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A Comparison of the Determination and Speciation of Inorganic Arsenic using General HPLC Methodology with UV, MS and MS/MS Detection

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Abstract

The determination and speciation of arsenic in natural resources such as drinking water and agricultural soils has been a growing concern in recent years due to its many toxicological effects [1-3]. To speciate and quantitate concentrations of less than 1 ppm of arsenic, typically an ion chromatograph (IC) interfaced to an inductively coupled plasma mass spectrometer (ICP-MS) is employed [4-9]. This methodology may be very robust and sensitive, but it is expensive and not as ubiquitous as high performance liquid chromatography (HPLC) with ultraviolet (UV) absorbance detection or electrospray ionization mass spectrometry (ESI-MS). Anion exchange chromatography is a well-documented means of speciating arsenite (As(III), As_2O_3) and arsenate (As(V), AsO_4) using UV [10], conductivity [11], or ESI-MS detection [12, 13]. This paper demonstrates the utilization of common liquid chromatographic instrumentation to speciate and determines inorganic Arsenic compounds using UV or MS via selected ion recording (SIR) or multiple reaction monitoring (MRM) detection.   This paper describes the analysis of arsenite and arsenate samples prepared using both deionized and ground water. The limit of quantitation for the techniques described in this paper for samples spiked in ground water were 454 ppb (As(III)) and 562 ppb (As(V)) for UV detection, 45.4 ppb (As(III)) and 56.2 ppb (As(V)) for SIR detection, and 4.54 ppb (As(III)) and 5.62 ppb (As(V)) for MRM detection.

Keywords: Arsenic determination; Arsenic speciation; UV detection; MS and MS/MS detection

1. Introduction

Environmental sources of inorganic arsenic including, but not limited to, ground water and top soil are an important concern in certain parts of the world such as Bangladesh [14], Cambodia [15], India [16] and Vietnam [17] where significant endogenous levels have been observed. Efforts are being made to remediate endogenous levels of arsenic using various techniques [18, 19, 20] requiring analytical methodology to assess the remediation process. Inorganic arsenic speciation is critical for health risk evaluation due to the fact that arsenite is significantly more toxic than arsenate. Simple, robust methodology for the speciation and determination of arsenite and arsenate in suspect samples would be most valuable for safety assessment. The most common method used for Arsenic speciation and determination is IC-ICP-MS using anion exchange chromatography. IC-ICP-MS is a very robust, and sensitive (detection limit < 1 part per billion (ppb)) method. However, it is expensive, and primarily dedicated to elemental analysis. If low parts per million (ppm) to low parts per billion (ppb) sensitivity are all that is required, an attractive alternative would be to use common chromatographic equipment incorporating UV [21, 22, 23] and/or ESI-MS detection – which is the subject of this paper. Ideally, the detection limit would meet the target of the current EPA limit for Arsenic in drinking water of 10 ppb [24].

An ion chromatographic method was developed for the determination and speciation of arsenite and arsenate in both deionized and ground water samples. The method employs a Waters Acquity UPLC