

## Determination of Cr(III) and Cr(VI) in Environmental Waters by Derivative Flame Atomic Absorption Spectrometry Using Flow Injection On-Line Preconcentration with Double-Microcolumn Adsorption

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The species of Cr(III) and Cr(VI) in water samples were determined by flow injection on-line preconcentration and separation on two-microcolumn system-derivative flame atomic absorption spectrometry during a collaborative analysis for certification. The Cr(III) and Cr(VI) in water samples were retained on two microcolumns with ion exchange resin and were eluted directly to nebulizer by 15% HNO<sub>3</sub> and 8% NH<sub>4</sub>NO<sub>3</sub>, respectively. The characteristic concentration (at the sensitivity grade of 2 mV min<sup>-1</sup> for 1 min of preconcentration time) for Cr(III) and Cr(VI) were 0.130 and 0.0985 μg l<sup>-1</sup>, in the order which were 332- and 431-fold better than those of FAAS, and 45- and 47-fold better than those of FI-FAAS, respectively. The relative standard deviations were 3.27% and 3.66% with corresponding detection limits (3σ) of 0.244 and 0.235 μg l<sup>-1</sup>, respectively. The linear ranges of determinations for Cr(III) and Cr(VI) were 0~100 μgm l<sup>-1</sup> with correlation coefficients of 0.9984 to 0.9996. The satisfactory recovery of 94.4%~106% for Cr(III) and Cr(VI) could be obtained from water samples.

**Keywords:** Flow injection, On-line preconcentration, Derivative flame atomic absorption spectrometry, Chromium(III), Chromium(VI)

### INTRODUCTION

The chemical speciation of trace elements in environmental and biological samples is very important, because the effects of elements, especially trace heavy metals, on ecological and environmental systems are generally influenced by their chemical forms. Some elements in environmental samples not only exist in more than one valence state, but can also be present as cationic, anionic or neutral species. Cr(III) is present as several hydroxide species, including CrOH<sup>2+</sup>, Cr(OH)<sub>2</sub><sup>+</sup>, Cr(OH)<sub>3</sub>, Cr(OH)<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> and Cr<sub>3</sub>(OH)<sub>4</sub><sup>5+</sup>. Cr(VI) may be present in aqueous solutions as CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>-</sup>, H<sub>2</sub>CrO<sub>4</sub>, HCr<sub>2</sub>O<sub>7</sub><sup>-</sup>. Cr(VI) is reported to be toxic and carcinogenic to human even at relatively low concentration Levels [1],

whereas Cr(III) is considered essential for mammals for the maintenance of glucose, lipid, and protein metabolism [2].

A number of methods for the differential determination of Cr(III) and Cr(VI) by atomic absorption spectrometry with solvent extraction [3,4], ion exchange [5,6] and coprecipitation [7] have been described. Although many of the above schemes are highly selective and sensitive, the procedures are time-consuming, and the prolonged sample manipulation may disturb the natural chromium species [8]. The use of flow injection analysis coupled to flame atomic absorption spectrometry (FI-FAAS) has been demonstrated for rapid speciation of chromium. Sperling et al. [9] determined Cr(III) and Cr(VI) in waters by FAAS using flow injection on-line preconcentration with selective adsorption on activated alumina. The preconcentrated Cr(III) (pH 7) and Cr(VI) (pH 2) were eluted directly from the microcolumn into the nebulizer with 1.0 mol l<sup>-1</sup> nitric acid

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and 0.5 mol l<sup>-1</sup> ammonia, respectively. However, the operation was complex and the retention efficiency of Cr(III) on activated alumina was only 80%. The determination of different species of Cr has been successfully performed using a C<sub>18</sub> microcolumn [10-12]. The separation and preconcentration of Cr(III) and Cr(VI) were based on the selective sorption of the different reaction products of chromium with organic reagent at different pH values. The reagents used lead to contamination, and the methanol used as an eluant is toxic to human.

The sensitivity of derivative FAAS have been described for the direct determination of trace elements with 5~50 folds better than that of conventional FAAS [13]. It was used for direct determination of trace elements in environmental and biological samples in combination with atom trapping [14-17] and hydride generation [18,19] with a much higher sensitivity than conventional FAAS and HGAAS.

The main purpose of this work was to establish a simple, sensitive and reproducible method for the determination of Cr(III) and Cr(VI) by derivative FAAS combining with a double microcolumn on-line preconcentration flow injection system. The proposed method has been applied to the determination of Cr(III) and Cr(VI) in water samples with satisfactory results.

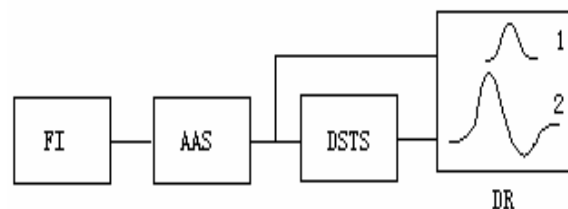
## EXPERIMENTAL

### Apparatus

A WFX-IF2 atomic absorption spectrometer (Beijing Second Optical Instrument Factory, Beijing, China) equipped with a chromium hollow cathode lamp (General Research Institute of Non-Ferrous Metals, Beijing, China) was used at the wavelength of 357.9 nm with a 1 nm slit width and a 7.5 mA lamp current.

A LZ2000 flow injection processor (Zhaofa Institute for microcolumns manufactured from Tygon tubing (20 × 3 mm id) packed with 0.1 g of 140-160 mesh type 732 strong Laboratory Automation, Shenyang, China) with two acidity cation exchange resins and type 717 strong alkaline anion exchange resin (both from Shijiazhuang Resin Factory, Shijiazhuang, China), respectively. The ends of the tube were fitted with cottonwool to retain the resin beads in the tube.

The laboratory-made derivative system was connected between the atomic absorption spectrometer and a



**Fig. 1.** The derivative measurement system of atomic absorption signal: (FI) flow injection on-line preconcentration system, (AAS) atomic absorption spectrometry, (DSTS) derivative signal treatment system, (DR) double-pen recorder. (1) The absorption signal of conventional on-line preconcentration-FAAS, (2) the absorption signal of on-line preconcentration-FAAS with derivative technique.

double-pen recorder. The derivative and conventional atomic absorption signals were recorded simultaneously at the 10 mV range. The measurement system is illustrated in Fig. 1.

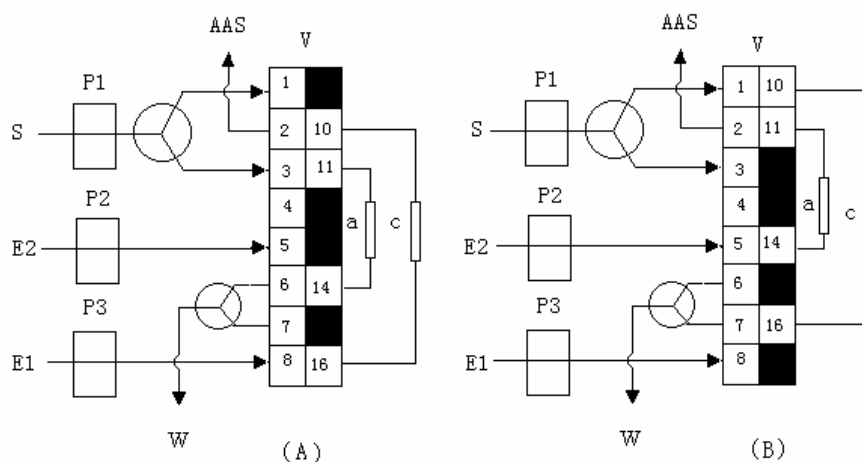
### Reagents

Standard solutions of Cr(III) and Cr(VI) were prepared by appropriate dilution of 1000 mg l<sup>-1</sup> stock solutions of chromium nitrate and potassium dichromate (The Chemical Regent Factory, Beijing), respectively.

All reagents used were of at least analytical grade. Sub-boiling distilled water was used throughout this work.

### Procedure

The flow injection manifold for on-line preconcentration and elution is shown in Fig. 2. Sample was passed sequentially through type 732 cation exchange resin microcolumn (c) and type 717 anion microcolumn (a) by using a peristaltic pump with a flow rate of 10 ml min<sup>-1</sup>. Preconcentration and determination of Cr(III) and Cr(VI) were performed sequentially by selecting the appropriate injection valve position and eluent solutions. At position A (Fig. 2), during the preconcentration step of Cr(III) on cation microcolumn, Cr(VI) just passed through cation microcolumn without being retained, meanwhile the retained Cr(VI) on anion microcolumn was eluted directly



**Fig. 2.** Flow injection manifold for on-line pre-concentration of Cr(III) and Cr(VI): (V) injection valve, (P1, P2, P3) peristaltic pumps, (a) anion microcolumn (c) cation microcolumn, (E1, E2) eluent, (S) sample, (W) waste.

to FAAS with 8% ammonium nitrate solution at a flow rate of  $4.0 \text{ ml min}^{-1}$  for a duration of 30 s. At position B (Fig. 2), during the pre-concentration step of Cr(VI) on anion microcolumn, the pre-concentrated Cr(III) just was eluted with 15% nitric acid directly to FAAS from cation microcolumn at a flow rate of  $4.0 \text{ ml min}^{-1}$  for a duration of 30 s. The conventional and derivative signals were recorded simultaneously by the double-pen recorder. The sensitivity grade of  $2 \text{ mV min}^{-1}$  was used for derivative signal processing.

## RESULTS AND DISCUSSION

### Characteristics of Derivative Signal

The derivative measurement system consists of a magnification and a differential unit. The output signal has a rigorous derivative relation with the input ones. The output signal of the system will keep in base-line when the variation of the input signal is zero. When the variation of the input signal is not zero, there is a corresponding polar output which is in direct relation to the variation of the input signal.

As shown in Fig. 3, the absorption signal of conventional FI-AAS is a pulse signal, and the signal of derivative FI-AAS consists of two parts, an upward peak and a downward peak, which correspond to the growth and decay sides of the conventional signal, respectively. The



**Fig. 3.** Absorption signal of conventional (A) and derivative (B) FI-FAAS.

total height of the up and down peaks, which is directly proportional to the concentration of chromium according to our experimental results and was considered for derivative FI-AAS.

### Effect of Flow Rate

The flow rate of sample passing through microcolumn is important for the pre-concentration. In general, sample flow rate for flow injection is limited by the backpressure produced by the column. The sorption efficiency is

decreased with increasing flow rate. No reduction in sorption efficiency was observed up to a flow rate of 10.0 ml min<sup>-1</sup> for 50 µg l<sup>-1</sup> of both Cr(III) and Cr(VI) at pH 6.0. A 10 ml min<sup>-1</sup> of sample flow rate and a 1 min of sorption time were used in the work.

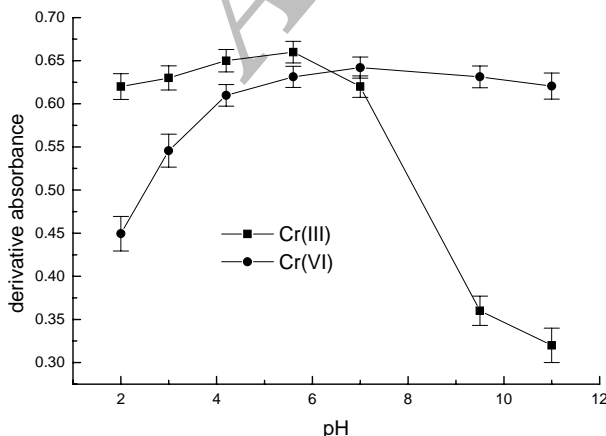
The effects of eluent flow rate in the range of 2.0~10.0 ml min<sup>-1</sup> on the derivative absorbance of Cr(III) and Cr(VI) were investigated. The derivative absorbance signal decreased with increasing flow rate, but lower flow rate led to elution peaks with wider tailing. A 4.0 ml min<sup>-1</sup> of eluent flow rate and a 30 s of eluted time were used in the work.

### Effect of Eluent Concentration

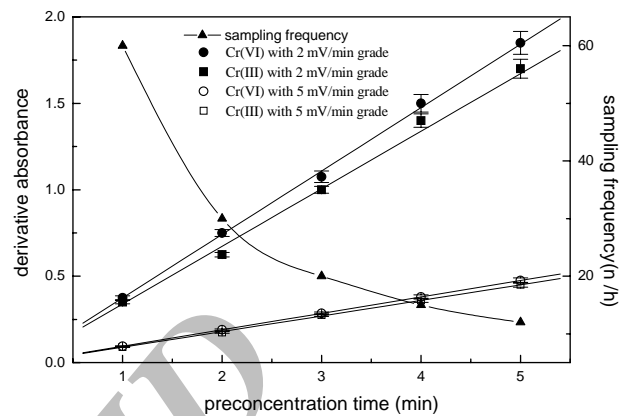
The effect of concentrations of nitric acid and ammonium nitrate used as eluent for Cr(III) and Cr(VI), respectively, in the range of 2%~20% on the derivative absorbance was investigated. The results showed that the derivative absorbances increased with increasing eluent concentration up to 12% for nitric acid and 6% for ammonium nitrate. With concentrations higher than 12% and 6% for nitric acid and ammonium nitrate, respectively, the derivative absorbances for Cr(III) and Cr(VI) no longer increased. Solutions of 15% nitric acid and 8% ammonium nitrate were used for complete elution of Cr(III) and Cr(VI) adsorbed on two microcolumn, respectively.

### Effect of Sample Acidity

The pH value of sample was adjusted by adding hydrochloric acid or sodium hydroxide solution for



**Fig. 4.** Effect of the pH of sample solution on the derivative absorbance.



**Fig. 5.** Effect of the preconcentration time on the derivative absorbance and sampling frequency.

preconcentration of Cr(III) and Cr(VI). Figure 4 shows that the derivative absorbance for Cr(III) and Cr(VI) depends on the pH value of sample solution. The derivative absorbance for Cr(VI) no longer increased when the pH value was higher than 4.0. For Cr(III), it was higher than 7.0. This may be due to the derivative absorbance decreasing rapidly when the pH value of formation of Cr(OH)<sub>3</sub> is in the range of 7.0-10.5 as described by Michael Sperling [9], so the Cr(OH)<sub>3</sub> cannot be retained by the resin in the range of pH 2-7, and Cr(VI), in the range of pH 4-11, were observed cation resin of less than 5%. A pH of 6 was selected for preconcentration of Cr. The derivative absorbance signal for both Cr(III), with relative change (III) and Cr(VI).

### Effect of Preconcentration Time

The effect of preconcentration time on preconcentration efficiency was tested by measuring derivative absorbance with 2 mV min<sup>-1</sup> and 5 mV min<sup>-1</sup> derivative sensitivity grades. Figure 5 shows that the derivative absorbance depends linearly on the preconcentration time for Cr(III) and Cr(VI) and that the smaller the number of derivative sensitivity grade (i.e., the higher the amplification), the higher is the derivative absorption signal with the same solution and same preconcentration time. For the determination of lower concentration of chromium the method can be modified by using a longer preconcentration period at the expense of a reduced sample throughput.

### Sensitivity, Detection Limit and Precision

The linear regression equations and correlation

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coefficients of the proposed method at different sensitivity grades for Cr(III) and Cr(VI) are listed in Table 1.

The calibration curves were linear in the concentration ranges of 0-100  $\mu\text{g ml}^{-1}$  for Cr(III) and 0-100  $\mu\text{g ml}^{-1}$  for Cr(VI) with correlation coefficients of 0.9984 to 0.9996. The sensitivity, detection limits and precision for FAAS, FIAAS and the proposed method are listed in Table 2. The characteristic concentration expressed as sensitivity is defined as the concentration that gives the derivative absorbance of 0.0044. The detection limit is the triple the standard deviation of a series of eleven measurements at blank level.

The sensitivities of the proposed method at the sensitivity grades of 2, 5 and 10  $\text{mV min}^{-1}$  for a preconcentration time of 1 min were 0.130, 0.335, and 0.65

$\text{mg l}^{-1}$  for Cr(III) and 0.0985, 0.219, and 0.457  $\mu\text{g l}^{-1}$  for Cr(VI). The sensitivities for Cr(III) and Cr(VI) at 2  $\text{mV min}^{-1}$  were 332 and 431-fold better than that of FAAS, and 45- and 47-fold better than that of conventional FI-FAAS under the same experimental conditions, respectively.

The detection limits at the sensitivity grade of 2  $\text{mV min}^{-1}$  for a preconcentration time of 1 min were 0.244  $\mu\text{g l}^{-1}$  for Cr(III) and 0.235  $\mu\text{g l}^{-1}$  for Cr(VI), which were improved by about 35-fold with respect to the conventional FI-FAAS.

### Interference Studies

Interference effects were investigated by determining the recoveries of chromium in the presence of different kinds of co-existing elements in water samples. No interference was observed up to 1800-fold Na(I), Ca(II), Mg(II), 1300-fold

**Table 1.** The Linear Regression Equations

Sensitivity range ( $\text{mV min}^{-1}$ )	Species	Regression line equation	Correlation coefficient
2	Cr(III)	$A = 3.55 \times 10^{-2}C + 0.001$	0.9986
	Cr(VI)	$A = 3.90 \times 10^{-2}C + 0.003$	0.9989
5	Cr(III)	$A = 1.37 \times 10^{-2}C + 0.002$	0.9996
	Cr(VI)	$A = 1.53 \times 10^{-2}C + 0.005$	0.9991
10	Cr(III)	$A = 6.32 \times 10^{-3}C + 0.001$	0.9984
	Cr(VI)	$A = 6.63 \times 10^{-3}C + 0.001$	0.9985

**Table 2.** Characteristic Concentration, Detection Limit and Precision

Method	Sensitivity range ( $\text{mV min}^{-1}$ )	Characteristic conc. ( $\mu\text{g l}^{-1}$ )		Detection limit ( $\mu\text{g l}^{-1}$ )		RSD <sup>a</sup> (%)	
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
FAAS		43.14	42.42	56.4	55.8	2.76 <sup>b</sup>	2.72 <sup>b</sup>
FI-FAAS		5.87	4.63	8.40	8.25	2.80 <sup>c</sup>	2.75 <sup>c</sup>
Proposal method	2	0.130	0.0985	0.244	0.235	3.27 <sup>d</sup>	3.66 <sup>d</sup>
	5	0.335	0.219	0.558	0.522	2.89 <sup>e</sup>	3.01 <sup>e</sup>
	10	0.650	0.457	0.696	0.667	2.23 <sup>f</sup>	2.22 <sup>f</sup>

<sup>a</sup> Based on 7 replicate measurements. Standard solution concentrations ( $\mu\text{g l}^{-1}$ ) are: <sup>b</sup> 1500, <sup>c</sup> 150, <sup>d</sup> 5.0, <sup>e</sup> 10.0, <sup>f</sup> 20.0.

**Table 3.** Results for Cr speciation in GBW 08607 Water

Cr Species	GBW 08607 Water ( $\mu\text{g l}^{-1}$ )	
	Certified	Found
Cr(III)	-	$499 \pm 12.5$
Cr(VI)	-	Not detected
Total Cr	$500 \pm 10$	$499 \pm 12.5$

Cd(II), Cu(II), Zn(II), Pb(II) for chromium solutions of 5-20  $\mu\text{g l}^{-1}$ . 90  $\mu\text{g ml}^{-1}$  of Fe(III), Fe(II) and Ni(II) interfered; however, the concentrations of above elements are below those in water samples. Therefore, no interferences had to be expected in the analysis of real samples.

### Sample Analysis

The results for Cr(III) and Cr(VI) species found in the water reference material (GBW08607) are shown in Table

3. The values obtained for Cr(III) and Cr(VI) in the water reference material (GBW08607) were in agreement with the standard values. This indicates the accuracy of the proposed method.

The contents of Cr(III) and Cr(VI) in tap water, synthetic water, electroplating wastewater and Minxin river water samples were determined. The results are shown in Table 4 along with the corresponding recoveries. The recoveries are in the range of 94.4%-106%.

## CONCLUSIONS

The derivative flame absorption spectrometry combined with flow injection on-line preconcentration on double-microcolumn is a simple and sensitive method for speciation of chromium in environmental water samples. The proposed method has higher sensitivity, lower detection limit and good reproducibility compared to those of FI-FAAS and FAAS. The proposed method is possible for the routine determination of the speciation of inorganic chromium in environmental water samples without

**Table 4.** Determination of Cr (III) and Cr (VI) in Water Samples

Sample	Conc. in spiked solution ( $\mu\text{g l}^{-1}$ ) Cr(III) + Cr(VI)	Cr(III)		Cr(VI)	
		Found ( $\mu\text{g l}^{-1}$ )	Recovery (%)	Found ( $\mu\text{g l}^{-1}$ )	Recovery (%)
Tap water <sup>a</sup>	0+0	Not detected		Not detected	
	5+5	5.27	105	5.15	103
	10+10	9.83	98.3	10.0	100
	15+15	15.0	100	14.6	97.0
Synthetic water <sup>b, c</sup>	25+0	24.5	98.1	-	-
	50+25	50.6	101	25.8	103
	75+50	73.2	97.6	53.1	106
	100+75	101	101	72.7	96.9
Electroplating waste water <sup>b</sup>	0+0	18.7	-	10.5	-
	5+5	23.4	94.4	15.9	107
	10+10	28.4	96.5	21.1	106
Minxin river water <sup>a</sup>	0+0	2.10	-	Not detected	
	5+5	6.89	95.8	5.09	102
	10+10	12.4	103	9.47	94.7

<sup>a</sup> Derivative sensitivity grade 2  $\text{mV min}^{-1}$ . <sup>b</sup> Derivative sensitivity grade 10  $\text{mV min}^{-1}$ .

complicated retreatment and with the advantages of simplicity, speed, less risk of contamination and lower cost.

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