

Traces of Heavy Metals in Toys

Toys must be safe. That is very clearly stated in the European Directive 88/378/EWG which stipulates the maximum permissible values of substances such as arsenic, lead, cadmium or antimony in toys. The amounts must be below the level which could be harmful for children. During the last few months, several cases were covered by the press where harmful amounts of heavy metals had been detected. With the growing media coverage of this problem, the insecurity of the consumers grows as well. Therefore, it is in the very own interest of toy manufacturers to prove by a reliable quality control the innocuousness of their products.

From Size Reduction to Analysis

Atomic Absorption Spectroscopy (AAS) is very suitable for the detection of traces of heavy metal in plastics. The method is easy and inexpensive and the results show good precision and accuracy. With AAS only dissolved substances can be analyzed, therefore, the sample must first be ground and then digested. Usually, the sample preparation takes up much more time than the actual analysis; moreover, it can be a source of errors not to be underestimated. If, for example, a sample is reduced in size with scissors or a household mixer, falsified analysis results due to contamination are inevitable.

With a plastic doll as an example, this article describes the exact working steps from the neutral-to-analysis sample preparation to the final analysis result. To control the accuracy of this method, reference materials were bought and analyzed as well.



HEAVY-DUTY CUTTING MILL SM 2000

- Feed material: soft, medium-hard, tough, elastic, fibrous
- Material feed size: < 60 x 80 mm
- Final fineness: 0.25 - 20 mm



MIXER MILL MM 400

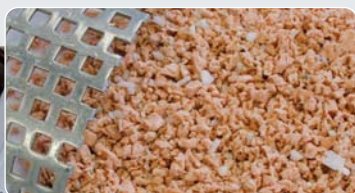
- Feed material: hard, medium-hard, soft, brittle, elastic, fibrous
- Material feed size: ≤ 8 mm
- Final fineness: ~ 5 µm





SM 2000

Preliminary and fine size reduction of the sample



First of all, the components of the doll are separated into 3 different analysis groups: body, hair and dress.

In a first step, the doll's body is pre-cut to a fineness of approximately 3 to 4 mm in RETSCH's **Heavy-Duty Cutting Mill SM 2000**. With its offset hard-metal cutters and powerful drive it is ideally suited for the preliminary size reduction even of heterogeneous sample materials. The sample is then divided into representative sub-samples with the help of the rotary tube divider PT 100 which provides a very high division accuracy. The sub-sample is further homogenized in the **Ultra Centrifugal Mill ZM 200**. It achieves a final fineness below 200 µm in a very short time and is gentle on the material. It is recommendable to use **dry ice as a grind-**

Microwave Digestion



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After the mechanical preparation of the doll, the next step is microwave digestion, before the sample is finally analyzed in liquid form. The objective is the complete digestion of the sample with the digestion solution containing all elements and compounds which are of interest in an unaltered quantity. Inorganic substances should be transformed completely into soluble components whereas organic substances should be mineralized.

The ground parts of the doll (approx. 500 mg) are weighed in the digestion container and 10 ml nitric acid are added. The digestion process is then started software-controlled. The temperature development of all samples is continually measured and adapted to the specified digestion profile, depending on the reaction development. After **only 30 minutes** the samples are digested and can now be filled to the nominal volume for the subsequent analysis in the Atomic Absorption Spectrometer.

For trace element analysis the following requirements have to be fulfilled:

- The digestion should be **easy** to carry out, i.e. without great effort and complicated instruments.
- The procedure should be **safe**, i.e. the microwave should possess all necessary safety features.
- The digestion process should be optimally adjusted to the complete analysis procedure so that, for example, the digestion acids don't cause a matrix extension.
- Digestion parameters should be recorded and controlled to guarantee **reproducible conditions**.

Nowadays it is no longer efficient to let the sample boil for hours in concentrated mineral acid on a heating plate.

Microwave digestion systems are designed to dissolve a solid sample in a very short time. This **time benefit** is achieved due to the direct heating of the solution by microwaves, the quick cooling down after digestion and temperatures far above the regular boiling point of the digestion acids.



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ing aid as cooling not only improves the breaking properties of the material but also helps to preserve volatile substances which might otherwise be affected by the frictional heat.

The doll's **hair and dress** are ground in the **Mixer Mill MM 400** which can process two samples of 20 ml within 1-2 minutes. The screw-top grinding jars are filled with sample material and are then **pre-cooled in liquid nitrogen** before being clamped into the mill.

All mills described here can be equipped with **heavy-metal-free grinding tools** thus avoiding the risk of falsifying the analysis results due to contamination.



MM 400

Analytics

The samples are analyzed with Graphite Tube AAS to allow for a low detection level. For this method, 5 to 50 microliters of sample solution are put into the graphite furnace and are then heated step by step to such a degree that the sample is atomized. Modern spectrometers with fixed lamps and a motor controlled mirror allow for the rapid, fully automatic quantitative analysis of several elements.

The doll was analyzed for traces of the toxic heavy metals arsenic (As), cadmium (Cd), lead (Pb) and antimony (Sb). The results:

| element | dress | hair | body |
|----------|--------|-------|--------|
| | mg/kg | mg/kg | mg/kg |
| arsenic | – | – | – |
| cadmium | – | – | 31 ± 1 |
| lead | – | – | – |
| antimony | 32 ± 3 | – | – |

Traces of cadmium were detected in the doll's body and of antimony in the dress. The concentrations are below the recommended limits for toys (Cd: 75 mg/kg; Sb: 60 mg/kg), however, the amount of antimony in the dress is already critical when compared to the values that voluntary seals of approval for ecologically compatible textiles such as Oeko-tex 100 recommend (30 mg/kg).

To verify the accuracy of the complete procedure, reference materials were analyzed as well. Five plastic samples were obtained from the Association of the German Automobile Industry (VDA) which contained different amounts of cadmium.

| sample | certified value | measured value |
|--------|-----------------|----------------|
| | mg/kg | mg/kg |
| 1 | 114.6 ± 2.1 | 114.0 ± 1.0 |
| 2 | 40.9 ± 1.2 | 40.5 ± 0.6 |
| 3 | 75.9 ± 2.1 | 75.7 ± 1.0 |
| 4 | 197.9 ± 4.8 | 196.8 ± 1.3 |
| 5 | 407 ± 12 | 403 ± 6 |



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As the analysis results (average of three independent microwave digestions) come very close to the reference values it can be summarized that the procedure described in this article is very well suited to analyze traces of heavy metals in toys. The results obtained are accurate and highly reproducible and the complete process can be carried out within a couple of hours.