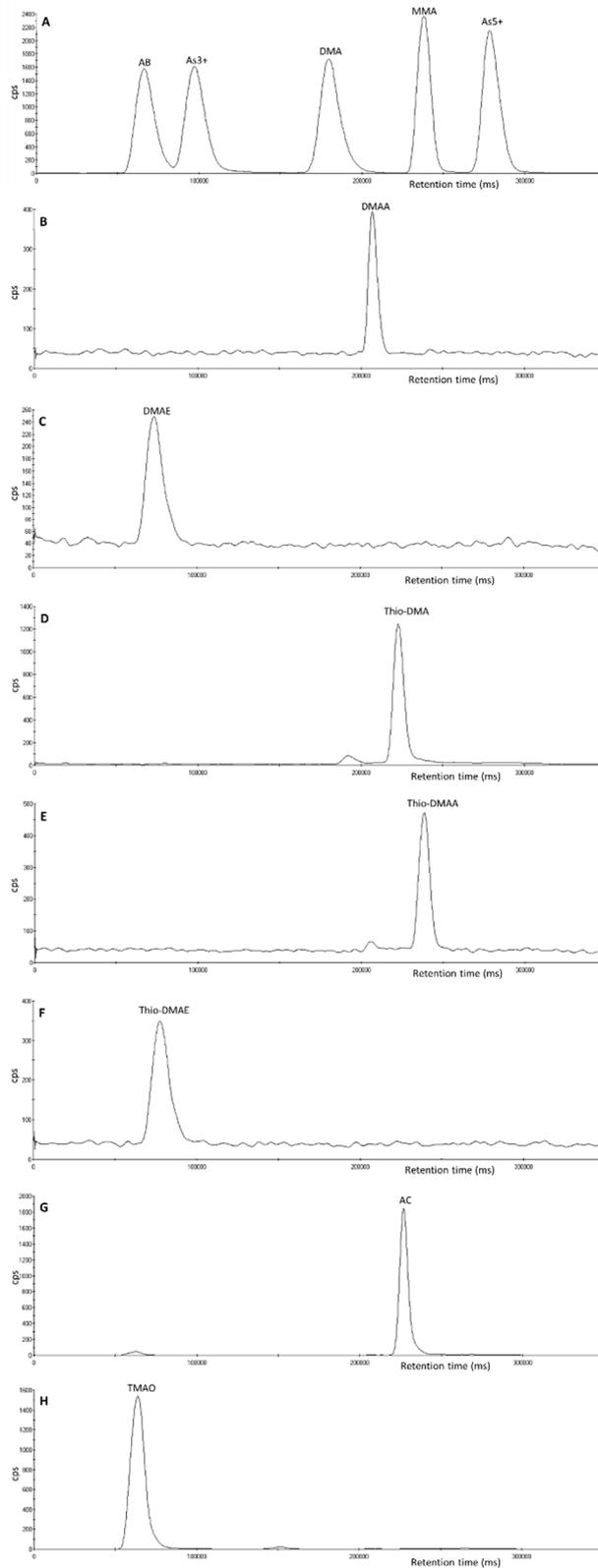


# Supplementary Materials: The Investigation of Unexpected Arsenic Compounds Observed in Routine Biological Monitoring Urinary Speciation Analysis

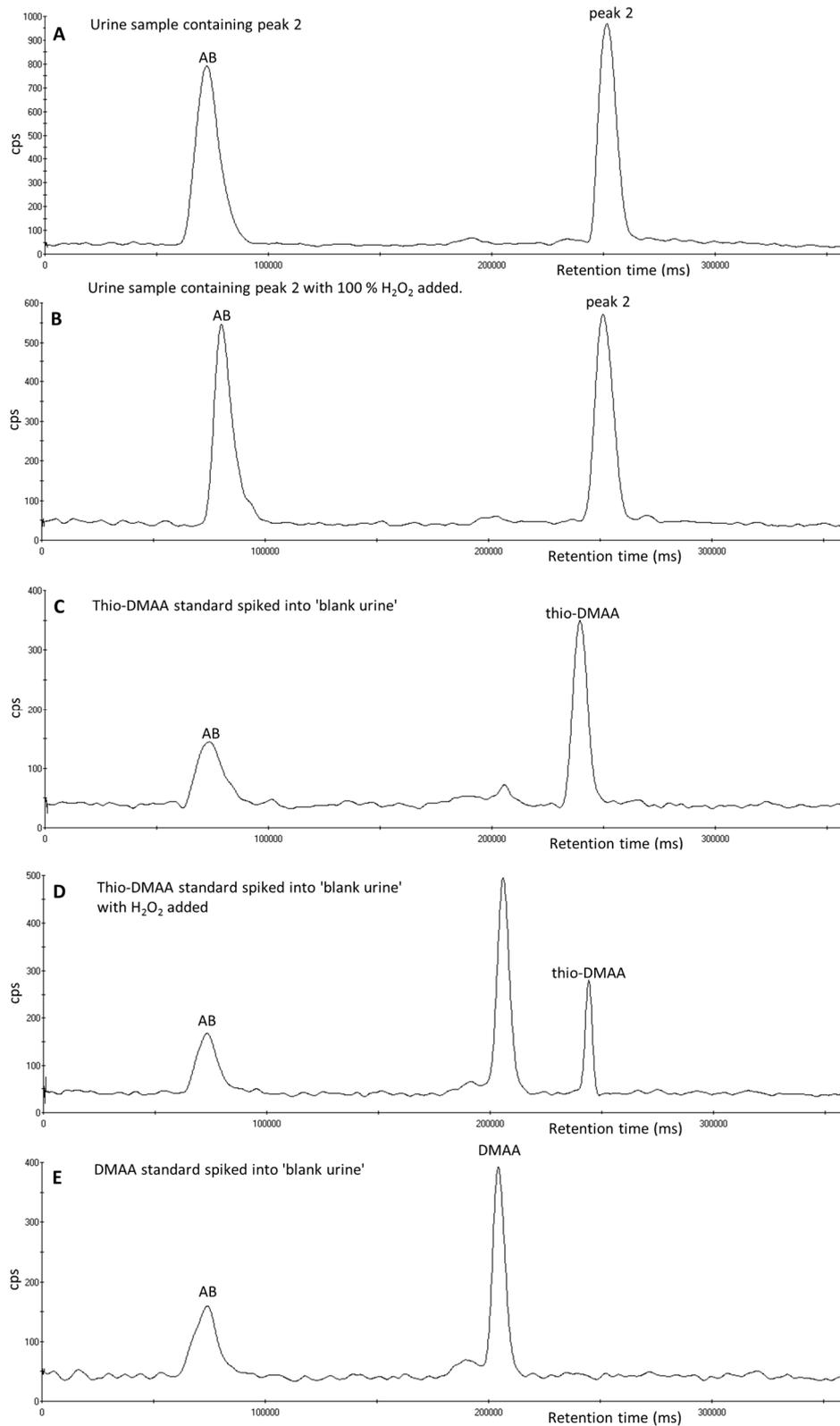
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Inorganic Arsenic	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{As}-\text{OH} \\   \\ \text{OH} \\ \text{As}^{5+} \\ \text{Arsenate} \end{array}$	$\begin{array}{c} \text{HO}-\text{As}-\text{OH} \\   \\ \text{OH} \\ \text{As}^{3+} \\ \text{Arsenite} \end{array}$
Methylated Metabolites	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{OH} \\   \\ \text{OH} \\ \text{MMA}^{5+} \\ \text{Monomethylarsonic acid} \end{array}$	$\begin{array}{c} \text{H}_3\text{C}-\text{As}-\text{OH} \\   \\ \text{OH} \\ \text{MMA}^{3+} \\ \text{Monomethylarsonous acid} \end{array}$
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\   \\ \text{OH} \\ \text{DMA}^{5+} \\ \text{Dimethylarsinic acid} \end{array}$	$\begin{array}{c} \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\   \\ \text{OH} \\ \text{DMA}^{3+} \\ \text{Dimethylarsinous acid} \end{array}$
Oxo-dimethylated Analogues	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_2-\text{C}(=\text{O})-\text{OH} \\   \\ \text{H}_3\text{C} \\ \text{DMAA} \\ \text{Dimethylarsinoylacetate} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_2-\text{CH}_2-\text{OH} \\   \\ \text{H}_3\text{C} \\ \text{DMAE} \\ \text{Dimethylarsinoylethanol} \end{array}$
Thio-dimethylated analogues	$\begin{array}{c} \text{S} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_2-\text{C}(=\text{O})-\text{OH} \\   \\ \text{OH} \\ \text{thio-DMAA} \\ \text{thio-dimethylarsinoylacetate} \end{array}$	$\begin{array}{c} \text{S} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_2-\text{CH}_2-\text{OH} \\   \\ \text{H}_3\text{C} \\ \text{thio-DMAE} \\ \text{thio-dimethylarsinoylethanol} \end{array}$
	$\begin{array}{c} \text{S} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\   \\ \text{OH} \\ \text{thio-DMA} \\ \text{thio-dimethylarsinate} \end{array}$	
Dietary Arsenic	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{As}^+-\text{CH}_2-\text{C}(=\text{O})-\text{OH} \\   \\ \text{CH}_3 \\ \text{AB} \\ \text{Arsenobetaine} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\   \\ \text{CH}_3 \\ \text{TMAO} \\ \text{Trimethylarsine Oxide} \end{array}$
		$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{As}^+-\text{CH}_2-\text{CH}_2-\text{OH} \\   \\ \text{H}_3\text{C} \\ \text{AC} \\ \text{Arsenocholine} \end{array}$

**Figure S1.** Structures of inorganic arsenic, methylated metabolites, oxo- and thio- dimethylated analogues and dietary arsenic compounds. The structures in blue indicate the seven arsenicals investigated in this study.



**Figure S2.** Chromatograms of seven additional arsenic species and their retention times analysed using an ESI OneFAST system coupled to a Dionex AG7 anion exchange column and ICP-MS using mobile phases 2 mM and 70 mM ammonium carbonate solution (A) the standard five arsenic species (B) DMAA, (C) DMAE, (D) thio-DMA, (E) thio-DMAA (F) thio-DMAE (G) AC and (H) TMAO.



**Figure S3.** Chromatograms of arsenic species analysed using an ESI OneFAST system coupled to a Dionex AG7 anion exchange column and ICP-MS using mobile phases 2 mM and 70 mM ammonium carbonate solution. (A) A urine sample containing peak 2. (B) The urine sample with 100 % *v/v* H<sub>2</sub>O<sub>2</sub> added. (C) A thio-DMAA standard spiked into 'blank urine' (only containing AB arsenic species). (D) The spiked urine sample from chromatogram C with 50 % *v/v* H<sub>2</sub>O<sub>2</sub> added. (E) DMAA standard spiked into 'blank urine' (only containing AB arsenic species).