Metrohm

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Determination of hexavalent and soluble trivalent chromium (Cr^{+6} and Cr^{+3}) species in soil, solid samples and pharmaceuticals using ion chromatography–inductively coupled plasma mass spectrometry (IC-ICP-MS) with speciated isotope dilution methodology (USEPA, SW846 method 6800 – SIDMS)

Branch

Dietary Supplements, Nutraceuticals, Pharmaceuticals, Public health

Keywords

IC-ICP-MS; Chromium; Trivalent Chromium; Cr^{+3}; Hexavalent Chromium; Cr^{+6}; Metrohm 850; Agilent 7700; Metrosep ASupp 4 250

Summary

While soil naturally contains a small amount of chromium (Cr) that comes from weathering of its bedrock, the element also enters the terrestrial environment through anthropogenic activities. Cr (III) and Cr (VI) are the prevalent forms of Cr in soil and other parts of the environment. The speciation analysis of Cr has received increasing interest because of the opposing properties of the two prevalent species. In soil, Cr (III) mainly exists as insoluble (hydr)oxides or adsorbs to humic acid and macromolecular clay compounds, whereas Cr (VI) occurs as anions (CrO_4^{2-} or $HCrO_4^-$) that are mobile under most conditions. Cr (III) is relatively innocuous and essential for the proper functioning of living organisms. However, Cr (VI) is toxic to both plants and animals because it is a corrosive, acute tissue irritant and carcinogen. In the present study, Cr (VI) and soluble Cr (III) were simultaneously determined by ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS) with speciated isotope dilution methodology. The soil was spiked with isotopically enriched analogues of the analytes, i.e. ^{50}Cr (III) and ^{53}Cr (VI), and both the endogenous and spiked analytes were extracted in a microwave using alkaline solution of ethylenediaminetetraacetic acid (EDTA). The extracts were analyzed by IC-ICP-MS, and the separated species were quantified using the mathematical relationships in speciated isotope dilution mass spectrometry (SIDMS, EPA Method 6800) with simultaneous correction for their method-induced transformations.

Direct separation of Cr (VI) and Cr (III) by chromatography is difficult because the species possess opposite charges in solutions. High-pressure gradient IC using Metrosep ASupp 4 column was employed to achieve baseline separation of the species prior to analysis on an Agilent 7700 ICP-MS instrument. The IC and ICP-MS instruments were synchronized using remote signal. The MagIC Net software controls the sample loading and gradient program while data handling and manipulation is accomplished with the Agilent MassHunter software.

Samples

- Analytes were extracted from soil, pharmaceuticals, and nutraceuticals in a microwave oven using 50 mM EDTA solution.
- Extracts were cooled and centrifuged.
- Supernatants were decanted, filtered and analyzed by IC-ICP-MS.
- For analysis of samples without extraction (e.g. aqueous samples), complexation of Cr(III) with EDTA can be achieved by mixing the sample with equal volume of 50 mM EDTA and heating the mixture in a microwave at 90 °C for 20 minutes.

Instruments

ProfIC Cation HP-Gradient	2.940.1440
Professional Sample Processor: Pump	2.858.0020
Remote box	6.2148.010
Cable for MagIC Net/Chemstation sync	6.2141.380
Metrosep ASupp 4 250/4.0	6.1006.430
Ethos Microwave	
ICP-MS Agilent 7700	

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Reagents

- Cr(VI), natural abundant, 10 mg L^{-1}, Applied Isotope Technologies
- Cr(III), natural abundant, 10 mg L^{-1}, Applied Isotope Technologies
- Cr(VI), enriched with ^{53}Cr, 700 mg L^{-1}, Applied Isotope Technologies
- Cr(III), enriched with ^{50}Cr, 95 mg L^{-1}, Applied Isotope Technologies
- Tetrasodium salt of ethylenediaminetetraacetic acid (EDTA), >99%, Fisher Scientific
- Ammonium hydroxide solution, 25–28% NH_3 in water, ACS, BDH
- Ultrapure water, resistivity 18.2 MΩ cm, Branstead NANOpure

IC Solutions

Eluent A	2.0 mM EDTA (pH 10) [isocratic]
Eluent B	N/A

Standard solutions

Mass bias standard solution containing 25 ng g^{-1} of Cr(III) and 25 ng g^{-1} Cr(VI) was prepared in 50 mM EDTA, and the solution was microwaved at 90 °C for 20 minutes.

IC Parameters

Flow	0.8 mL/min
Injection Volume	100 µL
Recording time	10 min
Temperature column	Off

Microwave parameters

Sample (dietary supplement, soil, pharmaceuticals) mass	0.25 g
Extraction solution	50 mM EDTA solution
Extraction solution volume	10.0 mL
Ramp time	10 min
Step 1. Heating temperature	90 °C for 5 minutes
Step 2. Cooling temperature	25 °C
Step 1. Heating temperature	110 °C for 5 minutes

Agilent ICPMS Parameters

RF power	1550 W
RF matching	1.8 V
Sampling depth	8 mm
Plasma gas flow rate	15 L min^{-1}
Carrier gas flow rate	0.95 L min^{-1}
Makeup gas flow arte	0.15 L min^{-1}
Collision gas (He) flow rate	4.0 mL min^{-1}
Spray chamber temperature	2 °C
Tuning solution	1 µg L^{-1} Li, Co, Y, Ce, and Tl in 2% HNO_3 solution

Data Acquisition Parameters

Monitoring masses (Cr)	50, 52 and 53 amu
Acquisition mode	Spectrum and time resolved analysis (TRA)

Results

The chromatographic condition achieved baseline separation between Cr (III) and Cr (VI) with Metrohm column in less than 10 minutes. Several standard reference materials (SRM) were analyzed in the study. The measured mass fractions of Cr (VI) in the soil SRMs statistically agreed with the certified values at 95% CL. The soluble Cr (III) found in all the SRMs were less than 3% of the total Cr in the corresponding samples.

Calculations

The data calculations were generated automatically by the Agilent Chem Station software.

Comments

pH of solution is the key to prevent inter-conversion of Chromium Specie

Appendix (List)

- Chromatograms
- Data
- Post Column Standard Recoveries (Replicates)

References

1. Mesay M. Wolle et al, *Optimization and validation of strategies for quantifying chromium species in soil based on speciated isotope dilution mass spectrometry with mass balance*, J. Anal. At. Spectrom. 29 (2014) 1640–1647.
2. Neus Fabregat-Cabello et al., *Fast and accurate procedure for the determination of Cr(VI) in solid samples by isotope dilution mass spectrometry*, Environ. Sci. Technol. 46 (2012) 12542–12549.

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Date

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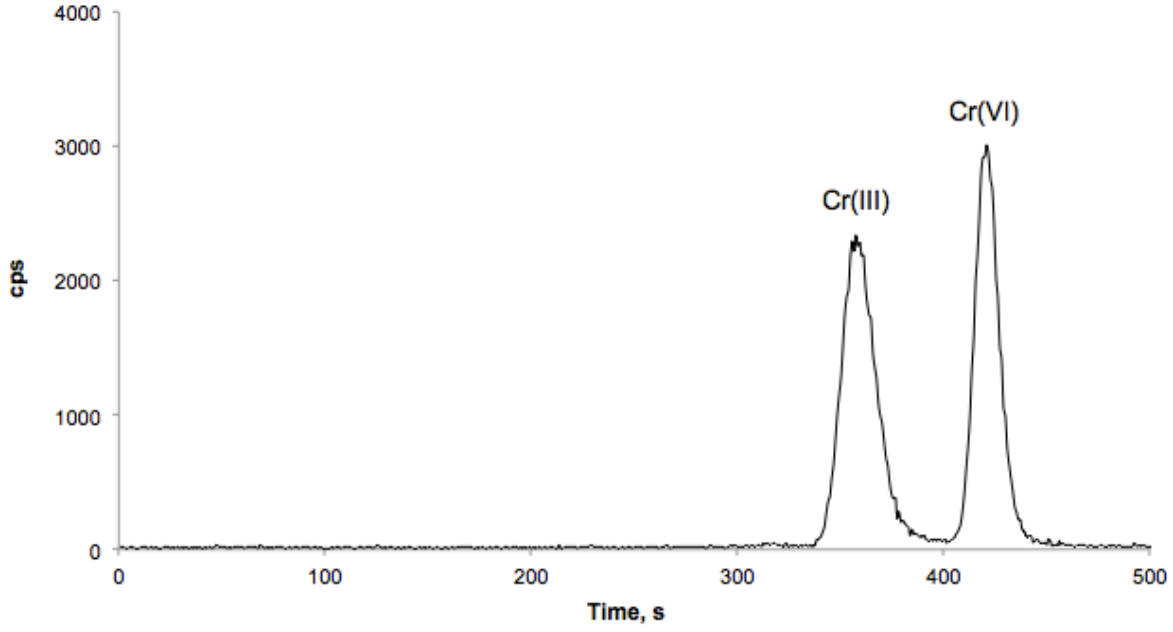
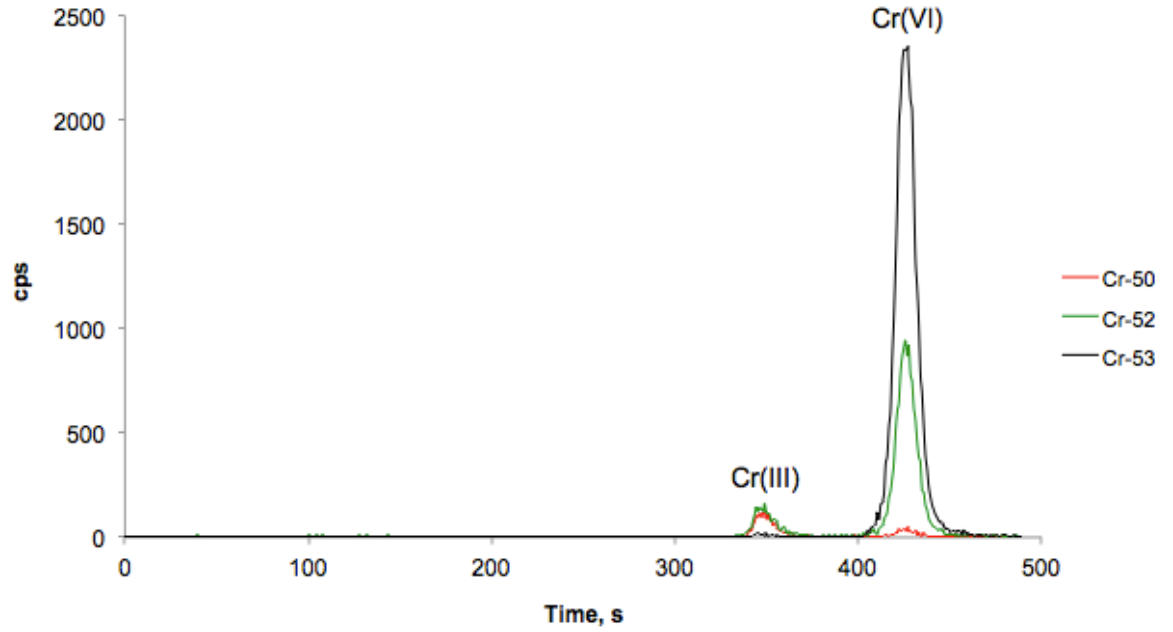
Appendix

Chromatogram for a standard solution containing 10.0 ng g^{-1} Chromium per species



Chromatogram for a microwave extract generated from a soil sample double-spiked with ^{50}Cr(III) and ^{53}Cr(VI).



Data for Several Global SRMs

	USEPA Methods for Analysis					
	Method 6800 (SIDMS)	Method 7199	Method 7194 (draft)			Direct Measurement after digestion
	Cr(VI)			Cr(III)	Cr(III)+Cr(VI)	Total Cr
	ug/g					
NIST 2700A_quartz	12.28	12.6	13.8	317.8	330.1	341
NIST 2700B_glass	11.85	10.4	12.46	668.9	680.7	667.6
Sigma SRM	54.04	55.1	56.8	99.23	158.8	152.2