APPLICATION BRIEF 000383

Ensuring toy safety from hexavalent chromium to meet European regulations using IC-ICPMS quantification

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Goal

To optimize the chromatographic method for hexavalent chromium [Cr(VI)] quantification and its migration process according to the EN 71-3: 2019[1] using the Thermo Scientific™ iCAP™ RQ ICP-MS in combination with the Thermo Scientific™ Dionex™ ICS-6000 Ion Chromatography System (or IC-ICPMS)

Introduction

Infants and children are more vulnerable to toxic metal exposure due to their tendency to lick, chew or swallow small pieces of toys, causing the accidental ingestion of chemical components released from the toy material. In order to decrease these exposure risks, European standards were developed to regulate the maximum concentrations of trace elements permitted in toys. However, in recent years, special attention has been focused on Cr(VI) as it has proven harmful effects on health and is strongly related to several types of cancer (Alvarez et al., 2021[2]). The Scientific Committee on Health and Environmental Risks (SCHER) proposed in 2015 to reduce the limit value for Cr(VI) to the current value of 0.005 mg/kg for liquid or sticky toy materials. A revised test method is expected to be available soon that will reliably measure concentrations down to 0.0025 mg/kg. The committee also recommended reviewing the available test methods for CR(VI) every two years to try to find one that reliably assesses even lower concentrations. The main objective is to limit any additional exposure to Cr(VI) in toys to the lowest achievable levels through the application of the best available technologies.

The iCAP RQ ICP-MS system enables fast method development with high accuracy and ultralow limits of detection, achieving the challenging regulatory demands. In combination with the ICS-6000 IC instrument, Cr(VI) can be he separated and detected from other oxidation states.

This Application Brief presents an updated method of AN43175[3] in order to ensure compliance with the EN 71-3: 2019 and to comply with current lower quantification limits.

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System configuration

With the goal of separating Cr(VI) and detecting this species with lowest possible quantification limits, a previously developed method using IC-ICPMS was optimized. For the separation the Dionex ICS-6000 ion chromatography system was utilized with two Dionex guard columns (NG-1 and AG-7) to improve the retention of any potential impurities, reduce the analysis time, and increase sample throughput. In addition, the high precision Thermo Scientific™ Dionex™ AS-AP autosampler was used, allowing sequential injections of different volumes of samples. Finally, the multi-pump configuration system enabled an efficient workflow with the iCAP RQ ICP-MS, facilitating the introduction of mobile phase, rinsing and ICP-MS tuning solution.

The outlet of the column was directly connected to a PFA-LC Nebulizer. The most abundant isotope, ^{52}Cr, was selected and analyzed using kinetic energy discrimination (KED) with pure helium as the collision gas to effectively eliminate polyatomic interferences.

Materials

Product	Part number
Thermo Scientific™ Dionex™ ICS-6000 SP Single Pumps	(P/N 22181-60001)
Thermo Scientific™ Dionex™ AS-AP Autosampler	(P/N 079656)
Thermo Scientific™ UltiMate™ 3000 TCC-3000SD Standard Thermostatted Column Compartment	(P/N 5730.0010)
Thermo Scientific™ IC/LC Connector Kit for iCAP™ Q/Qnova Series ICP-MS Systems	(P/N 1335350)
Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ Software ChromControl Plug-in	(P/N IQLAAGGA CBFAOVMBJD)

Standards preparation and calibration

Nitric acid (75mM) was used as an oxidizing agent in the the eluent, enabling the separation of both Cr(VI) and Cr(III). However, following the European standard EN 71-3:2019, the pH value was adjusted to 7.0 with an ammonia solution to maintain the stability of the hexavalent chromium.

A stock solution of Cr(VI) at 1 g/L was prepared in ultrapure water, and fresh standard solutions were prepared daily to create the calibration curve (Table 1 and Figure 1). The pH value was adjusted to 7.5 for all the standard solutions.

Table 1. Cr (VI) retention time and calibration

Cr(VI) theoretical concentration (µg/L)	Cr(VI) peak area	Cr(VI) concentration (µg/L)
0.02	8983	0.019
0.04	17838	0.040
0.08	35148	0.080
0.12	51646	0.119
0.16	69987	0.161

As a result of the optimized method conditions and the overall stability of the hyphenated IC-ICP-MS setup, Cr(VI) retention time (RT) was consistent and the corresponding peak was automatically and reliably detected using the tQuant feature set of the Thermo Scientific™ Qtegra™ ISDS software (Figure 2).

Based on calibration curve in Figure 1, the instrumental (3σ) detection limit (IDL) was calculated to 0.35 ng/L for Cr(VI).

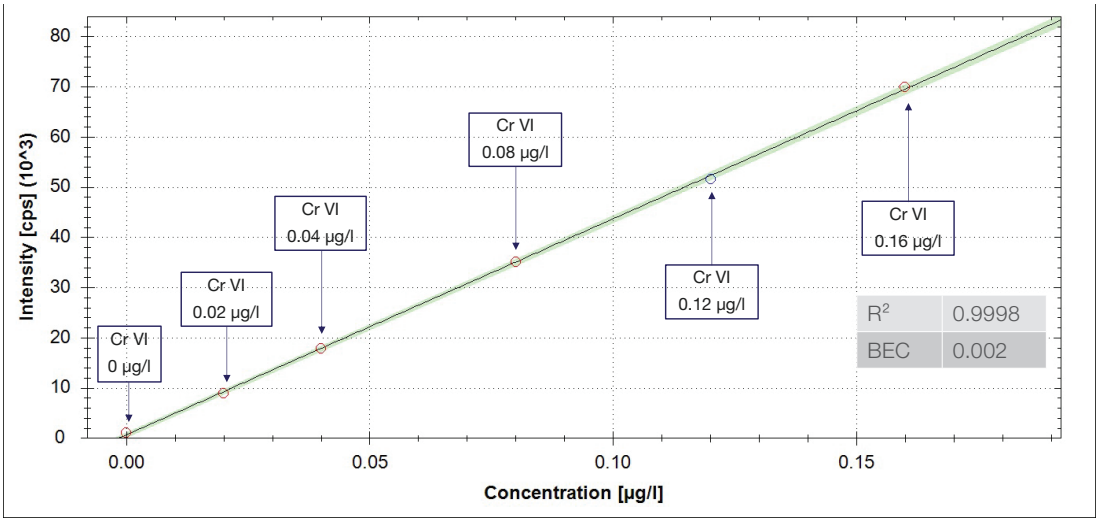

Figure 1. Cr(VI) calibration curve following EN 71-3:2019

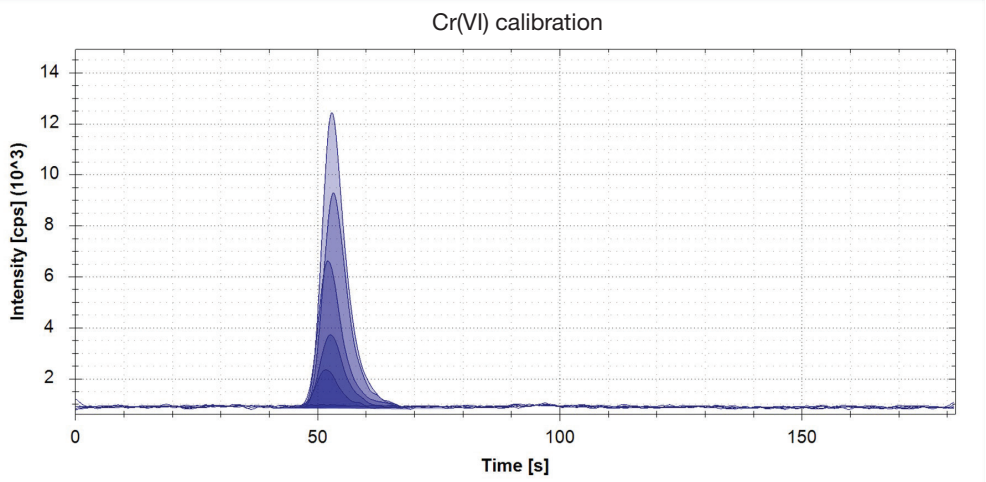

Figure 2. Cr(VI) retention time and calibration values

Migration process

The objective of the migration is to extract elements from toy materials under conditions simulating the contact of the material with gastric juices for a certain period after ingestion.

The migration procedure was used as described in the European standard EN 71-3:2019, with special efforts made to maintain the stability of the chromium species, which can be adversely impacted by redox potential and pH, causing inter-conversions between trivalent and hexavalent chromium, if not monitored. To mitigate this, alkaline conditions were used to maintain the stability of Cr(VI) once the migration is complete.

Analysis

Three different types of sample from toys were tested from categories II (liquid or sticky materials) and III (scraped-off materials): glue, paint and a plastic figure. The corresponding chromatograms of the migration extracts are shown in Figures 3, 4 and 5 and the spike recovery data is summarized in Table 2. The peak before Cr(VI) in the glue and paint samples represents unretained compounds and other chromium species that eluted in void volume of the column. In these analytical conditions (pH=7.5), only Cr(VI) is stable and is retained at about 50 sec. Other chromium species are not retained and are eluted in the void volume at approximately 25 seconds. This can be verified with chromium isotopes ^{52}Cr and ^{53}Cr.

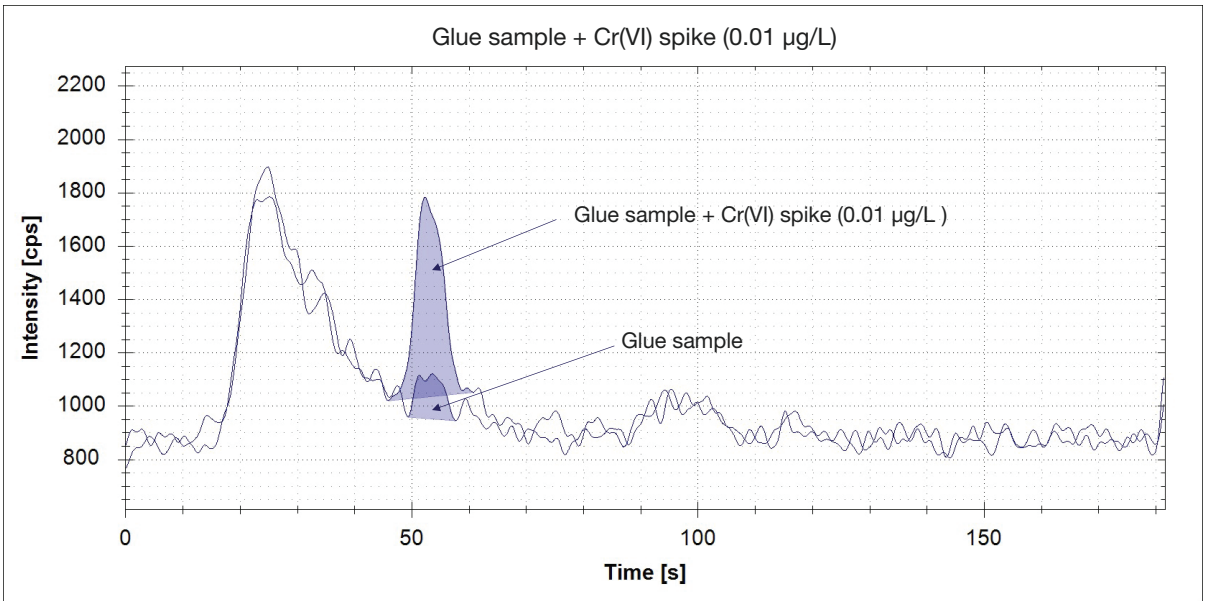

Figure 3. Glue sample spiked with Cr(VI) at 0.01 µg/L

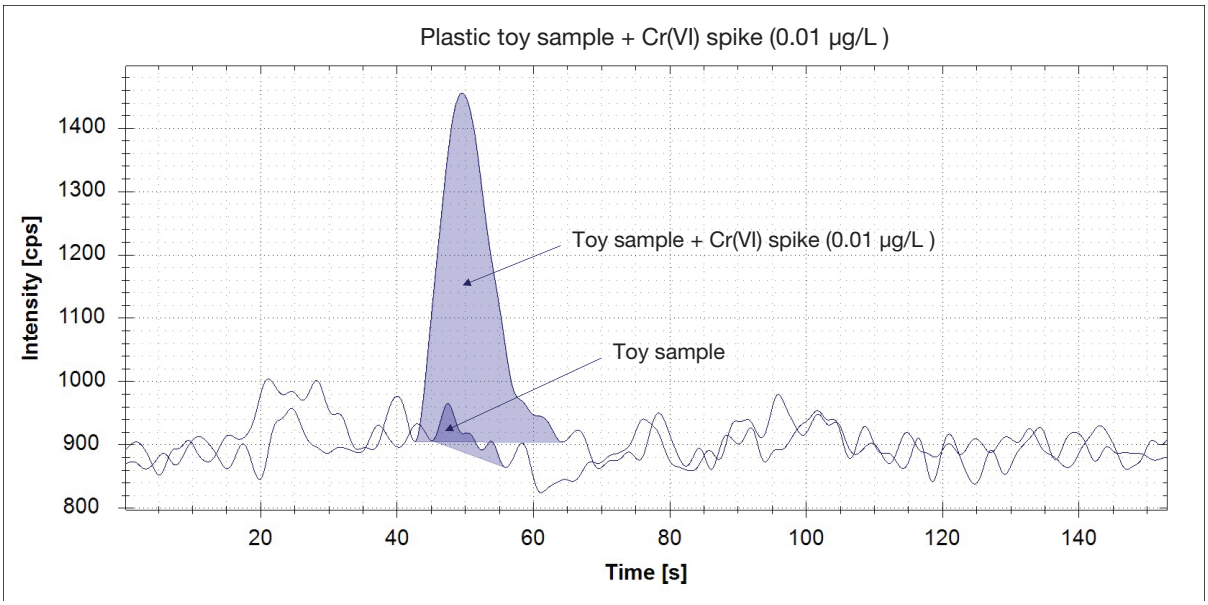

Figure 4. Toy sample spiked with Cr(VI) at 0.01 µg/L

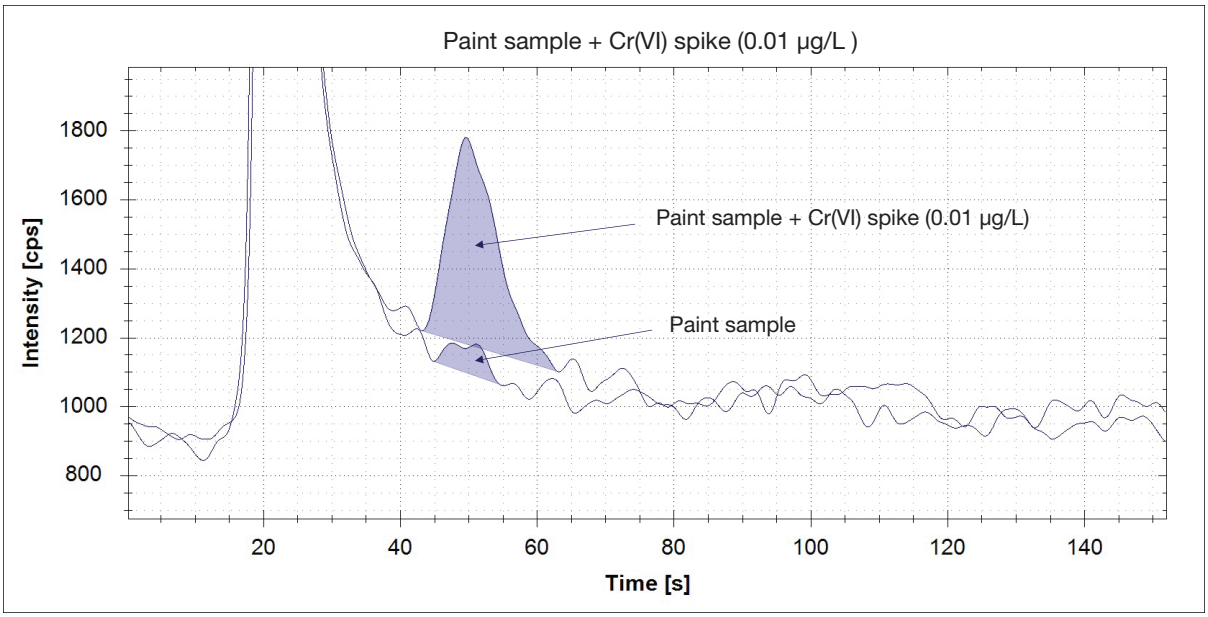

Figure 5. Paint sample spiked with Cr(VI) at 0.01 µg/L

Table 2: Spike and recovery data for different samples of toy materials

Sample type	Cr(VI) in µg/L	Cr(VI) spike (0.01 µg/L)	VI) spike recovery(%)
Glue (pH 7.46)	0.000	0.011	109
Plastic toy (pH 7.61)	0.000	0.010	98
Paint (pH 7.43)	0.000	0.010	103

Table 3. Experimental IC-ICPMS conditions vs. EN 71-3: 2019 recommendations

Parameters	Recommended conditions (EN 71-3: 2019)	Experimental IC-ICPMS conditions
Mobile phase	75 mM HNO_3 (pH=7.0)	75 mM HNO_3 (pH=7.0)
Flow	0.8 ml/min	0.7 ml/min
Column	Non-porous polymer phase with low ion exchange power (5µm x 4.6mm x 50mm)	IonPac NG1 (10µm x 2 x 50mm) + Ion Pac AG7 (10µm x 2 x 50mm)
Column temperature	Ambient	40°C
Injection volume	100 µl	100 µl
Analysis time	3 min	2 min

The samples from categories II and III were analyzed after the migration process and no Cr(VI) was detected. Spiked samples showed excellent recovery, RT stability, and there was no carry-over.

During this study, sample pH conditions were an important factor for Cr(VI) retention time stability and needed to be monitored during the migration process and before injection. Cr(VI) retention time was also affected by column temperature, so utilizing the column compartment allowed for better retention time stability for sequential samples.

This optimized method enabled a reduced runtime of 2 min (Table 3) with high accuracy by quantifying 0.002 µg/L Cr(VI), which corresponds to 0.25 µg/kg Cr(VI) in toys, 20 times lower than actual limit.

Conclusion

The goal of this study was to optimize IC-ICPMS conditions for Cr(VI) detection by modifying the conditions described in European standard EN 71-3:2019 in order to separate and quantify the lowest possible concentration of Cr(VI) in toys to meet current and potentially future regulations. To prove the stability and the powerful detection capabilities of the method, all samples were spiked with 0.01 µg/L Cr(VI), with high recoveries between 98-109% (Table 2).

The iCAP RQ is a dedicated ICP-MS system that can be used to detect low concentrations of total elements as required to meet current regulations. When coupled with the ICS-6000 ion chromatography system, this easy to set-up and reliable configuration can be adapted for quantifying chromium species in toy materials.

Reference

1. EN 71-3:2019. Safety of Toys – Part 3: Migration of certain elements
2. Alvarez, C. C., Gómez, M. E. B., & Zavala, A. H. (2021). Hexavalent chromium: Regulation and health effects. Journal of Trace Elements in Medicine and Biology, 126729.
3. Thermo Fisher Scientific Application Note 43175

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