DETERMINATION OF INORGANIC ARSENIC (III) AND ARSENIC (III PLUS V) USING AUTOMATED HYDRIDE-GENERATION ATOMIC-ABSORPTION SPECTROMETRY

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Abstract

A simple method was developed to analyze aqueous inorganic arsenic in the $\mu g \ L^{-1}$ range using automated hydride-generation atomic-absorption spectrometry. Total inorganic arsenic, As(III plus V), was determined by reducing As(V) to As(III) using KI then generating the hydride in 6 M HCl. Arsenic (III) was determined by generating the hydride at pH 4.0 to 4.5 using an oxalate buffer. Detection limits for the As(III plus V) and As(III) analytical methods were less than 0.4 μg As L^{-1}. Arsenic(V) was calculated by difference. Spiking of actual sample solutions with As(III) and As(V) showed the procedure to be accurate on solutions with initial pH values ranging from 2.7 to 9.8 and As(III)/As(V) ratios ranging from 1:4 to 4:1. Recoveries of As were within 1.5 μg As L^{-1} of added amounts ranging from 10.0 to 40.0 μg As L^{-1}, and standard deviations of triplicate analyses were within 0.4 μg As L^{-1}. Automated hydride generation allowed analysis at a rate of 53 samples per h, a significant rate increase over traditional batch hydride generators. Spontaneous oxidation of As(III) to As(V) was observed on spiked samples mixed 3 h before analysis.

Additional Index Words: Arsenite analysis, Arsenate analysis.

ARSENIC IS TOXIC to both plants and animals and has accumulated in some agricultural soils through the use of arsenical pesticides. Inorganic As is much more toxic in the trivalent than in the pentavalent form (USEPA, 1976). Because of the difference in toxicity, speciation of inorganic As is important. Separation of inorganic As(III) and As(V) species has been accomplished by selective extraction of As(III) using a variety of solvents (Puttemans and Massart, 1982; Amankwah and Fasching, 1985; Huang and Wai, 1986). While able to provide quantitative separation of As oxidation states, solvent extraction methods are time consuming. The rapid conversion of As(III) to As(V) can be problematic. Oxidation of As(III) has been found to occur within 5 h when present at the $\mu g \ L^{-1}$ level in unfiltered soil pore waters (Haswell et al., 1985) but was undetected in soil extracts containing 5 to 500 mg As(III) L^{-1} (Elkhatib et al., 1984a,b).

Hydride-generation atomic-absorption spectrometry of acid solutions is a popular method for determination of total inorganic As(III plus V) at the nanogram level. Selective analysis of the As(III) species can be achieved by maintaining the pH at 4 (Gupta and Chen, 1978) or 5 (Shaikh and Tallman, 1978; Howard and Arbab-Zavar, 1981) during hydride formation. Previous As speciation analyses have been carried out using batch type hydride-generators. Con-

tinuous flow hydride-generation technology offers improved precision and reduced analysis time by automating the sample presentation step (Voth-Beach and Shrader, 1985). A continuous flow through hydride-generation method for the determination of inorganic As(III) and As(III plus V) has been developed and is described below.

Apparatus

All As analyses were performed using a Perkin-Elmer model 3030B atomic-absorption spectrophotometer with an electrodeless-discharge lamp, and a Varian VGA-76 hydride-generator (Varian Instrument Group, Palo Alto, CA 94303). Atomic absorption analyses were carried out at a wavelength of 193.7 nm, slit width of 0.7 nm, and lamp power supply of 7 W using a reducing air/acetylene flame. Gaseous As hydride was formed by pumping 2.5 mL min^{-1} sample (or standard), 1.0 mL min^{-1} acid reagent, and 1.0 mL min^{-1} NaBH$_4$ reagent through a reaction coil and into a gas-liquid separator. An Ar carrier gas was used to strip the hydride from the liquid and carry it into an open-ended, air-acetylene heated-quartz cell. The continuous flow design of the VGA-76 hydride-generator produces a steady-state absorbance signal rather than the absorbance peaks generated by traditional batch hydride-generators. This design allows for signal integration over a period of time resulting in highly improved precision. Samples were analyzed at a rate of 53/ h using a Perkin-Elmer AS-50 autosampler (Perkin-Elmer Corp., Norwalk, CT 06856).

Reagents and Standards

Standard solutions were prepared from sodium arsenate and sodium m-arsenite obtained from Sigma Chemical Co. (Sigma Chemical Co., St. Louis, MO 63178). Standard solutions were prepared daily from dilutions of 10.0 mg As(III) L^{-1} and 10.0 mg As(V) L^{-1} stock solutions. Sodium borohydride was obtained from Aldrich Chemical Co. (Aldrich Chemical Co., Milwaukee, WI 53201), and sodium oxalate was obtained from Allied Chemical Corp. (Allied Chemical Corp., Morristown, NJ 07960). All remaining reagents were obtained from Baker Chemical Co. (Baker Chemical Co., Phillipsburg, NJ 08865). High purity Baker Instra-Analyzed HCl was used throughout this study.

As(III plus V) Analysis

Concentrations of As(III plus V) were determined using the method of Voth-Beach and Shrader (1985) as described below. Solutions containing 10.0 mL of sample (or standard), 10.0 mL of concentrated HCl, and 0.50 mL of urea reagent (80% w/v) were reduced by adding 0.50 mL KI reagent (40% w/v) 30 to 60 min prior to analysis. The hydride was generated using concentrated HCl and 0.35% NaBH$_4$/ 0.30% NaOH in deionized water. Standard concentrations of 10.0, 25.0, 50.0, and 75.0 μg As(III) L^{-1} were used. The standard curve was linear ($r^2 = 0.999$), however we used a third order polynomial.

As(III) Analysis

The reagent concentrations chosen enabled the buffering of samples having initial pH values ranging from 2.5 to 11.5 at a final pH from 4.0 to 5.0. No preparation of standards or samples was needed prior to As(III) analysis. The hydride was generated using 1.15% H$_2$C$_2$O$_4$/0.60% Na$_2$C$_2$O$_4$ in deionized water and the NaBH$_4$ reagent as above. Standards ranging from 10.0 to 75.0 μg As(III) L^{-1} as above were used. The standard curve was again linear ($r^2 = 0.998$), but we used a third order polynomial.

The capability of the As(III) procedure to determine As(III) in the presence of As(V) at various pH values was tested.

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Table 1. Arsenic concentrations and recoveries of spiked sample solutions.

Sample	Treatment (Sample plus) As(III)	As(V)	As(III plus V) Conc.	Recovery	As(III) Conc.	Recovery	As(V)† Recovery
				µg L⁻¹			
Imperial	0.0	0.0	13.7	–	1.3	--	--
soil	10.0	40.0	65.2	51.5	12.7	11.4	40.1
extract	25.0	25.0	64.9	51.2	27.7	26.4	24.8
	40.0	10.0	64.4	50.7	42.4	41.1	9.6
Colorado	0.0	0.0	0.0	–	1.1	--	--
River	10.0	40.0	51.3	51.3	12.5	11.4	39.9
water	25.0	25.0	51.1	51.1	27.4	26.3	24.8
	40.0	10.0	51.2	51.2	41.8	40.7	10.5
Imperial	0.0	0.0	0.0	–	0.4	--	--
Valley	10.0	40.0	51.1	51.1	11.7	11.3	39.8
drainage	25.0	25.0	50.6	50.6	26.6	26.2	24.4
water	40.0	10.0	50.5	50.5	41.3	40.9	9.6

† As(V) Recovered = As(III plus V) Recovered − As(III) Recovered.

Samples of a solution containing 25.0 µg As(III) L⁻¹ and 25.0 µg As(V) L⁻¹ were adjusted to pH values ranging from 2.5 to 10.7. These subsamples were analyzed for As(III) in triplicate. Samples with initial pH values of 2.7 to 9.8 displayed concentrations 24.4 ± 0.3 µg As(III) L⁻¹. Samples with initial pH values outside this range resulted in lower concentrations.

The capability of the As(III) procedure to determine As(III) in solutions of varying As(III)/As(V) ratio was tested by spiking actual sample solutions. Three solutions were prepared for this study: (i) a deionized water extract using 40.0 g L⁻¹ of Imperial soil [fine, montmorillonitic, (calcareous), hyperthermic, Vertic Torrifluvent], electrical conductivity EC = 0.26 dS m⁻¹; (ii) a synthetic Colorado River water, EC = 1.3 dS m⁻¹; and (iii) a synthetic Imperial Valley drainage water, EC = 3.9 dS m⁻¹. Compositions of the synthetic waters were obtained from Rhoades (1987, personal communication). The three spikes added to each solution varied in As(III)/As(V) ratio from 1:4 to 4:1 and are shown in Table 1. Analyses of both As(III) and As(III plus V) were performed in triplicate on these sample solutions. Recoveries of As(III) and As(III plus V) were calculated as differences between concentrations found in spikes and concentrations of zero-added blanks. To avoid possible interconversion of As species, all added As(III), As(V), and sample solutions were mixed within 5 min of analysis. The As(V) stock solutions were oxidized by boiling in 5% HNO₃ for 15 min, cooled, and adjusted to pH 4.5 prior to mixing to assure that no As(III) contamination was present. In a separate experiment to determine whether rapid analysis was necessary to avoid changes in oxidation state, As(III) analysis was performed as above except that the mixed solutions were allowed to stand for three h prior to analysis.

To ensure that a matrix-effect correction for nonzero readings of the blank samples was justified, the above spiking procedure was repeated using the synthetic Colorado River water. On this run, the As(III) standards were made in a Colorado River water rather than a deionized water background. The As(V) solutions were oxidized as above. The As(III), As(V), and sample (or standard) solutions were mixed within 5 min of analysis, and analyses were performed in triplicate.

Results and Discussion

Trial runs had established that samples ranging in pH from 2.5 to 11.5 could be buffered to pH 4.0 to 5.0, and that samples ranging from pH 2.7 to pH 9.8 were within the proper range for As(III) analysis. These results indicate that samples buffered to pH 4.0 to 4.5 are within the proper range for As(III) analysis. Detection limits, calculated as three times the standard deviation of six blank readings, for the As(III plus V) and As(III) analytical methods were less than 0.4 µg As L⁻¹.

Table 1 shows the As(III plus V), As(III), and As(V) concentrations and recoveries of sample solutions spiked with varying As(III)/As(V) ratio. Recovery concentrations of As(V) were calculated as the difference between As(III plus V) and As(III) recoveries. Standard deviations of all triplicate analyses in this study were 0.4 µg As L⁻¹ or less. The concentrations of spiked samples when analyzed using standards made in a Colorado River water background were within 0.2 µg As L⁻¹ of the original Colorado River recovery concentrations thus justifying the correction for matrix induced nonzero blank readings. Recoveries of added As(III plus V), As(III), and As(V) deviated 1.5 µg As L⁻¹ or less from expected values at all addition ratios. Recoveries were independent of EC value in the range of 0.26 to 3.9 dS m⁻¹.

During the experiment where solutions were mixed three h before analysis, the resulting As(III) recoveries deviated by +0.1 to −10.2 µg As(III) L⁻¹ from the expected values with standard deviations of triplicate analyses ranging up to 7.3 µg As(III) L⁻¹. The As(III plus V) recoveries, on the other hand, were unaffected by the 3-h delay in analysis suggesting that the loss of As(III) was due to conversion of As(III) to As(V). Preservation of µg L⁻¹ levels of As(III) for up to 6 weeks can be achieved in interstitial water samples by acidification to pH 2 and refrigeration near 0°C (Aggett and Kriegman, 1987).

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