Speciation of Cr(III) and Cr(VI) by IC-ICP-MS and Empower 3

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Introduction

Speciation analysis for chromium is increasingly becoming a regulatory requirement to assess the quality of drinking water. With the public health goal in California set to just 20 ng/L Cr(VI), the sensitivity of the technique and accuracy at low levels becomes even more important.

One of the most sensitive analysis techniques for this task is IC-ICP-MS. Systems with a metal-free flow path are one option to guarantee inertness and to achieve low backgrounds for the benefit of this trace analysis. The use of EDTA as complexing agent is very common in the field of chromium speciation. Around 90% of existing methods are using EDTA as an additive to the mobile phase or for the sample preparation.

This work shows the impact of EDTA additions to the eluent. Additionally, it highlights the professional hardware and software data handling of this sophisticated hyphenated system.

Hardware

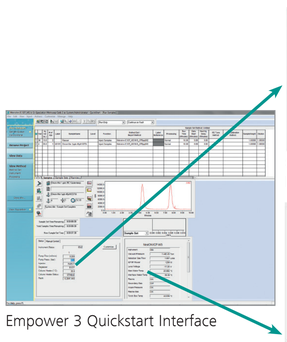
PerkinElmer NexION 350D ICP MS (left) coupled to Metrohm Professional IC Vario One and Professional Sample Processor (right).

Operating Conditions NexION ICP-MS	
Plasma Gas Flow	15 L/min
Isotope m/z	52
RF Power	1300 W
Nebulizer	Glass Concentric
Spray Chamber	Quartz Cyclonic
Gas Mode	DRC (Ammonia)
Gas Flow	0.7
Dwell Time	900 ms
RPq-Value	0.6

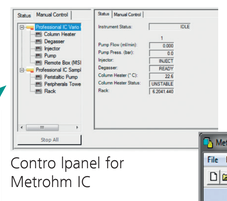
Operating Conditions Professional IC Vario One	
Flow IC Pump	0.2 mL/min
Column	Metrosep Carb 2 - 100/2.0 + Guard Column
Column Pressure	~ 60 bar
Column Temperature	20 °C
Injection Volume	20 µL
Run Time	10 min
Eluent	100 mmo/L Nitric acid 156 mmol/L Ammonium hydroxide (pH 9)
EDTA-Solution	20 mmol/L EDTA in eluent (pH 3.9)

Software

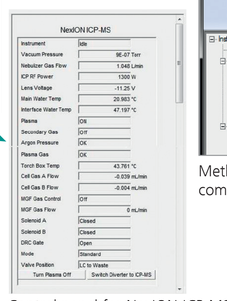
A new speciation method based on anion exchange using a Metrohm 940 Professional IC Vario One with Metrohm 858 Professional Sample Processor coupled to a PerkinElmer NexION 350D ICP-MS is shown in this work. Furthermore, the software featured takes full control of the entire speciation system. Productivity and ease of use are enhanced significantly. The entire system operates under Empower 3 Software.



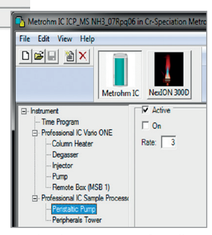
Empower 3 Quickstart Interface



Contro lpanel for Metrohm IC



Control panel for NexION ICP-MS



Method parameters for all components

«Empower 3 is Waters' compliant-ready chromatography data software (CDS) package for advanced data acquisition, management, processing, reporting, and distribution.»

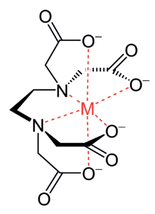
Empower 3 allows data acquisition and control of a variety of instruments, including HPLC, UHPLC, and GC. The software permits control of advanced detection techniques such as MS, ICP-MS, and PDA without outsourcing to third party vendors. Thus, there is no need for multiple software packages and the system operates from a single PC.

Experimental Setup

A series of experiments was carried out to investigate the appropriate EDTA concentration for the new method with the Column Metrosep Carb 2. Samples and standards where prepared in eluent and spiked subsequently with EDTA solution. To speed up the complexation process all samples and standards were heated to 60 °C for 1 h.

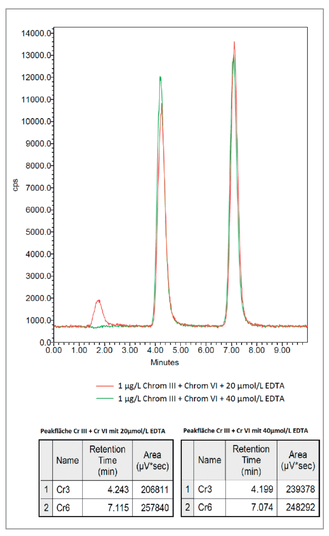
The mobile phase was adjusted to pH 9 and EDTA was prepared as a separate solution with 20 mmol/L. Initially the influence of EDTA concentration was tested.

EDTA –Metal Complex



The influence of the column temperature was investigated. All of the following experiments were carried out at 20 °C.

Spike experiments were conducted to check for species stability and quantitative complexation.



Peakfläche Cr III + Cr VI mit 20µmol/L EDTA

	Name	Retention Time (min)	Area (µV*sec)
1	Cr3	4.243	206811
2	Cr6	7.115	257840

Peakfläche Cr III + Cr VI mit 40µmol/L EDTA

	Name	Retention Time (min)	Area (µV*sec)
1	Cr3	4.199	239378
2	Cr6	7.074	248292

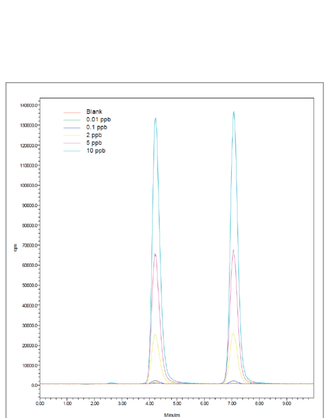
Influence of different EDTA concentrations on the complexation of Cr(III).

Calibration

Two test series were carried out at low and high EDTA concentrations.

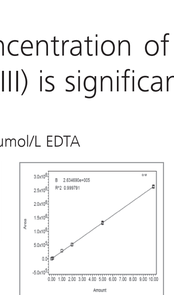
c = 40 µmol/L EDTA

The minimum concentration for a entire complexation of Cr(III) and a good chromatographic separation of both species on the Metrosep Carb 2 was determined to be 40 µmol/L EDTA. Additional a common EDTA concentration level from literature (500 µmol/L) was tested as well.



Calibration data for 40 µmol/L EDTA

	STD-Value [µg/L]	Calc. Value Cr(III) [µg/L]	Calc. Value Cr(VI) [µg/L]
1	0.01	0.010	0.013
2	0.10	0.095	0.108
3	1.00	0.984	1.020
4	2.00	1.97	1.96
5	5.00	4.98	4.99
6	10.0	10.0	9.98



The calibration with 40 µmol/L EDTA shows good recovery throughout.

Empower calculates all essential calibration and results data automatically.

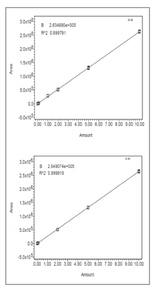
c = 500 µmol/L EDTA

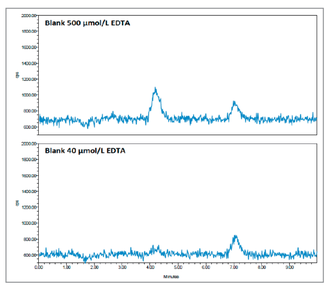
Both EDTA levels work for a successful calibration. Although the calibration with 500 µmol/L EDTA looks very promising, the recovery is slightly better with a lower EDTA concentration, especially for the low concentration levels.

At higher concentration of EDTA the blank contamination for Cr(III) is significantly higher as well.

Calibration data for 500 µmol/L EDTA

	STD-Value [µg/L]	Calc. Value Cr(III) [µg/L]	Calc. Value Cr(VI) [µg/L]
1	0.01	0.008	0.003
2	0.10	0.098	0.098
3	1.00	–	1.11
4	2.00	1.95	1.96
5	5.00	5.00	4.99
6	10.0	9.98	9.98





Results

A commercial bottled water sample with a high mineral content was tested to examine the influence of EDTA concentration.

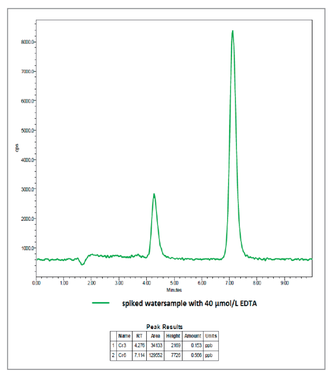
The sample was spiked with 0.5 µg/L of a mixture of Cr(III) and Cr(VI). For both EDTA concentrations, a 5-fold determination was carried out.

c = 40 µmol/L EDTA

The results shown below indicate that a concentration of 40 µmol/L EDTA is insufficient to completely complex Cr(III). With 30%, the spike recovery was consequently very poor. Thus a poor spike recovery of 30% for Cr(III) was calculated. A good recovery of 111% for Cr(VI) was observed. Unspiked samples gave no Cr(III) and no Cr(VI) concentration after blank correction.

Spike recovery for 40 µmol/L EDTA

Water Sample with 40 µmol/L EDTA	Cr(III) [µg/L]	Cr(VI) [µg/L]	Spike conc. Cr(III)/(VI) [µg/L]
	0.139	0.560	0.5
	0.196	0.564	0.5
	0.153	0.566	0.5
	0.143	0.531	0.5
	0.124	0.559	0.5
Recovery	**30%**	**111%**	

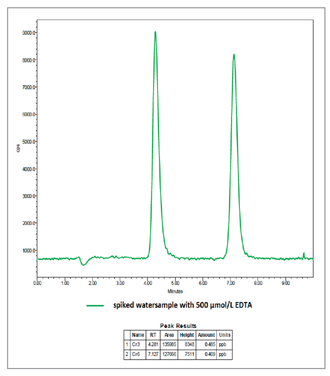


c = 500 µmol/L EDTA

At the higher level of EDTA spike recoveries for both chromium species were good, indicating that Cr(III) is quantitatively complexed and both chromium species are stable.

Spike recovery for 500 µmol/L EDTA

Water Sample with 500 µmol/L EDTA	Cr(III) [µg/L]	Cr(VI) [µg/L]	Spike conc. Cr(III)/(VI) [µg/L]
	0.475	0.484	0.5
	0.485	0.469	0.5
	0.478	0.462	0.5
	0.462	0.463	0.5
	0.465	0.464	0.5
Recovery	**95%**	**93%**	



The optimal amount of EDTA could differ from standard to sample. Full complexation of Cr(III) is already achieved with EDTA concentrations of 40 µmol/L in ultrapure water standards. Depending on the sample matrix higher EDTA concentrations might be required. A significantly higher concentration of 500 µmol/L is more appropriate for a wide range of different samples.

Conclusions

This poster demonstrates the feasibility of coupling a Metrohm IC system to a PerkinElmer NexION ICP-MS, operated under Empower 3 Software.

Using a Metrosep Carb 2 column, the chromatographic separation of both species was achieved with a high resolution. Low background and high sensitivity allow determination in the low ng/L range.

Optimal separation and full complexation of Cr(III) is already possible with EDTA concentrations from 40 µmol/L in low matrix solutions and may need to be increased depending on the sample matrix.

Handling of the system was easy and user friendly. It was shown that speciation of Cr(III) and Cr(VI) can be carried out on this system utilizing a professional data system for acquisition, processing, and reporting.

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