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Improved chromatographic separation of thio-arsenic compounds by reversed-phase high performance liquid chromatography-inductively coupled plasma mass spectrometry

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Abstract

A new group of arsenic species, thio-arsenicals, have recently been reported in several natural samples such as molluscs, algae, and urine. These compounds are the sulfur analogues of oxo-arsenicals, a large group of naturally-occurring compounds, whereby the arsinoyl (As=O) group is substituted by an arsinothioyl group (As=S). The most common separation technique for oxo-arsenicals is anion-exchange HPLC with polymer-based columns, but under these conditions the thio-arsenicals show strong retention, resulting in unacceptably long analysis times and broad peaks. We report the development of a reversed-phase HPLC method, with ICPMS detection, which allows separation of the known thio-arsenicals within 15 min with significantly improved peak shapes. The detection limit is about 0.6 μg As/L based on 10 μL injection volume. Further, we have applied the method to the identification and quantification of thio-arsenic species in two standard reference materials, BCR 710 oyster tissue and NIES 18 human urine.

Keywords: HPLC–ICPMS; Arsenic; Thio-arsenicals; Speciation analysis; Reversed-phase

1. Introduction

Speciation analysis, the determination of the different species of an element, is of particular importance for investigating the transformation of elements in environmental and biological systems. Speciation analysis has been widely used in the field of arsenic research – arsenic occurs naturally as many different species, some of which are toxic, and understanding the processes of arsenic biotransformation is of fundamental biochemical and toxicological interest with implications for human health.

Foremost amongst the currently used arsenic speciation methods is high performance liquid chromatography coupled to an inductively coupled plasma mass spectrometer (HPLC–ICPMS) [1]. The ICPMS can serve as a robust, sensitive, element-selective detector, thereby allowing the analysis of samples with a minimum of sample preparation. Most of the 50 or more arsenic compounds identified as natural products have, until recently, constituted just two major groups, namely tetra alkylarsonium compounds (e.g. arsenobetaine), and trialkylarsine oxides (e.g. oxo-arsenosugars). These compounds are polar, and depending on pH, are present in solution as charged species, and hence they have all been amenable to HPLC separations based on ion-exchange or ion-pairing mechanisms. Since the early report [2] of anion- and cation-exchange HPLC to separate arsenicals in biological samples, there have been several hundred further studies using this basic separation principle.

In 2004, however, a thio-arsenical, thio-dimethylarsenoacetate (thio-DMAA; see Fig. 1 for structures and abbreviations of arsenic compounds), was reported by Hansen et al. [3] as a natural constituent of the urine of a particular breed of sheep that grazes on algae (which contain large concentrations of oxo-arsenosugars). That work heralded thio-arsenicals as a new group of significant arsenic compounds, because, as predicted by Hansen et al., subsequent work has shown the presence of several other thio-arsenicals in biological samples. Thus, up to four thio-arsenosugars, have been reported in various species of molluscs [4–8] and algae [9,10], and thio-DMA, thio-DMAE,

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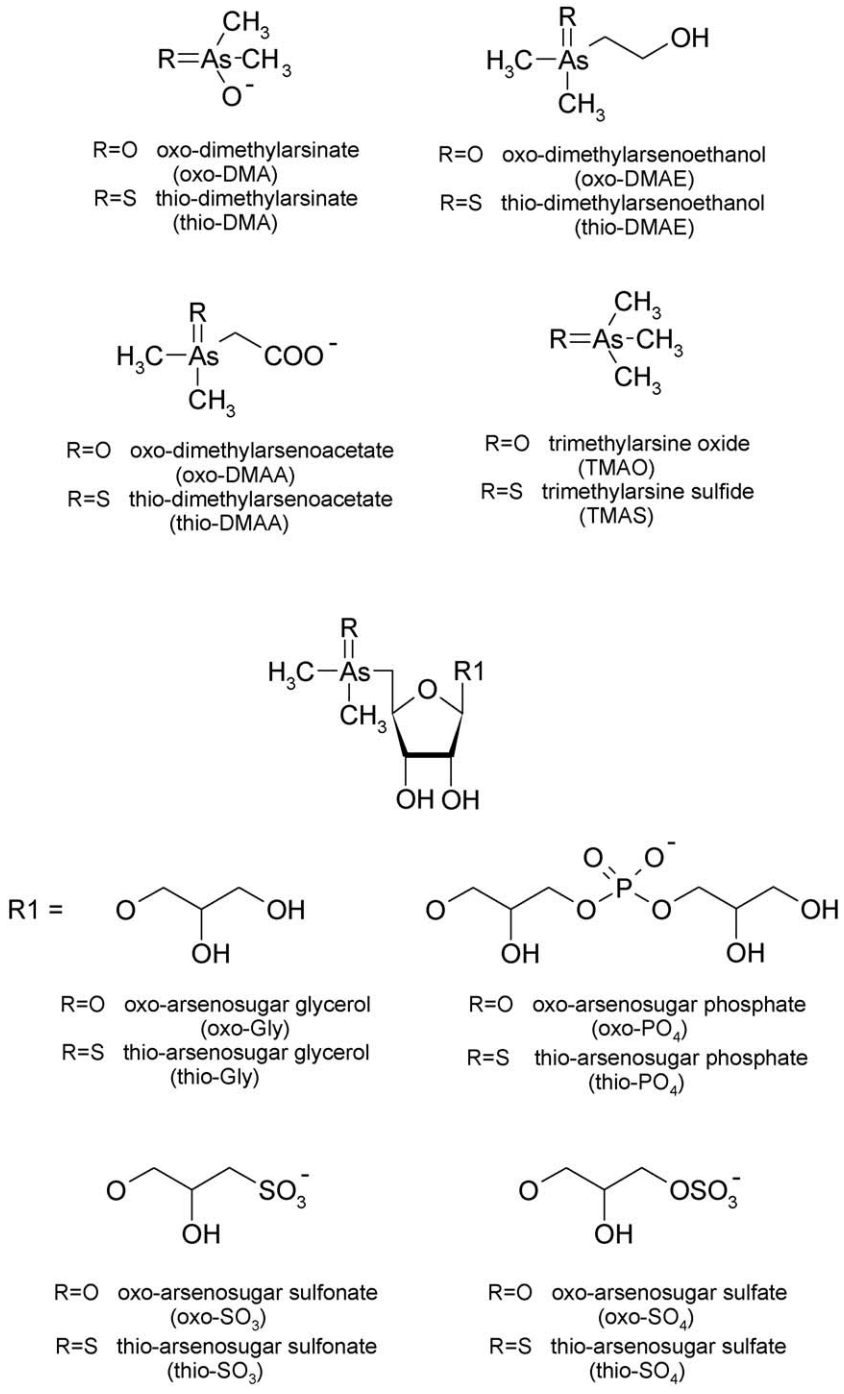

Fig. 1. Structures and abbreviations of arsenic compounds used in this work.

and a thio-arsenosugar, in addition to thio-DMAA, have been identified as urinary metabolites of an oxo-arsenosugar [11].

The established ion-exchange methods for separating arsenic compounds showed limitations when applied to thio-arsenicals, as illustrated by attempts to separate them on the anion-exchange column PRP-X100, which has a backbone of polystyrene divinylbenzene copolymer [11]. Under conditions commonly used for oxo-arsenicals, the thio-arsenicals showed very long retention times and broad peaks. Addition of methanol to the mobile phase significantly decreased the retention times but could not sufficiently improve the peak broadening. This unusual and strong retention was ascribed, at least in part, to interaction of the less polar thio-compounds with the hydrophobic column backbone, and suggested that efficient chromatography of these compounds might be effected under reversed-phase conditions.

It now appears probable that thio-arsenicals will prove to be widespread in nature and will eventually be shown to constitute a third major group of naturally-occurring arsenic compounds. Their detection in natural samples, however, requires the application of a suitable analytical method. Preliminary use