DIONEX

Technical Note

TN 24
July 1991

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Determination of Chromium by Ion Chromatography

INTRODUCTION

Chromium exists primarily in two oxidation states, trivalent Cr(III) and hexavalent Cr(VI). The uncomplexed trivalent species is the chromic ion, Cr^{3+}. This species is soluble in acidic solutions but precipitates as the hydroxide in alkaline solutions. The ligand exchange kinetics of Cr(III) are very slow and account for its low reactivity in environmental and biological systems.

The hexavalent species exists primarily as the chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ion, depending upon the pH of the solution. In acidic solutions, dichromate dominates; whereas in basic solutions, chromate dominates. In either state, Cr(VI) is a strong oxidizer and therefore harmful in environmental and biological systems.

Three methods are presented in this technical note for the determination of chromium in various sample matrices.

The need for various industries to determine the trivalent and hexavalent species of chromium has led to the development of Method A for the rapid speciation of chromium at ppb levels. Method A utilizes a postcolumn reaction with a color reagent. It is a very selective and sensitive method, allowing determination of Cr(III) (chromic ion) and Cr(VI) (chromate/dichromate ion). Using direct injections of 250 µL, the minimum detection limits are below 100 ppb for Cr(III) and 1 ppb for Cr(VI).

The need to determine total chromium content in industrial waste waters and solid waste extracts has necessitated the development of a method for analyzing samples that have undergone standard oxidation and digestion procedures. One such procedure is an alkaline persulfate digestion, which introduces high levels of sulfate. Method B is tailored for such samples. As in Method A, Method B also utilizes a postcolumn reaction with a color reagent. This method is used to determine Cr(VI) only. Using the suggested digestion procedure, the detection limit is about 5 ppb.

Method C allows the determination of inorganic anions in addition to chromate by anion exchange and chemically suppressed conductivity. The detection limit for Cr(VI) is below 500 ppb by direct injection.

STANDARDS

Trivalent and hexavalent chromium salts are available from chemical supply companies. Reagent grade $Cr(NO_3)_3 \cdot 9H_2O$ should be used as a chromic ion source. The standard should be slightly acidified (pH 3-4) using HNO_3. Chromate standards may be prepared from the sodium or potassium salts of chromate or dichromate. No pH adjustment is suggested. To prepare 1,000-ppm standards of the metals from pure salts, dissolve the weights of salt listed below in 1 L of water. Add 2 drops of concentrated nitric acid to the Cr(III) standard.

Metal	Salt	Weight (g)
Cr(III)	$Cr(NO_3)_3 \cdot 9H_2O$	7.695
Cr(VI)	$Na_2CrO^4 \cdot 4H_2O$	4.494

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LPN 034350-01 5M 7/91

METHOD A: SIMULTANEOUS DETERMINATION OF TRIVALENT AND HEXAVALENT CHROMIUM

Analytes

Chromic ion (Cr^{3+}) and chromate (CrO_4^{2-}); didichromate ($Cr_2O_7^{2-}$) ions

Discussion of Method

In Method A, the visible absorbances of the Cr(III)-pyridine dicarboxylic acid (PDCA) complex and the Cr(VI)-diphenylcarbohydrazide (DPC) complex at 520 nm allow photometric detection of Cr(III) and Cr(VI). As shown in Figure 1, elution times are 3 minutes and 5 minutes for trivalent and hexavalent chromium, respectively.

The eluent system is PDCA based. The trivalent chromium is separated as the $Cr(PDCA)_2^-$ complex, while the hexavalent chromium is separated as the chromate ion, CrO_4^{2-}. Hexavalent chromium does not form a complex with PDCA. Because of the slow kinetics of ligand exchange for Cr(III), a pre-column derivitization with PDCA is used to form the Cr(III)-PDCA complex in the samples. At the nearly neutral pH of the eluent, Cr(VI) exists as divalent chromate. The Cr(III)-PDCA complex is a stable monovalent anion.

The pH values of the sample and eluent systems are critical to the efficiency of the separation. As shown in Figure 2, pH values of 6 or greater cause inhibition of the $Cr(PDCA)_2^-$ complex formation. pH values below 6 show a marked conversion of chromate ion to dichromate ion, which can be harmful to the column. The pH of the system and samples is therefore chosen to be 6.8 to allow optimum separation and detection of both species.

After separation, the Cr(VI)-DPC complex is formed using postcolumn derivitization. Using injection volumes of 250 µL (the standard loop must be replaced), determinations of Cr(III) and Cr(VI) are possible to detection limits of 30 ppb and 0.3 ppb, respectively.

The flow rates of the eluent and postcolumn reagent are critical to the analysis. The combined flow rate should be 1.5 mL/min. The eluent flow rate alone is 1.0 mL/min and the postcolumn reagent is 0.5 mL/min. Adjust the RDM flow rate after first measuring the flow rate of the eluent at the waste line outlet and then measuring the flow rate again after pressurizing the RDM.

In a variation of Method A, both Cr(III) and Cr(VI) are dettached at 365 nm. The absorbances of the Cr(III)-PDCA complex and the chromate ion at 365 nm require no postcolumn hardware for the detection of both oxidation states. The absorbance of chromate at 365 nm is not nearly as great as that of Cr(VI)-DPC complex at 520 nm, but the method is useful for samples that contain high concentrations of chromium, such as plating baths.

Recommended Equipment

Any Dionex Ion Chromatograph equipped with either a Variable Wavelength UV/Vis or a Visible Detector and either a Postcolumn Module or a Reagent Delivery Module.

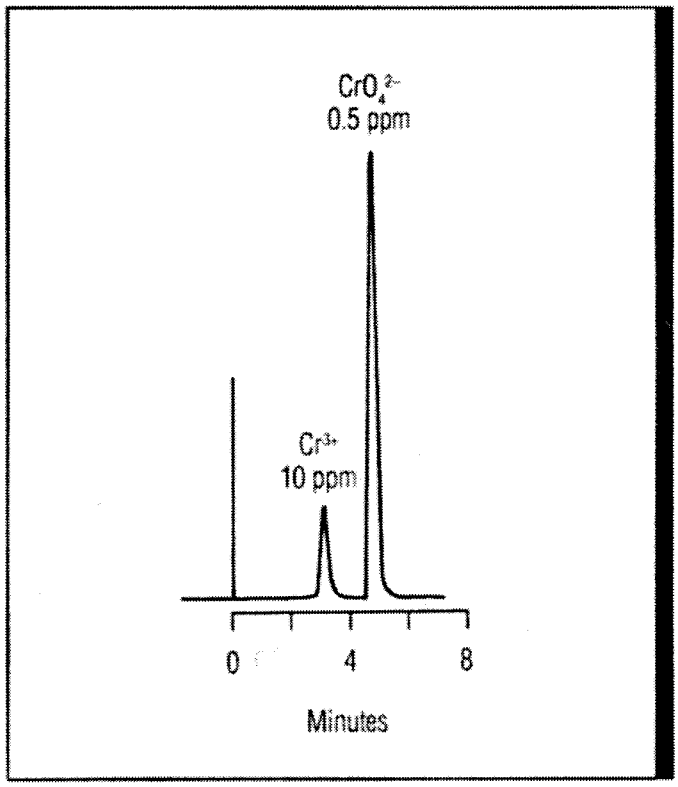

Figure 1 Trivalent and hexavalent chromium

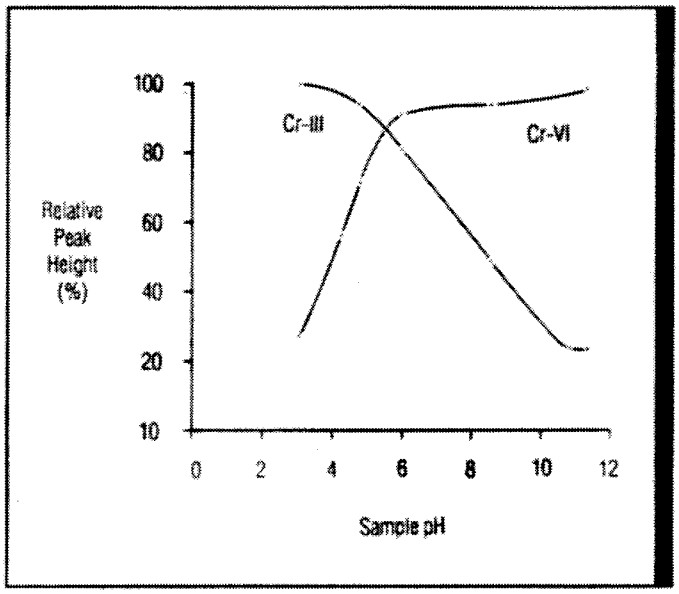

Figure 2 Peak height vs. sample pH for the determination of chromium (III) and (VI) by ion chromatography

Conditions

Sample Loop Volume:	250 µL
Columns:	HPIC-CG5 Guard and HPIC-CS5Analytical
Eluent:	2 mM PDCA, 2 mM Na_2HPO_4, 10 mM NaI, 50 mM $CH_3CO_2NH_4$, 2.8 mM LiOH
Flow Rate:	1.0 mL/min
Postcolumn Flow Rate:	2 mM DPC, 10% CH_3OH, 0.9 N H_2SO_4
Reagent Flow Rate:	0.5 mL/min
Mixing Device:	Membrane Reactor or Reaction Coil
Detector Wavelength:	520 nm

Solutions and Reagents

Eluent Stock:

Prepare by dissolving the following reagents in 18 MΩ deionized water: 20.0 mM (3.34 g/L) pyridine-2,6-dicarboxylic acid (PDCA), 20.0 mM (5.36 g/L) disodium hydrogen phosphate heptahydrate, 100 mM (15.0 g/L) sodium iodide, 500 mM (38.5 g/L) ammonium acetate, 28.0 mM (1.10 g/L) lithium hydroxide monohydrate. PDCA is slow to dissolve. Heat the solution before adding the remaining reagents to increase the rate of dissolution.

Eluent:

2 mM PDCA, 2 mM Na_2HPO_4, 10 mM NaI,
50 mM $CH_3CO_2NH_4$, 2.8 mM LiOH

Prepare by diluting 100 mL of the eluent stock to 1 L with 18 MΩ degassed deionized water. The pH of the diluted eluent should be between 6.70 and 6.80.

Postcolumn Reagent:

2 mM DPC, 10% CH_3OH, 0.9 N H_2SO_4

Prepare by dissolving 0.5 g of 1,5- diphenylcarbohydrazide (DPC) in 100 mL of HPLC grade methanol. Add to about 500 mL of degassed 18 MΩ deionized water containing 25 mL of 96% spectrophotometric grade sulfuric acid. Dilute to 1 L with degassed deionized water.

Sample Preparation

For typical waste water samples, adjust the pH of raw samples to a value of 6.8 with sodium hydroxide or hydrochloric acid. In a 100 mL volumetric flask, add 10 mL of the eluent stock solution to exactly 10 mL of sample. Heat the sample to boiling for 1 minute. Cool the sample to room temperature and dilute to 100 mL with deionized water. Calculations must account for the 1/10 dilution of the sample.

For plating bath samples 1/1,000 or 1/10,000 fold dilutions are necessary. Initial sample pH adjustments are typically necessary. Some plating baths require an intermediate ligand exchange process in the sample preparation to free the chromic ion for reaction with the PDCA. If this is found to be necessary, add 10 mL of plating bath to 10 mL of glacial acetic acid and dilute to 100 mL in a volumetric flask. After mixing, dilute this mixture 1/100 or 1/1,000 and prepare according to the standard preparation procedure.

METHOD B: PHOTOMETRIC DETERMINATION OF HEXAVALENT AND TOTAL CHROMIUM

Analytes

Cr(VI): Chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions.

Discussion of Method

In Method B, the visible absorbance of Cr(VI)-diphenylcarbohydrazide (DPC) complex at 520 nm allows photometric detection of Cr(VI). The eluent system is PDCA and NH_4OH based. The hexavalent chromium is separated as the chromate ion, CrO_4^{2-}, with PDCA acting as a divalent anionic eluent component and NH_4OH providing an alkaline environment. As shown in Figure 3, the elution time for Cr(VI) as chromate is about 3.5 minutes. The disturbance in the chromatogram is due to the high salt content in the sample.

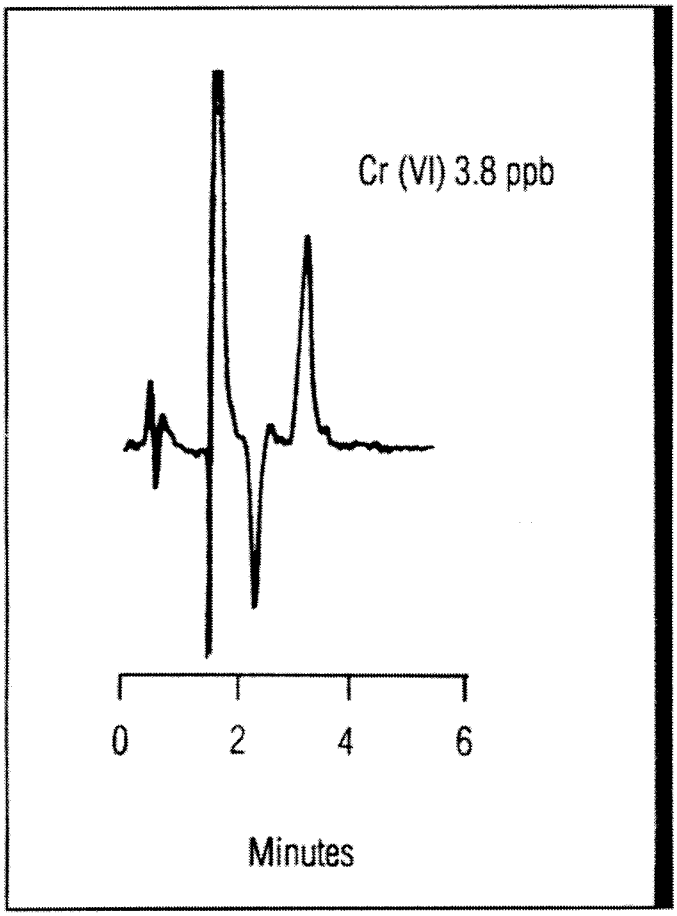

Figure 3 Total chromium in waste water

The pH values of the sample and eluent are critical to the efficiency of the separation. At pH values below 6, chromate ions are converted to dichromate ions. The result is poor separation and potential harm to the column due to the higher reducing power of dichromate ions.

After separation, the Cr(VI)-DPC complex is formed using postcolumn derivitization with DPC.

Flow rates must be measured at the waste line outlet. Adjust the RDM pressure after first measuring the flow rate of the eluent. The combined flow rate after pressurizing the RDM should be 1.5 mL/min, when the eluent flow rate alone is 1.0 mL/min.

Using injection volumes of 100 µL, determination of Cr(VI) in samples taken through the suggested digestion procedure is possible to detection limits of 5 ppb.

Recommended Equipment

Any Dionex Ion Chromatograph equipped with either a Variable Wavelength UV/Vis or a Visible Detector and either a Postcolumn Module or a Reagent Delivery Module.

Conditions

Sample Loop Volume:	100 µL
Columns:	HPIC-CG5 Guard and HPIC-CS5 Analytical
Eluent:	10 mM PDCA, 148 mM NH_4OH
Flow Rate:	1.0 mL/min
Postcolumn Reagent:	2 mM DPC, 10% CH_3OH, 1.8 N H_2SO_4
Reagent Flow Rate:	0.5 mL/min
Mixing Device:	Membrane Reactor or Reaction Coil
Detector Wavelength:	520 nm

Solutions and Reagents

Eluent:

Dissolve 1.67 g of pyridine-2,6-dicarboxylic acid (PDCA) and 10 mL of 29% reagent grade ammonium hydroxide per liter of water.

Postcolumn Reagent:

Prepare by dissolving 0.5 g of 1,5-diphenylcarbohydrazide (DPC) in 100 mL of HPLC grade methanol. Add to about 500 mL of degassed 18 MΩ deionized water containing 50 mL of 96% spectrophotometric grade sulfuric acid. Dilute to 1 L with degassed 18 MΩ deionized water.

Sample Preparation

Free Hexavalent Chromium:

The samples may be injected directly after adjustment of pH. The pH of the samples and prepared standards must be adjusted to a value above 7 with sodium hydroxide.

Total Chromium:

These samples are oxidized using an alkaline persulfate digestion. Persulfate oxidizes organics and lower oxidation states of chromium. The method is derived from ASTM Method D1687-80 (Method C) and is as follows:

1. Pipet 25 mL of sample into a 100 mL volumetric flask.
2. Add 1 mL of 50% NaOH and 0.80 g of $(NH_4)_2S_2O_8$. Swirl to dissolve the persulfate.
3. Gently boil the sample for 10 min or long enough for all color to disappear.
4. Cool the sample and dilute to 100 mL with deionized water.

The sample is ready for injection. Calculations must account for the four-fold dilution of the sample.

The sample preparation procedure for total chromium is designed to ensure complete oxidation of the sample, while maintaining a total salt concentration in the sample acceptable for chromatography.

It is possible that samples containing high levels of oxidizable material will require additional persulfate. If the amount of dissolved salts exceeds 2%, it is probable that some dilution will be necessary to prevent sulfate from overloading the column.

METHOD C: CONDUCTIMETRIC DETERMINATION OF HEXAVALENT CHROMIUM

Analytes

Chloride, sulfate, and chromate.

Discussion of Method

In Method C, the divalent chromate anion is detected by conductivity. This detection method also allows the determination of other ionic species in the sample, such as chloride and sulfate, which are resolved by the chromatographic separation. As with Method A, the anionic and cationic character of the CS5 column used allows the separation of Cr(VI) as the chromate ion, CrO_4^{2-}. The primary use of this method is the simultaneous determination of chromate and sulfate in chromium plating baths.

As shown in Figure 4, the elution times are 3.5 and 12 minutes for sulfate and chromate, respectively. Using an injection volume of 15 µL, determination of Cr(VI) is possible to below 500 ppb.

Recommended Equipment

Any Dionex Ion Chromatograph equipped with a Conductivity Detector Module or a Dionex QIC Analyzer.

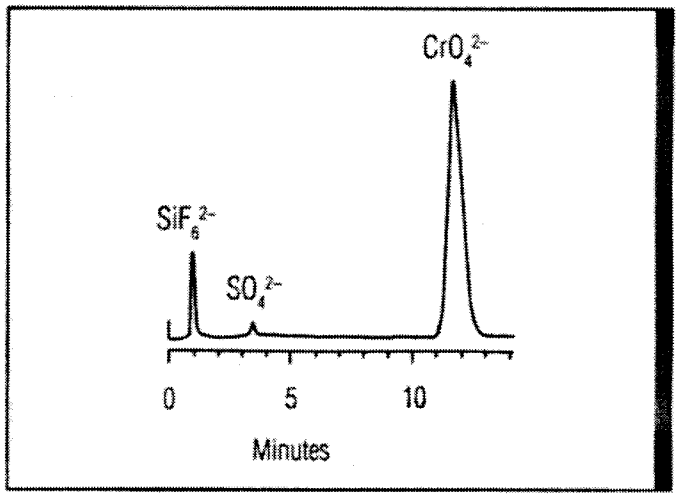

Figure 4 Chromate bath

Conditions

Sample Loop Volume:	15 µL
Columns:	HPIC-CG5 Guard and HPIC-CS5 Analytical
Eluent:	5 mM Na_2CO_3, 1 mM $NaHCO_3$
Flow Rate:	1.7 mL/min
Suppressor:	Anion MicroMembrane (AMMS)
Regenerant:	25 mN H_2SO_4
Regenerant Flow Rate:	3 mL/min

Solutions and Reagents

Eluent:

5 mM Na_2CO_3, 1 mM $NaHCO_3$

Dilute 10 mL of 0.5 M Carbonate Anion Eluent Concentrate (P/N 37162) and 2 mL of Bicarbonate Anion Eluent Concentrate (P/N 37163) per liter of 18 MΩ deionized water. Or dissolve 0.530 g sodium carbonate (anhydrous) and 0.084 g sodium bicarbonate per liter of 18 MΩ deionized water.

Regenerant:

25 mN H_2SO_4

Dilute 1 bottle (400 mL) of Anion Suppressor Sulfuric Acid Regenerant (P/N 37164) with water in a 4-L container. Or add 3 mL of concentrated sulfuric acid to 3 L of water in a 4-L container, fill to 4 L.

Sample Preparation

In a 100 mL volumetric flask, add exactly 100 µL of sample and dilute to 100 mL with eluent.