Application Note AN-M-013

Chromium speciation by IC-ICP-MS

Analysis of Cr(III) and Cr(VI) in water using Metrohm IC coupled to Agilent's ICP-MS entirely operated in ICP-MS MassHunter

Differentiation between trivalent (Cr(III)) and hexavalent chromium (Cr(VI), chromate) is crucial due to their contrasting toxicological profiles. Cr(III) is an essential nutrient for glucose and lipid metabolism, while Cr(VI) is highly toxic and carcinogenic, even at low levels [1,2]. Consequently, determining total chromium content alone is often insufficient for accurate risk assessment. To distinguish between these two species, various analytical techniques have been developed. Aside from chromatography using ion-pairing on C8 or C18 columns [3], the coupling of ion chromatography (IC) with inductively coupled plasma mass spectrometry (ICP-MS) has gained prominence due to its high sensitivity and precision.

This Application Note details the approach as stated in ISO 24384 [4], using an EDTA-chelating treatment, subsequent separation of Cr(III) and Cr(VI) by anion-exchange chromatography, and mass detection by ICP-MS. Incorporation of Metrohm IC into Agilent's ICP-MS MassHunter software via the Metrohm IC driver streamlines the process, saves time, and enhances the efficiency and safety of the entire analytical procedure.

SAMPLE AND SAMPLE PREPARATION

Samples (tap water from Herisau, Switzerland) and standards (from 0.1 to 20 µg/L, containing Cr(III) and Cr(VI)) were prepared as described in ISO 24384 [4] by a chelating treatment before their analysis with IC-ICP-MS.

For the chelating treatment, a 0.025 mol/L EDTA solution was used (9.31 g of ethylenediamine-N,N,N′,N′-tetraacetic acid disodium salt (Supelco) in 1000 mL ultrapure water (UPW)). A 2 mL portion of the EDTA solution was transferred into a 20 mL volumetric flask and then filled up to the mark with the standard respective volumes of 100 µg/L stock solutions for Cr(III) (prepared from chromium(III) chloride hexahydrate, Sigma-Aldrich), Cr(VI) (prepared from chromate standard for IC, Supelco), and UPW or sample solution. The pH was adjusted to pH 6.9 ± 0.1 with nitric acid or sodium hydroxide. After gently mixing, the solutions were transferred to screw-capped test tubes and heated at 70 ± 3 °C for 60 minutes.

EXPERIMENTAL

After the chelating pretreatment for the sample and standards, speciation analysis was performed by coupling IC with ICP-MS (Figure 1).

Control of both devices in ICP-MS MassHunter (Agilent ICP-MS MassHunter 5.3, version D.0103) is enabled using the Metrohm driver for IC (Metrohm IC Driver 1.0, ICP-MS MassHunter) (Figure 2). The remote box (Remote Box MSB, 6.2148.010) and the connection box (IC equipment, connection Agilent ICP-MS, 6.05330.400) are mandatory to guarantee bidirectional communication (e.g., to stop both instruments in case of an emergency).

Sample and standard handling was performed using the 889 IC Sample Center – cool (Figure 1), increasing stability of the liquids to be measured. A full-loop injection (250 µL) on to the separation column was performed by the extremely fast 889 autosampler.

Figure 1. Setup for chromium speciation in water with a Metrohm 940 Professional IC, an 889 IC Sample Center – cool, and a 7850x ICP-MS from Agilent Technologies.

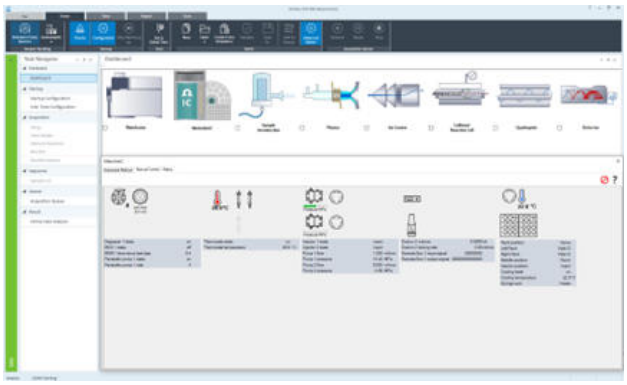

Figure 2. With the help of the Metrohm IC Driver 1.0, ICP-MS MassHunter (6.6090.100), full control of both devices (IC and ICP-MS) is possible in ICP-MS MassHunter as a single-software solution.

The separation of Cr(III) and Cr(VI) was achieved on a Metrosep Carb 2 - 100/4.0 separation column (equipped with a Metrosep Carb 2 guard column) using isocratic conditions and a ammonium nitrate eluent (150 mmol/L nitric acid, Sigma-Aldrich, puriss. p.a., 65%) and 234 mmol/L ammonia solution (ACS reagent, 28–30%, Sigma-Aldrich) at pH 9 ± 0.1.

The calibration (0.5–20.0 g/L) was performed by the injection of single standards in the given range. By using the Metrohm intelligent Partial-Loop Injection Technique (MiPT), the overall performance could improve by producing the calibration from a single standard.

The ICP-MS (7850x, G8422A) was operated in TRA-mode (time-resolved analysis) using He (4.2 mL/min) as the collision gas to reduce mass interferences [**4**]. The isotopes ^{52}Cr and ^{53}Cr were monitored (RF power 1550 W, nebulizer gas flow 1.07 L/min) with an integration time per mass of 0.3 seconds. Only the data for ^{52}Cr were used for data evaluation and quantification of Cr(III) and Cr(VI). To ensure the full capability for the evaluation of chromatographic data in Agilent ICP-MS MassHunter 5.3 was available, the software was upgraded with the Chromatographic Software Package.

RESULTS

With the increased strength of the eluent compared to the example in ISO 24384, and an eluent flow rate of 1.0 mL/min, Cr(III) and Cr(VI) were separated in less than four minutes (**Figure 3**). Compared to a 2 mm column, the 4 mm version (with the same length) has a higher capacity. Especially for water sources with a higher matrix load, the analysis is more robust and does not suffer from a matrix overload of the column.

The spike tests with recoveries of 99.7% and 114.0% for Cr(III) and Cr(VI), respectively, show the reliability of the whole analysis (**Tables 1 and 2**). The calibration in the range of 0.1 to 20 g/L yielded R values between 1.0 and 0.998 for both species (Cr(III) and Cr(VI)). Peak heights for the lowest standard (0.1 g/L) were above 2500 cps (with the blank lower than 150 cps) and show that calibration below the level as adapted from ISO 24384 is possible.

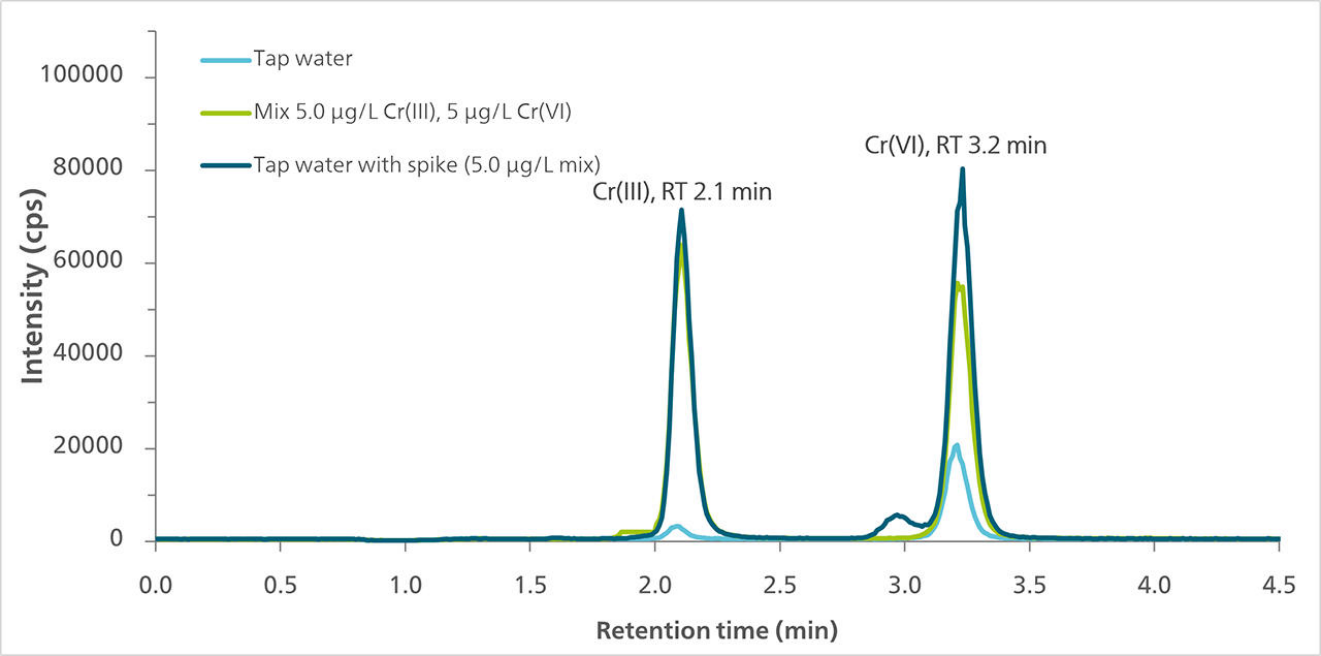

Figure 3. Chromatogram overlay of a 5 µg/L mixed standard and both a spiked and unadulterated tap water sample (250 µL injection volume). The chromatograms display the intensities measured for m/z 52. Elution took place on a Metrosep Carb 2 - 100/4.0 separation column using an ammonium nitrate eluent at isocratic conditions with a flow rate of 1.0 mL/min.

Table 1. Results for the analysis of 52Cr(III) in tap water and spiked tap water. The recovery yielded 99.7% for 52Cr(III).

^{52}Cr(III)			
Sample	**RT (min)**	**Area**	**Conc. (g/L)**
5 g/L mixed standard	2.11	380574	5.0
Tap water	2.10	15018	0.2
Spiked tap water (5 g/L mix of Cr(III) and Cr(VI))	2.11	394429	5.2

Table 2. Results for the analysis of 52Cr(VI) in tap water and spiked tap water. The recovery for 52Cr(VI) was calculated at 114%.

^{52}Cr(VI)			
Sample	**RT (min)**	**Area**	**Conc. (g/L)**
5 g/L mixed standard	3.21	362578	5.0
Tap water	3.22	129449	1.8
Spiked tap water (5 g/L mix of Cr(III) and Cr(VI))	3.23	542830	7.5

CONCLUSION

This Application Note specifies a sensitive and reliable method for the determination of hexavalent and trivalent chromium in water by ion chromatography coupled to inductively coupled plasma mass spectrometry after a chelating pretreatment as described in ISO 24384.

EDTA is used as complexing agent to form a stable anionic complex with Cr(III), facilitating its separation from Cr(VI) via anion-exchange chromatography. The use of a high-capacity anion-exchange column, i.e., the Metrosep Carb 2, enables baseline separation of the two species and guarantees robustness, high recoveries, and accuracy even for water sources with a higher matrix load. The ammonium nitrate eluent without additional additives is preferred to maintain the sensitivity and selectivity of the ICP-MS detection at *m/z* = 52.

The entire analysis is managed using Agilent's ICP-MS MassHunter with the **Metrohm IC Driver 1.0 for ICP-MS MassHunter**, providing a unified software solution for **user-friendly sensitive Cr(III) and Cr(VI) speciation**. This setup ensures maximum analytical safety through bidirectional communication. It is also less prone to manual errors (e.g., during device control or making data entries in the software), ensures data integrity, and enhances the overall efficiency through a reduced workload.

REFERENCES

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CONTACT

CÔNG TY TNHH
METROHM VIT NAM
Tòa nhà Park IX, s 08 ng
Phan ình Giót, Phng Tân
Sn Hòa
null Thành ph H Chí Minh
info@metrohm.vn

CONFIGURATION

Metrosep Carb 2 - 100/4.0

The Metrosep Carb 2 - 100/4.0 IC column is particularly suitable for the determination of carbohydrates using alkaline eluents and pulsed amperometric detection. The high-capacity anion exchanger column is based on a styrene-divinylbenzene copolymer. It is stable in the range of pH = 0 - 14 and provides separation of glucose, fructose, and sucrose. It is also suitable for the analysis of some sugar alcohols and oligosaccharides. Short analysis times can be achieved on the 100 mm version of the Metrosep Carb 2 separation column.