Application Note 43175

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

Daniel Kutscher, Shona McSheehy Ducos, Lothar Rottmann, Thermo Fisher Scientific, Germany

Key Words
Chromium, Ion Chromatography (IC), Speciation, Toys

Goal

To address the need for trace elemental and hexavalent chromium determination (as defined in EU directive 2009/48/EC) migrating from toy materials.

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 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 stabilization and quantification of Cr (VI) after migration from toy material 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 (TiO_2) raw material that is commonly used as a white pigment in many different toy products.

In order 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 71-3:2012[1]. This Standard Operating Procedure (SOP) has been recently updated and at the time of publication 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 to maintain the original species distribution.

Thermo SCIENTIFIC

Species distribution can be maintained by adjusting the pH of the sample higher than 7.1 so that the oxidation potential of the chromate ion is decreased. All samples were therefore diluted as follows: 1 equivalent of 1 mol L^{-1} NH_4OH was added to 4 equivalents of migration solution. Repeated analyses showed that Cr (VI) in the samples was stable for at least 24h of these solutions. Using this method however, Cr (III) is prone to hydrolysis and eventual 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. $CaCO_3$) 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, this system 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 ($^{40}Ar^{12,13}C$) are not observed. Nevertheless, both $^{52,53}Cr$ isotopes were monitored using He Kinetic Energy Discrimination (KED) mode to remove possible interferences (e.g. $^{37}Cl^{16}O$) 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 SC-4Q 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 50 mm), Dionex AG-7 (2 x 50 mm)
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 ^{88}Sr 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 in Table 2, the measured values agree well with the expected concentrations.

The three migration solutions were analyzed after neutralization as previously described. 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 EU 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 lowest concentration standard: 0.05 ng mL^{-1} Cr (VI) which is easily distinguished from the baseline. The instrumental (3σ) detection limit (IDL) was calculated to be 0.9 ng L^{-1} for Cr (VI).

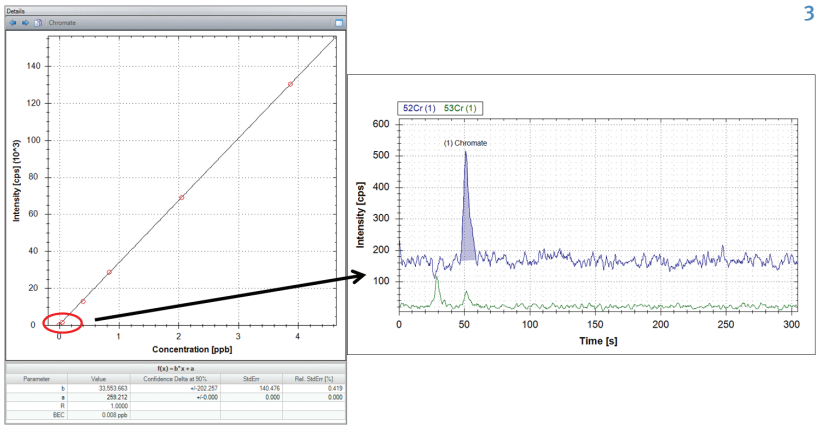

Figure 1. Calibration graph and chromatogram for the lowest concentration Cr standard (0.05 ng mL^{-1}).

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.

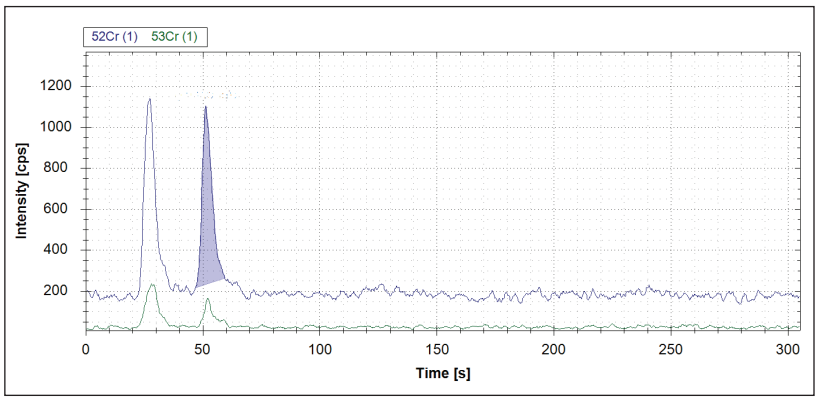

Figure 2. Chromatogram of an ink sample subjected to the migration procedure outlined in SOP EN 71-3:2012.

The results from all analyses 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 NH_4OH 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 is 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 instrumental set up is totally metal free. Detection power is not affected in subsequent speciation analyses since the dilute HNO_3 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

Africa-Other +27 11 570 1840
Australia +61 3 9757 4300
Austria +43 810 282 206
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China 800 810 5118 (free call domestic) 400 650 5118
Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland +358 9 3291 0200
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9494
Italy +39 02 950 591
Japan +81 45 453 9100
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Norway +46 8 556 468 00
Russia/CIS +43 1 333 50 34 0
Singapore +65 6289 1190
South Africa +27 11 570 1840
Spain +34 914 845 965
Sweden +46 8 556 468 00
Switzerland +41 61 716 77 00
UK +44 1442 233555
USA +1 800 532 4752

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific

AN43175-EN 0516C