

# Chromate in Toys, Leather, and potable Water

## Ion Chromatography with Inline Sample Preparation

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Generally speaking, chromate Cr(VI) is classified as allergenic, carcinogenic, and extremely toxic and is subject to strict monitoring. Cr(VI) can occur in various concentrations in different areas, e.g., drinking water, toys, or textile and leather products. Metrohm has developed ion chromatographic determination methods for determining Cr(VI) in various concentration ranges (ng/L to mg/L) with Inline Sample Preparation techniques for various matrices.

**The method can be almost entirely automated. In the following we present the analysis of hexavalent chromium in toys, leather, and drinking water.**

### Chromate in toys according to DIN EN 71-3

Children are exposed to heavy metals from a wide variety of sources. In particular, Cr(VI) represents a potential hazard, as it is absorbed from food and drinking water, from the air, from textiles, and from toys. Analytical determination of the Cr(VI) content in toys is described in the European Standard DIN EN-71-3-2013 (Safety of toys Part 3 – Migration of certain elements), as well as in the EU directive 2009/48/EC. The limit values that apply to Cr(VI) according to the EU directive are listed in Table 1. According to DIN EN 71 Part 3 the user is free to choose whichever analysis method he or she prefers, as long it is validated. Metrohm has developed an ion chromatography method for this application that uses Inline Preconcentration and Inline Matrix Elimination. The method can be almost entirely automated.

**Table 1: The three types of toy materials and their migration limits for Cr(VI) according to EU directive 2009/48/EC, plus some examples**

Toy material group	Dry, brittle, powder-like or pliable toy materials	Liquid or sticky toy materials	Scraped-off toy materials
Examples	Colored pencil leads, chalk, wax crayons, modeling clay	Finger paint, varnish, liquid ink in pens, soap bubble solution, glue sticks	Varnish coatings, polymers and similar, paper, cardboard, glass, ceramics, metallic materials, wood, leather
Migration limit	0.02 mg/kg	0.005 mg/kg	0.2 mg/kg

### Sample digestion using synthetic gastric juice

Chromium(VI) is extracted from the toy material at body temperature using hydrochloric acid. This type of sample digestion simulates how gastric juice dissolves out the harmful substance from swallowed toy material. The sample that is obtained using this method is then manually neutralized and diluted. Dilution is required because the high ion concentration present in the sample – which is caused by hydrochloric acid extraction and subsequent neutralization – does not permit preconcentration of chromium(VI).

### Automation improves convenience and safety

All the remaining steps are automated. To start with, the entire sample flow path is equilibrated using sample. A Dosino then feeds a defined sample volume onto the preconcentration column (Figure 1).

The Dosino allows to control with accuracy the injection volume, and this is what forms the basis of reliable determination, especially when dealing with low analyte concentrations. Equally important for the sensitivity, however, is the post-column reaction of Cr(VI) with 1,5-diphenylcarbazide that results in the formation of VIS active complexes. As illustrated in Figure 2, the method presented accurately determines hexavalent chromium in the single digit ppt range, easily complying with the 10 ppt limit set by the EU directive 2009/48/EC.

### Chromate in leather according to DIN EN ISO 17075

The Cr(VI) that may form during the chrome tanning process is regarded as allergenic and carcinogenic. Causes of the Cr(VI) load in leather include, among other things, contamination of the Cr(III) salts by Cr(VI) compounds.

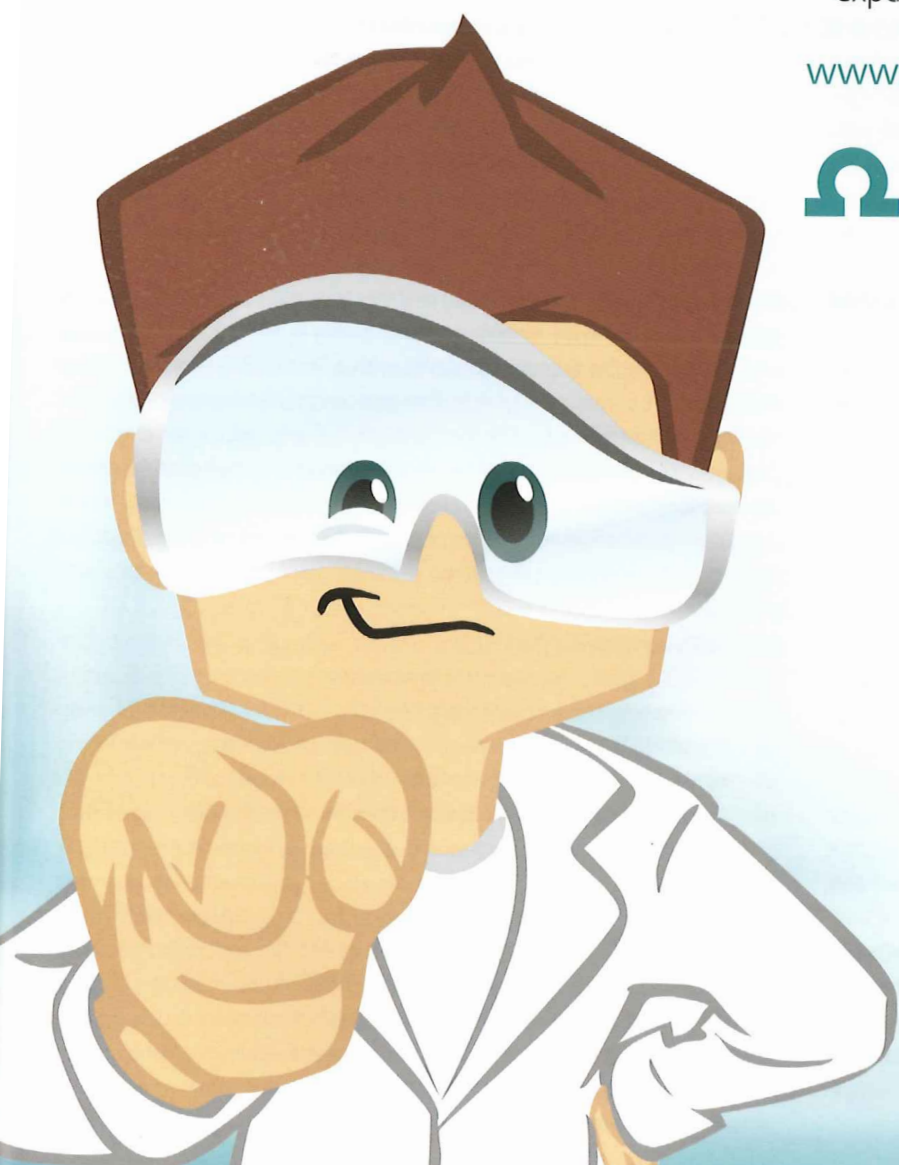
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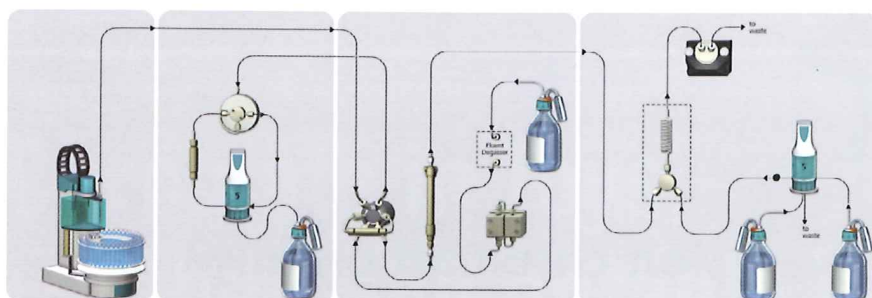


Fig. 1: Diagram of the IC system for the determination of chromium(VI) in toy samples. Following manual extraction, dilution, and neutralization of the samples, the fully automated analysis process takes place according to the measurement setup shown above. Dosing the sample and post-column reagent using Dosinos rather than pumps offers a number of benefits, as it allows not only exceptionally precise control of the sample volume, but also post-column reagent dosing that is synchronized with the column flow – as well as automatic switching between the post-column reagent and rinsing solution. The setup can be easily modified for analyzing leather or drinking water samples.

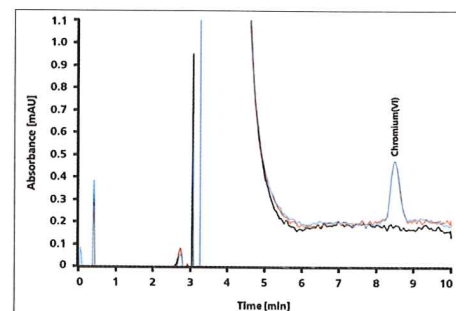


Fig. 2: Two determinations of a standard solution containing 0.04 µg/L chromium(VI) in a matrix corresponding to that of a neutralized migration solution – this contains HCl, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (red and blue). The reference curve (black) shows the chromatogram of ultrapure water.

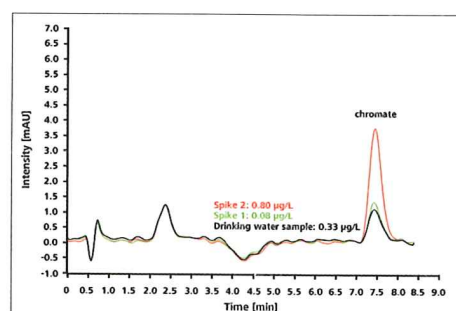


Fig. 3: Chromate determination in a drinking water sample – once unspiked and once spiked with 0.08 µg/L and 0.8 µg/L Cr(VI). Recoveries were between 99.8 and 99.9%. Column: Metrosep A Supp 5 - 150/4.0; eluent: 12.8 mmol/L Na<sub>2</sub>CO<sub>3</sub>, 4 mmol/L NaHCO<sub>3</sub>, 2.5 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.7 mL/min.

In addition, excess Cr(III) salts that are not bound to the collagen in the skin of the leather may oxidize to form chromium(VI) under certain conditions. The Cr(VI) content in leather is determined in accordance with DIN EN ISO 17075:2007. Strongly coloured leather extracts disrupt the determination of chromium(VI) and require filtration of the extracts. Metrohm has developed an ion chromatography method for this application using Inline Dialysis for automatic sample preparation and UV/VIS detection following post-column reaction. Before injection of the sample on the separation column, the high-molecular compounds of the sample matrix are separated from Cr(VI) with Inline Dialysis. In the second step, chromatographic separation takes place on an anion exchanger before post-column reaction with 1,5-diphenylcarbazide, as already described in the toy section.

#### Advantages of the method in comparison with the photometric method with solid-phase extraction:

- **Cost savings**  
The moderate price of the membrane for Inline Dialysis keeps operating costs very low in comparison with solid-phase extraction.
- **Time savings**  
The automatic sample preparation of the next sample is already taking place with Inline Dialysis during the running time of the chromatogram of each sample.
- **Increased detection sensitivity**  
Detection sensitivity can be enhanced considerably in comparison with the conventional photometric method thanks to the sensitivity of the UV/VIS detector after post-column reaction.

#### Chromate in mineral and drinking water according to EPA 218.7

Cr(VI) is a highly toxic contaminant of drinking water. Even the smallest quantities are hazardous to human health. Even though the RoHS Directive has severely restricted the use of Cr(VI) compounds in Europe since 1 July, 2006, chromate nonetheless remains a widespread pollutant in the environment. Some pigments formerly used in dyes also contained Cr(VI) compounds. These chromate pollutants appear in the environment when decontamination is done improperly. The carcinogenic Cr(VI) finds its way into the soil and over time also into our water. The EU limit value for total chromium, which corresponds to both the WHO limit value and to the German Drinking Water Ordinance, is still set at 50 µg/L.

There are ongoing discussions as to whether this limit value should be considerably lowered. We developed an exceptionally sensitive ion chromatography method for the detection of Cr(VI), with a limit of determination of less than 0.02 µg/L chromate (Figure 3). The application is also in compliance with the limit value stipulated in EPA Standard 218.7. If required, the sample can be prepared for injection using Inline Ultrafiltration in an automated sequence. As described earlier, detection takes place by post-column reaction with 1,5-diphenylcarbazide and subsequent detection at 540 nm. The procedure is controlled using the intelligent ion chromatography software MagIC Net.

- [1] EU Directive 2009/48/EC
- [2] DIN EN 71-3:2013-07: Safety of toys - Part 3: Migration of certain elements.
- [3] U.S. Environmental Protection Agency, Method 218.7, Version 1.0, Cincinnati, Ohio, USA (2011).
- [4] Metrohm Whitepaper WP-001EN: Chromium(VI) determination in children's toys
- [5] Metrohm Application Note AN-U-015: Chromium(VI) in a leather extract.
- [6] Metrohm Application Note AN-U-057: Chromate in drinking water by ion chromatography with PCR and UV/VIS detection, according to EPA Method 218.7.

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