Plastics Analysis

Solid Sampling: Environmental Monitoring

Introduction

Due to growing international concern, governments around the world are setting in place regulatory guidelines to restrict the migration of certain toxic substances from manufactured materials into the environment. Elements of particular concern include: Al, Cr, As, Cd, Hg & Pb. Getting polymeric materials into an aqueous solution is not trivial. Laser ablation solid sampling is a micro-destructive technique that reduces sample preparation times dramatically, enabling high sample throughput. The data presented here describes a unique, laser ablation solid sampling method that displays real promise as a viable technique capable of accurate multi-elemental quantitative analysis.

Ecotoxicological Concerns

The European Union and the United States have defined regulations to protect their citizens from pathways for migration of these elements into biological systems.[1,2] Parenteral nutrition products (IV bags, catheters, tubing and product containers) are in direct contact with the human blood stream. Consumer plastics (computer hardware and peripherals, product packaging, etc.) incinerated or deposited into landfills, may transfer trace elements into the local ecosystem, a concern of health officials.

Methodology

Though plastics have trace level components that are generally homogenous at a macroscopic level (millimeter range), there is often a high level of micro-heterogeneity (hundreds of microns spatial scale).

Evidence suggests that larger sampling volumes will be required to achieve good analytical precision in these sample types.[3] Implementation of a large beam, ultraviolet (266nm) laser ablation system **(Fig. 3a)** in conjunction with a unique, particle filtering device **(Fig. 3b)** has been used to improve the accuracy and precision of such micro-heterogeneous samples.

With laser ablation beam diameters » 500μm and a per sample volume of » 2 mm^3, sampling precisions can be improved significantly

Polyolefins such as polyethylene (PE) and polypropylene (PP) represent 48% of the polymer material currently produced.[3] BCR 681 and 680 are trace element standards in a polyethylene matrix; certified by the Institute for Reference Materials and Measurements (IRMM).

Each BCR 600 series "pellet" is approximately 2.5mm^3, weighing ca. 10mg. They were prepared for analysis by slicing in half, lengthwise and embedding in adhesive putty, so that the flat surface faces upward **(Fig. 1)**. Sample material was ablated via an automated line raster (**Fig. 2)** measuring 800μm x 2500μm with an optically imaged, square aperture. Helium sample cell gas carried the dry aerosol which was subsequently mixed with argon before entering the ICP, as described previously.[4] The laser and ICP parameters are listed (**Table 1)**. The ICP-MS data was intentionally run in a reduced sensitivity mode due to the high signal level for some of the elements characterized. Other spectrometer settings (RF power and lens offsets) are not shown as it is expected that different MS systems will have different optimal settings. The carbon isotope at mass 13 was used as an internal standard for all analyses.

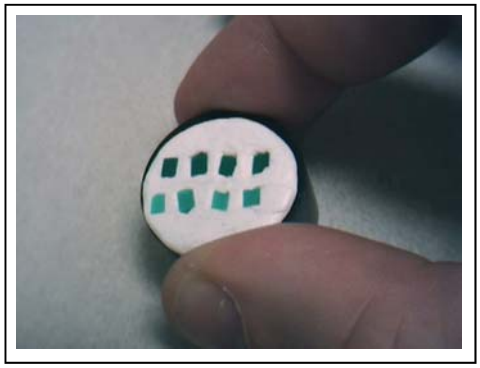


Figure 1: Placement of multiple samples & standards in sample cell, for analysis.

Figure 2: Image of a 800μm x 2500μm line ablation in SRM BCR 610 plastic

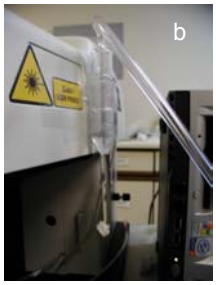
NEW WAVE RESEARCH

Particle Filtering

Filtering of larger particles created in the ablation process has been found to improve analytical precision and reduce elemental fractionation in 266nm ablation.[5-7] Unlike the bubbler device, described here, other devices are not designed to handle large particle loading and would require frequent cleaning.

Bubbler:

- Removes large particles
- Low maintenance - handles large particle load
- Entrained water vapor may enhance particle digestion in ICP.[8]
- Especially well suited to bulk analysis of solids
- May be used as a particle trap for subsequent aqueous analysis



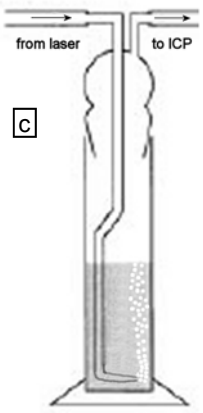


Figure 3: (a) UP-266 MACRO, large beam UV laser ablation system with (b) bubbler, particle filtering device. Schematic diagram of bubbler (c).

Laser Parameters

Aperture	V-adj.	Spot Size	Power	Pulse Freq.	Scan Speed
610um square	1.4	800um^2	3J/cm^2	10Hz	200um sec^{-1}

ICP Parameters

He Cell Gas	Ar Makeup Gas
0.4 L/min	0.6 L/min

Table 1: Operating Parameters

Results

Mass	Element	Run1	Run2	Run3	Run4	Run5	Mean	%RSD	Cert.
27	Al	19	19	20	20	20	20	2.4%	19
53	Cr	18.7	20.5	19.7	17.4	20.0	19.3	6.3%	17.7
75	As	3.25	3.53	3.79	3.60	3.67	3.6	5.7%	3.93
79	Br	82	82	86	85	85	84	2.1%	98
111	Cd	18.2	18.3	17.8	18.6	17.9	18.1	1.7%	21.7
202	Hg	3.8	3.8	4.0	3.9	3.9	3.9	2.2%	4.5
208	Pb	14.2	13.8	13.2	13.4	13.6	13.6	2.9%	13.8

Table 2: BCR 681 - LA-ICP-MS data

Mass	Element	Run 1	Run 2	Run 3	Run 4	Run 5	Mean	%RSD	Cert.
27	Al	46	48	45	47	50	47.1	3.8%	51.0
53	Cr	107	111	107	106	121	110.3	5.7%	114.6
75	As	32	32	32	33	34	32.7	2.8%	30.9
79	Br	784	815	798	815	876	817	4.3%	808
111	Cd	130	133	128	134	139	132.8	3.1%	140.8
202	Hg	25	26	26	27	28	26.6	3.4%	25.3
208	Pb	97	103	99	100	106	100.9	3.6%	107.6

Table 3: BCR 680 - LA-ICP-MS data

Conclusion:

Large beam UV laser ablation is particularly well-suited to bulk analysis of solids. It has the capacity to average micro-heterogeneities inherent in many materials and can improve detection limits of trace element constituents. Integrating a particle filtration system eliminates large particles, present in 266nm aerosols, improving analytical precision. The bubbler device, described here, has the additional benefit of reducing MTBC as well as isolating sampled material in solution for subsequent aqueous analysis. Though the data herein is preliminary it shows much promise. In these experiments sample size was limited. In subsequent experiments we will take full advantage of the technique, using samples of greater dimension. By increasing spot size and integration time, our data will improve further.

References:

1. OJEC, 15.8.2002, *Commission Directive 2002/72/EC*
2. USGPO, Code of Federal Regulations, Title 21, Vol. 4, 2002, Section 201.323
3. *The certification of the mass fraction of As, Br, Cd, Cl, Cr, Hg, Pb and S in two polyethylene CRMs BCR-680 and BCR-681*, BCR Information, ECJRC - IRMMA, 2000, Lamberty, W. Van Borm. & Ph. Quevauviller
4. *The Helium Effect*, Technical Note, New Wave Research, 2003
5. *App. Surf. Sci.,* 1998, **127-129**, Figg, D.J., Cross, J.B. & Brink, C.H.
6. *JAAS,* 2002, **17**, Guillong, M., Gunther, D.
7. *Spectrochim. Acta Part B,* 2003, **58**, Guillong, M., Kuhn, H.-R. & Gunther, D.
8. *JAAS*, 2003, **18**, Aeschlimen, D.B., Bajic, S.J., Baldwin, D.P. & Houk, R.S.

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