FIFAAS) in water samples were found to be less than the detection limit of this procedure which equaled 0.03 μgml^{-1} for Cr^{+3} and Cr^{+6}. But the atomic signal for standard solutions shows a good separation of both chromium species when a mixture of both chromium species was used in the range of 0.05, 0.1, 0.2, 0.4, 0.8 μgml^{-1}. It shows good linear calibration graphs for both species as shown in Figures 2a. and 2b. Characteristic mass of Cr^{+3} = 0.045 µg/ml and Cr^{+6} = 0.007µg/ml.

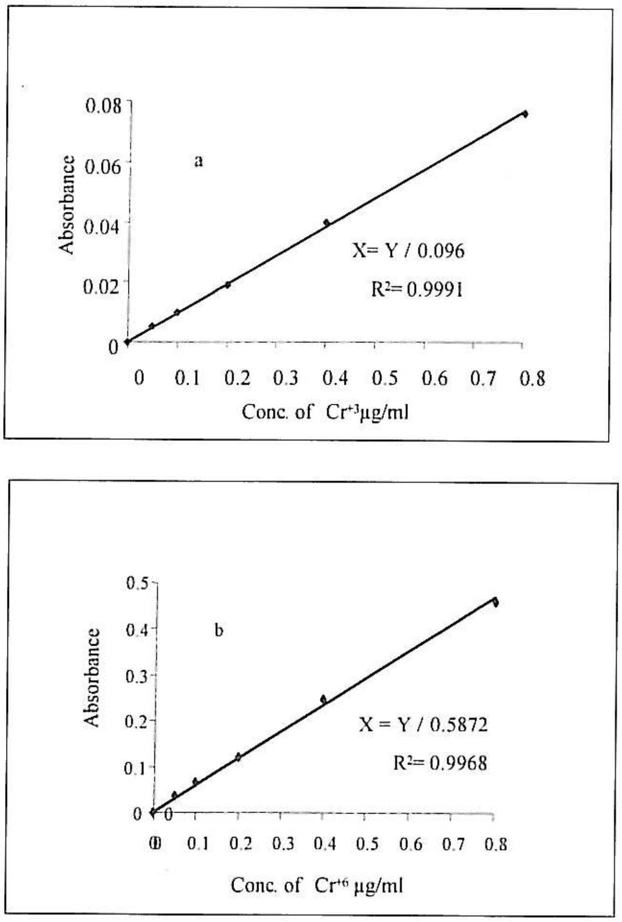

Fig. 2. Calibration curve for (a) Cr^{+3} and (b) Cr^{+6} obtained by FIFAAS.

Analytical line 357.9 nm for chromium AES was used for its maximum sensitivity and lower detection limit. This was used for determination of Cr^{+3} and Cr^{+6} by DCPAES. Figure 3 clearly shows a good dynamic range of 0.01,0.05, 0.1, 0.5 μgml^{-1} -for good separation of the two chromium species when optimum conditions were used, such as acid concentration flow rate, separation column capacity, injection loop capacity and ammonia concentration. 1000 µl of the mentioned standard containing both species was loaded into the injection port to the sample loop via injection valve with a stream of 0.01M HNO_3 solution was passed through the nebulizer immediately after the sample and standard. The atomic emission signal of Cr^{+3} was recorded as shown in Figure. 3. As soon as the emission signal got to the baseline, 1 ml of ammonia solution (2M) was injected. An atomic emission signal of Cr^{+6} was clearly recorded. As in Figure 3, by this technique, good broadening emission peak of Cr^{+3} and a sharp one of Cr^{+6} were obtained.

The calibration graphs of Cr^{+3} and Cr^{+6} using aqueous standard solution were straight lines with good linearity. All the plots passed through the origin. Results are depicted in Figures 4a and 4b. The limit of detection for both chromium species using DCPAES when water samples were analyzed for Cr^{+3} = 0.003 µg/ml and Cr^{+6} = 0.002 µg/ml. However, analysis of water samples collected at

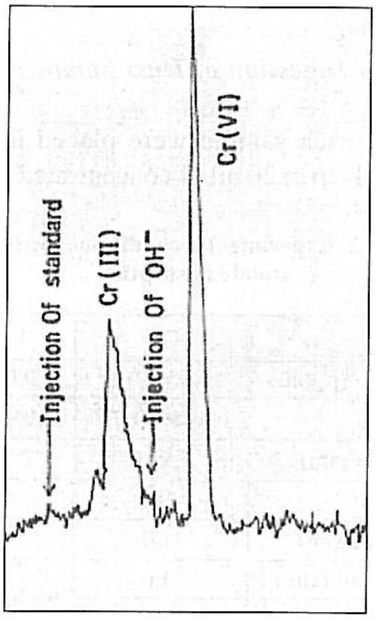

Fig. 3. Recorded signals for standard solution of Cr^{+3} and Cr^{+6} using DCPAES. Concentrations are in µg/ml.

the source in Tripoli city of Cr^{+3} and Cr^{+6} were found to be below the detection limit of this technique. This detection limit was calculated as three times the standard deviation of blank reading. It is clear that no contamination of chromium species was present in the sample that might cause toxicity to humans, but it may need further pre-concentration for the larger samples collected.

Table 4, shows the results of Cr^{+3} and Cr^{+6} concentrations (average of four determinations) and associated relative standard deviation for a selected group of dust sample. As seen, it is quite clear that maximum (1.57 $\mu g ml^{-1}$) characteristic mass of Cr^{+3} was found in sample $6A_2$, whereas minimum (0.97 $\mu g ml^{-1}$) content was found in samples $3A_3$, $10A_3$. Cr^{+6} content of the all samples was found to be less than 0.05 $\mu g ml^{-1}$. This value was calculated from the atomic signals obtained for 10 times the value of detection limit for each sample.

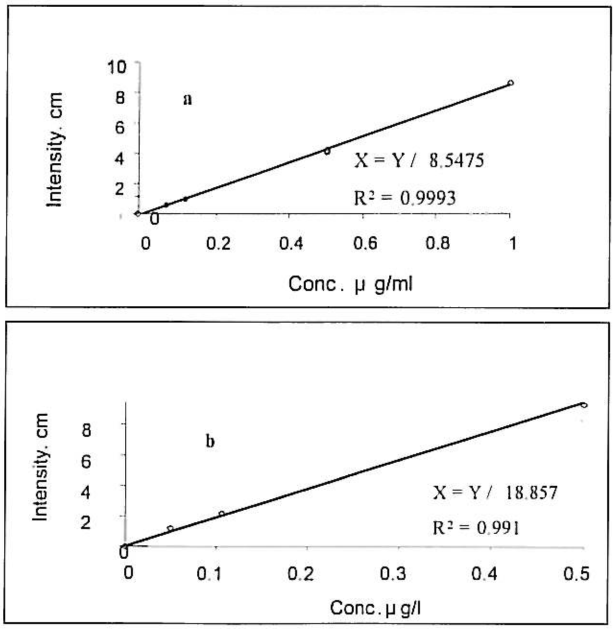

Fig. 4. Calibration curve for (a) Cr^{+3} and (b) Cr^{+6} obtained by DCPAES.

Table 4. Repetitive chromium species in dust sample

Sample	Cr^{+3} (conc.μg/ml)	Cr^{+6} (conc.μg/ml)
$2A_2$	1.09 ± 3.0%	< 0.05
$3A_2$	0.97 ± 7.9%	< 0.05
$4A_3$	1.45 ± 0.8%	< 0.05
$5A_3$	1.35 ± 9.2%	< 0.05
$6A_2$	1.57 ± 0.8%	< 0.05
$9A_3$	0.99 ± 6.7%	< 0.05
$10A_3$	0.97 ± 2.2%	< 0.05
10B	1.15 ± 5.5%	< 0.05

No. of replicate n = 4

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