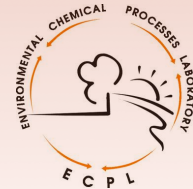# Investigating the Occurrence of Inorganic and Methylated Arsenic Species in Atmospheric Particles by Using Dual Column HPLC – arsine generation – ICP-MS: Overcoming Existing Analytical Method Limitations

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INTRODUCTION

Arsenic (As) is a ubiquitously distributed metalloid in the earth's crust, emitted into the atmosphere mainly in particulate form from natural sources or as a result of anthropogenic activities.

Five different species of As have been detected in atmospheric particulate matter (PM). Two of them are inorganic (arsenite iAs(III) and arsenate iAs(V)) and three of them are methylated (methylarsonate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO)). The two inorganic species of As are reported to be far more toxic than the methylated ones [1]. Although the methylated species have been detected in PM since the late 70's and 80's [2, 3], most of the recent studies focus mainly the two inorganic species of As and less on the DMA and MA, almost totally ignoring the presence of TMAO [4] with one exception [5]. **In most cases researchers that have used anion exchange HPLC - ICP-MS based methods for arsenic speciation analysis in atmospheric particles have failed to chromatographically separate iAs(III) from TMAO.** Thus in several studies the observed nonretained chromatographic peak that could correspond to any of the two has almost always been assigned to be iAs(III). This shortcoming in the applied analytical methodology not only fails to detect TMAO but could also lead to a possible overestimation of the iAs(III) concentration.

AIM OF THE STUDY

The objectives of the present study were to develop a one-step chromatographic approach for the complete separation of all As species which have been reported to date to be present in atmospheric particulate matter, i.e. iAs(III), iAs(V), MA, DMA and TMAO and to apply this method to atmospheric PM.

EXPERIMENTAL

The samplings were conducted under the "Hazardous CHEmicals and MIcroorganisms transported by SAharaN Dust Into the Mediterrranean – CHEMISAND" project. Air monitoring usually took place during days with strong or weak Saharan dust outbreak events. Moreover, for comparison purposes, some samples were taken before and after the Saharan dust events.

A. Sample Collection

Sampling site: is semi-rural located at the northern front of the Department of Chemistry, UoC.

Sampling duration: Twenty four (24) hours.

Sampling Period	PM aerodynamic Diameter	Number of samples	Sampler Type – Filter Type
27/11/2012 - 14/03/2013	PM2.1	13	High Volume – Quartz or Cellulose
21/05/2013 - 20/11/2014	PM2.5	33	Low Volume – Quartz
	PM10	33	

Table 1: Sampling details

B. Sample Extraction

A portion of the filter was ultrasonicated with ultrapure water for 90 minutes at 50-55 ºC.
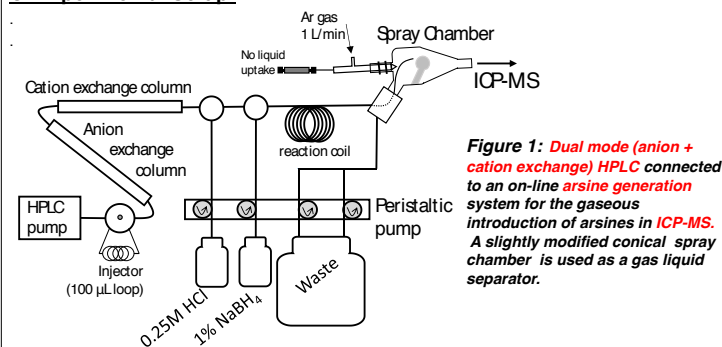
C. Experimental Setup:

Figure 1: Dual mode (anion + cation exchange) HPLC connected to an on-line arsine generation system for the gaseous introduction of arsines in ICP-MS. A slightly modified conical spray chamber is used as a gas liquid separator.

HPLC SYSTEM
- Columns: Hamilton PRP-X100, 250 × 4.1 mm anion exchange column and Agilent Zorbax 300 SCX 150 × 4.6 mm cation exchange column
- Injection loop: 100 μL
- Mobile Phase: 10 mM $(NH_4)_2HPO_4$ acidified with acetic acid to pH 4.2.
- Flow rate: 1 mL min^{-1}

ARSINE GENERATION SYSTEM
- HCl 0.25 M, flow rate of 1.4 mL min^{-1}
- NaBH$_4$ 1%, flow rate of 1.1 mL min^{-1}

CONCLUSIONS

A dual mode (anion + cation exchange) HPLC-Arsine Generation-ICP-MS system has been set to efficiently separate and quantify all five As species which have been reported to be present in atmospheric particulate matter. Application to water extracts of particulate matter, which in most cases was enriched by airborne Saharan dust, provided results for the concentration of the five species. iAs(V) and TMAO were the main species detected in most samples.
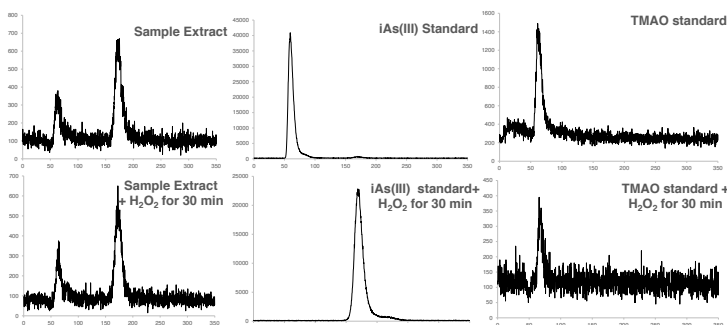
RESULTS

Figure 2. Preliminary HPLC-ICP-MS experiment pointing out the co-elution of iAs(III) with TMAO when using a single anion exchange column by addition of H$_2$O$_2$.
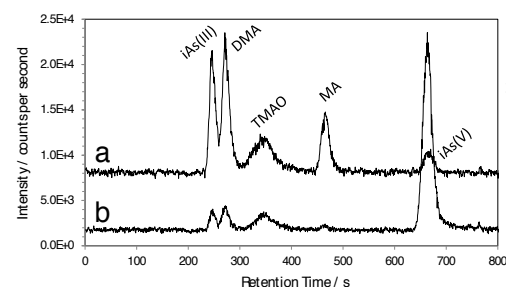

Table 2. Limits of detection in μg As L^{-1} (a) and in terms of pg As m^{-3} (b) using a mean volume of 6.4 m^3 sampled air.

	LODs(a)	LODs(b)
iAs(III)	0.010	2.400
DMA	0.016	3.600
TMAO	0.025	5.800
MA	0.015	3.400
iAs(V)	0.050	11.700

Figure 3. Chromatograms using the experimental set up established in the present study of a) standard solution containing the 5 arsenic species at 0.8 μg L^{-1} As for each species, (b) an atmospheric PM water extract.

Table 3. Descriptive statistics of the concentrations in pg As m^{-3} of each As species identified in PM water extracts and of their concentrations summary.

| PM2.1	iAs(III)	DMA	TMAO	MA	iAs(V)	SUM
Min	b.d.l.	b.d.l.	6.8	b.d.l.	12.9	26.1
Max	4.7	9.2	59.6	b.d.l.	269.4	305.3
Average	2.9 ± 1.0	3.6 ± 2.6	26.3 ± 14.1	b.d.l.	97.5 ± 78.1	129.2 ± 85.8
PM2.5	iAs(III)	DMA	TMAO	MA	iAs(V)	SUM
Min	b.d.l.	b.d.l.	b.d.l.	b.d.l.	33.1	50.7
Max	8.9	26.2	77.6	b.d.l.	491.1	512.7
Average	3.4 ± 2.4	6.9 ± 5.4	28.4 ± 19.6	b.d.l.	155.7 ± 108.8	187.3 ± 110.4
PM10	iAs(III)	DMA	TMAO	MA	iAs(V)	SUM
Min	b.d.l.	b.d.l.	b.d.l.	b.d.l.	36.3	50.4
Max	10.8	25.4	90.0	5.3	689.8	718.2
Average	4.3 ± 2.4	6.8 ± 6.3	35.8 ± 24.8	3.3 ± 1.1	168.6 ± 147.0	209.7 ± 149.2
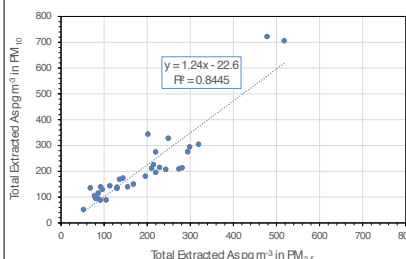
Figure 4. Correlation of total extracted As in PM$_{2.5}$ and PM$_{10}$ in water extracts as a summary of individual species As concentration
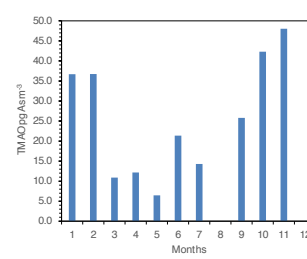

Figure 5. Annual arsenic concentration as TMAO variation

European Winter Conference on Plasma Spectrochemistry
Münster, Germany, February 22-26, 2015
EWCPS 2015

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