SPECIATION OF ARSENIC IN GROUNDWATER AND TECHNOLOGIES FOR REMOVAL OF ARSENIC IN DRINKING WATER IN THE SPIRO TUNNEL BULKHEAD, PARK CITY, UTAH, USA

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ABSTRACT

Application of an anion exchange resin column was performed to speciate of arsenic (III) and (V) in drinking water. This methodology was used to analyze water samples collected from the study of arsenic removal by two technologies, reverse osmosis membrane filtration and chemical coagulation/ filtration in pilot scale in anticipation of EPA's new arsenic drinking water standard of 10 μg/L takes effect 2006. This EPA treatment technology project was to collect data on the performance of two existing water treatment processes to remove arsenic on pilot scale. Total arsenic concentrations were reduced by reverse osmosis from an average 60 μg/L in the source water to less than 1 μg/L, and chemical coagulation reduced total arsenic from an average 60 μg/L to 4 μg/L. The work reported here will focus on obtaining accurate readings for arsenic valence states (III) and (V), given the Edwards [17] method for arsenic speciation. Separation of arsenic As(III) and As(V) by speciation in field samples, was performed using an anion exchange resin column. The chloride interferences that affect the determination of ^{75}Arsenic from chloride (35 isotope) molecular species ($^{40}Ar^{35}Cl$), were corrected using chloride measurements in all samples using equation: $[^{75}As(corr)] = [^{75}As] - 3.127 \times \{[^{40}Ar^{37}Cl] - 0.815\,[^{82}Se]\}$. The use of sulfuric acid in the preservation procedure

created interferences with ICP-MS in the range one µg/L of arsenic. The problem of interference in determination of isotope ^{75}As is due to sulfur ^{34}S isotope which is present in sulfate. The (^{34}S isotope, 4.21%) forms the polyatomic species (mass 75) (^{40}Ar^{34}S^{1}H) and species (mass 74) (^{40}Ar^{34}S) which interferes with the determination of ^{75}As isotope.

The method detection limit, MDL, for arsenic for ICP-MS was determined to be 0.1 µg/L. Our spiked matrix recoveries, spiked blank samples, and reference materials deviate only a few percents from the listed true values.

Keywords: Arsenic speciation; Reverse osmosis treatment; Coagulation filtration treatment; Water treatment

INTRODUCTION

Some water systems in the U.S. western states, parts of Midwest, and New England have arsenic concentrations in groundwater which tend to be higher than 50 µg/L [1]. The U.S. Geological Survey has prepared a map that identifies the location and concentration of arsenic contaminated groundwater sites in the United States. This map can be accessed on www.usgs.gov. Arsenic occurs naturally and can contaminate drinking water through the erosion of rocks and minerals or through human activities such as fossil fuel burning, paper production, cement manufacturing, and mining. Natural contamination of groundwater by arsenic has become a crucial water quality problem in many parts of the world, particularly Bangladesh, West Bengal, India and Vietnam [2-7]. The World Health Organization has a 10 µg/L guideline. It is provisional from 1993 because of the lack of suitable testing methods, but based on heath concerns alone, the guideline should be lower still. The current maximum contaminant level (MCL) of arsenic in drinking water is 50 µg/L in the United States [8], 10 µg/L in the European Union and 25 µg/L in Canada [9].

The epidemiological studies of populations exposed to arsenic in drinking water show that elevated levels can lead to skin, bladder, lung, and prostate cancer, with risk to exposure comparable to that of radon and second hand tobacco smoke. Non-carcinogenic effects of ingesting arsenic include cardiovascular diseases, diabetes, and anemia, as well as reproductive and developmental, immunological and neurological effects [10-12].
Inorganic As(III) and As(V) are the major species in groundwater [2,13]. Highly toxic As(III) may also be converted to less toxic forms such As(V) or methylated forms such as monomethylarsonate (MMA) and dimethylarsinate (DMA) in surface waters. In natural waters, soluble arsenic is virtually always present in the oxidation states of either +3(III) or +5(V) valence. An organic species (methylated) has been reported by other authors, but concentrations of the organic compound rarely exceed 1µg/L and it is considered of little or no significance as a drinking water

contaminant. In oxygenated waters, the As(V) valence is dominant, existing in the forms of $H_2AsO_4^{-1}$, $HAsO4^{-2}$ and AsO_4^{-3}. In waters containing little or no oxygen (anoxic), As(III) exists in the nonionic form, (H_3AsO_3) below a pH of 9.22, and the anionic form, $H_2AsO_3^-$ at a pH above 9.22.

A natural source of ground water with high arsenic was used for these studies. The feedwater from the Spiro Tunnel Bulkhead (Park City, Utah) has the total arsenic levels which have averaged 60 µg/L. Results of the dissolved arsenic analysis showed that 70 % of the arsenic present in the feedwater was in dissolved form. Arsenic speciation for valence states (III) and (V) showed that arsenic (V) represented 76 % of the dissolved arsenic in the source water. Antimony levels in the feedwater averaged 8.7 µg/L, where the U.S. MCL is 6 µg/L.

This paper reports the performance of innovative technologies for removal of arsenic in drinking water at Park City, Utah. Two technologies were applied: (a) reverse osmosis membrane filtration [14,15] (two vendors), and (b) chemical coagulation/filtration [16] (two vendors). This paper will provide information on correlation of the speciation of arsenic (III and V) removal from drinking water by reverse osmosis and chemical coagulation /filtration technologies in pilot scale. The anion exchange resin column speciation method is based on application of sulfuric acid during separation/preservation [17]. The high concentration of sulfate created interferences with ICP-MS in lowest range one µg/L of arsenic. The U.S. Environmental Agency created the Environmental Technology Verification (ETV) Program to facilitate the development of innovative treatment technologies.

METHODS

Test Site. The verification testing site was the Park City Spiro Tunnel Filtration Plant in Park City, Utah. The source of water was Spiro Tunnel Bulkhead water, which is considered a ground water source under the State of Utah source protection program. Water is developed from water bearing fissures in an abandoned silver mine tunnel. A two meter-bulkhead built approximately three km into the tunnel holds back the water and creates a reservoir. The tunnel is located 300 m or more under remote unoccupied forest in a mountainous region. The water is piped to the treatment plant through a 30 cm diameter pipe at a flow rate of 4400 L per minute (L/min), and enters the city treatment plant which was built in February 1993. The nominal capacity is 3800 L/min, and the treatment plant is located 300 m away from the Tunnel portal and is designed to remove iron, manganese, and arsenic from the raw water. The water is considered stable with respect to quality and quantity, and is known to contain arsenic. For the municipal supply, it is currently diluted with treatment plant finished water to form a blend of the approximately 35 µg/L arsenic that meets the present arsenic standard of 50 µg/L. For this test, only the untreated, unblended Spiro

Tunnel Bulkhead supply was used. This source is one of five active sources serving the municipality: 2 tunnels, 2 deep wells, and a spring. None of the other sources contain significant quantities of arsenic. The water system serves 6500 residents, and as much as 20000 people per day during the winter season.

Technology description

NSF International's consultant operated four treatment systems at Park City, Utah under a grant from the U.S. Environmental Protection Agency. Two of these systems used reverse osmosis, and two used coagulation filtration technology described in more detail below. The purpose of that project was to conduct independent testing of arsenic treatment systems which were available on the USA market for treating public water supply sources.

(a) Reverse Osmosis (RO) processes are generally used to remove ionic solids, such as arsenic, sodium, chloride, and other dissolved materials from drinking water. RO membranes will also remove particulate contaminants, but high particulate loads can lead to membrane fouling. Certain polymer membranes can reject more than 99% of all ionic solids and have a molecular weight cut-off in the range of 50 to 100 daltons.

The Park City membrane model was a spiral wound polyamide membrane with fiberglass outer wrap. The molecular weight cut-off was approximately 100 dalton. RO membranes are designed to reject dissolved salts and operate at pressures that are typically an order of magnitude higher than membrane filtration processes designed to remove only particulate matter such as microfiltration. RO operating pressure requirements are a function of the concentration of the contaminants in the feedwater. Higher contaminant levels in the water will require higher pressure to effect the separation. The Park City membrane model was rated for a maximum pressure of 24 atm and normal design pressure of 8.5 atm.

RO membranes reject salts utilizing a mechanism that is not fully understood. Some experts endorse the theory of pure water preferentially passing through the membrane; other attribute it to the effect of surface charge of the membrane of the polymer on the polarity of the water immediately adjacent to the membrane surface [14, 15].

(b) Chemical Coagulation/Filtration. Iron hydroxide can be used to remove arsenic from drinking water. Two primary removal mechanisms exist: adsorption and precipitation-coagulation. Chemical coagulation is commonly used for removal of iron from source waters. This process involves (1) oxidation of iron, Fe(II) and arsenic, As(III) to the relatively insoluble Fe(III) in order to form precipitates and converted soluble As(V); and (2) As(V) attaches to the iron hydroxides through adsorption-coprecipitation and filtration of the coagulated from the water. The most

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common oxidants used to precipitate soluble iron are air, chlorine, and potassium permanganate. Chemical coagulation /filtration processes are used to adsorb the soluble As(V) better than As(III) species and that can be removed with a backwashing media filter [16]. The Watermark Technologies, LLC Model 5 uses insoluble ferric hydroxide, $Fe(OH)_3$ (precipitate from $FeCl_3$ and NaOCl: $2Fe^{+3} + 6ClO^- + 6OH^- \rightarrow 2\ Fe(OH)_3 + 2ClO_3^- + 4Cl^-$) to adsorb ionic arsenic. The Model 5 consists of metering pumps to feed $FeCl_3$ and NaOCl to the feedwater stream, a retention tank to facilitate coagulation, and a repressurization pump to feed coagulated water to a multi-media filter to continuously remove the precipitate with adsorbed arsenic species. At four hour intervals, a timer initiated a five-minute backwash at 76 L/min per 0.1 square meter of surface area, followed by one minute for media settling.

Tab. 1. Performance of reverse osmosis and coagulation/filtration
treatment systems for arsenic (total) removal

Manufacturer	Arsenic Feed μg/L	Arsenic Product μg/L	Arsenic % Rejection
Reverse Osmosis Units			
Koch TFC – ULP4 [18]	60	0.9	98.5
Hydranautics ESPA2-4040 [19]	65	0.5	99.2
Coagulation /Filtration Systems			
Watermark Technologies eVOX Model 5 [20]	71.4	4.1	94.3
Kinetico Microlite Model CPS100CPT [21]	65	2.9	95.5

The Watermark Model 5 is designated for small system applications or groups of individual homes, this sized unit would serve up to 15 - 20 people. The footprint of the unit is approximately 1.1 m^2. The Watermark Model 5 removed arsenic species from the feedwater supply to an average concentration of less than 4.7 μg/L.

The second coagulation and filtration system studied utilizes also $FeCl_3$ and NaClO, (see reaction above) and is manufactured by Kinetico Incorporated Macrolite System in the USA. The Macrolite model consist of metering pumps to feed $FeCl_3$ and NaOCl to feedwater stream, two retention tanks to facilitate coagulation, and a repressurization pump to feed coagulated water to the Macrolite media filter to continuously remove the precipitate with adsorbed arsenic species. The Macrolite Model is designated for small system applications; this sized unit would serve 15 - 20 people. The footprint of the unit is approximately 2.1 m^2, including retention tanks. The Macrolite Model removed arsenic species from the

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feedwater supply to an average concentration of less than 3 μg/L. Filtration processes for both units were operated at 139 – 203 L/m^2. The results of these studies are presented in the Table 1.

Sampling Arsenic and Field Speciation Procedure

Earlier studies of the determination of Arsenic species concluded that no effective method exists for preserving As(III) and As(V) in water field samples [16,23]. In response, a field speciation of arsenic technique has been developed by using an anion exchange resin column (Dowex 1- X8, 100-200 mesh, acetate form) [17,22,24,25]. For this study, the EPA decision was made to utilize a field speciation technique and 0.05 % H$_2$SO$_4$ was used instead of 1 % HCl to acidify samples prior to resin treatment [17].

We analyzed three types of containers labeled A, B, and C, which correspond to container A (Total As) contained 1% HNO$_3$ (v/v) in a 250 mL unfiltered water sample, container B (Dissolved As (III and V)) contained 0.05 % H$_2$SO$_4$ (v/v) in 125 mL filtered water sample through a 0.45 μm disc filter, and container C (Dissolved As (III) only) held 20 mL of the eluate from the resin column of solution from container B plus 0.5 mL 1:1 HNO$_3$. Sulfuric acid was used to acidify the sample in container B because nitric acid (an oxidizing agent) could damage the resin or form nitric acid-arsenic redox couples [16, 17].

A portion of the acidified sample in container B was run through the resin column, and the resin retained the As(V) (e.g., H$_2$AsO$_4$$^{-1}$) and allowed As(III) (e.g., H$_3$AsO$_3$) to pass through the column. The dissolved As(V) concentration was calculated by subtracting dissolved As(III) from the total dissolved arsenic concentration of the sample in container B.

We found that the use of sulfuric acid in this method created interferences with the inductively coupled plasma mass spectroscopy analyzing the arsenic range less than one μg/L. Sulfate interferences were not accounted by Edwards for inductively coupled plasma mass spectrometry.

Concerns have been expressed by the ICP-MS analyst of difficulties analyzing arsenic samples acidified with 0.05% sulfuric acid (especially containers labeled B). If the concentration of the matrix element in a sample is high, the signal intensity of peak in the ICP-MS is decreased (internal standard failed) due to the plugging of the sampling system at the sampling interface of the instrument. The cone surface turned brownish, and these difficulties were observed after analyses of about 10 samples not diluted with DI water requiring cleaning to reestablished optimum analytical conditions. Slightly less interference was found in containers C which contained a combination of sulfuric acid and nitric acid. The concentration of sulfate and other particles in containers labeled C is partially reduced by passing a sample B through an anion exchange resin column, when As(V) is selectively removed [17]. As it would be expected, a dilution factor of 2 and 10 was applied to the samples in containers B, and we were then able to

analyze samples acidified with sulfuric acid. It appeared that after the samples were diluted, interference was reduced.

In order to understand better interferences from sulfate, an experiment was run using four grades of sulfuric acid:

I. Optima grade, < 0.5 μg/L (calc. As conc. in 0.05 % sulfuric acid is about 0.00025 μg/L)

II. Certified grade < 1 μg/L (calc. As conc. in 0.05 % sulfuric acid is about 0.0005 μg/L)

III. ACS reagent grade < 10 μg/L (calc. As conc. in 0.05 % sulfuric acid is 0.005 μg/L).

IV. Certified ACS < 1 μg/L (used for the EPA study in April 2000), (calc. As conc. in 1 % sulfuric acid is about 0.0005 μg/L).

Nitric acid certified ACS (As < 3 μg/L) was used in our study (calculated As conc. in 1 % nitric acid is about 0.003 μg/L).

The reading of arsenic from different grades of sulfuric acid from ICP-MS was performed: 0.05 % H_2SO4 in DI water solution gave a reading of arsenic I Optima (0.28 μg/L), II Certified (0.24 μg/L), III ACS Reagent (0.28 μg/L) and IV Certified ACS plus (0.36 μg/L), and in 1 % nitric acid in DI water the reading of arsenic was less than (0.1 μg/L). To examine the strength of I Optima sulfuric acid present in 1% nitric acid DI solution versus the arsenic signal obtained, six samples were measured: 0.005 % H_2SO_4 (< 0.1 μg/L As), 0.01 % (< 0.1 μg/L), 0.02 % (0.10 μg/L), 0.03 % (0.15 μg/L), 0.04 % (0.27 μg/L), and 0.05 % (0.36 μg/L).

Results from the analysis of spiked DI water with nitric acid and sulfuric acid indicated that the presence of sulfuric acid increased levels of measurement interference by 10 times the concentration of contaminants compared to the sample acidified with nitric acid. Our investigations concluded that contamination by arsenic from high purity of sulfuric acid itself (comparable to nitric acid) can be excluded because concentration of arsenic in 0.05 % sulfuric acid is not detectable (0.005 to 0.00025 μg/L). To better understand the possible source of potential error in arsenic quantification by ICP-MS see discussion " Interferences in determination of arsenic by ICP-MS".

Analytical Procedures

All of the methods used were standard EPA methods. Determinations of As, Sb, Al, and Mn in analyzed water were accomplished by ICP-MS and ICP (Fe, Mg only) using EPA Method 200.8 and 200.7, respectively. ICP-MS analyses were conducted on a Perkin-Elmer Sciex model ELAN 6000 equipped with an crossflow pneumatic nebulizer and an automatic sampler. ICP was also Perkin Elmer model Optima 3000. Yttrium ($^{88.9}$Y) was added to all samples run by ICP-MS spectrometer as an internal standard to correct for instrument drift. Because arsenic is monoisotopic, all measurements were at a mass/charge ratio of 75. To eliminate interference from a chloride

molecular species ($^{40}Ar^{35}Cl$), all data were corrected using chloride measurements in all samples. The MDL determined for arsenic was 0.1 µg/L. All the unfiltered water samples (e.g., in bottle A) were digested using EPA Method 200.8 prior to analysis. Filtered water samples (i.e., in bottles B and C) were analyzed directly without digestion.

RESULTS AND DISCUSSION

Arsenic removal with reverse osmosis technology. The feedwater from Spiro Tunnel Bulkhead had the following average water quality during the verification test period (results from reverse

Tab. 2. Average Analytical Results of Groundwater from the Spiro Tunnel Before and After Removal of Arsenic in Drinking Water by Reverse Osmosis Membrane Filtration by KOCH Membrane System (KOCH) [18] and Hydranautics ESPA2-4040 (HYDRA [19].

Parameter[a-f], Unit	Number of samples	Feedwater KOCH	Feedwater HYDRA	Permeate water KOCH	Permeate water HYDRA
Turbidity, NTU	34	1.44	1.44	< 0.1	< 0.1
TDS, mg/L	10	543	547	10	11
Alkalinity, mg/L	10	147	145	5	3
As (total), µg/L	34	60	65	0.9	0.5
As (tot. solub.), µg/L	34	42	42	1.3	0.8
As (III, solub.), µg/L	34	8	7	0.6	0.5
As (V, solub), µg/L	34	32	35	0.8	0.5
Antimony, µg/L	34	8.7	8.6	< 3	< 3
pH	34	7.31	7.33	5.94	5.55
Fluoride, mg/L	4	0.17	0.16	< 0.05	< 0.05
Iron, mg/L	5	0.16	0.14	< 0.02	< 0.02
Manganese, µg/L	5	15	15	< 5	< 5
Sulfate, mg/L	4	274	277	< 20	< 20
Magnesium, mg/L	4	39.5	39.5	< 1.0	< 1.0
Chloride, mg/L	4	5.5	5.5	< 3	< 3
Permeate flow, L/min				3.8	3.0

SRM[a] (% recovery) 97 - 105   CSTD[b] (% recovery) 94 - 104
LSB[c](% recovery) 94 - 103   LSBD[d] (% recovery) 93 - 104
LSM[e] (% recovery) 95 - 107   LSMD[f] (% recovery) 95 - 106

[a]Reference standard, [b]Continuing standard, [c]Lab spike blank, [d]Lab spike blank duplicate, [e]Lab spike matrix, [f]Lab spike matrix duplicate.

Accuracy is expressed as a ratio a LSB and LSBD, or a LSM and a LSMD; the precision is determined by calculating the difference between the results found for the LSB and LSBD, and then dividing the difference by the average of the two results.

Osmosis two units are very close - see Table 2: TDS 543 mg/L, pH 7.32, iron 166 μg/L, sulfate 274 mg/L, alkalinity 147 mg/L.

The total arsenic concentration in the feedwater averaged 60 μg/L over thirty-four day test period. Results of the dissolved As analysis showed that 70% of the As present in the feedwater was in the dissolved form. Arsenic speciation for the valence states (III) and (V) showed that arsenic (V) represented 76% of the dissolved arsenic in the feedwater. The KOCH of membrane module reduced total arsenic to an average of 0.9 μg/L and Hydranautics module reduced the total arsenic in the feed stream to 0.5 μg/L in the permeate. The KOCH membrane module reduced the dissolved arsenic in the feedwater from an average of 42 μg/L to less than 1.3 μg/L and the Hydranautics module reduced the total arsenic in the feed stream to 0.8 μg/L in the permeate. The dominant arsenic species in the Spiro Tunnel water was As(V). The feedwater average concentration of As(V) was 32 μg/L and was reduced to an average level of 0.8 μg/L in the treated water. Arsenic (III) was also rejected by the membrane, reducing the average feedwater level of 8 μg/L to 0.6 μg/L in the permeate. A summary of the concentrations of arsenic species and other parameters in both the feedwater and filtrate streams is presented in Table 2.

In all cases the permeate concentrations were below the current EPA MCL of 50 μg/L and below the promulgated new standard of 10 μg/L. The KOCH and HYDRA reverse osmosis modules effectively and consistently removed/rejected all forms of arsenic present in the feedwater.

An important parameter of reverse osmosis membrane performance is TDS rejection, which is the ability of the module to reduce total dissolved solid concentration in a feedwater stream.

Reverse osmosis membrane technology also reduced the concentration of TDS, total hardness, sulfate and antimony in this water supply, allowing it to meet the recommended or statutory limits.

Total arsenic concentrations were reduced by reverse osmosis from an average 60 μg/L in the source water to less then 1 μg/L, and chemical coagulation reduced total arsenic from an average 60 μg/L to 4 μg/L.

Arsenic removal with chemical coagulation/filtration. During initial operations, without chemical coagulation, the media filter removed approximately 49 % of the total As in the feedwater stream and approximately 11.5 % of dissolved As was removed. Because iron is already present in the tunnel water, and this supply is exposed to the air, it is suspected that the resulting iron hydroxide adsorbed a portion of the arsenic (V), which was almost 93 % removed by the media filter.

During the test period, while coagulant chemicals were being fed to the feedwater stream, approximately 95 % of the average total arsenic removed by this system. The Watermark module removed approximately 89 % of the average dissolved As in the feedwater and all the filtrate samples were at or

below 4 μg/L. The dissolved As (V) and dissolved As (III) species were removed to an average of 4 μg/L and 0.7 μg/L, in the filtrate, respectively. A summary of the concentrations of arsenic species and other parameters in both the feedwater and filtrate streams is presented in Table 3. Iron in the feedwater stream was at an average concentration of 300 μg/L and was consistently removed to below the method reported limit (20 μg/L) in all samples collected.

EPA has estimated that 2% of all US water supply sources exceed 10 μg/L and therefore will need treatment to reduce arsenic below the new MCL. Because arsenic species are important to consider when applying treatment (one of the forms, arsenate, is an anion as discussed earlier), accurate measurement is essential, especially at low levels. The current speciation procedure suggested by Edwards [17], includes sulfuric acid which causes positive interference at levels one μg/L when arsenic is measured by ICP-MS.

Tab. 3. Analytical Results of Groundwater from the Spiro Tunnel Before and After Removal of Arsenic Using Chemical Coagulation-Filtration by Watermark Technologies (WATER) [20] and Kinetico Incorporated Macrolite System (KINETICO) [21].

Parameter[a-f], Unit	Number of samples	Feedwater		Permeate water	
		WATER	KINETICO	WATER	KINETICO
Turbidity, NTU	25	1.51	1.75	0.06	0.1
Alkalinity, mg/L	22	144	143	138	139
As (total), μg/L	22	71.4	65	4.1	2.9
As (tot. solub.), μg/L	22	42	41	4.7	1.5
As (III, solub.), μg/L	22	2.5	2.7	0.7	0.7
As (V, solub), μg/L	22	39.5	38.3	4.0	0.8
Antimony, μg/L	22	9.1	9.0	8.7	8.6
pH	31	7.30	7.24	7.20	7.15
Fluoride, mg/L	5	0.17	0.16	< 0.05	< 0.05
Iron, mg/L	14	0.30	0.30	< 0.02	0.06
Manganese, μg/L	2	16.3	14.2	< 5	5.9
Sulfate, mg/L	2	277	307	272	301
Permeate flow, L/min				3.8	13.0

SRM[a] (% recovery) 96 - 105   CSTD[b] (% recovery) 93 - 103
LSB[c](% recovery) 96 - 106   LSBD[d] (% recovery) 95 - 106
LSM[e] (% recovery) 94 - 107   LSMD[f] (% recovery) 94 - 106

[a]Reference standard, [b]Continuing standard, [c]Lab spike blank, [d]Lab spike blank duplicate, [e]Lab spike matrix, [f]Lab spike matrix duplicate.

Accuracy is expressed as a ratio a LSB and LSBD, or a LSM and a LSMD; the precision is determined by calculating the difference between the results found for the LSB and LSBD, and then dividing the difference by the average of the two results.

Interferences in determination of arsenic by ICP-MS

Matrix effects are obviously a source of potential error in ^{75}As quantification by inductively coupled plasma mass spectrometry by presence (a) chloride and (b) sulfate, and requiring the appropriate correction method. Spectral interferences can exist in two forms: atomic ion or polyatomic ion overlap or from non-spectral matrix effects originating from the plasma. If an isobar nuclide is contained in the sample, it becomes a problem to determine the target nuclide and its isobar peak position in the mass spectrum.

(a) The chloride interferences that affect the determination of isotope ^{75}Arsenic is an appreciable interference from a chloride (35 isotope) by forming molecular species (^{40}Ar^{35}Cl), all current data were corrected using chloride measurements in all samples using equation: $[^{75}$As(corr)$] = [^{75}$As] - 3.127 x $\{[^{40}$Ar^{37}Cl$] - 0.815 [^{82}$Se$]\}$:

Case study. As chloride concentration in sample increases (from 500 to 3000 ppm) 10 ppm arsenic recovery also increase, but remained constant after correction (all concentrations in ppm).

Chloride, ppm	0	500	1000	1500	2000	2500	3000
As, measured, ppm	9.78	11.67	12.95	15.01	18.28	18.45	21.45
As, corrected, ppm	9.65	9.74	8.84	8.84	9.43	8.30	8.66

(b) The sulfur interferences that possibly affect the determination of ^{75}Arsenic isotopes is an appreciable interference from a sulfur (^{34}S isotope) molecular species (mass 75) (^{40}Ar^{34}S^{1}H) and molecular species (mass 74) (^{40}Ar^{34}S). Relative abundance of natural isotopes of sulfur are: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%) and isotope ^{36}S (0.02%). This work suggests that the problem of positive interference at low levels of arsenic is due to a sulfate (^{34}S isotope) effect and problem require basic studies to create a new equation for correction of arsenic in presence of high level of sulfate ion. Interferences from sulfate presence are observed in our studies because our detection limit was very low 0.1 μg/L, for higher MDL's and low concentration of sulfate interferences are not observed. The ICP-MS studies of arsenic with preservation of sulfuric acid preformed by Edwards [17] for MDL 0.5 μg/L, any technical difficulties with the ICP-MS con changes, internal standard and interferences were not presented.

In the our study, the arsenic speciation procedure with sulfuric acid [17], which was applied by the EPA project manager are explained in this

work by additional studies analyzing four manufactures sulfuric acid. We proved that observed interferences are not related to contamination of arsenic in the sulfuric acid reagent.

CONCLUSIONS

A number of different treatment technologies exist for removing arsenic from drinking water [26]. Among these are ion exchange, activated alumina, reverse osmosis, nano-filtration, electrodialysis reversal, coagulation and filtration, lime softening. Some newer technologies of research interest are iron-oxide coated sand, granular ferric hydroxide, iron filings, sulfur modified iron, greensand filtration, iron addition and microfiltration, and conventional iron and manganese removal. Two for the former processes were studied here.

The groundwater at Spiro Tunnel study of arsenic removal by two reverse osmosis membrane filtration and chemical coagulation/filtration on pilot scale showed the promise of both technologies as a practical means of purification. The speciation of arsenic during a treatment process is of great interest to researchers.

Total arsenic concentrations by reverse osmosis were reduced from an average 60 μg/L in the source water to less then 1μg/L (99 %), As(V) soluble reductions at 98 %, and As(III) soluble reductions at 93 %, and chemical coagulation/filtration reduced total arsenic from an average 60 μg/L to 3 μg/L (95 %), As(V) soluble reductions at 90-98 %, and As(III) soluble reductions at 73 %.

Attempts to acidify water samples with 0.05 % sulfuric acid showed technical difficulties when an ICP-MS technique was used and interferences from sulfate in the arsenic range one μg/L. From the arsenic results presented in this paper, we recommend that for future method description for speciation of arsenic in water, sulfuric acid as the preservative should be avoided.

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