

CHROMSYMP. 2143

## **Determination of dissolved hexavalent chromium in industrial wastewater effluents by ion chromatography and post-column derivatization with diphenylcarbazide**

ELIZABETH J. ARAR\*

*Technology Applications, Inc., 26 West Martin Luther King Drive, Cincinnati, OH 45219 (U.S.A.)*  
and

JOHN D. PFAFF

*U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, OH 45268 (U.S.A.)*

---

### ABSTRACT

A proposed EPA method for the determination of dissolved hexavalent chromium in drinking water, groundwater and industrial wastewater effluents was developed using existing ion chromatographic techniques. Two solid waste matrices were briefly investigated. Aqueous samples were passed through a 0.45- $\mu\text{m}$  filter and the filtrate was either (1) left unadjusted, (2) adjusted to pH 8 or (3) adjusted to pH 10 prior to analysis by ion chromatography. The method detection limits were 0.3–0.4  $\mu\text{g/l}$ . When analyzed within 24 h, the two pH levels and the unadjusted sample yielded *ca.* 100% recovery of spikes. No oxidation of trivalent chromium to hexavalent chromium was observed at pH 7, 8 or 10 when aqueous samples were spiked with 50 mg/l Cr(III).

---

### INTRODUCTION

Current U.S. Environmental Protection Agency (EPA) methods for dissolved hexavalent chromium are Methods 218.4 and 218.5 [1]. Method 218.4 is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK) followed by flame atomic absorption spectrometry. Method 218.5 is based on coprecipitation of lead chromate with lead sulphate, which is resolubilized as Cr(III) prior to analysis by furnace atomic absorption spectrometry. Ion chromatography (IC) has proved to be a useful technique for the determination of hexavalent and trivalent chromium in various aqueous matrices [2–5]. Recent developments in IC have resulted in the coupling of anion exchange IC with post-column derivatization of Cr(VI) with diphenylcarbazide and detection of the colored complex at 520 nm [6]. This techniques does not suffer from the interferences common to the diphenylcarbazide spectrophotometric method when other potentially reactive metals are present in the sample because the Cr(VI) is separated from the matrix prior to color development. The primary focus of this work was to apply this existing ion chromatographic method to

wastewater and to determine a sample preparation and preservation step that would work well for most types of wastewater effluents regulated by the Environmental Protection Agency.

## EXPERIMENTAL

The most challenging problem in the determination of Cr(VI) is the preservation of its oxidation state. Cr(VI) exists predominantly as  $\text{HCrO}_4^-$  in acidic solution and is a strong oxidizer. It is reduced to Cr(III) in the presence of organics or the oxides of nitrogen and sulfur. Conversely, Cr(III) in an alkaline medium will oxidize to Cr(VI) in the presence of oxidants such as Fe(III), oxidized Mn or dissolved oxygen [7,8]. At  $\text{pH} \geq 6.5$  Cr(VI) exists predominantly as  $\text{CrO}_4^{2-}$ , which is less reactive than  $\text{HCrO}_4^-$ . For this reason, two pH values (8 and 10) were chosen at which the samples were stabilized after filtration through a  $0.45\text{-}\mu\text{m}$  filter. A 1.0 M sodium hydroxide solution (ultrapure grade; Aesar, Seabrook, NH, U.S.A.) was used to adjust the pH of the samples. Five types of water (ASTM Type I water, drinking water, groundwater, primary municipal wastewater effluent and electroplating wastewater effluent) were spiked at 0.1 and 1.0 mg/l. Additionally, two solid waste samples (treated municipal sludge and electroplating waste) were spiked with Cr(VI), extracted at various pH values, filtered and adjusted to the same pH values as aqueous samples. Solid samples were extracted and analyzed on the day of collection. Aqueous samples were analyzed on the day of collection and the day after. Some of the aqueous samples were analyzed again 4–15 days after collection. All sample solutions were stored at  $4^\circ\text{C}$  and allowed to equilibrate to ambient temperature prior to analysis by IC.

### *Verification of ion chromatographic method*

The instrumental operating conditions were as follows: instrument, Dionex 4506i ion chromatograph, AI450 software and Dionex VDM-2 detector; guard column, Dionex IonPac NG1; separation column, Dionex IonPac AS7; eluent, 250 mM ammonium sulfate–100 mM ammonium hydroxide solution at a flow-rate of 1.5 ml/min; Post-column reagent, 2 mM diphenylcarbazide–10% (v/v) methanol–1 N sulfuric acid at a flow-rate of 0.5 ml/min; Detector, visible (530 nm).

The IC method, which was developed by Dionex, was not altered in any way [6]. The linear range, precision, accuracy and detection limit were initially investigated by fortifying ASTM Type I water with Cr(VI) as  $\text{CrO}_4^{2-}$ . The linear range was tested by preparing eight standards covering the estimated linear range (0.5  $\mu\text{g/l}$ –10.0 mg/l). A single injection was made of each standard and the peak height used in preparing a calibration graph. A log–log plot of peak height vs. analyte concentration was constructed and the correlation coefficient used to determine the working linear range.

The analytical precision for a single calibration was determined by the reproducibility of the measured peak height for eight consecutive injections of a low standard (0.5  $\mu\text{g/l}$ ) and a high standard (1.0 mg/l) and reported as relative standard deviation (R.S.D.). Accuracy was determined by the analysis of high- and low-concentration quality control samples and blinds obtained from another laboratory. Results within 10% of the true values were accepted. The method detection limit (MDL) of Cr(VI) in the various matrices was determined by taking seven replicate

aliquots of a single sample that did not contain a level of Cr(VI) exceeding five times the estimated MDL in ASTM Type I water. The MDL for each matrix is defined as the standard deviation ( $s$ ) of the seven replicate analyses multiplied by the Student's  $t$  value for a 99% confidence level [9].

## RESULTS

### *Verification of ion chromatographic method*

The correlation coefficient for a log-log plot of peak height *vs.* concentration was 0.99988 for a concentration range covering four orders of magnitude. The analytical precision as determined by the R.S.D. of the peak height of eight consecutive injections of a low and a high standard was 4.9% for a 0.5  $\mu\text{g/l}$  standard and 0.57% for a 1.0 mg/l standard. Two Cr(VI) standards of known concentrations were obtained from another laboratory together with two samples of unknown concentration. The low standard (4.0  $\mu\text{g/l}$ ) and the low unknown (2.0  $\mu\text{g/l}$ ) were both found to be within 10% of their nominal concentrations. The high standard (1.0 ml/l) and the high unknown (0.5 mg/l) were both found to be within 3% of their nominal concentrations.

### *Aqueous sample analysis*

MDLs for each water matrix are listed in Table I. MDLs were determined using a 250- $\mu\text{l}$  sample loop with a detector setting of 0.002 a.u.f.s. The instrumental detection limit, which was determined based on a chromatographic method by Knoll [10], was 0.15  $\mu\text{g/l}$  in ASTM type I water.

TABLE I  
METHOD DETECTION LIMITS FOR Cr(VI) IN WATER AND WASTEWATER

Matrix type	Retention time (min)	Method detection limit <sup>a</sup> ( $\mu\text{g/l}$ )
Reagent water	3.80	0.4
Drinking water	3.80	0.3
Groundwater	3.80	0.3
Primary sewage wastewater	3.80	0.3
Electroplating wastewater	3.80	0.3

<sup>a</sup> MDL concentrations are calculated for final analysis solution.

Sample collection sites were all within a 1-h drive of the laboratory, making it possible to filter, preserve and analyze the samples within 4 h of collection. Samples were stored on ice from the time of collection until received in the laboratory, at which time they were filtered, adjusted to pH 8 or 10 and left without pH adjustment. For each pH value spikes of 100 and 1000  $\mu\text{g/l}$  were made. Each sample was analyzed immediately and on the next day. Recoveries for the same-day analysis and at a later date if performed are given in Table II. Native Cr(VI) was not found in any of the water sample at any of the pH values.

TABLE II  
RECOVERIES OF Cr(VI) IN WATER AND WASTEWATER

Matrix type	pH	Spike level ( $\mu\text{g/l}$ )	Recovery (%)		
			Day 0	Day 1	Day $n^a$
Reagent water	7	100	100	98	98
		1000	100	95	94
	8	100	102	96	100
		1000	96	98	94
	10	100	100	94	98
		1000	100	94	97
Drinking water	7	100	105	105	108
		1000	98	95	93
	8	100	103	100	101
		1000	100	104	103
	10	100	99	100	98
		1000	99	99	97
Groundwater	7	100	94	94	No data
		1000	99	97	No data
	8	100	105	101	No data
		1000	90	95	No data
	10	100	98	98	No data
		1000	96	99	No data
Primary municipal wastewater effluent	7	100	96	96	81
		1000	101	102	99
	8	100	100	100	90
		1000	83	83	86
	10	100	100	100	100
		1000	104	104	111
Electroplating wastewater	7	100	102	99	No data
		1000	97	92	No data
	8	100	102	100	No data
		1000	98	95	No data
	10	100	99	103	No data
		1000	101	103	No data

<sup>a</sup> The reagent water and drinking water were re-analyzed on the fifteenth day after collection. The primary municipal wastewater effluent was re-analyzed on the fifth day after collection.

### Solid waste samples

Solid waste samples were obtained from a municipal wastewater treatment plant and an electroplating plant. Solid samples were treated with the same timeliness as aqueous samples. A 10-ml volume of the moist sample was placed in a 50-ml metal-free centrifuge tube. ASTM Type I water (25 ml) was added prior to the addition of the Cr(VI). The tube was capped, shaken thoroughly, placed in an ultrasonic water-bath for 15 min and centrifuged for 20–30 min at 2000 rpm (675 g). A 10-ml volume was filtered for each pH value to be investigated. The pH of the extraction solution was checked and in both solid waste extract samples had remained at 7. Recoveries of Cr(VI) at various spike levels and at various pH values are given in Table III for the municipal sludge cake. As a neutral extraction yielded nearly zero

TABLE III  
RECOVERIES OF Cr(VI) FROM MUNICIPAL SLUDGE CAKE

Spike level (mg/l)	pH of extraction solution	Recovery (%)	Blank concentration ( $\mu\text{g/l}$ )
0.2	7	< 10	< MDL
2.0	7	< 10	< MDL
0.2	8	< 10	< MDL
4.0	9.5	76.5	No data
4.0	13	76.5	7.9

TABLE IV  
RECOVERIES OF Cr(VI) FROM ELECTROPLATING SOLID WASTE

Spike level (mg/l)	pH of extraction solution	Recovery (%)	Blank concentration ( $\mu\text{g/l}$ )
1.0	8	61.9	No data
1.0	9	56.4	20.3

recoveries even when the pH of the filtrate was adjusted to 8 or 10, an extraction at pH 8 was attempted for the sludge cake. An extraction with the eluent (pH 9.7) and an extraction with 0.1 *M* sodium hydroxide solution (pH 13) were also attempted. The recoveries were improved but were still considered poor.

Only two pH values were examined for the electroplating waste, distilled, deionized water at pH 8 and 9 being used as the extracting solution. Recoveries of a 1.0 mg/l spike are given in Table IV together with the Cr(VI) concentration found in a blank. At this point it was decided that solid waste would require more method development than was planned in this assignment and it was excluded from the final proposed method. It should be noted, however, that the analytical technique using IC would remain the same.

## DISCUSSION

As a pH of 7, 8 or 10 had little effect on the recovery of spikes in wastewaters when analyzed within 24 h of collection, the final proposed method recommends an adjustment to pH 9–9.5 using a concentrated buffer solution. The buffer is a 10-fold more concentrated form of the IC eluent. The buffer works well on samples at high or low pH and requires less precise addition than the 1.0 *M* sodium hydroxide solution.

As solid waste samples present special problems, they are not included in the method. The presence of Cr(VI) in the unspiked sludge cake found when the pH of the extraction solution was 13 but not at pH 8 raises the issue of a possible change in the oxidation state of chromium. Extraction solutions of higher pH may either solubilize otherwise insoluble chromates or they may oxidize available Cr(III) in a reactive matrix such as sludge waste.

It is recommended that all samples be analyzed within 24 h of collection, although drinking water samples have a longer holding time. As wastewater matrices will vary, it is the responsibility of the monitoring laboratory to show that the specific matrix type under study is stable for longer than the recommended 24 h.

#### ACKNOWLEDGEMENTS

The authors gratefully thank Theodore M. Martin, U.S. EPA, Cincinnati, OH, Stephen E. Long, Technology Applications, Cincinnati, OH, and Robert Joyce, Dionex, Sunnyvale, CA, for their many contributions to this work. This work was funded by the United States Environmental Protection Agency under Contract No. 68-03-3352 to Technology Applications.

#### REFERENCES

- 1 *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1983.
- 2 S. Ahmed, R. C. Murthy and S. V. Chandra, *Analyst (London)*, 115 (1990) 287.
- 3 H. C. Mehra and W. T. Frankenberger, Jr., *Talanta*, 36 (1989) 889.
- 4 D. Molina and M. T. Abell, *Am. Ind. Hyg. Assoc. J.*, 48 (1987) 830.
- 5 T. Williams, P. Jones and L. Ebdon, *J. Chromatogr.*, 482 (1989) 361.
- 6 *Dionex Technical Note*, No. 26, Dionex, Sunnyvale, CA, 1990.
- 7 R. Bartlett and B. James, *J. Environ. Qual.*, 8 (1979) 31.
- 8 V. J. Zatka, *Am. Ind. Hyg. Assoc. J.*, 46 (1985) 327.
- 9 J. A. Glaser, D. L. Foerst, G. D. McKee, S. A. Quave and W. L. Budde, *Environ. Sci. Technol.*, 15 (1981) 1426.
- 10 J. E. Knoll, *J. Chromatogr. Sci.*, 23 (1985) 422.