Screening Technique for Lead and Cadmium in Toys and Other Materials Using Atomic Absorption Spectroscopy

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Even though it is well known that metals such as lead and cadmium are toxic, especially to young children, children's toys as well as other consumer products still contain these metals. For example, polyvinyl chloride (PVC) polymers often contain lead or cadmium compounds as stabilizers. When PVC polymers break down, due, for example, to exposure to UV radiation as in the case of the miniblind scare in 1996 *(1),* the lead and cadmium may form a dust-like powder that can be readily ingested by children. Unfortunately, in spite of the known toxicity of these metals, some vinyl toys still contain lead and cadmium. A report by Greenpeace in 1996 showed that approximately 20% of the 131 brand-name vinyl consumer products for children purchased in different North American cities contained lead and cadmium *(2).* A plastic harmonica and a toy dragon recently purchased locally were found to contain 20 ppm and 1300 ppm lead and 7 and 38 ppm cadmium, respectively. Both of these objects are likely to be placed in the mouth by small children. Even government regulations permit the presence of lead. According to the Canadian Hazardous Products Act (Item 9 of Part 1, Schedule 1) a toy product may not contain "more than 0.5% weight to weight of lead in the total solids" in the coatings used on toys *(3).* Unfortunately, no level of lead intake by children is safe, since lead is a cumulative poison, affecting the nervous system. This article describes a simple procedure to quickly screen different consumer products for the presence of lead, cadmium, and other metals.

The banning of tetraethyl lead in gasoline in 1991, the use of lead-free solder for joining copper water pipes, and the restricted use of lead-based paint pigments have all contributed to reduced exposure to lead *(4).* Nevertheless, many products, both old and new, still contain unacceptable levels of toxic metals.

Several articles have been published in this *Journal* describing methods of testing for lead in paint chips or ceramic objects using chemical methods *(5).* The Occupational Safety and Health Administration branch of the U.S. Department of Labor has an excellent site describing the evaluation of commercial test kits for lead *(6).* Test kits are also available for cadmium, nickel, or mercury. Many of the toxic metals, though, may not be readily detectable in plastic toys by these chemical test methods, as the metal ions are trapped in the polymeric structure; it is only when the polymer degrades (e.g., exposure to sun or chewed by children) that the metal ions may be freed and ingested.

For a quantitative analysis of metals in polymers, the sample is normally oxidized at a high temperature in a muffle furnace, the resulting ash dissolved in acid, and the solution analyzed for the metals of interest using atomic absorption or inductively-coupled plasma spectroscopy. The sample preparation steps are time-consuming, precluding the use of these methods as a screening tool. With so many consumer products on the market, it is virtually impossible to test them all for the presence of toxic metals. Of special concern are plastic toys for children.

Test for PVC

The polymer of primary concern for toxic metals is polyvinyl chloride (PVC), since it appears to be the only polymer that is often stabilized with lead or cadmium salts; these metallic ions are added to prevent the formation of HCl, which could lead to degradation of the polymer, by reacting with chloride ions to form insoluble chloride salts. To determine whether the polymer contains chlorine, the Beilstein test, a common test for halogens used in introductory organic chemistry, may be used *(7).* This test is based on the principle that copper halides vaporize readily, giving off a blue–green colored flame owing to the presence of copper. To perform this test, copper wire (18 or 20 gauge), inserted into a cork (to serve as an insulated handle), is heated in a blue Bunsen burner flame. The hot wire is touched to an inconspicuous part of the plastic toy (or other object) to be tested in order to melt some of the polymer onto the wire; the wire is then reheated in the flame. A blue–green colored flame, which may persist only a few seconds, indicates the presence of a halogen (excluding fluorine) and suggests that the polymer may be PVC.

Screening Test for Lead and Cadmium (or Other Metals)

The atomic absorption spectrometer (AAS) requires that the metallic atoms be in the gaseous state. This is normally accomplished by aspirating a solution of the sample into a high-temperature flame. The absorption of radiation from an appropriate hollow cathode lamp is compared to prepared standards to determine the quantity of the element in the sample. To use the AAS as a screening device, the spectrometer is set to zero absorbance at the appropriate wavelength. The sampling wire is heated red-hot to ensure that none of the metal is present, as evidenced by zero absorption. A portion of the sample is then placed on the wire and heated directly in the flame, while monitoring the absorbance of the radiation.

For screening samples, nichrome wire (inserted into a cork stopper) works better than copper wire owing to its higher melting point. With a lead hollow cathode lamp and the wavelength selector set to 217.0 nm, the presence of lead may be readily detected in the sample. Absorption of radiation when the sample is heated in the flame indicates the presence of lead; no change in absorption suggests a very low level or absence of lead. Similar tests can be done for other metals using the appropriate hollow cathode lamp and wavelength.

Techniques for Specific Types of Samples

Plastic Objects

After ensuring that the wire is clean, touch the hot wire to the plastic object in an inconspicuous place. Immediately place the wire into the flame and observe the absorbance reading. Continue to heat the wire until the absorbance reading drops to zero before testing the next sample.

Paint chips

Form a small loop on the end of the nichrome wire. After heating the wire, dip it into deionized water. While wet, place a small paint chip on the wire loop (the water helps to keep the chip in place by capillary action). Slowly bring the wire into the flame, so that the water is first evaporated, followed by fusing the chip onto the wire. Continue to heat the wire until red-hot while monitoring the absorbance.

Solder

Lead-free solder looks the same as lead-based solder. To test the solder used for copper water pipes or other applications, simply rub the end of the cooled nichrome wire against an exposed portion of the solder. Then heat the wire as before.

Jewelry or Seals on Wine Bottles

Some inexpensive children's necklaces and bracelets contain high levels of lead. Soft metallic seals used on some wine bottles may also contain lead. To test jewelry or seals, rub a nichrome wire against them and heat in the AAS flame to reveal the presence or absence of lead.

Hazards

Due to the potential release of UV radiation from the high-temperature flame, students should wear protective UV absorbing safety glasses, since the protective door or shield mounted on most instruments must be kept open to allow the students to place the wire in the flame. In addition, the instrument should be properly vented to remove toxic combustion products.

Detection Limit

To determine the detection limit of this method, white PVC siding known to be free of lead and cadmium was shredded using a fine-toothed power saw and collected using a nylon stocking attached to vacuum cleaner. A 1.00 mL solution of the metal standard at the appropriate concentration was added to 1.00 g of the shredded PVC, thoroughly mixed and then dried. For example, adding 1 mL of 100 ppm Pb^{2+}/g PVC is equivalent to 100 ppm Pb on the PVC. The PVC was then tested using the above method for the presence of metal. The lowest detection limit is difficult to determine since the quantity of sample transferred to the wire (and hence into the flame) varies. Nevertheless, the approximate detection limits obtained by this procedure were 100 ppm (or 0.01% by mass) for lead and 10 ppm (or 0.001% by mass) for cadmium; at these levels, an absorbance of about 0.2 was observed.

A few of the substances tested are listed in Table 1. Fortunately, most of the recent vinyl products tested negative for lead and cadmium (including toys, vinyl siding, and binders). Nevertheless, there are still far too many products that children may put into their mouths that contain these toxic elements.

Table 1. Results of Testing Selected Consumer Products

Item Tested	PVC	Presence of Pb	Presence of Cd
Toy soldier (from dollar store)	Yes	Yes	Yes
Toy harmonica (from dollar store)	Yes	Yes	Yes
Toy horn	No	No	No
Vinyl Barbie case	Yes	No	No
Fisher Price ring set	Yes	No[a]	No
Vinyl binder (old)	Yes	Yes	No
Vinyl binder (recent)	Yes	No	No
Insulation on household wire	Yes	Yes	No
Insulation on wire from low-voltage power supply	Yes	Yes	No
Vinyl Suitcase	Yes	Yes	Yes
Vinyl siding (old)	Yes	Yes	No
Vinyl siding (recent)	Yes	No	No
Old house paint	No	Yes	No

[a]Several different sets were tested. In one set, the smallest (red) ring tested positive for lead, but none of the others.

Conclusion

This screening technique avoids expending a lot of preparation time on samples known to contain low levels of hazardous metals; only samples testing positive for the desired elements need to be analyzed quantitatively using standard sample preparation methods.

This technique can easily be adapted as a lab activity in courses for nonscience majors, such as consumer chemistry or environmental science, since very little skill or understanding of AAS is required. Once the instructor sets up the spectrometer, the students can readily test their own samples with minimal instruction or supervision. The only difficulty lies in having to change the lamp and wavelength to test for a different element (unless, of course, you have an old AAS that could be resurrected to serve as a screening instrument!).

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