

Children's Products

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Determination of Hexavalent Chromium in Toys by using UV/Vis Spectrometry

analysis of such elements is important to ensure safety. The European standard EN 71 specifies safety requirements for toys. EN 71, Part 3 contains one section entitled "Migration of certain elements". In this section it defines the limits for element migration from toy materials including hexavalent chromium. In EN 71, Part 3, the limit specified for migration of chromium is not more than 60 mg/kg. In the environment, chromium is found in several different forms including two oxidation states as trivalent i.e., Cr(III) and hexavalent i.e., Cr(VI). Cr(III) is considered to be an essential nutrient for the body. In contrast Cr(VI) is relatively mobile in the environment and is acutely toxic and carcinogenic. It is widely used in electroplating, stainless steel production, leather tanning, paint, and textile manufacturing.

Introduction

Toy safety is a joint responsibility among governments, the toy industries, regulatory bodies and parents. The toy safety regulations are intended to reduce potential risks children could be exposed to when playing with toys. Enforcement of the regulations aims to identify those toys that do not comply with the legislation and remove them from the market. The toxic elements that may be present in toys are heavy metals such as antimony, arsenic, chromium, lead, mercury, etc., which can accumulate in the body and may cause adverse effects. Therefore,



Figure 1. LAMBDA XLS+ UV/Vis spectrometer.
Wavelength: 540 nm; Measurement Mode:
Absorbance; Cell 10 mm.

During the analysis, sample preparation was carried out using European method EN 71, Part 3, specifying extraction of sample by hydrochloric acid for 2 hours at 37 °C in darkness followed by colorimetric determination of hexavalent chromium by 1,5-diphenylcarbazide reagent.

Experimental

The analysis was carried out using PerkinElmer® LAMBDA™ XLS+ UV/Vis spectrometer as shown in Figure 1.

Apparatus and reagents

Table 1. List of apparatus and reagents used.

pH meter
Volumetric flasks, volume 100 mL
Erlenmeyer flasks, volume 250 mL
Water bath
Boiling chips
Eppendorf® micropipettes
Sodium hydroxide, 1N
Potassium dichromate, dried
Nitric acid, concentrated
Sulfuric acid, concentrated
Sulfuric acid, 0.2 N
Phosphoric acid, concentrated
Hydrochloric acid, 0.1 M
1,5 Diphenylcarbazide
Acetone

*The reagents, chemicals, standards used were of ACS grade.

Chromium stock solution (500 mg/L): Dissolved 141.4 mg of potassium dichromate in water and diluted to 100 mL.

Chromium standard solution (5 mg/L): Diluted 1.0 mL of above chromium stock solution to 100 mL.

Diphenylcarbazide solution: Dissolved 250 mg of 1,5-diphenylcarbazide in 50 mL acetone and stored in brown bottle.

Series of reference solutions were prepared by pipetting suitable volumes of above chromium standard solution, as shown in Table 2, into 100-mL volumetric flasks.

Table 2. Calibration solutions.

	Amount of chromium standard solution (5 mg/L) in 100 mL	Concentration (mg/L)
Blank	–	0
Reference 1	2 mL	0.10
Reference 2	4 mL	0.20
Reference 3	6 mL	0.40
Reference 4	8 mL	0.60
Reference 5	10 mL	0.80
Reference 6	20 mL	1.00

Absorbance measurement of calibration solutions:

Background correction was performed with blank solution and absorbance of calibration reference solutions were measured at 540 nm using 10 mm cell. Figure 2 shows the calibration graph.

Sample analysis: Different toy samples selected for analysis were, 'yellow plastic'; 'green fabric' and 'toy coated with paint'. 100 mg of test portion of sample was taken and cut into small pieces. For toy sample with paint coating, the coating layer was scraped off for analysis. The test portion so prepared was mixed for about 1 minute with 5 mL of 0.1 mol/L hydrochloric acid at 37 °C ±2 °C. pH of the solution was adjusted to between 1 and 1.5 with 2 mol/L hydrochloric acid. The mixture was protected from light, kept at 37 °C ±2 °C and agitated for 1 hour continuously and then allowed to stand for 1 hour at 37 °C ±2 °C. Then the solution was filtered immediately through a membrane filter and diluted to about 90 mL with distilled water. The pH of the solution was adjusted to 2.0 ±0.5 using phosphoric acid and 0.2 N sulfuric acid. The solution was transferred to a 100-mL volumetric flask and diluted up to the mark with distilled water. 2 mL of diphenylcarbazide solution was added to the solution and allowed to stand 10 minutes for full color development. An appropriate portion was transferred to a 1 cm absorption cell and measured the absorbance at 540 nm with the blank as a reference.

Results and discussion

Calibration – linearity

The seven different levels of calibration standards were prepared in the range from 0.1 mg/L to 1.0 mg/L with reagent blank as first level. Results showed linearity with a good correlation co-efficient of 0.9997. The calibration curve is shown in Figure 2.

Spike recovery studies:

A recovery study was performed at 0.5 mg/L concentration in three replicates. The results are summarized in Table 3. As seen in table, the recoveries are good, approximately 105 percent. This demonstrates that the extraction is not causing transformation of the Cr(VI) spike to Cr(III).

Table 3. Replicate spike recoveries.

Sample	% Recovery
Sample 1	104.8
Sample 2	104.6
Sample 3	104.6

Method detection limit: 10 replicate reagent blank solutions were prepared to make an estimate of method detection limit. To determine method detection limit, seven replicate aliquots of fortified reagent water (0.01 mg/L) were prepared and processed through entire analytical method. The method detection limit was calculated as follows,

MDL = (t) X (s) where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. [t = 3.143 for seven replicates].

s = standard deviation of replicate analyses.

The method detection limit found to be 0.003 mg/L.

Sample analysis: Results obtained for different toy samples are presented in Table 4. The yellow paint exceeds the limit specified in the current standard for total chromium (60 mg/Kg). The anticipated revision to the EU standard recommends a limit of 0.02 mg/Kg hexavalent chromium in a dry, brittle or pliable toy, much lower than the current standard and based on the species. The detection limit measured here is sufficient for the new regulatory level if a larger sample is taken for extraction or a smaller dilution is used.

Table 4. Sample analysis results (calculations are based on total amount extracted and dilution factor).

Sample	Cr +6 – UV result (mg/Kg)	Total Chromium – ICP result (mg/Kg)
Yellow Plastic	5.4	29.9
Green Fabric	ND	2.6
Blue Paint-1	7.2	89.5
Blue Paint-2	11	66.9
Yellow Paint-1	430	1790
Yellow Paint-2	360	1870
Red Paint-1	ND	58.4
Red Paint-2	ND	47.4

*ND: not detected

The total amount of chromium in the extracts was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with resulting values in Table 4. Since the total chromium value is made up of both Cr(III) and Cr(VI) this is a good indication of the maximum amount of Cr(VI) that might be present. This provides an order-of-magnitude confirmation of the analysis.

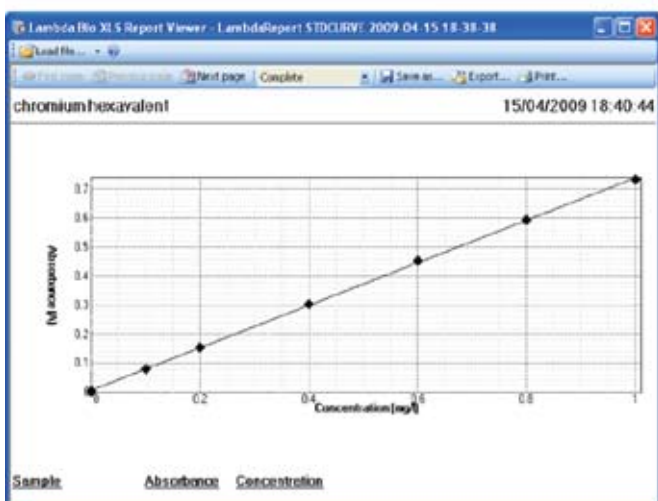
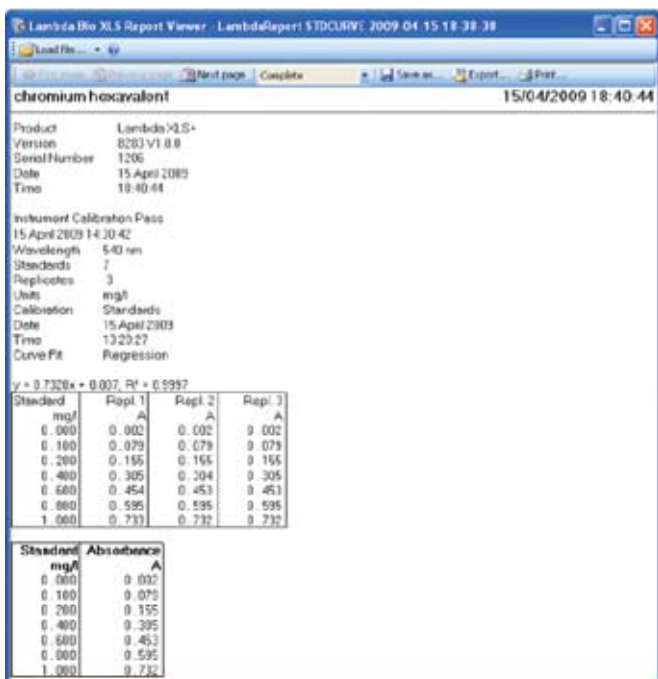


Figure 2. Calibration graph.



Figure 3. Toy samples.

Conclusion

The LAMBDA XLS+ UV/Vis spectrometer can be used to measure Cr(VI) contents in toys. The detection limit is sufficient to determine Cr(VI) at low levels and can be improved by taking a larger sample for extraction and reducing the dilution factor if the new revisions to EN 71 require it. Linearity and spike recoveries further validate the performance of this methodology.

The sample extraction used here may not be representative of the extraction that may be recommended in the final revision of EN 71 specifically for Cr(VI), but represents a reasonable approach to demonstrate the resulting analysis.

Overall, the capability to measure Cr(VI) using the UV/Vis procedure with the LAMBDA XLS+ has been successfully demonstrated.

References

1. Standard Methods for the Examination of Water and Wastewater", Method 3500-Cr, American Public Health Association.
2. EN 71-3:1995 Safety of Toys – Part 3 Migration of certain elements.
3. 40 CFR, Part-136 Appendix B – Definition and Procedure for the Determination of the Method Detection Limit.