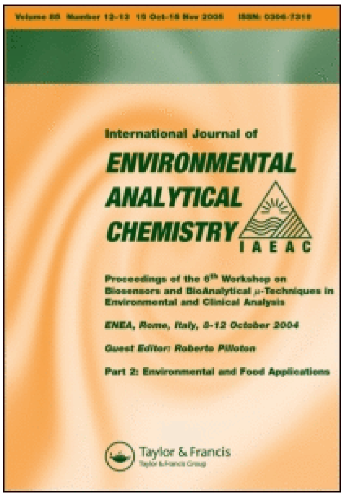

**International Journal of Environmental Analytical Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Speciation of Cr III and Cr VI in Aqueous Samples by Coprecipitation/Slurry Sampling Fluorination Assisted Graphite Furnace Atomic Absorption Spectrometry

Lei Wang[a]; Bin Hu[a]; Zucheng Jiang[a]; Zhiqing Li[a]
[a] Department of Chemistry, Wuhan University, Wuhan, Hubei, P.R. China

**To cite this Article** Wang, Lei , Hu, Bin , Jiang, Zucheng and Li, Zhiqing(2002) 'Speciation of Cr III and Cr VI in Aqueous Samples by Coprecipitation/Slurry Sampling Fluorination Assisted Graphite Furnace Atomic Absorption Spectrometry', International Journal of Environmental Analytical Chemistry, 82: 6, 387 — 393

**To link to this Article: DOI:** 10.1080/03067310290007813

**URL:** http://dx.doi.org/10.1080/03067310290007813

*Intern. J. Environ. Anal. Chem.*, Vol. 82, No. 6, pp. 387–393

Taylor & Francis
Taylor & Francis Group

# SPECIATION OF $Cr^{III}$ AND $Cr^{VI}$ IN AQUEOUS SAMPLES BY COPRECIPITATION/SLURRY SAMPLING FLUORINATION ASSISTED GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

LEI WANG, BIN HU*, ZUCHENG JIANG and ZHIQING LI

*Department of Chemistry, Wuhan University, Wuhan, Hubei, 430072, P.R. China*

*(Received 30 March 2001; In final form 2 January 2002)*

A $Pb(PDC)_2$ coprecipitation separation and preconcentration combined with slurry sampling fluorination assisted electrothermal atomic absorption spectrometry with PTFE as chemical modifier has been developed for the speciation of $Cr^{III}$ and $Cr^{VI}$. Base on the variation of the pH, this method can soundly separate $Cr^{III}$ and $Cr^{VI}$ at pH 4.0 and 9.0, respectively. The experimental conditions of the coprecipitation and GFAAS determination were investigated systematically. Under the optimum conditions, the linear range of $Cr^{III}$ and $Cr^{VI}$ was from 0.5 to 80 ng/ml, and detection limit was 0.02 ng/ml with the RSD of 3.2% for $Cr^{VI}$ ($n=9$, $C=1$ ng/ml) and 3.9% for $Cr^{III}$ ($n=9$, $C=1$ ng/ml). The proposed method has been applied for the analysis of $Cr^{III}$ and $Cr^{VI}$ in natural water and tea infusion samples with satisfactory recoveries.

*Keywords:* Speciation of chromium; Lake water; Tea infusion; APDC; GFAAS

## INTRODUCTION

Chromium exists in natural water in two stable oxidation states: $Cr^{III}$ and $Cr^{VI}$. $Cr^{III}$ is considered to be essential to mammals for the maintenance of glucose, lipid, and protein metabolism, whereas $Cr^{VI}$ is a toxic and carcinogenic form [1–3]. $Cr^{III}$ and $Cr^{VI}$ can enter the environment by variable ways. Precise knowledge of the concentrations of different chromium species in a system is of great significance to an accurate assessment of the environment. Therefore, the development of speciation techniques for Cr is necessary for analytical chemists [4].

The speciation of chromium can be achieved by different methods. Generally, the analytical methods contain two steps: separation of one or both the considered species from the original matrix, and then the step of determination of each one of them. Separation techniques employed include solvent extraction and solid extraction [5,6], electrochemical methods [7], ion-exchange separation [8,9], high performance liquid

---

*Corresponding author. Fax: +86-27-87647617. E-mail: binhu@whu.edu.cn

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310290007813

chromatography [10,11], capillary electrophoresis [12,13] and coprecipitation [14–17]. Atomic absorption [6,10,18] or plasma emission spectrometry [12]/ICP mass spectrometry [13] are frequently utilized as the means of detection.

Owing to its rapidity, simplicity and good separation efficiency, the coprecipitation separation technique is still considered to be one of the effective separation methods for $Cr^{III}$ and $Cr^{VI}$. Coprecipitation reagents for separation of Cr speciation include: hydroxides of $Fe^{III}$ [19] or $Al^{III}$ [16], the sulphate of lead [17] and organic reagent APDC [14,15] etc.

With high sensitivity, low detection limits, low sample volume requirement and slurry sampling, graphite furnace atomic absorption spectrometry (GFAAS) has been widely used for the determination of trace elements speciation. In our previous work [18], using PTFE as chemical modifier, a method was reported for determination of the trace chromium in water sample by GFAAS. The detection limit of this method was superior to that of conventional GFAAS and the matrix interferences were also reduced significantly.

The aim of this work is to develop a simple, rapid and sensitive technique for determination of $Cr^{III}/Cr^{VI}$ speciation, in which the coprecipitation separation system is combined with GFAAS determination. Furthermore, the PTFE emulsion was used to reduce the interferences caused by matrix and improve the sensitivity for AAS determination. The proposed method has been successfully applied for the separation and determination of trace amount of $Cr^{III}/Cr^{VI}$ in lake water and tea infusion with satisfactory results.

## EXPERIMENTAL

### Apparatus and Operating Conditions

A 180–50 atomic absorption spectrometer fitted with deuterium background corrector, a GA-3 graphite atomizer system and an automatic sampling system (Hitachi, Ltd., Tokyo, Japan) was employed. The instrument was operated via a microcomputer. The parameters of graphite furnace were set in it. All data were processed with Origin 5.0 data analysis software. An SY1200 Ultrasonic wave generator (Shanghai Shengyuan Ultrasonic Instrument Company, Shanghai, China) was used for dispersing the slurry sample.

The operating conditions used are given in Table I.

TABLE I Spectrometer operating conditions and graphite furnace heating program

| | |
|---|---|
| Wavelength/nm | 357.9 |
| Slit/nm | 1.3 |
| Current of hollow cathode lamp/mA | 7.5 |
| Cuvette | Pyrocoated tube |
| Graphite furnace heating program | Drying: 20–105°C; ramp 10 s, hold 20 s<br>Ashing: 105–1300°C; ramp 10 s, hold 30 s<br>Atomization: 2700°C; hold 6 s |
| Signal mode | Peak height |
| Recording mode of recorder | DIR (20 s) |
| Ar flow rate/ml/min | 200 ml/min (the flow was stopped during atomization) |

### Standard Solution and Reagents

All chemicals used, except where stated, were analytical reagent grade. Doubly distilled water was used throughout.

Stock standard solutions of 1.000 mg/ml $Cr^{III}$ and 1.000 mg/ml $Cr^{VI}$ were prepared from analytical-reagent grade $Cr(NO_3)_3$ and $K_2Cr_2O_7$ by dissolving corresponding salts in doubly distilled water, respectively. Pb solution (0.1000 mg/ml) and solution (1.000 mg/ml) of $K^+$, $Na^+$, $Ca^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Mg^{2+}$, $Fe^{3+}$ and $PO_4^{3+}$ were prepared as conventional methods.

*APDC solution* (1.000 mg/ml). Dissolve 100 mg APDC (Shanghai Third Reagent Factory, Shanghai, China) in 100 ml water. The pH 7.0–10.0 buffers were prepared by $NH_4Cl$ and $NH_3 \cdot H_2O$; pH 2.0–6.0 acetate buffers were prepared by NaOAc and HOAc.

A 60% m/v PTFE emulsion ($d < 1$ µm, viscosity $7 \times 10^{-3}$–$1.5 \times 10^{-2}$ Pa s, Shanghai, Organic Chemistry Institute, Shanghai, China) was commercially available.

### Coprecipitation Separation Procedure

3.0 ml water sample were added into a 10 ml centrifuge tube, then added with 0.5 ml 0.1 mg/ml Pb solution. one millilitre 1 mg/ml APDC solution, and diluted to 6 ml with pH 4.0 buffer. After vigorous shaking the solution was let it stand for 2 h. In the centrifuged solution (2000 rpm, 15 min), $Cr^{VI}$ can be coprecipitated with $Pb(PDC)_2$ completely, and $Cr^{III}$ was left in the solution. Pipetted out the upper clarified solution, and kept it in another tube. After adjusting this clarified solution to pH 9.0 with ammonia solution, Pb, APDC solution and pH 9.0 buffer were added. In this case, the $Cr^{III}$ can also be coprecipitated with $Pb(PDC)_2$ completely.

### Slurry Sample Preparation

The sample slurry is prepared by adding 0.2 ml 6% PTFE slurry to the precipitate. The enrichment factor of 15 can be obtained by the above operation (from 3.0 to 0.2 ml). The concentration of PTFE was chosen following a previous study [18]. Then, an ultrasonic wave generator dispersed the mixture for 20 min. The resulting slurry samples were introduced directly into the GFAAS for the determination of $Cr^{III}$ and $Cr^{VI}$ by the autosampler.

### Determination

A 10 µl volume of slurry samples were introduced into the pyrolytic graphite–coated graphite tube with autosampler. After being dried and pyrolysed, the analyte was vaporized and atomized. The intensity values of absorption signal of the analyte and background were displayed on the screen of microcomputer. The peak height was used for quantification. The aqueous standards with 6% PTFE chemical modifier were used for making the calibration curve for the analytes determination.

## RESULTS AND DISCUSSION

### Optimization of Coprecipitation Conditions

As shown in the literature [15,20], at acidic pH, only $CrO_4^{2-}$ can be coprecipitated with $Pb(PDC)_2$. At pH of 9.0, the hydroxide ion $[Cr(H_2O)_5(OH)]^{2+}$ is probably formed, which can give soluble dimmers and polymers and can be coprecipitated with $Pb(PDC)_2$. The experimental results (Fig. 1) show that:

(i) It is possible to coprecipitate $Cr^{VI}$ and $Cr^{III}$ in the pH 3.5–4.5 and 8–9.5, respectively. It is noted that the effect of pH on the coprecipitation of $Cr^{III}$ in the pH range of 3–6.5 were also investigated and the results showed that the recovery of $Cr^{III}$ in the pH 3–6.5 was less than 40%. Thus, the acidity of pH 4.0 and 9.0 was selected;
(ii) $Cr^{VI}$ and $Cr^{III}$ can be completely coprecipitated by 1 mg APDC and 50 µg Pb;
(iii) A standing time of 2 h is required for complete coprecipitation of the analytes.

### Effect of Coexisting Ions on Separation

The advantage of using the coprecipitation is that the major interfering elements do not form the complexes with coprecipitation reagents. Most of the coexisting ions are still in solution under the separation conditions.

Table II lists the coexisting ions and their maximum concentrations tested. It was found that $10^4$ fold excess of coexiting ions did not have significant effect on the separation and determination.

### The Optimization of ETAAS Measurement

Figure 2 shows the pyrolysis and atomization curves of the analyte in the coprecipitation slurry with PTFE and Fig. 3 indicates the effect of pyrolysis time on absorption signal and background. As it can be seen, the choice of pyrolysis time is important,

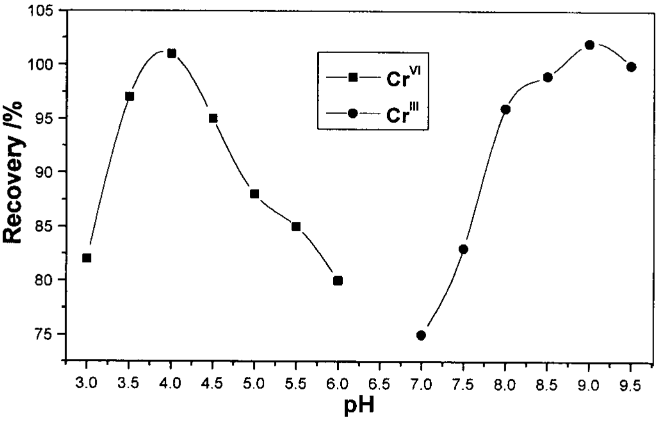

FIGURE 1 The optimization of acidity for the two-step coprecipitation.

TABLE II The effect of coexisting ions[a]

| *Coexisting ions* | *Concentration* (mg/ml) | *Recovery* (%) | | *Coexisting ions* | *Concentration* (mg/ml) | *Recovery* (%) | |
|---|---|---|---|---|---|---|---|
| | | *Cr$^{III}$* | *Cr$^{VI}$* | | | *Cr$^{III}$* | *Cr$^{VI}$* |
| K$^+$ | 0.4 | 102.2 | 99.2 | Al$^{3+}$ | 0.4 | 99.0 | 102.7 |
| Na$^+$ | 3 | 100.7 | 101.5 | Fe$^{3+}$[b] | 0.4 | – | 103.5 |
| Ca$^{2+}$ | 0.4 | 102.0 | 100.4 | Cu$^{2+}$ | 0.4 | 98.4 | 99.3 |
| Mg$^{2+}$ | 0.3 | 101.8 | 101.4 | NH$_4^+$ | 0.5 | – | 101.7 |
| Zn$^{2+}$ | 0.1 | 98.2 | 103.4 | PO$_4^{3+}$ | 0.5 | 100.3 | 101.1 |

[a] The maximum concentrations of coexisting ions that have been tested in this work.

[b] At pH 9.0, there were visible brown precipitation, when the concentration of Fe$^{3+}$ above 10 μg/ml.

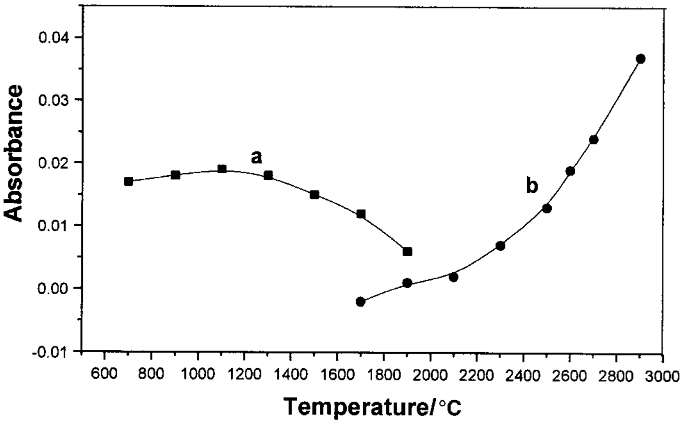

FIGURE 2 (a) Pyrolysis curve (atomization temperature: 2700°C) and (b) atomization curve (pyrolysis temperature: 1300°C). (Cr, 25 ng/ml; other conditions were listed in Table I).

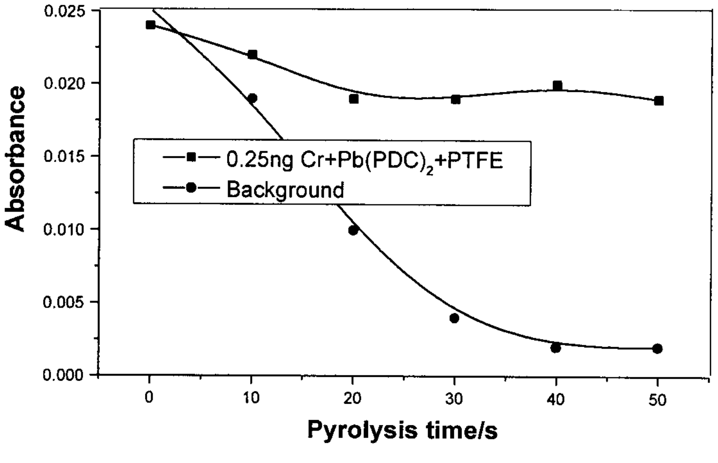

FIGURE 3 Dependence of Cr absorption and background on pyrolysis time (pyrolysis/atomization temperature: 1300/2700°C, Cr, 25 ng/ml).

and the longer pyrolysis time is beneficial to the separation of background absorption. As a result, a temperature of 1300°C and holding time of 30 s were chosen for the further studies. Under these conditions, the matrix could be removed during the pyrolysis period in the presence of PTFE as chemical modifier.

## The Influence of PTFE on the Signal Profile

As a refractory element, Cr easily forms carbide in the graphite furnace, which is difficult to be decomposed, and sometimes completely suppresses the analyte signal. As reported before [18], the addition of PTFE clearly enhanced the analytical sensitivity of Cr, increased the analyte ashing temperature and therefore allowed the higher matrix pyrolysis temperature and significantly reduced the matrix interference. The result in Fig. 4 supports this conclusion further.

The signal profiles of Cr both in aqueous solution and in slurry were comparatively investigated and similar profiles were obtained. Based on this result, the calibration graphs can be performed with aqueous standard solution containing PTFE emulsion without matrix matching.

## Precision and Detection Limit

According to the definition of IUPAC, the detection limit ($3\sigma$) is 0.02 ng/ml (enrichment factor of 15) with relative standard deviation of 3.2 ($n=9$, 1 ng/ml $Cr^{VI}$) and 3.9% ($n=9$, 1 ng/ml $Cr^{III}$). The linear range of $Cr^{III}/Cr^{VI}$ covers from 0.5 to 80 ng/ml.

## Sample Analysis

The surface water sample (sampled in East lake, Wuhan, China) was filtered through 0.45 μm membrane before analysis. The tea leaves (Langxi, Anhui, China) were dried at 80°C for 2 h, then ground to a fine powder in an agate mortar. Tea powder (0.5 g)

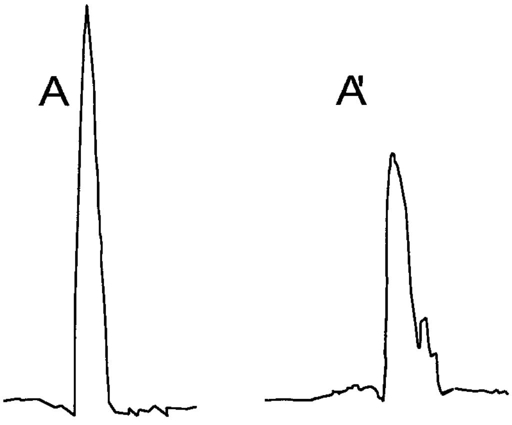

FIGURE 4 Typical signal profile of Cr (Cr, 0.25 ng; PTFE, 6%; APDC, 1 mg; Pb, 50 μg). (A) Cr + $Pb(PDC)_2$ + PTFE; (A′) Cr + $Pb(PDC)_2$.

TABLE III The standard recovery analysis results of water samples and tea infusion, results given are mean ± standard deviation ($n = 9$)

| *Sample* | *Cr* (ng/ml) | | *Cr found* (ng/ml) | | *Recovery* (%) | |
|---|---|---|---|---|---|---|
| | $Cr^{III}$ | $Cr^{VI}$ | $Cr^{III}$ | $Cr^{VI}$ | $Cr^{III}$ | $Cr^{VI}$ |
| Lake water | 0 | 0 | 0.48 ± 0.03 | 0.29 ± 0.02 | – | – |
| | 1.0 | 0 | 1.50 ± 0.04 | 0.30 ± 0.03 | 102 ± 0.4 | – |
| | 0 | 1.0 | 1.48 ± 0.02 | 1.28 ± 0.05 | – | 99 ± 0.5 |
| | 1.0 | 1.0 | 1.52 ± 0.04 | 1.28 ± 0.03 | 104 ± 0.4 | 99 ± 0.3 |
| Tea infusion | 0 | 0 | 0.57 ± 0.01 | 0.27 ± 0.02 | – | – |
| | 1.0 | 0 | 1.56 ± 0.03 | 0.29 ± 0.02 | 99 ± 0.3 | – |
| | 0 | 1.0 | 0.60 ± 0.02 | 1.31 ± 0.02 | – | 104 ± 0.2 |
| | 1.0 | 1.0 | 1.62 ± 0.03 | 1.33 ± 0.01 | 105 ± 0.3 | 106 ± 0.1 |

was infused with 50 ml boiling water for 10 min (10 mg powder in 1 ml infusion). The mixture was filtered and the resulting tea infusion was analysed subsequently.

Three millilitre water sample or tea infusion were pipetted into a centrifugal tube and operated as the procedure described previously. The analytical results of the samples together with the recovery are given in Table III.

## Acknowledgements

Financial support from Wuhan Municipal Science and Technology Commission and Wuhan University is greatly acknowledged.

## References

[1] J.F. Pankon and G.E. Janauer, *Anal. Chim. Acta*, **69**, 97–104 (1974).
[2] D. Rai, B.M. Sass and D.A. Moore, *Inorg. Chem.*, **26**, 345 (1987).
[3] J.O. Nriagu and E. Nieboer, *Chromium in the Natural and Human Environments*. John Wiley and Sons, New York (1988).
[4] K. Wang, *Trace Elements in Life Science*, Zhongguojiliang Press, Beijing, p. 172 (1996).
[5] E. Vassileva, K. Hadjiivanov, T. Stoychev and C. Daiev, *Analyst*, **125**, 693–698 (2000).
[6] D.M.A. Cerezo, M.L. Estelles and A.R.M. Aucejo, *Talanta*, **51**, 531–536 (2000).
[7] H. Ohura, T. Imato, I. Matsuo and S. Yamasaki, *Bunseki Kagaku*, **49**, 59–64 (2000).
[8] J. Wang, K. Ashley, D. Marlow, E.C. England and O. Carlton, *Anal. Chem.*, **71**, 1027–1032 (1999).
[9] E.M. Alonso, S.J. Hill, M.E. Foulkes and J.S. Crighton, *J. Anal. At. Spectrom*, **14**, 187–192 (1999).
[10] J. Posta, H. Berndt, S.K. Luo and G. Schaldach, *Anal. Chem.*, **65**, 2590–2595 (1993).
[11] M. Derbyshire, A. Lamberty and P.H.E. Gardiner, *Anal. Chem.*, **71**, 4203–4207 (1999).
[12] Y.Y. Chan and W.T. Chan, *J. Chromatogr. A*, **853**, 141–149 (1999).
[13] I. Stewart and J.W. Olesik, *J. Chromatogr. A*, **872**, 227–246 (2000).
[14] N. Lavi and Z.B. Afassi, *Analyst*, **115**, 817–822 (1990).
[15] C. Lan, C. Tseng, M. Yang and Z.B. Alfass, *Analyst*, **116**, 35–38 (1991).
[16] L. Li, Y. Feng and G. Huang, *Spectroscopy and Spectral Analysis*, **18**, 354–358 (1998).
[17] T.D. Martin and J.K. Riley, *Atomic Spectroscopy*, **3**, 174–179 (1982).
[18] F.Y. Wang and Z.C. Jiang, *J. Anal. At. Spectrom*, **13**, 539–542 (1998).
[19] A.J. Pik, J.M. Eckert and K.L. Williams, *Anal. Chim. Acta*, **124**, 351–356 (1981).
[20] S. Tong, *Huaxue Tongbao*, **9**, 13–15 (1985).