On-Line Chromium (Cr^{3+} / Cr^{6+}) Speciation by FI-ICP-OES

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Introduction

Over the past several years, numerous papers concerning the determination of Cr^{3+} and Cr^{6+} in various samples have been published. The reason for this interest is governed by the fact that chromium toxicity depends critically on its oxidation state. The two primary oxidation states of chromium (Cr^{3+} and Cr^{6+}) in natural waters differ significantly in biological, geochemical and toxicological properties(1-2). While Cr^{3+} is considered essential in mammals for the maintenance of glucose, lipid, and protein metabolism, Cr^{6+} is known to be toxic to humans because of its ability to oxidize other species and its undesirable effects on the lung, liver and kidney. Because of different toxicities and bio-availability of chromium species, the analysis of total chromium does not give full information about possible health hazards. Therefore, it is important to monitor the concentration of the individual chromium species as well as the total content in the environment. Traditional methods for the speciation of inorganic chromium are relatively time-consuming, involving species separation based on solvent extraction (3), co-precipitation (4), electrochemical separation (5), ion exchange, solid-phase extraction, or selective volatilization in combination with graphite furnace atomic absorption spectroscopy. In the present work, an on-line FI-ICP-OES method is proposed for the pre-concentration of Cr^{3+} and Cr^{6+}. The determination was performed by ICP-OES associated with a FI methodology. The goal of this work was to establish a fully automated method for the determination of Cr^{3+} and Cr^{6+} which is easily controlled, has high sensitivity, and is reproducible.

Experimental

Instrumentation

A PerkinElmer Optima™ 5300 DV ICP-OES (inductively coupled plasma optical emission spectrometer) (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) with WinLab32™ v3.1 software was used. A PerkinElmer FIAS™-400 system was used as the flow injection accessory, which is also controlled with the WinLab32 v3.1 software.

The FIAS-400 system, equipped with an AS-91 autosampler, was connected directly to the Optima 5300 DV nebulizer by means of narrow-bore Teflon® tubing and used for on-line pre-concentration of chromium. The automatic operation of the injection valve and two multi-channel peristaltic pumps were programmed using the spectrometer software (PerkinElmer ICP-OES WinLab32 v3.1). The internal gas flow of the FIAS-400 system was deactivated. Tygon peristaltic tubing (1.52 mm i.d.) was used to pump the sample and buffer, while 0.76 mm i.d tubing was used for eluent; PTFE tubing (0.3 mm i.d.) was used for all connections in order to minimize dead volume. A conically shaped activated alumina microcolumn (PerkinElmer, PN B050-9561, yellow) was used for speciation of Cr^{3+} and Cr^{6+}. Photos of the FIAS system and the column appear in Figures 1 and 2.

Figure 1. FI-ICP-OES with FIAS-400, Autosampler 91 and Optima 5300 DV ICP-OES

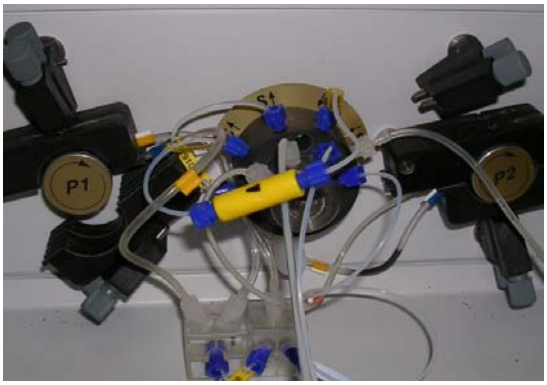

Figure 2. FIAS-400 and activated alumina mini column (yellow)

Time-resolved signals of chromium were displayed on the computer monitor along with peak area and integrated intensity values. A Scott spray chamber and cross-flow nebulizer were used for sample introduction into the ICP-OES. The operating conditions for FI-ICP-OES are summarized in Table I, and the flow injection program for FIAS 400 is shown in Table II. Using this program, a total sample volume of approximately 15 mL is used for the analysis: the flow rate is about 10 mL/ min, with the prefill step lasting 30 seconds and the load step requiring 60 seconds. All measurements were made using the transient scan mode with integration time of 50 ms for each Cr-species and 3 points per peak. Because transient signals are used, the peak area mode was used for all quantification work. Speciation conditions are shown in Table III.

Table I. FI-ICP-OES Operating Conditions

Plasma Gas	15 L/min
Auxiliary Gas	0.2 L/min
Nebulizer Gas	0.8 L/min
RF Power	1300 W
Plasma View	Axial View
Peak Processing	Peak Area
Signal processing	Transient
Points per peak	3
Integration time	50 ms
Wavelength	267.7 nm
Replicates	3

Table II. Flow Injection Program of FIAS 400

Step	Description	Time (sec)	Pump1 speed	Pump2 speed	Valve Position
Prefill		30	100	0	Fill
1	Load	60	120	0	Inject
2	Wash	30	0	120	Inject
3	Elute, Read	45	0	100	Fill
4	Wash	30	0	100	Inject

Table III. Speciation Conditions

	Cr^{3+}	Cr^{6+}
Buffer	Potassium sodium phosphate (pH 7)	Potassium chloride (pH 2)
Eluent	1.0 mol/L HNO_3	0.5 mol/L NH_4OH
Sorbent	activated alumina, acidic form	
Column	Conical shape, approx.40 mg of sorbent, yellow (PerkinElmer, P/N B050-9561)	

Reagents

All reagents used were of at least analytical grade. Stock standards of 1000 mg/L Cr^{3+} and Cr^{6+} were obtained from Sigma & Aldrich. Working standards were prepared by appropriate serial dilution. The buffers were purchased already prepared from Sigma & Aldrich and were potassium sodium phosphate at pH 7for Cr^{+3} (part number 456098-500mL) and potassium chloride at pH 7 for Cr^{+6} (part number 223581-500mL). Both chemicals were from Sigma & Aldrich, and 0.5 M ammonia solutions and 1 M nitric acid were prepared from the Aldrich chemicals, respectively. Ultrapure water (18MΩ cm^{-1}) was obtained from an EASYpure® RF (Barnstedt, Iowa, USA).

Sample Collection and Preparation

In order to avoid the reduction of Cr^{6+} with the organic matter present in natural water, the samples were not acidified at collection. The analysis was performed immediately after sampling in order to minimize the adsorption of chromium in solution on the walls of the container. All instruments used were previously washed with a 10 % (v/v) HNO_3 solution followed by the ultrapure water.

Procedure for FI-ICP-OES Measurement

A tubing diagram, schematic diagram of the FIAS-400 manifold and the sequence of its operation are presented in Figures 3, 4 and Table II, respectively. A prefill step flushes the tubing and mixing block with a sample and buffer solution by pump 1. In step 1, the sample is premixed in the mixing block with buffer solutions of pH 2.0 for Cr^{6+} or pH 7.0 for Cr^{3+}, respectively and passed through the analytical column (10 mL/min). The time selected for this step controls the volume of sample passed through the column. Following sample loading, the tube is washed with deionized water by pump 2 to remove residual sample in the lines. Retained Cr^{3+}or Cr^{6+} ions are then eluted with 1 M (mol/L) nitric acid or with 0.5 M(mol/L) ammonia, respectively, at a flow rate of 2.5 mL/min. The sample is introduced into the plasma in step 3 and then analyzed by ICP-OES. The total analytical time for the entire procedure is 3 minutes. In step 4, the valve is switched to the wash position to return the column to a neutral pH in preparation for loading the next sample. As can be seen in Figure 4, in the elution step the valve was switched to fill position and the retained chromium was eluted in countercurrent (i.e., reversal of the flow direction through the column during elution with respect to sample loading) with eluent at a flow rate 2.5 mL/min, directly into the nebulizer and subsequently to the plasma. Countercurrent elution subsequently improves the elution profile as compared to the unidirectional flow. Chromium was completely eluted from the column with 2.5 mL/min. The operating conditions were established and the determination was completed.

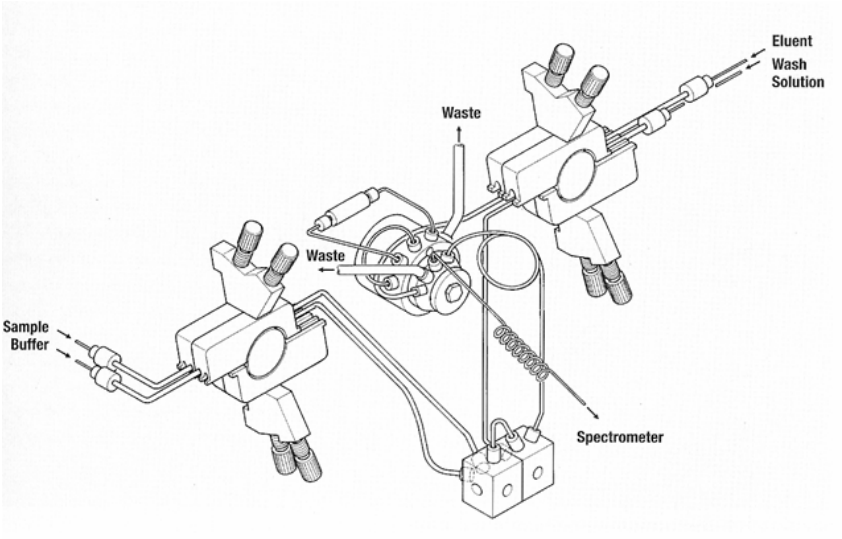

Figure 3. Tubing diagram of FIAS 400 for on-line chromium species determination

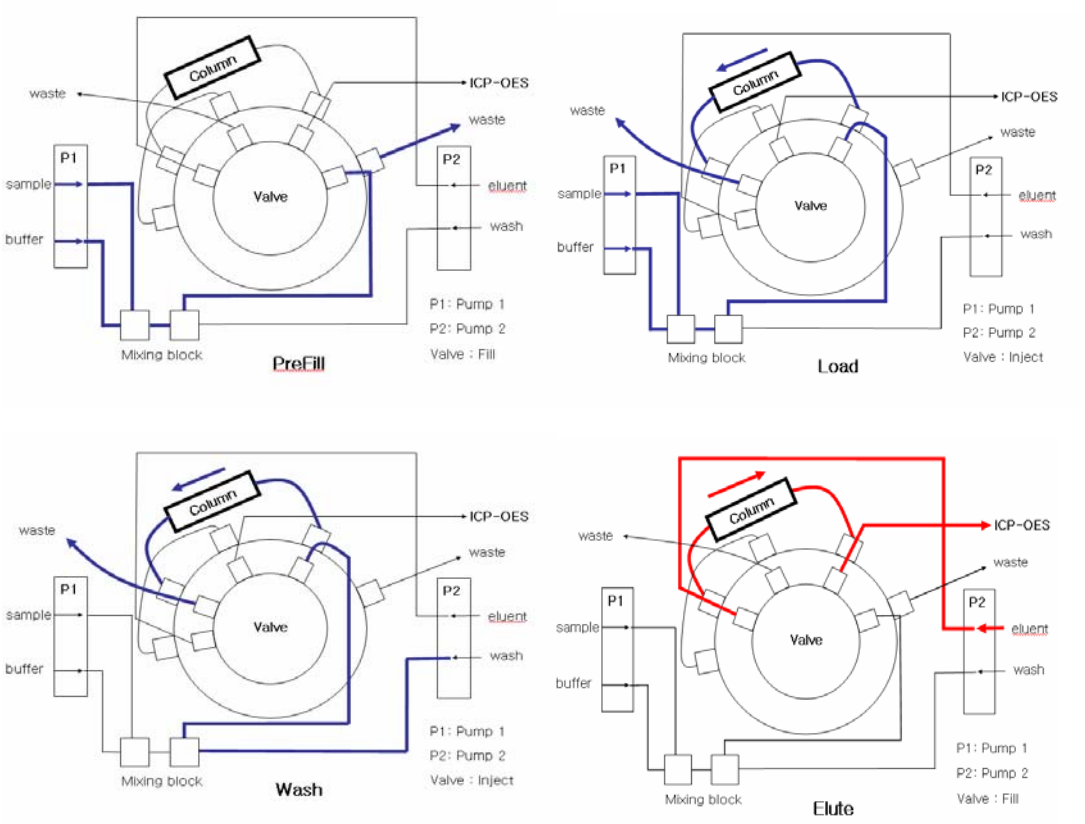

Figure 4. Schematic diagram of the system for FIAS-400 system for automated speciation of Cr^{3+} and Cr^{6+} species

Results

Figure 5 shows the peak profile for a 50 µg/L Cr^{6+} standard where 10 mL of the standard was pre-concentrated on the column. The relative standard deviation (RSD) for ten replicates containing 100 µg/L of Cr^{3+} and Cr^{6+} was less than 5%. As seen in Figure 6, the calibration graph for Cr^{6+} is linear with a correlation coefficient of 0.9999 from levels near the detection limits up to at least 100 µg/L. The detection limit, calculated as the amount of Cr required to yield a net peak that was equal to three times the standard deviation of the background signal (3δ), was 1 µg/L and 0.9 µg/L for Cr^{3+} and Cr^{6+}, respectively.

In routine practical applications, the recovery of Cr^{3+} and Cr^{6+} determined by the proposed procedure in some natural water samples ranged from 90 to 110 %, as shown in Table IV. Recoveries were determined by spiking water samples with different levels of the chromium species and measuring the results.

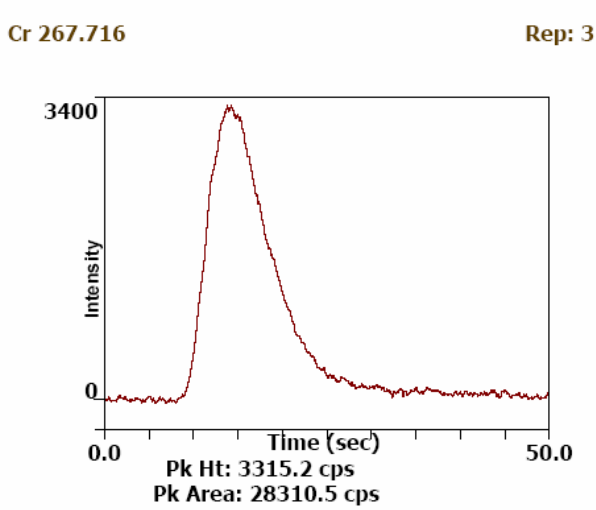

Figure 5. Peak profile obtained by preconcentration of 10 mL of Cr^{6+} using the system depicted in Figure 3. Loaded flow rate was 10 mL/min; the elution flow rate was 2.5 mL/min. Cr^{6+} concentration was 50 µg/L.

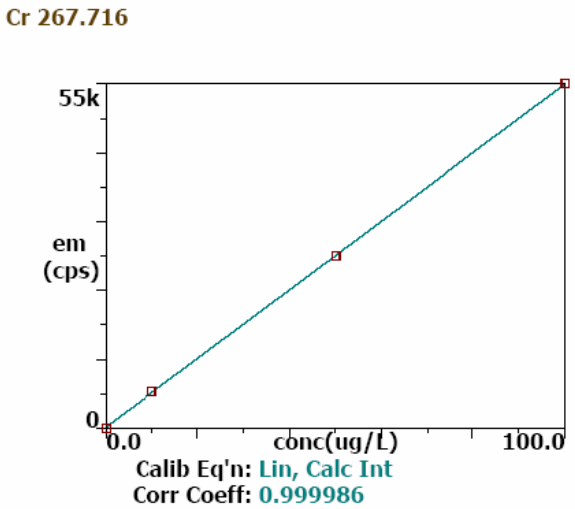

Figure 6. Calibration for Cr^{6+} using FIAS-400 with reference solutions containing 10, 50, 100 µg/L

Table IV. Recovery of Cr^{3+} and Cr^{6+} after spiking with known amounts of mixture to drinking water

Sample	Spike Conc (µg/L)	% Recovery Cr^{3+}	% Recovery Cr^{6+}
Drinking water	100	102	98
	50	96	102
	10	110	98

Conclusion

The Flow Injection Analysis System (FIAS) coupled with ICP-OES performs very well as a simple quantitative method for chromium speciation. This fully automated, on-line chromium speciation method was applied to a series of spiked natural water samples with very good recoveries and detection limits.

References

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