

Simultaneous Determination of Trivalent Chromium and Hexavalent Chromium Using Accelerated Solvent Extraction and Ion Chromatography

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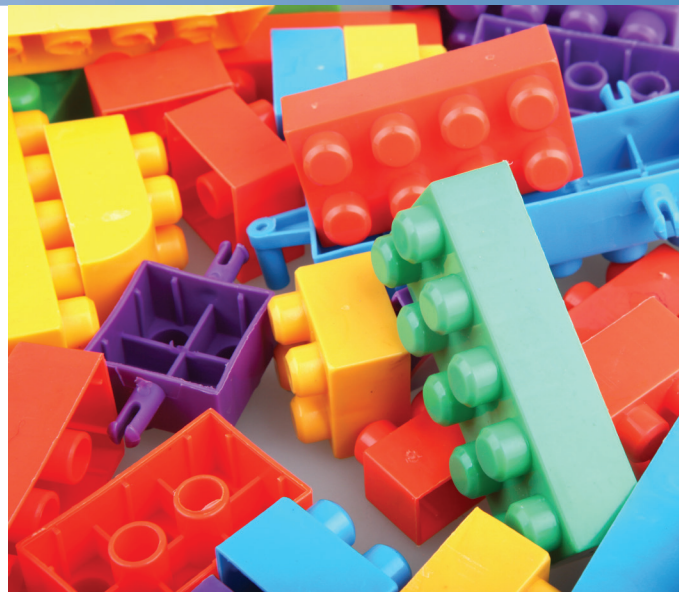
Key Words

Accelerated solvent extraction, ion chromatography (IC), trivalent chromium, hexavalent chromium

Introduction

In its natural state, chromium mainly occurs in its trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) forms. Trivalent chromium is an essential microelement for humans, and is nontoxic in normal doses in the food supply; at higher doses, however, trivalent chromium can exhibit cytotoxicity. Due to its highly oxidizing properties and its high skin permeability, hexavalent chromium is extremely toxic and has been confirmed to have a carcinogenic effect.¹ Hexavalent chromium compounds are widely used in the tanning, metallurgy, textile production, dyeing, chrome plating, and other industries. There are currently limit amounts for hexavalent chromium in all industries, such as the European Union's Toy Safety Directive of 2009 (2009/48/EC), which sets limit amounts for trivalent chromium and hexavalent chromium in all kinds of toys, with the minimum limit values for trivalent chromium and hexavalent chromium are 9.4 mg/kg and 0.005 mg/kg, respectively.

Since trivalent chromium and hexavalent chromium can interconvert under certain conditions and are both toxic to a certain degree, the simultaneous detection of trivalent chromium and hexavalent chromium content is of vital importance. Dionex, now part of Thermo Scientific, Technical Note (TN) 24: Determination of Chromium by Ion Chromatography detailed a simultaneous detection method for trivalent chromium and hexavalent chromium: precolumn and postcolumn derivatization is performed separately on the trivalent chromium and hexavalent



chromium, and an ultraviolet detector is used at 335 nm and 530 nm to detect trivalent chromium and hexavalent chromium,² respectively. The application described here is an improvement over the method used in TN 24. No derivatizing agent is pumped in the column, background noise is reduced, and the trivalent chromium detection limit is improved. Accelerated solvent extraction is used to extract the trivalent chromium, and hexavalent chromium, and the extract can be directly injected into the ion chromatograph to achieve the objective of simple, rapid detection.

For this study, samples consisted of a plastic toy building block and thread from a toy rag doll, both purchased at a local supermarket. The rubber sample came from a car tire, and the soil and solid waste sample were provided by a customer.

Accelerated Solvent Extraction Conditions

Instrument:	Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor System
Extraction Solvent:	2 mmol/L PDCA, 2 mmol/L KI, 100 mmol/L NH ₄ AC, 2.8 mmol/L LiOH
Temperature:	100 °C
Static Extraction Time:	5 min
Number of Cycles:	2
Rinsing Volume:	60%
Purge Time:	90 s
Extraction Cell:	Thermo Scientific™ Dionium™ Extraction Cell, 66 mL (P/N 068102)
Total Extraction Time per Sample:	18 min

Sample Pretreatment

Dry the soil sample in an oven at 50 °C. Powder the dried sample in a pulverizer. Crush solid waste into small particles with a stone grinder. Cut leather and textile samples with scissors into 0.2 × 0.2 cm pieces. Freeze and crush plastic and rubber samples. Combine a 10 g sample with an appropriate amount of Ottawa sand and mix. Transfer mixture to a 66 mL Dionium Extraction Cell with a glass fiber filter on the base. Perform accelerated solvent extraction and afterward, adjust the extraction solution volume to 100 mL. Filter through a 0.45 μm film, and then perform the IC analysis.

Ion Chromatography Conditions

Instruments:	Thermo Scientific™ Dionex™ ICS-1600 Reagent-Free™ Ion Chromatography (RFIC™) system, including: AXP Auxiliary Pump, VWD 3000 Variable Wavelength Detector, 375 μL knitted reaction coil
Columns:	Thermo Scientific™ Dionex™ IonPac™ CG5A Guard (4 × 50 mm) Dionex IonPac CS5A Analytical (4 × 250 mm)
Eluent:	2 mmol/L PDCA, 2 mmol/L KI, 100 mmol/L, NH ₄ AC, 2.8 mmol/L LiOH
Derivatization Reagent:	2 mmol/L DPC, 10% methanol (V:V), 2.5% sulfuric acid (V:V)
Eluent Flow Rate:	1 mL/min
Postcolumn Derivatization Pump Running Time:	6 min
Derivate Solution Flow Rate:	0.5 mL/min
Detector Wavelength:	335 nm (0–6 min), 530 nm (6–11 min)
Filling Volume:	250 μL

Results and Discussion

Selection of Ion Chromatography Conditions

Per TN 24, the postcolumn eluent was mixed with the postcolumn derivatization reagent throughout the entire process, resulting in an increase in background noise, and a drop in trivalent chromium detection sensitivity. As reported, the trivalent chromium detection limit is 23.3 μg/L. To increase the trivalent chromium detection limit when this method is used, no derivatization reagent was pumped in postcolumn, whereas when used to detect hexavalent chromium, the derivatization reagent was pumped in postcolumn to derivatize the hexavalent chromium. To enable the detection of hexavalent chromium, the postcolumn derivatization reagent was mixed with the postcolumn eluent, its pressure was stabilized, and the retention time interval for trivalent chromium and hexavalent chromium was extended.

In TN 24, 2 mM pyridinedicarboxylic acid (PDCA), 2 mM disodium hydrogen phosphate (Na₂HPO₄), 10 mM potassium iodide (KI), 50 mM ammonium acetate (CH₃CO₂NH₄), and 2.8 mM lithium hydroxide (LiOH) are used as the eluent. Where potassium iodide (KI) is mainly used for leaching, the experiment reduced the potassium iodide (KI) concentration as appropriate, enabling an extension of the retention time interval for trivalent chromium and hexavalent chromium. At the same time, the experiment used ammonium acetate (NH₄AC) and lithium hydroxide (LiOH) to adjust the pH value to between 6.70 and 6.80, so as to enable the separation and detection of two forms of chromium. After experimenting with adjustments, an eluent of 2 mmol/L PDCA, 2 mmol/L KI, 100 mmol/L NH₄AC, and 2.8 mmol/L LiOH was chosen.

By comparing postcolumn derivatization solution flow rates of 0.2 mL/min, 0.3 mL/min, 0.4 mL/min, and 0.5 mL/min, it was found that the flow rate had no major effect on derivatization with high concentrations of hexavalent chromium. However, when the concentration of hexavalent chromium is relatively low, a relatively high flow rate of derivatization solution is able to obtain a higher detection signal. Here a postcolumn derivatization reagent flow rate of 0.5 mL/min was used. At the same time, the effect of the reaction tube (375 μL and 750 μL) and the postcolumn reaction temperature (20 °C, 30 °C, and 40 °C) on the hexavalent chromium derivatization were compared, revealing that the reaction tube volume and reaction temperature had no visible effect on the derivatization. This method therefore used 375 μL and 30 °C as the reaction tube volume and postcolumn reaction temperature.

Optimization of Accelerated Solvent Extraction Conditions

For the simultaneous detection of trivalent chromium and hexavalent chromium, postcolumn derivatization was used for hexavalent chromium, whereas trivalent chromium required precolumn derivatization to form a stable compound with the PDCA derivatization reagent. In TN 24, the heating-to-boiling-point method was used to derivatize the trivalent chromium and PDCA. Here, the accelerated solvent extraction method was used to perform simultaneous trivalent chromium and hexavalent chromium extraction, and a derivatization reagent was added to the extraction solution so as to simultaneously achieve the objective of trivalent chromium precolumn derivatization.

According to the literature,^{1,2} when heated to boiling, the complex formed by PDCA and Cr (III) undergoes UV adsorption at 335 nm. Here, the IC eluent (2 mmol/L PDCA, 2 mmol/L KI, 100 mmol/L NH₄AC, 2.8 mmol/L LiOH) contains the derivatization reagent. Therefore, the IC eluent was used as the extraction solvent. After the extraction procedure, the extraction solution was cooled to room temperature, and the volume was adjusted to 100 mL by adding extraction solvent before the IC analysis. The extraction temperature was 100 °C, the static extraction time was 5 min, and two cycles were performed.

Accelerated Solvent Extraction Cell Selection

Accelerated solvent extraction uses extraction cells with two types of material—stainless-steel extraction cells and Dionium (zirconium alloy) extraction cells. In order to study the blanking values of the extraction cells of different materials, separate blanking value tests were performed on the stainless-steel extraction cells and Dionium extraction cells. When using stainless-steel extraction cells in the blanking test, the extraction solution exhibited a reddish color. After detection, 30 ng/mL of trivalent chromium was extracted from the stainless-steel extraction cells and no hexavalent chromium was detected (Figure 1). When the extraction was repeated with the stainless-steel extraction cells, the amount of trivalent chromium exhibited an impermissibly large change, making it unsuitable for the extraction of trivalent chromium or hexavalent chromium. When using Dionium extraction cells in the blanking test, no trivalent chromium or hexavalent chromium was detected. When the extraction was repeated with Dionium extraction cells, neither trivalent chromium nor hexavalent chromium was detected. Therefore, Dionium extraction cells were used as the accelerated extraction cells in this experiment.

Conversion Test

In order to prevent the trivalent chromium and hexavalent chromium from converting during accelerated solvent extraction, separate conversion tests were performed on the trivalent chromium and hexavalent chromium.

In independent trivalent chromium and hexavalent chromium standard samples of blanking samples, it was found that the spiked recovery rate of trivalent chromium reached exceeded 99%, whereas the spiked recovery rate of hexavalent chromium also reached 97%. This indicates that the trivalent chromium and hexavalent chromium did not convert into each other during the accelerated solvent extraction process.

Linearity, Detection Limit, and Spiked Recovery Rate

The Dionex ICS-1600 system detection limits for trivalent chromium and hexavalent chromium for this method ($S/N = 3$) were 5 ng/mL and 0.5 ng/mL, respectively, and these exhibited a good linear relationship within 50 ng/mL to 1000 ng/mL and 5 to 100 ng/mL, respectively. The existing equations were: $Y = 0.0038X - 0.0021$, and $Y = 0.0568X - 0.0152$, respectively, and the linear correlation coefficients were 0.9997 and 0.9992.

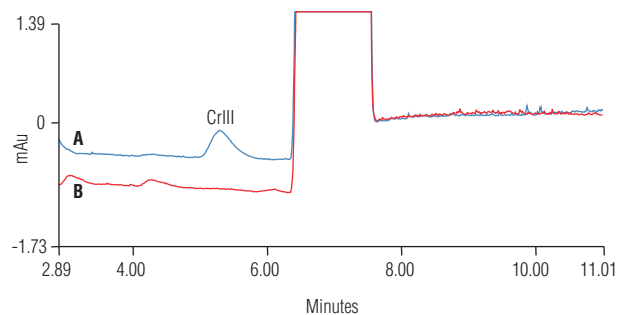


Figure 1. Stainless-steel extraction cell (A) and Dionium extraction cell (B).

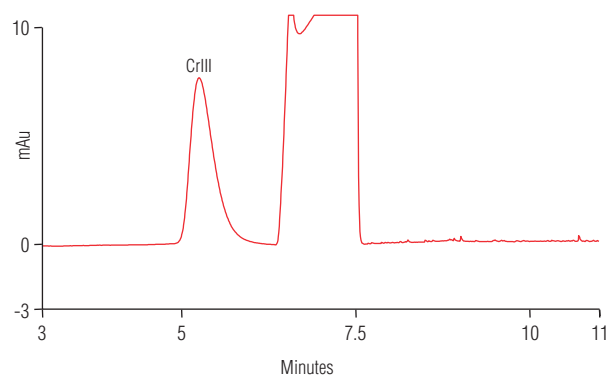


Figure 2. Trivalent chromium conversion test results.

Table 1. Spiked recovery rate results (n = 3).

NO.	Cr(III) Added Cr(III) ng/mL	Cr(VI) Added Cr(VI) ng/mL	Cr(III) Recovery Cr(III) %	RSD	Cr(VI) Recovery Cr(VI) %	RSD
1	50.0	5.0	90.5	4.5	97.4	3.1
2	100.0	10.0	95.7	3.7	99.5	2.2
3	500.0	50.0	98.3	3.1	101.2	1.9

A sample of 10 g was accurately weighed, and specific concentrations of trivalent chromium and hexavalent chromium were added and mixed to form a standard solution (Table 1). The samples were processed and then assayed. The recovery rate was calculated (Table 1) and ranges for trivalent chromium and hexavalent chromium were 90.5% to 98.3% and 97.4% to 101.2%, respectively, and RSD were 3.1% to 4.5% and 1.9% to 3.1%, respectively.

Sample Testing

This method was used to perform analysis and detection on soil, solid waste, leather, textiles, plastics, and rubber. A number of samples were taken, mixed with Ottawa sand and poured into an extraction cell into which a glass fiber mat had previously been placed. Samples then underwent accelerated solvent extraction, after which the extraction solution was washed to a constant volume using extraction solvent before undergoing IC analysis. Test results are given in Table 2.

Table 2. Detection results for each sample.

Sample	Cr(III)/ $\mu\text{g/g}$	Cr(VI)/ $\mu\text{g/g}$
Soil	0.182	BLD*
Solid Waste	0.103	BLD*
Leather	213	0.596
Textiles	3.10	BLD*
Plastics	0.095	BLD*
Rubber	0.186	BLD*

*Below limit of detection

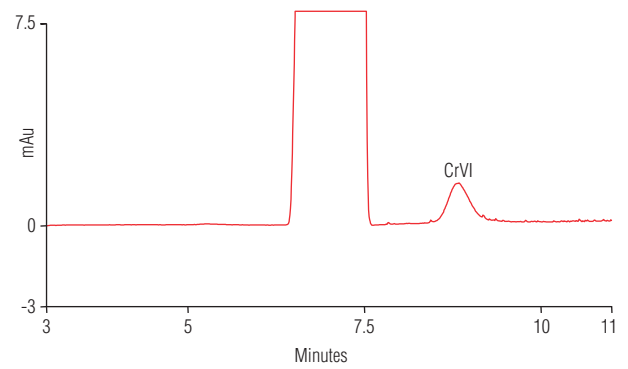
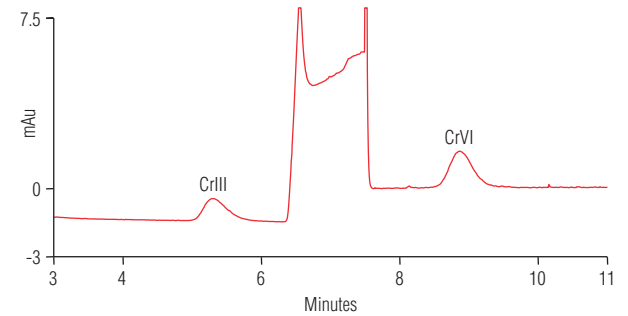


Figure 3. Hexavalent chromium conversion test results.

Figure 4. Standard sample, 100 $\mu\text{g/L}$ Cr (III) and 10 $\mu\text{g/L}$ Cr (VI).

Summary

Spiked recovery tests and stability tests on all of the matrix samples showed that the combination of an improved accelerated solvent extraction method with precolumn derivatization and IC with postcolumn derivatization is a perfect match for the simultaneous extraction, separation, and analysis of trivalent chromium and hexavalent chromium. This method is characterized by its simplicity, speed, and sensitivity.

References

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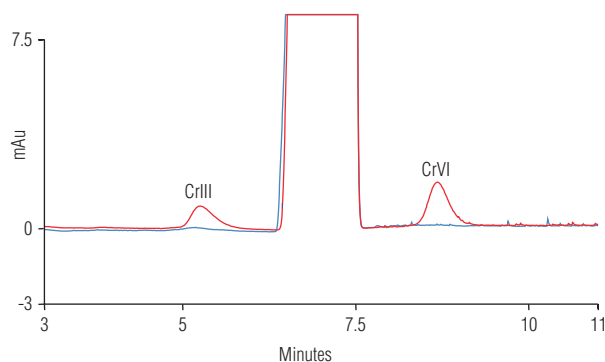


Figure 5. Sample (blue) and sample spiked with 100 µg/L Cr (III) and 10 µg/L Cr (VI) (red).

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