Chromate in toy migration solution

Stephanie Kappes and Alfred Steinbach

You may deem the chance slim that mythical monsters are hiding underneath your offspring's beds. However, danger might be lurking there in the form of toy blocks, action figures, or crayons. Hazardous substances found in everyday items, including toys, pose a particular threat to children. Even low concentrations have the potential to cause significant harm to their small bodies – and since children don't just discover the world through their eyes and hands, but by putting things in their mouths, too, they are at high risk of ingesting these substances

Metrohm International Headquarters; Herisau, Switzerland

New directive imposes tighter restrictions

National and EU-wide standards stipulate strict limit values for hazardous substances in toys. EU Directive 2018/725, also known as the "Toy Safety Directive", came into force on May 16, 2018, and has imposed tighter restrictions on the migration limits for some hazardous substances in toys – including the carcinogenic chromium(VI). The migration limit refers to the maximum quantity of a hazardous substance that a product is permitted to release. In the new directive, it is this type of value that now replaces the limit values expressed in terms of bioavailability that were defined in the previous version. The directive draws a distinction between three types of materials used in toys: (1) dry, brittle, powder-like, or pliable materials, (2) liquid or sticky materials, and (3) scraped-off materials. Each of these groups is subject to different migration limits according to the accessibility of the hazardous substances through sucking, licking, swallowing, or prolonged skin contact. The limit values that apply to hexavalent chromium according to the new EU Directive are listed in **Table 1**.

Free choice of test method

European standard EN 71 Part 3 outlines the test methods associated with the Toy Safety Directive, including sample preparation and results evaluation. Sample preparation involves producing a migration solution by releasing hazardous substances from the toy material under realistic conditions; that is, mimicking what happens when the material comes into contact with skin, is swallowed, or is put in the mouth, for instance. The user is free to choose whichever analysis method he or she prefers, as long as it is validated. Ion chromatography with UV/VIS detection following post-column derivatization is suitable for chromium(VI) determination in scraped-off toy materials, as well as dry, brittle, powder-like, or pliable materials, in accordance with the migration limits specified in **Table 1**. This method can be almost entirely automated. This, in combination with matrix elimination and preconcentration of chromium(VI), ensures highly reliable and precise analyses. To illustrate the method, the information that follows outlines the process of analyzing samples of finger paint, opaque white paint, colored pencils, inks, watercolors, and varnishes.

Table 1. The three types of toy materials and their migration limits for chromium(VI) according to EU directive 2018/725, plus some examples.

Category	I	II	III
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	0.053 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 (**Figure 1**). To start with, the entire sample flow path is equilibrated using sample. A Dosino then feeds a defined sample volume onto the preconcentration column. 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.

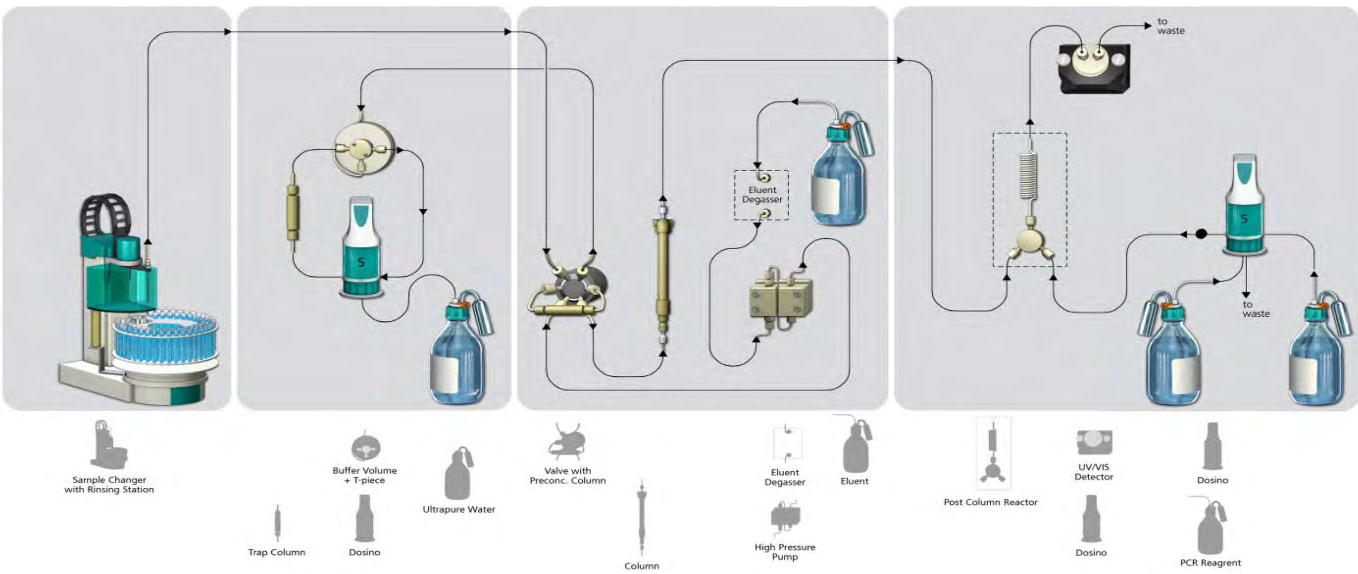

Figure 1. Diagram of the IC system for the determination of chromium(VI) in toy samples. Following manual extraction, dilution, and neutralization of the samples, the fully automated analysis process takes place according to the measurement setup shown above. Dosing the sample and post-column reagent 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.

Figure 2. 940 Professional IC Vario with 947 Professional UV/VIS Detector Vario, 943 Professional Reactor Vario and the 858 Professional Sample Processor.

Matrix elimination and preconcentration for reliable trace analysis

The preconcentration column contains an anion exchanger that binds chromium(VI). The cations in the sample and the organic matrix are eliminated by rinsing with 50% acetone, along with anions that bind weakly to the exchanger, such as chloride. Matrix elimination prevents interfering peaks, which compromise the evaluation of the chromium(VI) peak, and extends the service life of the analytical column. The acetone-containing rinsing solution eliminates not only ions and organic sample components, but also pigments: as pigments can interfere with VIS detection, it is crucial that they are thoroughly removed. During the process, the hexavalent chromium remains in the preconcentration column: Thanks to its lengthy retention time, up to 10 mL of rinsing solution can be used without eluting chromium(VI); this means that the majority of the matrix can be rinsed out.

Separation and detection

Chromium(VI) is released from the preconcentration column by the eluent and then proceeds via the separation column to the post-column reactor, where it is reacted with the post-column reagent 1,5-diphenylcarbazide (**Figure 3**). When combined with chromium(VI), 1,5-diphenylcarbazide forms optically active complexes that can be quantitatively determined using the UV/VIS detector because of their absorption in the VIS range. MagIC Net software is used to control the system and evaluate the measured data.

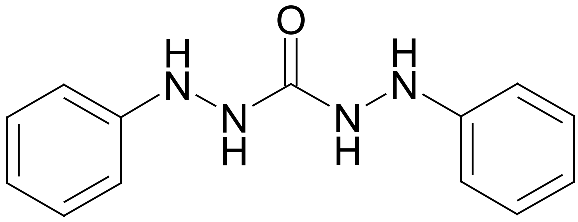

Figure 3. When combined with hexavalent chromium, 1,5-diphenylcarbazide forms complexes that can be detected using the UV/VIS detector thanks to their absorption in the VIS range.

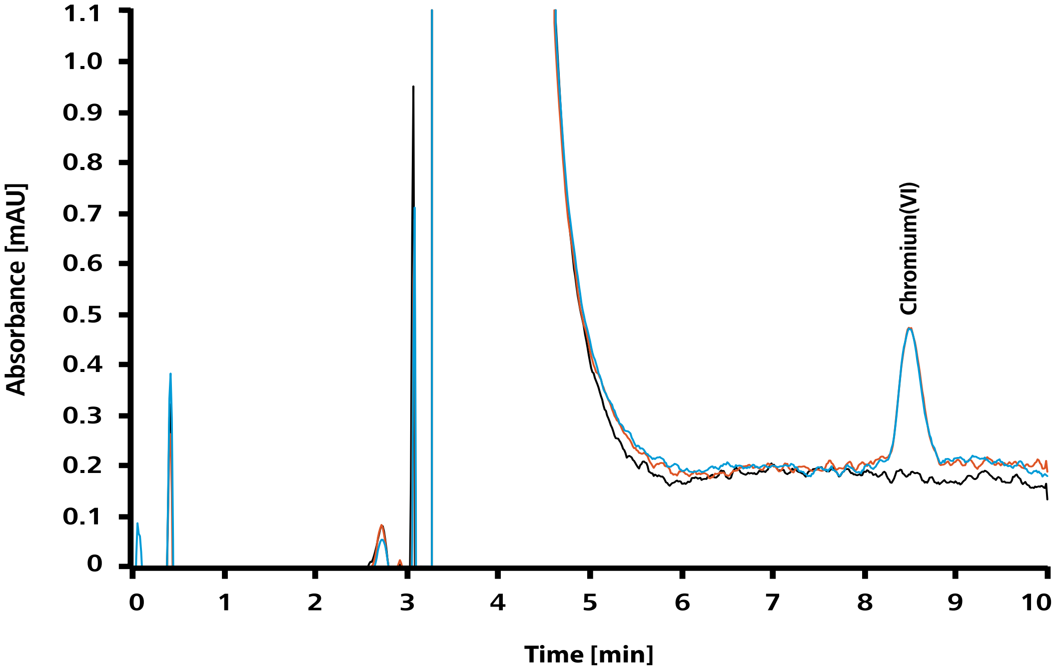

Figure 4. Two determinations of a standard solution containing 0.04 µg/L chromium(VI) in a matrix corresponding to that of a neutralized migration solution – this contains HCl, Na_2CO_3, $NaHCO_3$, and $(NH_4)_2SO_4$ (red and blue). The reference curve (black) shows the chromatogram of ultrapure water.

Summary

This article presents a straightforward and sensitive method for chromium(VI) determination in toy migration solutions. The toy migration solution is prepared according to DIN EN 71. VIS detection follows post-column reaction with diphenylcarbazide. The method presented accurately determines hexavalent chromium in the single-digit ppt range, complying to the limits for category I and III set by the EU Directive 2018/725.

References

[1] EU Directive 2018/725
[2] Metrohm Application Note AN-U-068
https://www.metrohm.com/en/applications/AN-U-068
[3] DIN EN 71-3:2019-08: Safety of toys - Part 3: Migration of certain elements.

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Contact: info@metrohm.com