



### Challenge

Meeting the low limits of migration defined in the norm EN 71-3 in migration solutions of a variety of toy samples.

### Solution

The unique sensitivity of the PlasmaQuant MS Q enables reaching lowest limits of detection in LC-ICP-MS.

## Determination of Hexavalent Chromium in Toy Samples According to EN 71-3

### Introduction

The safety of toys and children's products has been regulated for many years within the European Community under European Standard EN 71, which is a harmonized standard under Directive 2009/48/EC. Part 3 of the standard defines the migration of certain elements with the most recent update in 2021 as EN 71-3:2019+A1:2021 (defined as EN 71-3 in the rest of the note).

Measuring only the total concentration of a particular element in toy samples can often lead to errors in assessing toxicity, mobility, and bioavailability, as these effects can differ greatly between the various chemical species in which an element may occur. Chromium (Cr) is a good example of this, and in this case the key distinction is the ionic state of the chromium ion. Hexavalent chromium (Cr(VI)) is a known carcinogen whereas the trivalent form of chromium (Cr(III)) is less toxic and is an essential micronutrient. Nevertheless, chromium is widely used in numerous end products made of plastics, metalworking, and dyes/paints/inks.

As such, hexavalent chromium is regulated in the three categories of toy products as defined in EN 71-3 and shown in table 1:

- Category I: Dry, brittle, powder-like or pliable materials
- Category II: Liquid or sticky materials
- Category III: Scraped-off materials

Table 1: Categories of toy products according to EN 71-3 and the limits of migration of Cr(VI)

Toy material	Category I	Category II	Category III
Coatings of paints, varnishes, lacquers, printing inks, polymers, foams, and similar coatings			x
Polymeric and similar materials, including laminates, whether textile-reinforced or not, but excluding other textiles			x
Paper and paper board			x
Textiles, whether natural or synthetic			x
Glass, ceramic, metallic materials			x
Wood, fiber board, hard board, bone, leather, and other solid materials			x
Compressed paint tablets, materials intended to leave a trace, or similar materials in solid form appearing as such in the toy	x		
Pliable modeling materials, including modeling clays and plaster	x		
Liquid paints, including finger paints, varnished, lacquers, liquid ink in pens, and similar materials in liquid form appearing as such in the toy (e.g., slimes, bubble solution)		x	
Glue sticks		x	
Limit of migration of Cr(VI)	0.020 mg/kg	0.005 mg/kg	0.053 mg/kg

The limit of migration of hexavalent chromium is particularly challenging in category II because of a level as low as 0.005 mg/kg. Since the regulatory requirement distinguishes between the various forms of chromium, it is essential to separate and quantitatively analyze Cr(VI), where LC-ICP-MS is the recommended analytical instrumentation.

It is essential in such characterizations that the system being used has a metal-free fluid path, so it does not contribute toward the chromatographic Cr baseline, since this would adversely affect the limits of detection and quantification.

Apart from the need for a metal-free and inert fluid path in such applications, there are several other factors which may affect the accurate quantification of Cr(VI). Since mass spectrometric techniques are based upon m/z, carbon or

chloride from the mobile phase or sample may form  $^{40}\text{Ar}^{12}\text{C}$  and/or  $^{35}\text{Cl}^{16}\text{O}^1\text{H}$  polyatomic interferences on  $^{52}\text{Cr}$ , leading to inaccurate recoveries and raised baselines for Cr in LC-ICP-MS applications. This can be effectively dealt with by injecting a collision gas such as helium (He) at the tip of the skimmer cone where the high plasma density and temperature promote collisions of the interfering ions and the iCRC gas (He). Matrix effects caused by the variety and diversity of toy samples to be analyzed were successfully eliminated/reduced by eluting the migration solution through a SPE cartridge.

This application note shows the capabilities of the PlasmaQuant MS Q for the determination of the migration of hexavalent chromium from various toy products.

## Materials and Methods

### Instrumentation

The PlasmaQuant MS Q ICP-MS (Analytik Jena, Germany) was used in combination with the low-pressure, ion exchange liquid chromatography system and the fast injection valve (OneFast) from Elemental Scientific (Omaha, USA) for the separation of both chemical forms of Cr (Cr(III)

and Cr(VI)). This system is completely metal-free to achieve the best performances. The operating conditions of the ICP-MS and the LC systems are summarized in tables 2 and 3.

Table 2: PlasmaQuant MS Q operating conditions

Parameter	Setting
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.35 L/min
Nebulizer gas flow	1.05 L/min
iCRC gas setting	He – 0.12 L/min
Plasma RF power	1.40 kW
Dwell times	<sup>52</sup> Cr – 500 ms (2 points/sec)
Acquisition mode	Time resolved

Table 3: LC operating conditions

Parameter	Setting
Mobile phase	0.26 mol/L Ammonium Nitrate (ph 2)
Flow rate	170 µL/min
Elution	Isocratic
Run time	6 min
Column	Anion exchange (ESI)

### Samples and reagents

All samples were prepared according to the procedure described in EN 71-3. Approximately 0.5 g of the sample was accurately weighed and mixed with 25 mL solution of 0.07 mol/L hydrochloric acid. The mixture was checked for acidity, stirred for 1 h at 37 °C and then left unstirred for

another hour at 37 °C. The solution was filtered to separate the solid sample from the migration solution. According to chromium speciation requirements, the samples were neutralized after the migration step using ultrapure ammonia (Merck) (table 4).

Table 4: Neutralization of the samples following the migration step

Solution	Category I	Category II	Category III
Migration solution	4 mL	4 mL	4 mL
Ammonia	50 µL	50 µL	50 µL
Measuring solution final volume (ultrapure water)	20 mL	10 mL	50 mL

To eliminate/minimize potential matrix effects and chloride (<sup>35</sup>Cl<sup>16</sup>O<sup>1</sup>H) and/or carbon interferences (<sup>40</sup>Ar<sup>12</sup>C) that could affect the performance of Cr measurements, the neutralized solutions were filtered using a 0.45 µm syringe filter and then loaded onto a SPE cartridge (Chromafix PS-Ag<sup>+</sup>, Macherey-Nagel, Germany). The cartridge has been conditioned with 1 mL of ultrapure water added drop by drop before loading the sample. The first mL of migration solution was discarded, and the following 2 mL were kept for analysis. This step allows for the suppression of the matrix components, among them chloride and Cr(III), which are retained on the stationary phase of the cartridge, unlike Cr(VI).

The ammonium nitrate mobile phase was prepared in a plastic flask of 100 mL by adding a few mL of ultrapure water, 1 mL of a commercial Thulium solution at 1,000 mg/L, 3 mL of Suprapur® HNO<sub>3</sub>, 4.6 mL of Suprapur® ammonia and made up to volume with ultrapure water. The pH was adjusted between 1.8 and 2.0 by adding few drops of nitric acid or ammonia in a plastic cup.

## Results and Discussion

Calibration solutions were prepared from commercial 1,000 mg/L stock solutions of Cr(VI) and Cr(III) (Inorganic Ventures, USA) in ultrapure water with concentrations ranging from 0.015 to 0.50 µg/L (table 5). It is important to note that only Cr(VI) was quantified using this method, Cr(III) can be determined by the difference between the total amount of chromium and the amount of Cr(VI). The addition of Cr(III) into the calibration solutions was only used to evaluate the separation of both peaks. Speciation of both chromium species (Cr(III) and Cr(VI)) was performed using the isocratic LC method in less than 6 minutes.

Table 5: Cr(VI) standard solutions concentrations in µg/L

Species	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Cr(VI)	0.015	0.025	0.050	0.10	0.50

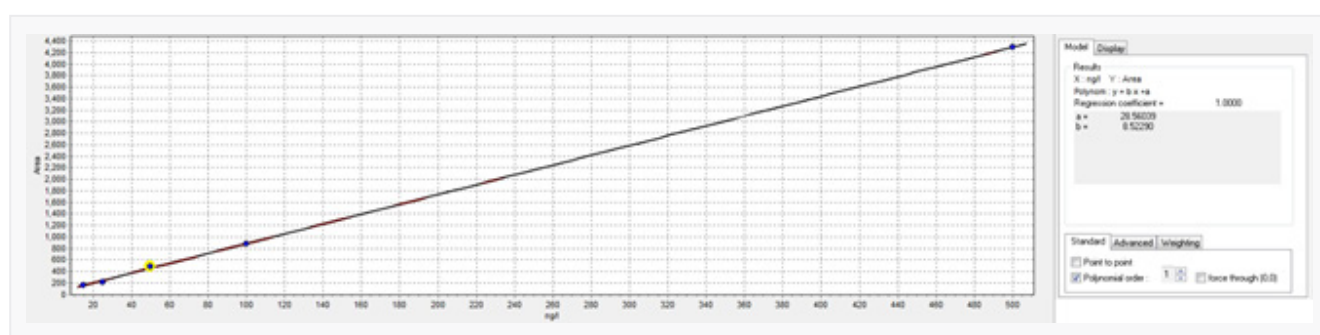


Figure 1: Calibration curve of Cr(VI) ranging from 0.015 to 0.500 µg/L

Excellent linearity was achieved ( $r^2 > 0.9999$ ), exceeding the required correlation coefficient of 0.99 as defined by EN 71.3. Excellent sensitivities and separation of both chromium peaks were also achieved as shown in figures 2 and 3. The peak of Cr(VI) can easily be distinguished from the baseline even at a concentration as low as 0.015 µg/L. At higher concentrations (0.5 µg/L), the separation of both chromium peaks is also very clear and allows the accurate measurement of hexavalent chromium. A method detection limit (MDL) of 0.003 µg/L was attained.

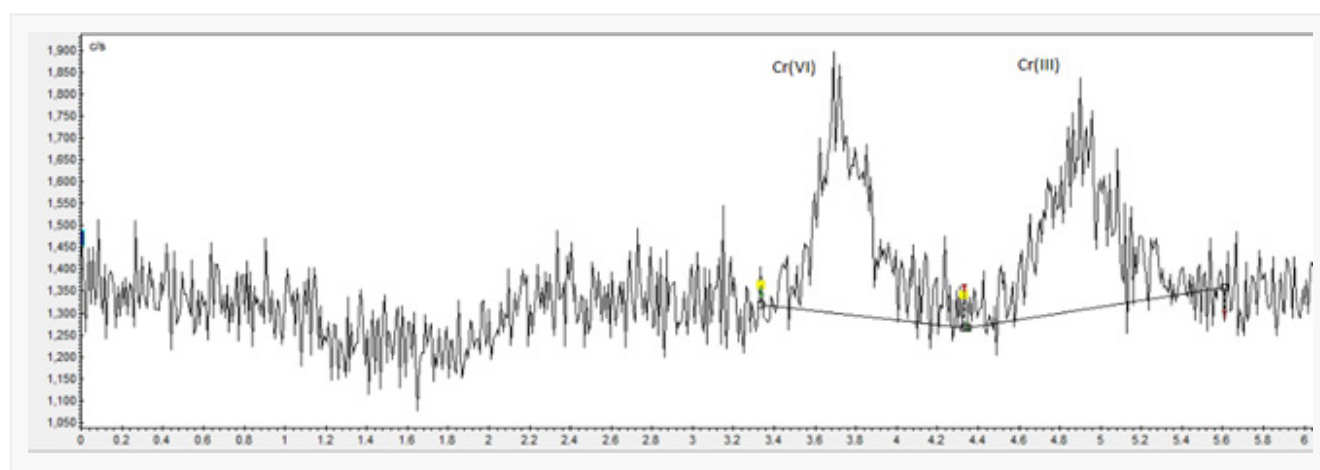


Figure 2: Chromatogram of the lowest standard solution at 0.015 µg/L

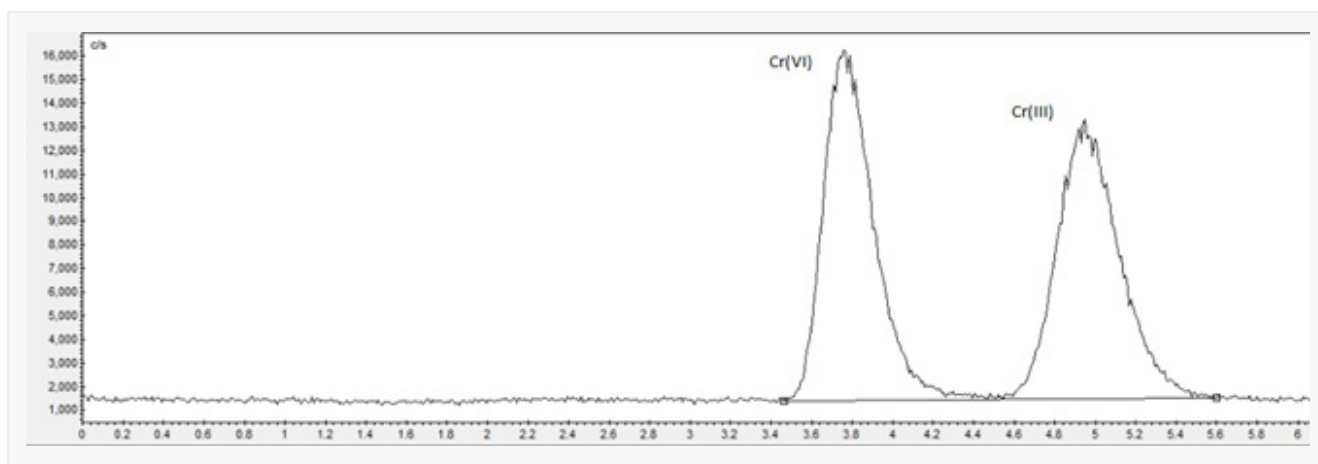


Figure 3: Chromatogram of the standard solution at 0.500 µg/L

To evaluate the performance of the method and compare it with external laboratories, several samples provided by the international proficiency test scheme TOYTEST (LGC, UK) were dispatched quarterly and analyzed using this method. Given that the reference concentration is widely above the calibration range, samples were diluted 1,000-fold prior to analysis. The results of nine different round robin tests are detailed in table 6. An excellent accuracy was achieved with Z-scores within  $\pm 1$  for most samples and recovery rates between 88% and 100%.

Table 6: Results of the determination of Cr(VI) in Toytest round robin test samples

Round robin test	Number of participants	Reported value [µg/L]	Reference value [µg/L]	Z-score	Recovery [%]
R83 (2020)	22	510.00	489.92	0.41	104
R84 (2020)	13	650.00	690.00	-0.58	94
R85 (2020)	14	481.00	480.25	0.02	100
R86 (2020)	26	300.00	339.70	-1.17	88
R89 (2021)	20	681.00	678.00	0.04	100
R90 (2021)	9	657.00	741.66	-1.14	89
R92 (2021)	50	431.00	395.00	0.91	109
R95 (2022)	15	545.00	520.50	0.47	105
R96 (2022)	14	722.00	707.70	0.20	102

A recovery test at low concentrations was carried out in a bubble solution (category II) where the limit of migration (0.005 mg/kg) defined in EN 71-3 is the most challenging to reach. A concentration of 0.020 µg/L of Cr(VI) (equivalent to 0.0025 mg/kg in the raw sample) was spiked into the migration solution and the measurements were repeated 10 times over 5 days of measurement. The mean of the measurements was  $0.022 \pm 0.003$  µg/L (n=10), showing the excellent accuracy and precision of the method, even at low levels.

## Conclusion

The developed method provides a robust and reliable tool for the quantification of hexavalent chromium in toy samples. Stable retention times and a clear separation of chromium peaks within six minutes underline the robustness of the method.

The excellent sensitivity of the PlasmaQuant MS Q allows to achieve the limits of migration for the three categories of toys defined in EN 71-3.



Figure 4: PlasmaQuant MS Q

## Acknowledgements

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