



Arsenic Speciation in LGC 6177 Landfill Leachates Quantification

Arsenic species quantification: ¹

Concentration of arsenic species [$\mu\text{g}/\text{kg As}$]		
Inorganic As ²	DMA ³	MMA ³
75.5	16.7	7.71

¹ Based on the average of all five sample bottles

² Sum total of AsIII and AsV

³ Concentrations reported as arsenic

Date of sample receipt 6th September 2010
Date of report 26th April 2012
Analyst Jennifer O'Reilly
Our reference No. AT20/10/3210-3214

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Method

Initial identification of arsenic species present in LGC 6177 landfill leachate solutions (bottles 1133, 1152, 1158, 1164 and 1166) was carried out in 2010 (final report dated: 4th October 2010) using HPLC-ICP-MS. Arsenic speciation analysis by HPLC-ICP-MS and retention time standards confirmed the presence of four main arsenic species, namely, arsenite (AsIII), arsenate (AsV), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA), which was re-verified prior to the current quantitative analysis. As a result, quantification studies were focussed on these four arsenic species. Concentrations of AsIII and AsV were combined and reported as total inorganic arsenic [$\mu\text{g}/\text{kg}$ As], since these species are subject to redox exchange during sample preparation.

Arsenic species quantification was performed using external calibration from a series of prepared stock standards over a range of 0 – 20 $\mu\text{g}/\text{kg}$ As for each species (Figure 1). Individual arsenic species concentrations were calculated based on integrated peak area responses for the external calibrants compared to the landfill leachate solutions.

Recovery measurements on leachates spiked with arsenic species was used to assess the accuracy of the method.

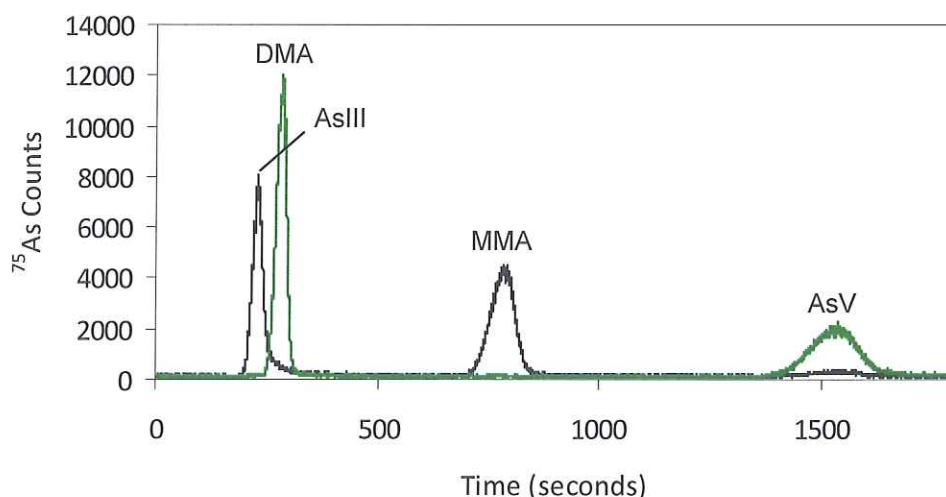


Figure 1: Typical chromatogram showing the 4 arsenic species under investigation (in elution order), each containing 20 $\mu\text{g}/\text{kg}$ As.

Reagents

The reagents (solid materials) used in the preparation of the arsenic species standards are the following:

- **As^{III}**: Sodium meta(arsenite) Aldrich Lot # BCBB711 AsNaO_2 129.91 g/mol
- **As^V**: Sodium arsenate dibasic heptahydrate Aldrich Lot # 0001376825 $\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ 312.01 g/mol
- **DMA**: Cacodylic acid Aldrich Lot # 0001404031 $\text{C}_2\text{H}_7\text{AsO}_2$ 138.0 g/mol
- **MMA**: Disodium methyl arsonate hexahydrate ChemService Lot # 429-110C 291.9 g/mol

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 7700x ICP-MS operating in Helium mode (4 ml/min) to minimise $^{40}\text{Ar}^{35}\text{Cl}^+$ 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 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 27 minutes, 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 landfill leachate (LGC 6177) as received on the 6th September 2010 (internal reference AT20/10/3210-3214) and subsequently stored at 4°C were re-analysed for the purposes of arsenic species quantification by anion-exchange HPLC-ICP-MS. An aliquot of sample solution (after shaking) was taken from each bottle and diluted 5-fold with mobile phase (20 mM NH_4HCO_3) prior to the determination of arsenic species concentrations (Figure 2). Repeatability measurements were carried out in triplicate on two of the landfill leachates (bottles

1133 and 1164). Standard addition experiments were also performed on one of the leachate solutions (bottle 1158) to establish individual arsenic species recoveries. The amount of each spiking solution added to the sample resulted in an approximate increase of 50% and 100% of the original arsenic species concentration (based on average species concentrations of all 5 sample solutions).

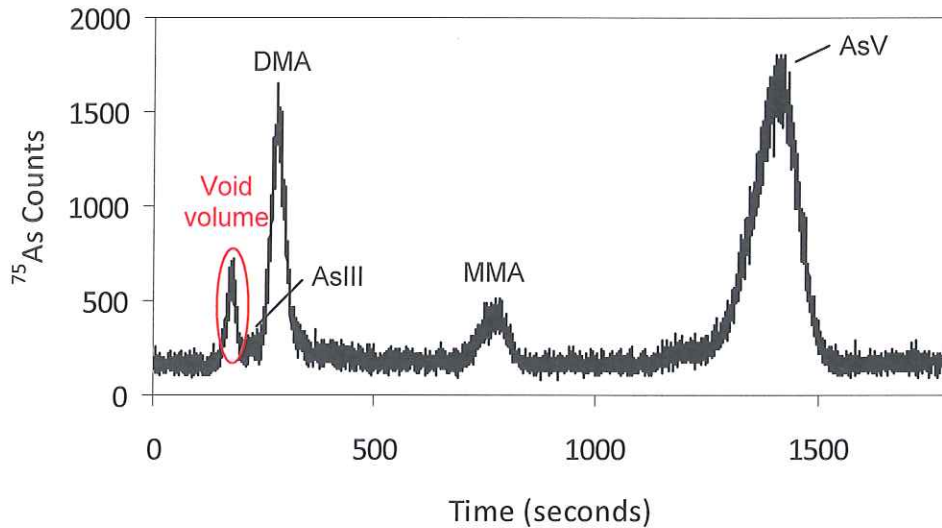


Figure 2: LGC 6177 landfill leachate bottle 1152 at a 5-fold dilution with mobile phase.

Results

The limit of detection (LOD) was calculated for each arsenic species under investigation by means of integrated peak areas. LODs were determined based on 3 x standard deviation of the blank (mobile phase; n = 5) divided by the gradient of the calibration graph (at 0, 1, 5 and 10 µg/kg As for each species). A summary of LOD values are shown in Table 1.

Table 1: LODs (3σ criterion) for each of the arsenic species present in the LGC 6177 landfill leachate solutions

LOD of each arsenic species [µg/kg As] (n = 5)		
Inorganic As ¹	DMA ²	MMA ²
0.025	0.018	0.020

¹ Taken as the LOD of the most dominant inorganic arsenic species (AsV)

² Concentrations reported as arsenic

Quantitative analysis carried out on aliquots from all 5 sample bottles of LGC 6177 (at a 5-fold dilution with 20 mM NH₄HCO₃) by HPLC-ICP-MS reported the following average arsenic species concentrations:

Table 2: Summary of arsenic species concentrations [$\mu\text{g}/\text{kg}$ As] in LGC 6177 landfill leachates (n = 5)

	Inorganic As¹	DMA	MMA
Concentration of arsenic [$\mu\text{g}/\text{kg}$]	75.5	16.7	7.71
Standard deviation	0.80	0.26	0.24
RSD %	1.06	1.56	3.09

¹ Sum total of AsIII and AsV

Two of the leachate solutions (bottles 1133 and 1164) were further analysed in triplicate for the purposes of repeatability (Table 3).

Table 3: Repeatability measurements for LGC 6177 landfill leachates (bottle 1133 and 1164)

	Inorganic As¹	DMA	MMA
Bottle 1133 (n = 3)			
Concentration of arsenic [$\mu\text{g}/\text{kg}$]	74.6	16.7	7.61
Standard deviation	0.65	0.34	0.05
RSD %	0.87	2.07	0.68
Bottle 1164 (n = 3)			
Concentration of arsenic [$\mu\text{g}/\text{kg}$]	76.2	16.7	7.82
Standard deviation	0.57	0.18	0.20
RSD %	0.75	1.06	2.56
Repeatability (% RSD)	0.81	1.57	1.62

¹ Sum total of AsIII and AsV

Standard addition experiments were undertaken to calculate arsenic species recoveries at two different spiking concentrations for each species using sample bottle 1158. Spiking was performed to increase all species concentrations by approximately 50%

and 100% of the original concentration within the sample (Figure 3). A summary of the results can be seen in Table 4.

Table 4: Standard addition recovery data (%) for LGC 6177 landfill leachates (bottle 1158)

	Inorganic As ¹	DMA	MMA
Standard addition (% of original concentration)			
50	98.2	102	101
100	106	107	109
Average % recovery	102	105	105

¹ Sum total of AsIII and AsV

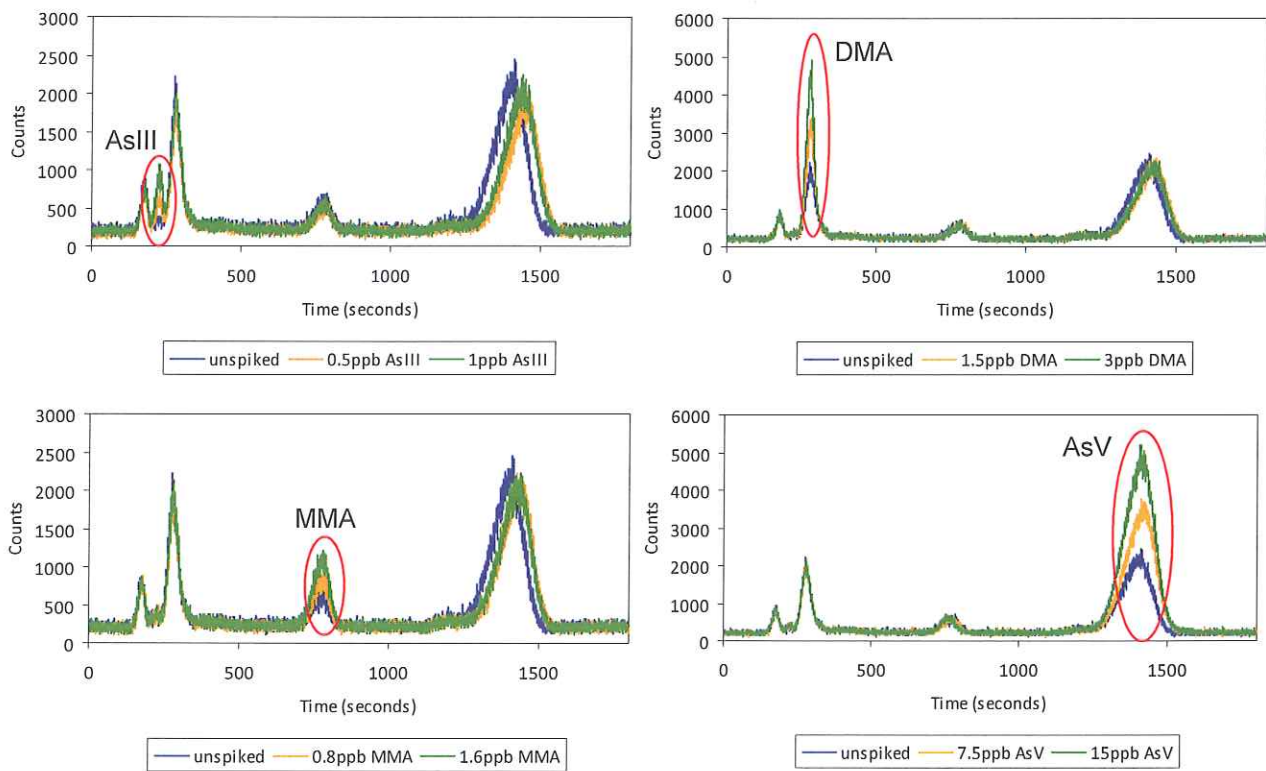


Figure 3: Chromatograms showing spike recovery addition for each arsenic species in LGC 6177 bottle 1158.