

The Migration of Elements from Toys and Speciation of Chromium (VI) in Toy Material Using a IC-ICP-MS Solution

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Key Words

Chromium, Ion Chromatography (IC), Speciation, Toys

Goal

To answer the need for trace level determination of several elements and hexavalent chromium that migrate from toy materials at limits outlined in EU directive 2009/48/EC.

Introduction

Hexavalent chromium (Cr (VI)) is highly toxic and classed as a carcinogen. Trivalent chromium (Cr (III)), however, is essential for enzymatic function in human metabolism. Discrimination between the oxidation states is therefore essential for an accurate risk assessment of chromium in materials we are exposed to.

The European Union directive for toy safety (2009/48/EC) is currently under revision, and the proposed limits for Cr (VI) content are analytically challenging with commonly used methods. For example, High Pressure Liquid Chromatography (HPLC) coupled to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) may not be suitable as high elemental chromium backgrounds push detection limits above the directive specified values. In this paper, the use of Ion Chromatography (IC) is shown to be a powerful alternative to HPLC, allowing the analysis of both Cr species in the low ng L⁻¹ range. Although IC chromatographic separation of the two species is simple, sample preparation plays an important role. Depending on sample conditions (e.g. pH), inter species conversion may occur prior to quantification producing inaccurate species distribution. In this application note, we present a method for total elemental quantification (TEQ) and for stabilization and quantification of Cr (VI) after migration from toy material and its sensitive detection at the 2009/48/EC directive required levels.



Sample and Calibration Solution Preparation

Three different samples were analyzed; finger paint, pen ink and a titanium dioxide (TiO₂) raw material that is commonly used as a white pigment in many different toy products.

To evaluate the method for the determination of total elemental concentrations, each element outlined in the EU directive was spiked into the finger paint sample at different concentrations and analyzed by ICP-MS.

All samples were subjected to the migration process as described in the European Standard EN 71-3:2012¹. This Standard Operating Procedure (SOP) has been recently updated and at the time of publication of this application note has not been officially released to the public. In the migration solution, Cr (VI) is prone to slow reduction in the acidic environment and a stabilization step is necessary after migration is completed to maintain the original species distribution.

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One way to accomplish this is to adjust the pH of the sample higher than 7.1 so that the oxidation potential of the chromate ion is decreased. Therefore, all samples were diluted as follows: 1 equivalent of 1 mol L⁻¹ NH₄OH was added to 4 equivalents of migration solution. Repeated analyses showed that Cr (VI) in the samples was stable for at least 24h under these conditions. Using this method however, Cr (III) is prone to hydrolysis and eventually precipitation. This is confirmed by an observed loss of Cr (III) in the sample after stabilization. The amount of Cr (III) present in a sample is therefore calculated by subtracting the amount of Cr (VI) determined in the speciation analyses from the chromium concentration determined from total elemental quantification.

An alternative approach that adjusts pH to approximately 4 would make the simultaneous analysis of Cr (VI) and Cr (III) possible but, as samples with a high content of basic material (e.g. CaCO₃) would require varying amounts of HCl for pH adjustment prior to migration, this approach is more time consuming and less reproducible.

Instrument Configuration

Total element quantification was carried out using a standard Thermo Scientific™ iCAP™ Qc ICP-MS equipped with a SC-4Q autosampler (Elemental Scientific, Omaha, NE, USA). Chromium (VI) was separated according to a previously published method (AN 43098) using a Thermo Scientific™ Dionex™ AG-7 anion exchange (guard) column. Prior to this column, a Dionex NG-1 column was used to remove organic compounds from the samples (e.g. dyes), that might affect the performance of the chromatographic separation. The separation was performed using a Thermo Scientific™ ICS-900™ ion chromatography system with an AS-DV™ autosampler coupled to the iCAP Qc ICP-MS. As part of the Thermo Scientific ion chromatography range, it is completely metal-free and thus ideally suited for trace metal speciation applications. Both the ICS-900 and AS-DV autosampler were controlled using the Thermo Scientific™ Chromeleon™ Chromatography Data System plug-in available in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ software (Qtegra ISDS). This integrated software package enables seamless control of both instruments within a single user interface and makes unattended routine speciation analysis possible. The eluent flow from the column was connected directly to the PFA-LC nebulizer of an iCAP Qc ICP-MS system configured with a connector kit specifically designed for coupling of IC or liquid chromatography systems. With this approach, dilute nitric acid is used as the eluent. Unlike organic eluents required by comparable separation techniques, dilute nitric acid is the ideal solvent for ICP-MS based analyses. By avoiding organic solvents, additional sample introduction techniques to remove excess carbon in the ICP ion source are not required so that a single instrumental configuration can be used for both total elemental and speciation analyses, driving simplicity. Elemental chromium contamination from nitric

acid can be effectively controlled since it can be either commercially sourced at high purity levels or distilled as required in the laboratory. As no complexing agent such as EDTA is required in this method, carbon based spectral interferences that interfere with the detection of Cr (⁴⁰Ar^{12,13}C) are not observed. Nevertheless, both ^{52,53}Cr isotopes were monitored using He Kinetic Energy Discrimination (KED) mode to remove possible interferences (e.g. ³⁷Cl¹⁶O) in Cl containing samples. The proprietary design of the iCAP Q Series' collision cell (QCell™) enables effective suppression of all polyatomic interferences while maintaining high sensitivity across the entire mass range.



General Analytical Conditions

The iCAP Qc ICP-MS was tuned daily and operated using the parameters shown in Table 1. For TEQ, an ESI-SC4Q autosampler was used and all elements were analyzed in a single operation mode using He KED. Ga (10 ng g⁻¹), Rh and Ir (1 ng g⁻¹ each) internal standards were added online using a T-piece. The detailed conditions for the chromatographic separation are summarized in Table 1 while a more detailed description of the method can be found in an earlier publication (AN 43098).

Table 1. Instrument operating parameters.

ICP-MS Parameter	
Nebulizer	Microflow PFA-ST for elemental analysis and PFA-LC for speciation
Nebulizer gas	0.99 L/min
Forward power	1550 W
QCell	4.4 mL/min 100% He, 3V KED
IC Parameter	
Column	Dionex NG-1 (2 x 50mm), Dionex AG-7 (2 x 50mm)
Eluent	0.35 mol/L HNO ₃
Elution mode	Isocratic @ 0.40 mL/min
Injection volume	10 µL

Results and Discussion

The finger paint sample was spiked and analyzed for total elemental content as prescribed in the updated SOP. The determined concentrations are summarized in Table 2.

Table 2. Total elemental quantification of the spiked finger paint sample.

Element	Concentration spiked [mg kg ⁻¹]	Concentration found [mg kg ⁻¹]	Recovery [%]
¹¹ B	170	171.0 ± 3.6	101 ± 2
²⁷ Al	1136	1165.4 ± 38.0	103 ± 3
⁵² Cr	5.68	5.54 ± 0.17	98 ± 3
⁵⁵ Mn	454	434.9 ± 14.5	96 ± 3
⁵⁹ Co	2.84	2.71 ± 0.11	96 ± 4
⁶⁰ Ni	5.68	5.33 ± 0.26	94 ± 5
⁶³ Cu	114	108.4 ± 2.2	95 ± 2
⁶⁶ Zn	586	595.3 ± 27.5	102 ± 5
⁷⁵ As	2.84	2.51 ± 0.09	88 ± 4
⁷⁸ Se	11.4	11.4 ± 0.07	100 ± 6
⁸⁸ Sr*	284	367.0 ± 18.5	129 ± 5
¹¹¹ Cd	0.57	0.56 ± 0.04	98 ± 7
¹¹⁸ Sn	568	535.9 ± 34.0	94 ± 6
¹²¹ Sb	11.4	9.87 ± 0.64	87 ± 6
¹³⁷ Ba	454	424.6 ± 24.9	94 ± 6
²⁰⁸ Pb	5.68	5.13 ± 0.32	90 ± 6

*The result for ⁸⁸Sr is biased by the high Sr content in the unspiked sample. Due to the limited sample amount it was not analyzed separately to quantify the original amount.

As it can be seen from the table, the values agree well with the expected concentrations.

The three migration solutions were analyzed after neutralisation as described previously. None of the samples were found to contain Cr at a measurable level, either as toxic Cr (VI) or non-toxic Cr (III). The three solutions were therefore spiked at different concentration levels of Cr (VI). The spike concentrations were set to match the directive defined limits for dry, brittle or powder-like toy materials and liquid or sticky toy materials. Taking into account the 50 fold dilution during the migration procedure, the final target concentrations were 0.1 and 0.4 ng mL⁻¹.

The system was calibrated using Cr (VI) standards from 0.05 ng mL⁻¹ to 4 ng mL⁻¹. Figure 1 shows the calibration graph obtained and the chromatogram for the standard with the lowest concentration: 0.05 ng mL⁻¹ Cr (VI) that is easily distinguished from the baseline. The instrumental detection limit (IDL) was determined using the 3σ criterion and was 0.9 ng L⁻¹ for Cr (VI).

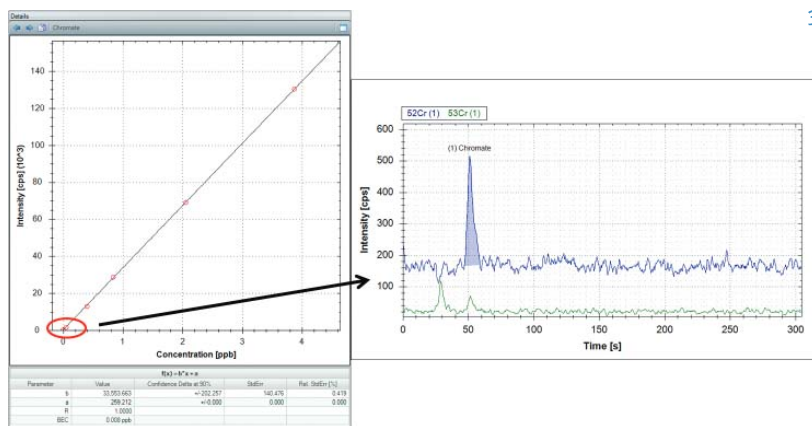


Figure 1. Calibration graph and chromatogram for the lowest concentration calibration standard (0.05 ng mL⁻¹).

The chromatogram for the ink sample spiked with approximately 0.10 ng mL⁻¹ is shown in Figure 2. The signal corresponding to Cr (VI) elutes after 50s. The signal eluting after approximately 30s coincides with the void volume of the column. The isotope ratio of this peak indicates that this signal is not caused by Cr containing species, but rather chlorine containing species (that result in spectral interferences such as ³⁷Cl¹⁶O) that are concentrated on the columns and are hence visible despite the use of KED.

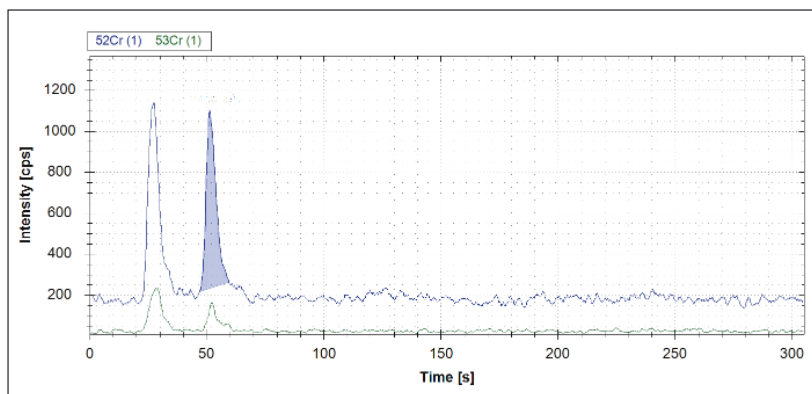


Figure 2. Chromatogram of an ink sample subjected to the migration procedure outlined in SOP EN 71-3:2012.

The results of all analysis are summarized in Table 3. The obtained values for the spike recovery indicate the accuracy of the method. Injection three was made on the day following the first two injections, indicating that the stabilization procedure using NH₄OH has indeed prevented reduction of Cr (VI) that has migrated from the sample material.

Table 3. Hexavalent Chromium concentration found in the various toy samples.

Sample	Amount spiked [ng mL ⁻¹]	Found Injection 1 [ng mL ⁻¹]	Found Injection 2 [ng mL ⁻¹]	Found Injection 3 [ng mL ⁻¹]	Average Recovery [%]
Finger paint	0.27	0.26	0.30	0.34	110 ± 15
TiO ₂	0.27	0.24	0.25	0.26	92 ± 4
Ink 1	0.27	0.23	0.27	0.25	88 ± 3
Ink 2	0.10	0.09	0.10	0.09	87 ± 4

Conclusions

The iCAP Qc ICP-MS was proven to be a powerful tool for the total elemental quantification and chromium speciation analyses in toys and toy related materials. Elemental concentrations in toy leachates can be determined with good accuracy and precision. The combination of IC with ICP-MS is a powerful tool for the speciation analysis of Cr (VI) in toy samples as the set up is totally metal free. Detection power is not reduced in subsequent speciation analyses since the dilute HNO₃ IC eluent is chromium free and does not generate additional spectral interferences. This combination of advantages allows the low level detection of toxic Cr (VI) at the single digit ng L⁻¹ level that is necessary to comply with both current legislation and future proof against any upcoming regulatory challenges.

Parts Used in this Note

Part	Thermo Scientific Catalogue Number
ICS-900 with AS-DV autosampler	1343380
Dionex IonPac AG-7, 50 x 2 mm	063099
Dionex NG-1, 50 x 2 mm	SP4356
IC/LC connector kit (N.B. included in PN 1343380)	1335350

Chemicals Used in this Note

Chemical	Fisher Scientific Catalogue Number
Optima grade Nitric Acid	A467-500
Multielement Solution 2	CLMS-2

For more information on chemicals please contact your local Fisher Scientific organization and/or visit: www.fishersci.com or www.acros.com

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