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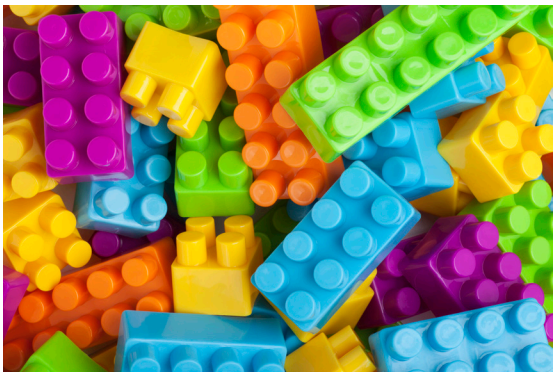
Applications Note

Automated Screening for Toxic Metals in Plastics Using SolidSample ICPMS

Introduction



Regulatory guidelines restrict the levels of toxic elements in manufactured plastics – especially Cr, As, Cd, Hg & Pb – to restrict pathways for migration of these elements into biological systems. Parenteral nutrition products (IV bags, catheters, tubing and product containers) are in direct contact with the human blood stream. Plastics used to contain foodstuff or used in the preparation of food, and plastics used in the manufacture of children's toys present a route for toxic elements to enter the body orally. Consumer plastics (computer hardware and peripherals, product packaging, etc.) incinerated or deposited into landfills may transfer trace elements into the local ecosystem.

Here we describe a rapid and sensitive method for screening plastic raw materials and plastic products for trace metal content using a SolidSample ICPMS robotized LA-ICPMS system.

SolidSample ICPMS

SolidSample ICPMS from Elemental Scientific Lasers (ESL) is designed to directly determine elements in solid materials with minimal sample preparation. Some plastics – especially those designed to resist corrosion – can be difficult to acid-digest for elemental determination. SolidSample ICPMS samples directly from the solid plastic, thereby avoiding acid digestion. Additionally, the absence of water and various acids (e.g. HNO_3, H_2SO_4 and HCl) typically used in solution/digestion ICPMS greatly simplifies the mass spectrum.

SolidSample ICPMS is a next-generation, single-unit instrument that fully automates the process of sample handling, laser sampling, ICPMS detection, data reduction and report generation. SolidSample ICPMS is suitable for medium throughput (<50 samples per day) up to high throughput (>1000 samples per day).

Figure 1. SolidSample ICPMS configured for high-throughput analysis of plastic samples.

Method

Three samples of polyvinyl chloride (PVC) plastic material with known concentrations of trace elements were provided for analysis. The white samples were blanks, the yellow samples had elevated levels of Cr and Pb, and the green samples had elevated levels of Br. Two reference materials – BCR681 and IMEP10 – were used for calibration. Each sample was analyzed six times, and ^{13}C was used as an internal standard. The entire experiment was run twice to demonstrate inter-batch reproducibility.

A NWR213 laser ablation system connected to a quadrupole ICPMS was used to determine trace elements in the samples. Due to some potential polyatomic interferences (e.g. $^{40}Ar^{12}C^+$ interferes with $^{52}Cr^+$, and $^{40}Ar^{35}Cl^+$ interferes with $^{75}As^+$) a KED method was used whereby He was introduced to the collision cell in the ICPMS. A test comparison of standard and KED methods demonstrated lower backgrounds and higher sensitivity for the KED method.

Table 1. Parameters used for determination of trace metals in plastic.

Parameter	Setting
Laser Ablation System	NWR213
Laser Repetition Rate	20 Hz
Laser Scan Speed	200 µm/s
Laser Spot Size	100 µm
Fluence	9 J/cm^2
He flow rate	0.9 L/min
Ar flow rate	0.8 L/min
ICPMS System	Quadrupole with KED mode
Isotopes	^{13}C, ^{52}Cr, ^{75}As, ^{79}Br, ^{111}Cd, ^{202}Hg, ^{208}Pb
He collision cell flow rate	5 mL/min

Results

The calibrations for selected elements are shown in Figure 2 and full quantitative results are shown in Table 2. Precision and accuracy was improved by normalizing elemental signals to those of ^{13}C (applied to all data). Limits of detection range from 48 ng/g to 140 ng/g for As, Br, Cd, Cr, Hg and Pb and 4.8 µg/g for Br. KED mode has enhanced detection limits and accuracy for all elements compared to a no-gas method.[1] Br was not detected in the white and yellow samples, while the green samples were determined to contain 435 and 443 µg/g Br in the two batch analyses, compared to a manufactured value of 450 µg/g. Recovery for Cr and Pb in both of the yellow samples were both 100%. No false positives for any elements in any samples were detected above the LOD's, and all the detected values were well in excess of the LOD's.

Calibration Curves

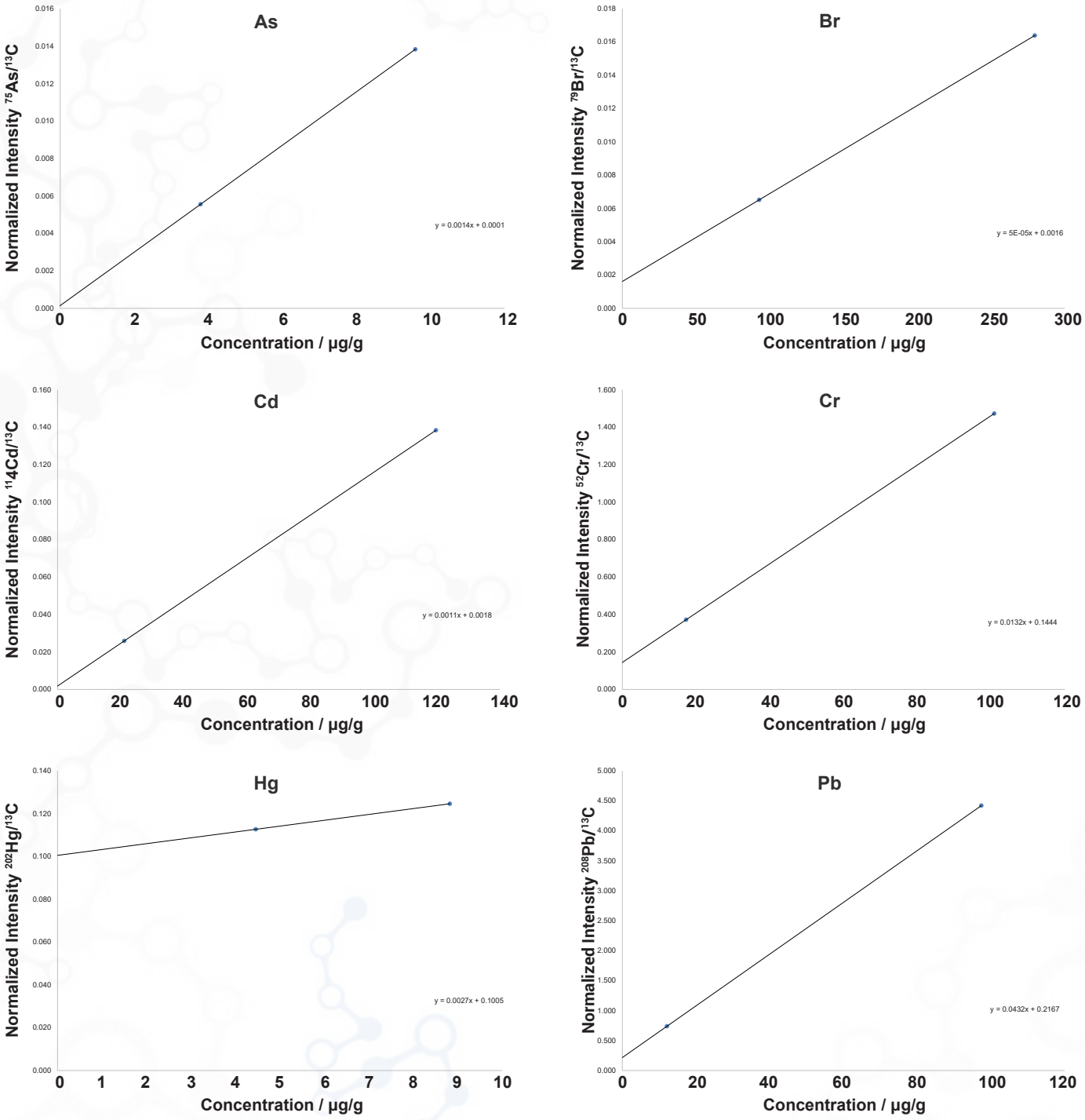


Figure 2. Example calibration curves for Cd and Pb achieved using SolidSample ICPMS.

[1] This study was previously run using a standard no-gas method. % recovery for Pb, Cr and Br were all >10% away from the true value, with poorer matching between batch 1 and 2. False positives for Br were reported for the white and yellow samples where none should be detected. Limits of detection were between 2 and 9 times poorer than the He KED method.

Table 2. Quantitative data for toxic elements in three test samples (in duplicate).

Element		White A	White B	Yellow A	Yellow B	Green A	Green B	LOD
As	Measured Value (µg/g)	< DL	< DL	< DL	< DL	< DL	< DL	0.094 µg/g
	Reference Value	0	0	0	0	0	0	-
Br	Measured Value (µg/g)	< DL	< DL	< DL	< DL	435 ± 13	443 ± 8	4.8 µg/g
	Reference Value	0	0	0	0	450	450	-
Cd	Measured Value (µg/g)	< DL	< DL	< DL	< DL	< DL	< DL	0.24 µg/g
	Reference Value	0	0	0	0	0	0	-
Cr	Measured Value (µg/g)	< DL	< DL	2487 ± 95	2487 ± 46	< DL	< DL	0.14 µg/g
	Reference Value	0	0	2480	2480	0	0	-
Hg	Measured Value (µg/g)	< DL	< DL	< DL	< DL	< DL	< DL	0.048 µg/g
	Reference Value	0	0	0	0	0	0	-
Pb	Measured Value (µg/g)	< DL	< DL	8919 ± 410	8935 ± 606	< DL	< DL	0.063 µg/g
	Reference Value	0	0	8900	8900	0	0	-

Conclusions

The methodology for determination of trace metals in plastics has been proven, is easily adaptable to large numbers of samples using SolidSample ICPMS technology and outperforms XRF. Existing worldwide limits for Cd and Pb in plastics range from 10 µg/g to 75 µg/g. SolidSample ICPMS can easily achieve these limits and actually exceeds these limits by several orders of magnitude, thus future-proofing the method in the case of reduced safety limits in the future.

SolidSample ICPMS is a rapid means to screen plastic samples with little-to-no sample preparation. Expensive and dangerous methods of sample digestion have been eliminated.

SolidSample ICPMS can also be employed as a pre-screening tool as any samples with high concentrations of a target metal can be selected based on data and re-analyzed with automated speciation analysis using ESI's prep*FAST* IC. For example, if the sample is high in chromium, the prep*FAST* IC can be used to determine which form of chromium is present, Cr III which is non-toxic or Cr VI which is toxic.

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