Setting standards in analytical science

Report reference AT20/10/3210-3214

Arsenic Speciation in LGC 6177 Landfill Leachates

Percentage arsenic species contribution*:

	Percentage As species (%)			
AsIII	**AsV**	**DMA**	**MMA**	**AsB**
< 1	**73**	**16**	**11**	**n.d.**

*Based on the average of all five sample bottles
AsIII: arsenite; AsV: arsenate; DMA: dimethylarsinic acid; MMA: monomethylarsonic acid; AsB: arsenobetaine
n.d. not detected

Date of sample receipt 6th September 2010

Date of report 4th October 2010

Analyst Jennifer O'Reilly

Our reference No. AT20/10/3210-3214

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Procedures

Arsenic speciation was performed on five replicate landfill leachate CRM solutions (LGC 6177) for the purpose of arsenic species preliminary identification by HPLC-ICP-MS. The five arsenic species under investigation were arsenite (AsIII), arsenate (AsV) and other widely reported compounds in the +5 oxidation state: dimethylarsinic acid (DMA), monomethylarsonic acid (MMA) and arsenobetaine (AsB). Arsenic species selection was based on the availability of arsenic standards in our laboratory. Preliminary identification of arsenic species in the extracts was achieved by HPLC-ICP-MS analysis of unspiked and spiked samples with individual arsenic species standards at 10 µg/kg As. The retention time for each of the arsenic species investigated is shown (Fig. 1).

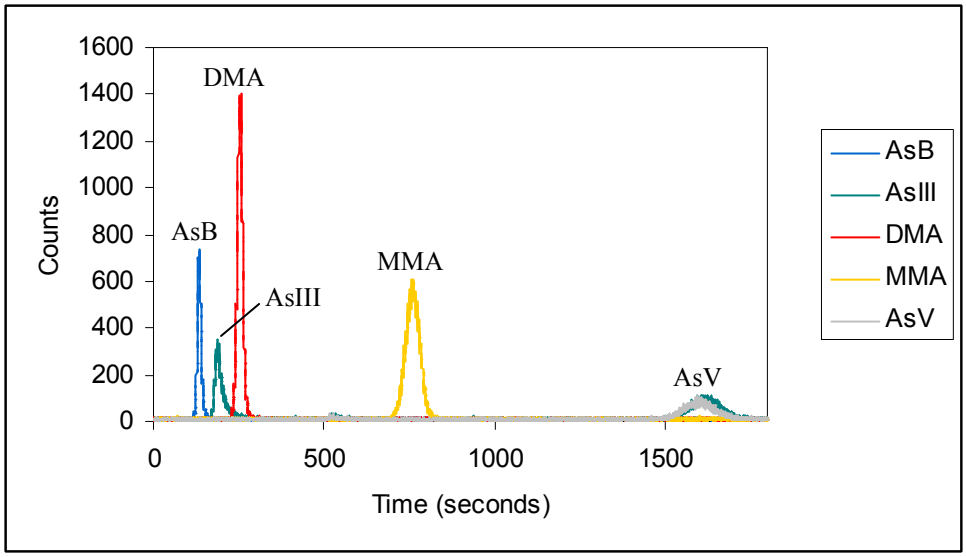

Figure 1: Overlaid chromatograms of 5 individually analysed arsenic species standards under investigation, each at 10 µg/kg.

Instrumentation

The chromatographic separation was carried out using an Agilent Technologies 1100 Series HPLC. Anion-exchange HPLC was performed using a Hamilton PRP-X100 column (250 mm x 4.1 mm id x 10 µm) directly coupled to an Agilent 7500ce ICP-MS operating in Helium mode (4 ml/min) to minimise $^{40}Ar^{35}Cl^{+}$ interferences for element-specific detection at ^{75}As. Samples were introduced into the plasma *via* a

microflow quartz concentric nebuliser and a cooled Scott type double pass spray chamber. Each analysis comprised a 30-35 minute isocratic chromatographic run using 20 mM ammonium hydrogen carbonate (pH 9.0) containing 1% (*v/v*) methanol as the mobile phase. Baseline separation of the detected arsenic species was achieved within either 27 or 33 minutes (depending on sample dilution), at a flow rate of 1.0 ml/min and an injection volume of 50 µl.

Sample collection and preparation

Five sample bottles of the material (LGC 6177) were received on the 6th September 2010 (internal reference AT20/10/3210-3214) and stored at 4^{o}C until HPLC-ICP-MS analysis. Each sample replicate was initially diluted 20-fold with mobile phase (20 mM NH_4HCO_3) prior to arsenic species detection (Fig. 2), providing a chromatographic run time of 30 minutes. To investigate analytical performance at higher matrix concentrations, a 10-fold dilution was also carried out on two of the undiluted leachate samples (Bottles 1133 and 1152); this appeared to yield data of comparable quality, but increased the chromatographic run time to 35 minutes (Fig. 3). The concentration of each arsenic species chosen to spike the sample was optimised to double the initial peak height.

Results

Excellent repeatability was obtained for all 5 bottles analysed at a 20-fold dilution (Fig. 2) as well as the duplicate analysis of two bottles at a 10-fold dilution (Fig. 3). Based on the overall chromatographic peak area, the percentage contribution of each of the arsenic species (identified from spiked samples (Fig. 4)) was as follows: AsIII <1%; DMA 16%; MMA 11% and AsV 73%. There was no detectable level of arsenobetaine (AsB) for any of the extracts, as also observed for other environmental matrices.

The preliminary spiking experiments suggest that the landfill leachate CRM contains concentrations of the identified species ranging up to around 10 µg/kg, mainly in the

+5 oxidation state. However, we would need to take further steps, including calibration, to quantify arsenic species in this matrix.

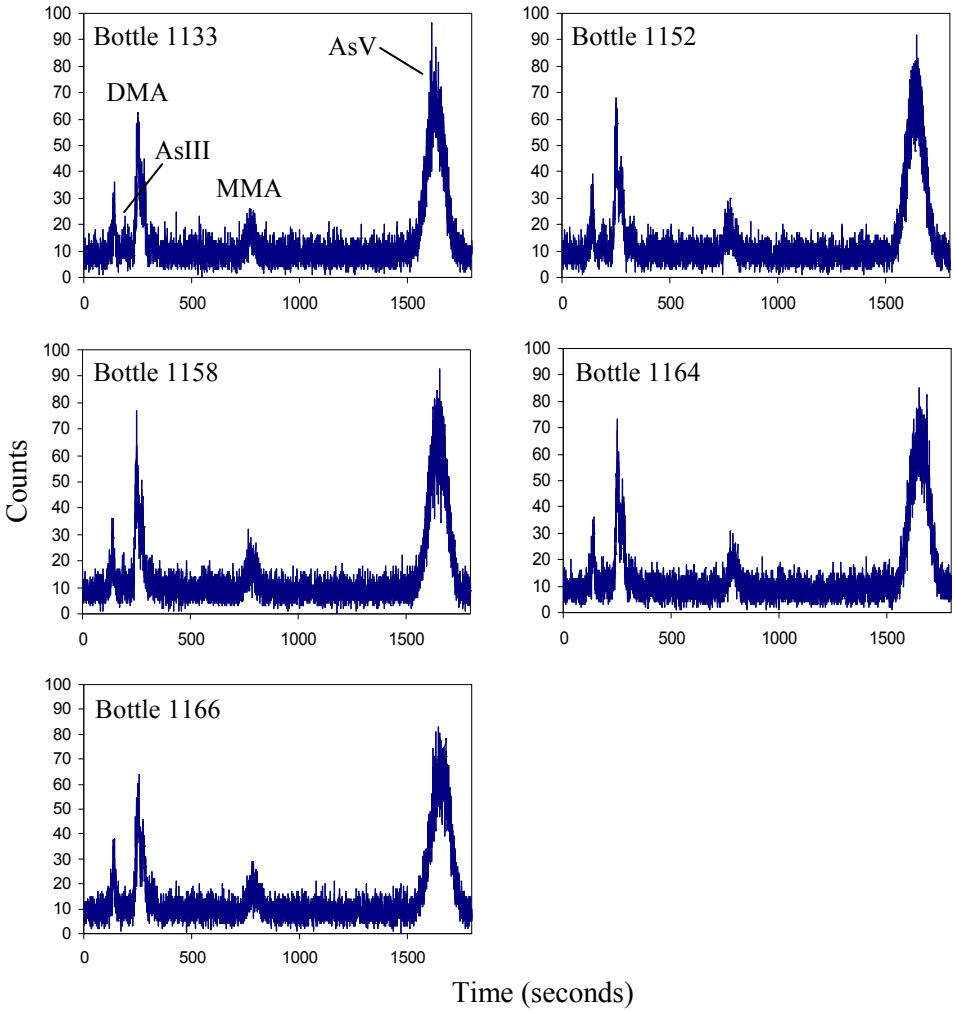

Figure 2: Chromatograms for the five individual replicate LGC 6177 samples (at a 20-fold dilution) by HPLC-ICP-MS.

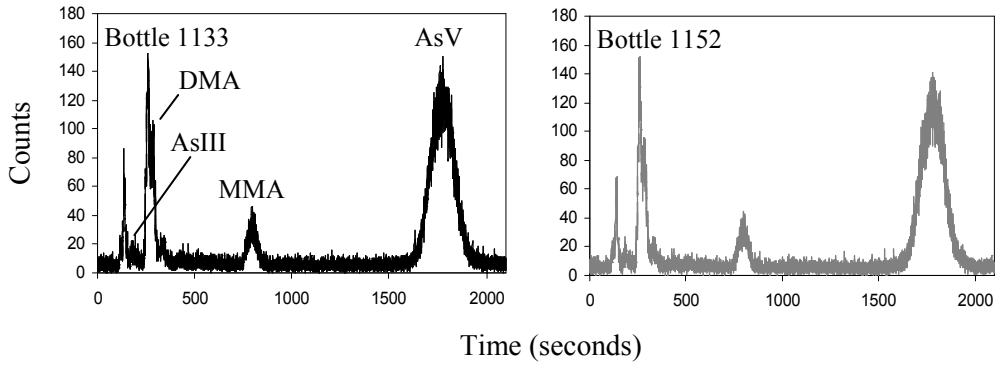

Figure 3: Comparison of two sample extract chromatograms at a 10-fold dilution.

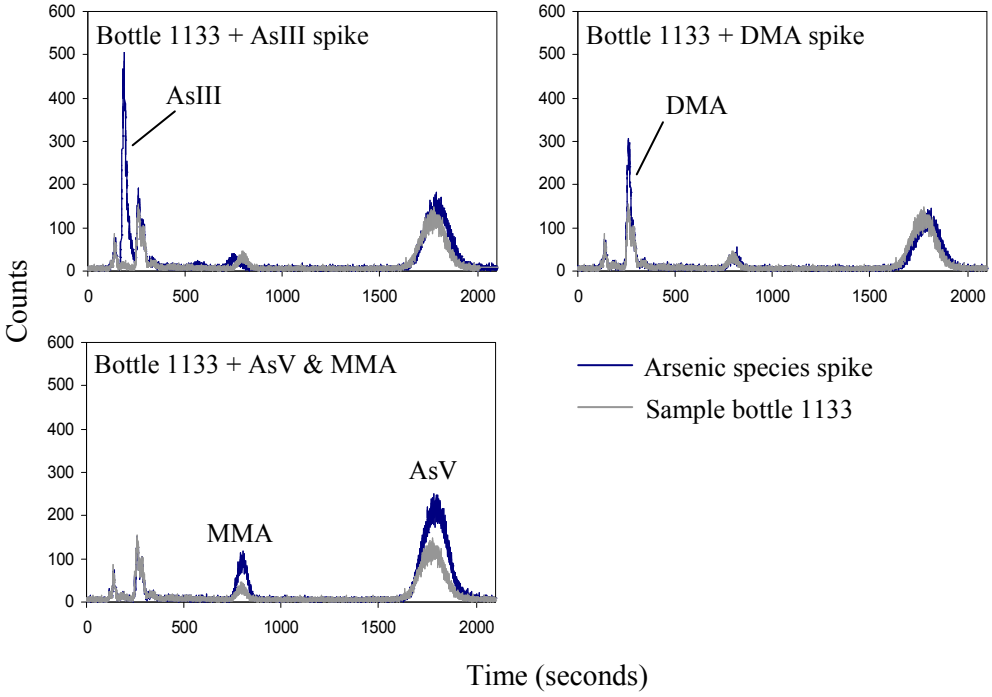

Figure 4: Spiked arsenic species in a 10-fold dilution of landfill leachate (LGC 6177 Bottle 1133).