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A rapid colorimetric method for measuring arsenic concentrations in groundwater

R.K. Dhar[a,b,c,*], Y. Zheng[a,b,c], J. Rubenstone[c], A. van Geen[c]

[a] *School of Earth and Environmental Sciences, NSB D-216, Queens College, City University of New York, 65-30 Kissena Building, Flushing, NY 11367, USA*
[b] *Graduate School and University Center, City University of New York, NY, USA*
[c] *Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA*

Abstract

The arsenic content of groundwater consumed by millions of people in the developing world has become a major health concern. We report here an optimization of the colorimetric method of Johnson and Pilson (1972) to accurately measure As concentrations in the <0.03–5.3 μmol L^{-1} (<2–400 μg L^{-1}) range in groundwater containing 2–30 μmol L^{-1} dissolved phosphate. The optimization includes increases in the concentrations of potassium iodate, ascorbic acid, antimonyl tartrate used for sample pre-treatment and color development that significantly lowered the detection limit and shortened the reaction time. Mean recovery obtained for a suite of groundwater samples from Bangladesh spiked with As in the 0.13–13 μmol L^{-1} (10–1000 μg L^{-1}) range, the linear range of the method, was 97 ± 5% ($n = 10$). The colorimetric method agrees within 5 μg L^{-1} for As concentrations up to 0.67 μmol L^{-1} (50 μg L^{-1}) and within 4% in the 0.67–5.3 μmol L^{-1} (50–400 μg L^{-1}) range with As analysis of the same Bangladesh groundwater samples by high-resolution inductively coupled-plasma mass spectrometry.

1. Introduction

Arsenic concentrations in drinking water far exceeding the guideline value of the World Health Organization (WHO) [1,2] of 0.13 μmol L^{-1} (10 μg L^{-1}) are reported in many parts of the world and pose a serious health hazard to tens of millions people [3–5]. The most devastating case of chronic As exposure is found in Bangladesh [6]. Since the spatial distribution of As in aquifers of the region is highly variable [7–10], the ability to distinguish high and low As wells through rapid and reliable testing in the field is critical.

Most colorimetric methods for measuring As are based on the Gutzeit [11] method. This classic approach is based on the generation of arsine gas by reduction of As under acid conditions following the addition of zinc powder, and quantifying the arsine by trapping it either in a silver diethyldithiocarbamate solution [12] or on paper impregnated with mercuric bromide. The Gutzeit method [13] suffers from difficulties in the quantitative evolution of small quantities of arsine gas. Several inter-comparisons with laboratory results have indicated an effective detection limit of 1.3 μmol L^{-1} (100 μg L^{-1}) As for various field kits based on this method [5,14–16]. The suppression of an interference by hydrogen sulfide in some groundwaters also requires an additional step in the procedure [6]. Finally, Hussam et al. [17] demonstrated that workers using arsine-based kits in poorly ventilated environments can be exposed to dangerous levels of AsH$_3$, the most toxic form of As.

* Corresponding author. Tel.: +1 718 997 3331/392 6781; fax: +1 718 997 3299.
 E-mail addresses: rdhar@gc.cuny.edu, rdhar@ldeo.columbia.edu (R.K. Dhar).

Johnson [18] and Johnson and Pilson [19] first proposed an elegant modification of the standard molybdate-based method for measuring phosphate (P) in natural waters as an alternative to the Gutzeit method. The key to Johnson and Pilson's modification is that As(V) and phosphate form a complex with reduced molybdate that strongly absorbs in the infrared, while As(III) does not. Dissolved As can therefore be quantified from the difference in absorbance between a sample aliquot that is pre-treated to oxidize As(III) (absorbance due to P and As) and another sample aliquot pre-treated to reduce As(V) (absorbance from P only). For a seawater matrix, Johnson and Pilson [19] showed that their method was convenient, sensitive, and precise ($\pm 1.5\%$) at As levels as low as $\sim 0.013\,\mu mol\,L^{-1}$ ($1\,\mu g\,L^{-1}$). The method has been used widely by researchers since then, without significant modification, for analysis also of As in freshwater containing 0–$10\,\mu mol\,L^{-1}$ of phosphate [20–22]. Most of these recent studies report a detection limit of $\sim 0.26\,\mu mol\,L^{-1}$ ($20\,\mu g\,L^{-1}$) and a reaction time of at least 1 h [23]. We report here a series of modifications to the Johnson and Pilson [19] procedure that significantly reduce both the detection limit and the reaction time.

From the perspective of a molybdate-based method, the main difference between seawater and freshwater, and reducing groundwater in particular, is that P concentrations frequently exceed maximum seawater levels of $3\,\mu mol\,L^{-1}$ by an order of magnitude [22–24]. Our initial tests of the original method with Bangladesh groundwater indicated a systematic 0.4–$2.6\,\mu mol\,L^{-1}$ (30–$200\,\mu g\,L^{-1}$) underestimate in inferred As concentrations at P concentrations in the 20–$80\,\mu M\,L^{-1}$ range. We evaluate here the performance of the optimized method in the laboratory and in the field by analyzing a set of groundwater samples from Bangladesh spanning a wide range of As and P concentrations.

2. Experimental

2.1. Instrumentation

The instrument used for most of the optimization experiments was a portable single-beam Hach DR2010 UV–vis spectrophotometer. A more precise double-beam Shimadzu Pharmaspec 1700 spectrophotometer with a stable read-out at the fourth decimal place was used to determine the detection limit and to measure As concentrations for actual samples in the laboratory and in the field. Unlike previous studies [19,22,25] reporting different absorbance spectra for P, As, and P + As–molybdate complexes (with maxima centered at 880, 850, and 865 nm, respectively), the absorbance spectra of arseno–molybdate and phospho–molybdate complexes formed using optimized reagent concentrations are very similar and show a broad maximum centered between 875 and 880 nm. Unless noted, absorbance was measured at 880 nm throughout this study.

2.2. Standards

Stock solutions of $13.3\,mmol\,L^{-1}$ ($1000\,mg\,L^{-1}$) As(V) and As(III) were prepared by dissolving analytical grade (Sigma) sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium *m*-arsenite ($NaAsO_2$) in deionized water. The As(V) solution was preserved with 1 mL/100 mL of concentrated HCl; the As(III) solution with 1 mg/mL of ascorbic acid [26]. Secondary As standards ($0.13\,mmol\,L^{-1}$) were prepared by diluting the stock solutions. A stock solution of $10\,mmol\,L^{-1}$ phosphate was prepared by dissolving KH_2PO_4 in deionized water; a secondary standard of $1\,mmol\,L^{-1}$ P was prepared by further dilution.

2.3. Reagent preparation

The reagents are identical to those of Strickland and Parsons [18,19]. Deionized ($18\,M\Omega$) water and trace-metal grade acids were used for all reagents, standards, and blank solutions. The optimization of the method, described in subsequent sections, resulted in the following final procedure:

(1) A $\sim 2\,mmol\,L^{-1}$ KIO_3 oxidizing solution for treating one sample aliquot is prepared by dissolving 0.0425 g of potassium iodate in 100 ml deionized water containing 2% hydrochloric acid.
(2) The reducing solution [18,19] for treating the other sample aliquot requires the preparation of 14% $Na_2S_2O_5$ ($736\,mmol\,L^{-1}$), 1.4% $Na_2S_2O_3$ ($89\,mmol\,L^{-1}$), and 10% H_2SO_4 ($1.8\,mol\,L^{-1}$). These three solutions are then mixed in ratios of 2:2:1, respectively. The mixed reducing solution is stable for 6 h below 30 °C.
(3) The color reagent that is added to both reduced and oxidized sample aliquots requires the preparation of 10.8% L-ascorbic acid $C_6H_8O_6$ ($613\,mmol\,L^{-1}$), 3% ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ($24\,mmol\,L^{-1}$), 0.56% antimony potassium tartrate $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$ ($8\,mmol\,L^{-1}$), and 13.98% H_2SO_4 ($2.5\,mol\,L^{-1}$). The preparation of these solutions follows the standard procedure [18,19], with the exception of the higher concentrations of ascorbic acid and antimonyl tartrate determined from the optimization.

Mixing procedure: The solutions of ascorbic acid, ammonium molybdate solution, and potassium antimonyl tartrate are first combined. Sulfuric acid must be added to the mixed solution immediately after the addition of potassium antimonyl tartrate to avoid the generation of turbidity in the color reagent. The mixing ratios of the four reagents are 2:2:1:5, respectively. The solution is stable for 6 h below 30 °C.

2.4. Procedure: sample pre-treatment, standard additions, and blank correction

All samples were acidified to 1% HCl immediately after collection. Samples cannot be acidified with nitric acid for analysis by the molybdate method. The presence of ni-

trate leads to color instability [21], inhibits complex formation in the oxidized aliquot, and enhances it in the reduced aliquot. Standard reference materials that are acidified with nitric acid, such as the natural water standard NIST 1640, can therefore not reliably be analyzed by this colorimetric method.

Acidified samples are analyzed by pipetting two 5 ml aliquots into 10 ml vials (Evergreen 240-3615-060). One aliquot is treated with 0.5 ml of oxidizing reagent and the other with 0.5 ml of mixed reducing reagent. If data on As speciation is desired, 0.5 ml of a 2% HCl is added to a third aliquot. The desired redox state of As in both pre-treated aliquots is reached in 10 min and remains stable for at least 3 h. After waiting for at least 10 min, 0.5 ml of color reagent is added to each vial. The color reagent is mixed thoroughly with the sample immediately after addition by shaking and allowed to react for at least 10 min before measuring the absorbance. The calibration slope usually was obtained by two to three replicated analyses of a series of sub-samples that were spiked with standard solutions of As(III) and As(V) to increase the total As concentration by 0.13, 0.67, 2.6, 5.2, 13.3 $\mu mol\,L^{-1}$ (10, 50, 200, 400, 1000 $\mu g\,L^{-1}$) and with P standard solutions to increase concentration by 10, 20, 40 $\mu mol\,L^{-1}$, respectively.

One peculiarity of the formation of As–molybdate complexes encountered during this study is that samples containing very little P must be spiked to at least 2 $\mu mol\,L^{-1}$ P (i.e. to ~0.05 absorbance for a reduced aliquot) because of a P dependence of the rate of color development for As (see Sections 3.1 and 3.3). Reagent blanks were therefore also determined by analyzing acidified deionized water spiked with 2 $\mu mol\,L^{-1}$ P with each set of analyses. A higher absorbance value was consistently observed for the reduced aliquot of spiked deionized water relative to the oxidized aliquot. Differences in absorbance between oxidized and reduced sample of this such solution averaged -0.0010 ± 0.0005 ($n = 5$) for different batches of reagents, which is equivalent to a correction of ~0.05 $\mu mol\,L^{-1}$ (4 $\mu g\,L^{-1}$) in As concentration.

3. Results

3.1. Rate of color development

The reaction rate was increased by raising the concentration of potassium antimonyl tartrate, following the suggestion of Murphy and Riley [27]. The optimal Sb level was determined by spiking deionized water with 13.3 $\mu mol\,L^{-1}$ (1000 $\mu g\,L^{-1}$) As, with equal proportions of As(III) and As(V), and 20 $\mu mol\,L^{-1}$ of phosphate, using optimized KIO_3 and ascorbic acid concentrations determined in parallel experiments. Potassium antimonyl tartrate concentrations in the color reagent of 0.14% (the original conditions of Johnson and Pilson [19]), 0.28%, 0.56% and 1.4% were compared. On the basis of these results, a concentration of 8 $mmol\,L^{-1}$ (0.56%) was selected, four times the concen-

tration used by Johnson and Pilson [19] to analyze seawater. Acidified Bangladesh groundwater containing 10 $\mu mol\,L^{-1}$ P was spiked with As to a concentration of ~10.7 $\mu mol\,L^{-1}$ (800 $\mu g\,L^{-1}$) and analyzed using the optimal level of Sb. Maximum absorbance was reached in less than 10 min for both the oxidized and the reduced aliquot (data not shown). The absorbance difference reached a stable value in 10 min and remained constant (±0.001) for an additional hour. However, groundwater obtained from a site in Vineland, NJ, that is naturally low in P (<2 $\mu mol\,L^{-1}$) required ~45 min for full color development under the optimized condition. This confirmed that low-P samples must be spiked to at least 2 $\mu mol\,L^{-1}$ P for As analysis by this method (Section 2.4). Full color development is reached in 8 min for both deionized water (~3 $\mu mol\,L^{-1}$ spiked P) and groundwater (~8.5 $\mu mol\,L^{-1}$ P) spiked with 0.13 $\mu mol\,L^{-1}$ (10 $\mu g\,L^{-1}$) As.

3.2. Oxidizing reagent

Arsenic concentrations in reducing groundwater can exceed 13 $\mu mol\,L^{-1}$ (1000 $\mu g\,L^{-1}$), predominantly in the form of As(III) [28–30]. Experiments were therefore conducted to adjust the conditions of the oxidizing pre-treatment by varying KIO_3 concentrations between 0.25 $mmol\,L^{-1}$, the original conditions of Johnson and Pilson [19], and 3 $mmol\,L^{-1}$. For these experiments, deionized water was spiked with 0, 20, 40, 60, and 80 $\mu mol\,L^{-1}$ P as well as 13 $\mu mol\,L^{-1}$ (1000 $\mu g\,L^{-1}$) As(V) and 13 $\mu mol\,L^{-1}$ (1000 $\mu g\,L^{-1}$) As(III). Because these experiments were conducted at an early stage, absorbance was read at 865 nm instead of 880 nm, the optimal wavelength determined subsequently, and with a color reagent containing 5.4% ascorbic acid instead of the optimal level of 10.8%. The results show maximum absorbance for an oxidized sample aliquot at a KIO_3 concentration of 2 $mmol\,L^{-1}$ (eight-fold higher than the conditions of Johnson and Pilson [19]), suggesting that As(III) is entirely oxidized under these conditions (Fig. 1a). Absorbance differences decrease at lower KIO_3 concentrations, indicating incomplete oxidation of 13 $\mu mol\,L^{-1}$ As(III) at >20 $\mu mol\,L^{-1}$ P concentrations. The reductions in absorbance difference of 0.004 and 0.026 at 1.0 and 0.5 $mmol\,L^{-1}$ KIO_3, respectively, relative to 2 $mmol\,L^{-1}$ are equivalent to an underestimate in As concentration of 0.27 and 1.7 $\mu mol\,L^{-1}$ (21 and 130 $\mu g\,L^{-1}$). No color was formed after 3 h at a KIO_3 concentration of 3 $mmol\,L^{-1}$, indicating that the subsequent reduction of molybdate by the color reagent was inhibited by an excess of oxidant (Fig. 1a).

3.3. Elimination of P dependence

The experiments that led to an increase in the optimal concentration of potassium iodate (Section 3.2) also showed a systematic decline in the difference in absorbance between oxidized and reduced aliquots with increasing P concentration, regardless of the KIO_3 concentration, and at a constant
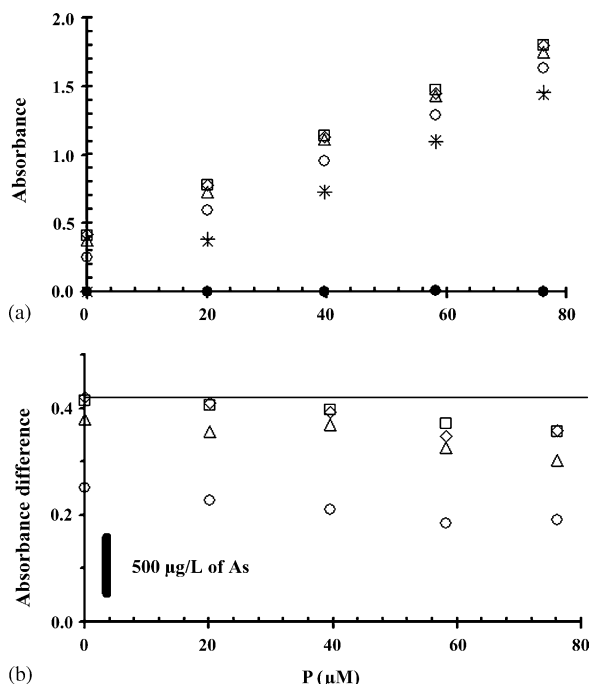
Fig. 1. (a) Absorbance of oxidized and reduced complexes at various KIO$_3$ concentrations [3 mM (●), 2 mM (□), 1 mM (◇), 0.5 mM (△), 0.25 mM (○)]. The sample analyzed is deionized water spiked with 26.6 µmol L^{-1} (2000 µg L^{-1}) mixed As [As(III)/As(V) = 1:1] and incremental P (20–80 µmol L^{-1}) concentrations. An additional reduced aliquot (×) without As spike was included to compare to the reduced aliquot with mixed As spike (+). (b) Absorbance difference between oxidized and reduced complexes for the same set of experiments.

As(III + V) concentration (Fig. 1b). This P dependence, which to our knowledge has not been reported previously, translates into an underestimate of As concentrations of 0.4–2.7 µmol L^{-1} (30–200 µg L^{-1}) in water containing 20–80 µmol L^{-1} P. The origin of the P dependence of the absorbance difference between oxidized and reduced aliquots was investigated by measuring, in addition, color development for samples without pre-treatment. These experiments were conducted with LDEO tap water containing <0.001 µmol L^{-1} (<0.1 µg L^{-1}) As and 4 µmol L^{-1} P, and with additions of 12, 25, 48 µmol L^{-1} P. Under the initial conditions of Johnson and Pilson [19], modified by increasing the concentrations of KIO$_3$ and Sb, the reduced aliquot produced the highest absorbance, followed by the untreated and the oxidized aliquots (Fig. 2a). This suggested that KIO$_3$ in the oxidizing reagent suppressed the color formation and/or that S$_2$O$_5$/S$_2$O$_3$ in the reducing reagents enhanced color formation. Lowering the S$_2$O$_5$/S$_2$O$_3$ concentration led to insufficient reduction of the As(V) spike, however. Therefore, the amount of ascorbic acid in the color reagent was instead increased to compensate for the suppression caused by the higher KIO$_3$ concentration. The P dependence of the absorbance difference between oxidized and reduced or untreated aliquots was considerably reduced when the concentration of ascorbic acid in the color reagent was doubled to 10.8%, which is close to saturation (Fig. 2a).
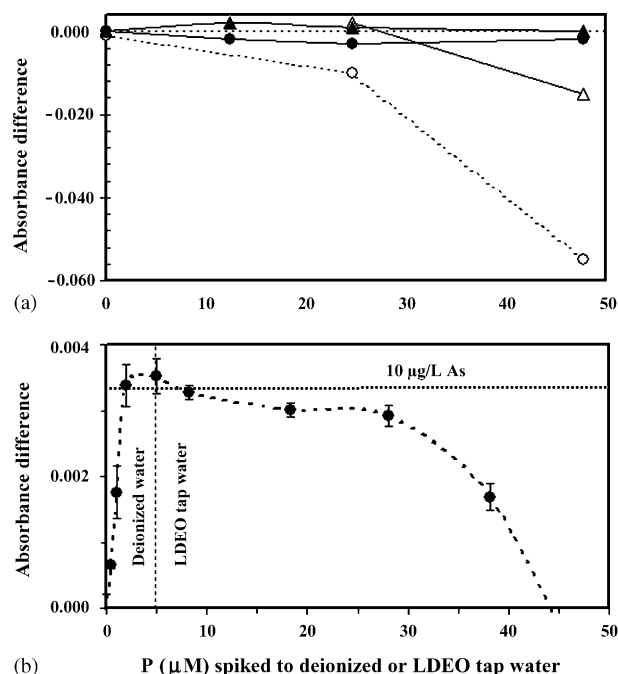

Fig. 2. (a) Absorbance difference between oxidized and reduced/untreated complexes for LDEO tap water spiked at various P levels at two different concentrations of ascorbic acid in the color reagent. Open circle (○) and open triangle (△) show the absorbance difference between oxidized–reduced and oxidized–untreated complex, respectively, with 5.4% ascorbic acid. Solid circles (●) and triangles (▲) show absorbance differences for [oxidized–reduced] and [oxidized–untreated] aliquots, respectively, using 10.8% ascorbic acid. (b) Absorbance differences (●) between oxidized and reduced complexes under optimized conditions (10.8% ascorbic acid) for deionized water and Lamont–Doherty Earth observatory (LDEO) tap water spiked at various P concentrations are also shown.

As a final test, deionized water spiked with 0.13 µmol L^{-1} (10 µg L^{-1}) As and 0, 0.5, 1, 2, 5 µmol L^{-1} P and LDEO tap water spiked with 0.13 µmol L^{-1} (10 µg L^{-1}) As and 0, 10, 20, 30, 40 µmol L^{-1} P, was treated with the optimized reagents and the higher ascorbic acid concentration. Measurements with the double-beam spectrophotometer show a plateau in absorbance difference corresponding to 0.13 ± 0.01 µmol L^{-1} (10 ± 1 µg L^{-1}) across the 2–30 µmol L^{-1} range in P concentrations (Fig. 2b). The series of experiments also confirms that samples must contain at least 2 µmol L^{-1} P to obtain accurate results.

4. Discussion

4.1. Detection limit and precision

The precision and detection limit of the colorimetric method was evaluated with repeated analyses of HCL acidified deionized water, LDEO tap water, and acidified Bangladesh groundwater with the double-beam spectrophotometer (Table 1a). Replicate analyses of deionized and LDEO tap water containing <0.001 µmol L^{-1} (0.1 µg L^{-1})

Table 1
Detection limit, accuracy and precision

Sample identification	Phosphate (μM)	Mean absorbance difference	Arsenic (μg L^{-1}) This method	HR ICP-MS
(a) Detection limit in the different matrices				
Deionized water	2 (spiked)	0.0001 ± 0.00015	0.4 ± 0.7 ($n = 5$)	<0.1
LDEO tap[a]	8.2	0.0000 ± 0.00013	0.1 ± 0.6 ($n = 6$)	<0.1
BGW-1	3	0.0001 ± 0.00023	0.3 ± 1.0 ($n = 3$)	0.6
BGW-2	5	-0.0004 ± 0.00036	-1.8 ± 1.5 ($n = 4$)	0.1

Sample identification	Phosphate (μM)	Spiked arsenic (μg L^{-1})	Arsenic (μg L^{-1}) This method
(b) Recovery of arsenic in LDEO tap water			
LDEO tap	8.2	0	0.1 ± 0.6 ($n = 6$)
LDEO tap	8.2	10	12 ± 1 ($n = 5$)
LDEO tap	8.2	50	53 ± 1 ($n = 4$)
LDEO tap	8.2	100	100 ± 1 ($n = 4$)
Spiked LDEO tap[b]	45	320	314 ± 4 ($n = 3$)

Shimadzu UV–vis spectrophotometer was used for all colorimetric measurements. Bangladesh groundwater (BGW) samples were analyzed in the field.

[a] LDEO tap water is from a groundwater source.

[b] Laboratory control sample [31] and measured arsenic by HR ICP-MS 320 ± 2 μg L^{-1} ($n = 26$).

As indicate a detection limit of $\sim$0.026 μmol L^{-1} (2 μg L^{-1}), calculated as three times the standard deviation of replicate absorbance differences measured for each sample. This is not inconsistent with a slightly lower reproducibility of $\pm$1–1.5 μg L^{-1} (Table 1a) obtained for two low-As groundwater samples containing 3 and 5 μmol L^{-1} P analyzed in the field in Bangladesh under sub-optimal conditions (i.e. under generator power and high humidity). With the single-beam spectrophotometer, the detection limit could not be lowered beyond 0.09 μmol L^{-1} (7 μg L^{-1}). This is the result of the lower precision of the single-beam instrument, possibly compounded by a display limited to the third decimal place since a 0.001 absorbance difference between an oxidized and a reduced aliquot corresponds to $\sim$0.05 μmol L^{-1} (4 μg L^{-1}) in As concentration.

4.2. Accuracy based on comparison with HR ICP-MS

Arsenic concentrations determined by colorimetry were compared with measurements by high-resolution inductively coupled plasma-mass spectrometry (HR ICP-MS). This reference method requires only 0.5 mL of samples diluted 10-fold in 2% HNO$_3$ and is applicable to a wide range of matrices [31]. The selection of a resolution of 12 000 eliminates the isobaric interference with As determinations from Ar–Cl. The method has a detection limit of 0.001 μmol L^{-1} (0.1 μg L^{-1}) As and a precision of $\sim$2%. Samples were acidified to 1% HCl immediately after collection for HR ICP-MS analysis within 10 days of sample collection.

The optimized method was used in Bangladesh to analyze in the field a representative suite of 10 groundwater samples containing 2–36 μmol L^{-1} P (Table 2). The same samples were also spiked with 1.3 μmol L^{-1} (100 μg L^{-1}) As. HR ICP-MS measurements for the combined set of samples span a range of 0.001–4.9 μmol L^{-1} (0.1–370 μg L^{-1}) As and indicate a mean recovery of the spike of 101 ± 5%. The

colorimetry results obtained in the field are consistent with the HR ICP-MS results within 0.067 μmol L^{-1} (5 μg L^{-1}) in the <0.03–0.67 μmol L^{-1} (2–50 μg L^{-1}) As range and within 5% at higher concentrations (Table 2). The mean recovery calculated on the basis of the colorimetric measurements (97 ± 5%) indicates no significant matrix dependence of the response [22], even though the samples also spanned a wide range of Si (400–1200 μmol L^{-1}) and Fe (4–180 μmol L^{-1})

Table 2
Comparison of field analyses with the laboratory analyses of same samples including spikes by HR ICP-MS

Sample identification	Phosphate (μM)	Arsenic (μg L^{-1}) This method	HR ICP-MS
BGW-1	36	13 ± 1 ($n = 5$)	13.4
Spiked (+100 μg L^{-1})		108	112
BGW-2	23	34 ± 1 ($n = 2$)	38.7
Spiked (+100 μg L^{-1})		122	135
BGW-3	24	41 ± 1 ($n = 2$)	42.7
Spiked (+100 μg L^{-1})		130	137
BGW-4	31	78 ± 1 ($n = 2$)	84.5
Spiked (+100 μg L^{-1})		166	180
BGW-5	3	<2 ± 1 ($n = 3$)	0.6
Spiked (+100 μg L^{-1})		101	99
BGW-6	2	44 ± 1 ($n = 5$)	39.3
Spiked (+100 μg L^{-1})		143	153
BGW-7	5	67 ± 1 ($n = 5$)	59.5
Spiked (+100 μg L^{-1})		178	165
BGW-8	19	228 ± 3 ($n = 4$)	225
Spiked (+100 μg L^{-1})		322	333
BGW-9	5	<2 ± 1 ($n = 4$)	0.1
Spiked (+100 μg L^{-1})		103	112
BGW-10	33	223 ± 1 ($n = 6$)	243
Spiked (+100 μg L^{-1})		322	372

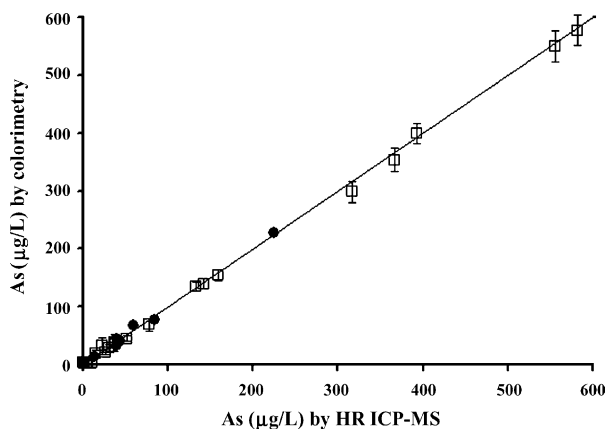Bangladesh groundwater (BGW) samples analyzed in the field.

Fig. 3. Comparison of As concentrations in a set of Bangladesh groundwater samples ($n = 10$) determined with a double-beam spectrophotometer in the field and HR ICP-MS (●). Also shown is a set of measurements ($n = 28$) with a single-beam spectrophotometer (□). Errors bars indicate the estimate uncertainty determined by propagating the most significant digit (0.001) of readings for the single-beam instrument. Error bars also include absorbance underestimation (0.001) due to high P ($>40\,\mu M$) and S.D. of 3 or more replicates.

concentrations [10,29]. Other potential interferences were not tested, but seem unlikely given the wide range of applicability of the phosphate method itself and the good match between colorimetric and HR ICP-MS for a broad suite of groundwater samples. A larger set of Bangladesh groundwater samples ($n = 28$) was also analyzed in the laboratory with the single-beam spectrophotometer. Although the measurements are less precise because of the limits the instrument, they are also consistent within $0.13\,\mu mol\,L^{-1}$ ($10\,\mu g\,L^{-1}$) for As concentrations up to $0.67\,\mu mol\,L^{-1}$ ($50\,\mu g\,L^{-1}$) and within 4% in the $0.67–8.0\,\mu mol\,L^{-1}$ ($50–600\,\mu g\,L^{-1}$) with the HR ICP-MS data (Fig. 3).

5. Conclusion

The method of Johnson and Pilson [19] optimized for measuring As in groundwater offers several significant advantages over existing methods relying on arsine generation. The method is relatively fast and the detection limit is below the WHO guideline value for As in drinking water of $0.13\,\mu mol\,L^{-1}$ ($10\,\mu g\,L^{-1}$), even if a portable and moderately priced single-beam spectrophotometer is used. The reagent cost is on the order of US$ 0.01 per test. No toxic arsine is generated and no major interferences were identified across a representative range of sample matrices.

As previously pointed by Johnson and Pilson [19], the method can also be slightly modified to determine inorganic speciation by including a sample aliquot without pretreatment in the analysis. Our preliminary tests also indicate that no colored complex is formed with organic species such as monomethyl arsonic acid (MMA) and dimethyl arsinic acid (DMA). This suggests that the concentration of organic As species could potentially be determined by difference relative to a measurement of total As by, for instance, HR ICP-MS.

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