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# Determination of inorganic arsenic in water by a quartz crystal microbalance

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A quartz crystal microbalance sensor has been developed for the determination of inorganic arsenic species in water. The gold electrode surface was modified by a self-assembled layer of dithiothreitol, and the frequency change of the modified crystal was proportional to the arsenic concentration from 0 to around  $50 \mu\text{g L}^{-1}$ , a range which spans the current US EPA maximum contaminant level of  $10 \mu\text{g L}^{-1}$  in drinking water. As dithiothreitol is capable of reducing arsenate to arsenite, the sensor detects both species. The method was applied to the determination of arsenic in spiked rain, tap, pond and bottled water; recoveries not significantly different from 100% were obtained for a number of spike additions of less than  $10 \mu\text{g L}^{-1}$ . Arsenic was only detected in the bottled water sample, at a concentration of  $8 \mu\text{g L}^{-1}$ . This method is simple, fast, and inexpensive compared with other conventional arsenic detection methods, and has the potential to be used in the field.

## Introduction

The contamination of groundwater by inorganic arsenic is a serious problem all over the world.<sup>1</sup> The World Health Organization recommends that the maximum concentration of arsenic in drinking water is  $10 \mu\text{g L}^{-1}$ , though for some countries, such as Bangladesh,  $50 \mu\text{g L}^{-1}$  is still the action limit.<sup>2</sup> To accurately determine the arsenic concentration in water samples, many methods that include atomic spectrometry techniques, such as AFS,<sup>3</sup> ICP-MS,<sup>4</sup> ICP-AES,<sup>5</sup> and HG-AAS<sup>6</sup> have been developed. All of these techniques have detection limits low enough to allow reliable measurement of concentrations at  $10 \mu\text{g L}^{-1}$  and can tolerate the matrix effects from a variety of water samples, so that analysis is possible with minimum sample preparation by direct introduction of the sample into the instrument. However, these instruments are large and expensive, and they need

supplies of stable power and gases. Some require additional high purity reagents (for hydride generation) and some have relatively long analysis times. Countries, such as Bangladesh, that need to monitor the arsenic content of millions of tube wells need access to low-cost, field-portable methodologies, for which the options are limited.<sup>7</sup> For measurements in the field, colorimetric test kits have been used for a long time, but they suffer from issues of accuracy and precision and can give rise to rather large numbers of false positive and false negative values.<sup>8</sup> Most of these fields test kits are based on the “Gutzeit” method, *i.e.* Gutzeit’s modification of Marsh’s original method,<sup>9</sup> in which the inorganic arsenic in a water sample reacts with zinc in acid solution to form arsine gas that, in turn, reacts with a mercury or silver salt impregnated into a filter paper strip exposed to the head-space of the reaction vessel. Mercuric bromide is used in most commercially available versions of the test, giving rise to a yellow-brown coloration. Some of the more severe criticisms of the performance of these kits no longer apply, as manufacturers have responded with improved versions.<sup>10,11</sup> As a portable instrument, electrochemistry instrumentation, which can perform anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV) has some advantages over the various “naked-eye” arsenic test kits. These electrochemical techniques are able to determine arsenic at trace levels within few minutes. In addition, these techniques can also distinguish between different oxidation states, are easy to operate and, compared with other instrumental techniques, are comparatively cheap. However, these methods also suffer from interferences and matrix effects, which means that voltammetric methods are rarely used for arsenic determination in complex matrixes, such as food samples. As Idowu *et al.* point out: “it is unlikely that such methods could ever be made robust enough ... electrodes are notoriously fickle”.<sup>12</sup> Thus, accurate, fast measurement of arsenic in the field remains a technical challenge.<sup>7</sup>

One candidate technology is the quartz crystal “microbalance” (QCM), so called because a small change in mass of the piezoelectric crystal affects the frequency of vibration, which can be readily measured by a relatively inexpensive instrument.

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The devices were first used for sensing the adsorption of analytes from the vapor phase<sup>13</sup> (by coating the crystal with a suitable adsorbent), but as the crystals will oscillate in water, procedures have been developed for sensing a variety of species in solution, including anions, such as phosphate, sulfate and selenite, for which the surface of the crystal was coated with an appropriate sensing material.<sup>14–16</sup>

Dithiothreitol (DTT), HSCH<sub>2</sub>CH(OH)CH(OH)CH<sub>2</sub>SH, the threo isomer of 2,3-dihydroxy-1,4-dithiobutane [IUPAC (2*R*,3*R*-) 1,4-bis(sulfanyl)butane-2,3-diol] has been used for inorganic arsenic detection by Kalluri *et al.*<sup>17</sup> and Forzani *et al.*<sup>18</sup> Kalluri and co-workers reported a DTT, glutathione (GSH) and cysteine (Cys) modified gold-nanoparticle-based dynamic light scattering assay for label-free detection of arsenic, with detection limit of 10 pg L<sup>-1</sup>. Forzani and co-workers developed a surface plasmon resonance sensor with DTT as the “recognition element” to detect total arsenic in ground water. Since DTT has two sulfur-containing groups, one can form a sulfur–gold bond with the surface of the sensing electrode and the other can form a sulfur–arsenic bond with the arsenic species in water. DTT can also reduce arsenate to arsenite, thus, this method can be used for the determination of arsenate without adding other reducing agents.<sup>13</sup>

We have developed a QCM procedure, in which the gold electrode was modified with DTT, as a potential portable arsenic sensor, which responds within 5 min and measures arsenite concentrations in a variety of water samples over the range 1 to 50 µg L<sup>-1</sup>.

## Experimental

### Apparatus

Measurements were made with a QCM200 Quartz Crystal Microbalance Digital Controller equipped with the QCM25 5 MHz Crystal Oscillator (Stanford Research Systems, Sunnyvale, CA, USA). The 2.54 cm diameter crystals are contacted on both sides by chromium/gold electrodes whose surface areas are 1.37 and 0.20 cm<sup>2</sup>, respectively. The crystal was mounted in a Kynar® holder so that the larger chromium/gold electrode surface was exposed to the solution. Frequency data were recorded by the LabVIEW software, which was download from the Stanford Research System website.

### Reagents

Analytical reagent grade chemicals were used. 1,6-Hexanedithiol, dithiothreitol (C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>), sodium arsenate, sodium arsenite, hydrogen peroxide and sulfuric acid were all purchased from Fisher Scientific (Pittsburgh, PA, USA). Ethylenediaminetetraacetic acid disodium salt was purchased from Mallinckrodt Chemical Inc. (St Louis, MO, USA). All working solutions were prepared in deionized distilled water (18.0 MΩ cm) obtained from a Barnstead E-Pure water system (Dubuque, IA, USA).

### Measurements

Sodium arsenite (0.173 g) and of sodium arsenate (0.417 g) were separately dissolved into 10.0 mL of water, in order to make 10.0 g L<sup>-1</sup> (as As) solutions. Solid DTT (0.154 g) was dissolved in

10.0 mL of water in order to make a 15.4 g L<sup>-1</sup> (0.100 M) stock solution. The lower concentration solutions, 1.50 mg L<sup>-1</sup> (20.0 µM) arsenite 1.50 mg L<sup>-1</sup> (20.0 µM) arsenate, 3.09 mg L<sup>-1</sup> (20.0 µM) DTT and 1.54 mg L<sup>-1</sup> (10.0 µM) DTT, were prepared from the stock solutions by step-wise dilution. Solutions of low DTT concentration were freshly prepared before each experiment and purged with nitrogen gas for 4 min.

The gold electrode surface was modified with 1,6-hexanedithiol (HDT) as an alternative to DDT; 0.118 g of solid HDT was dissolved in 10 mL of 5% ethanol to make an 11.8 g L<sup>-1</sup> (0.100 M) stock solution. The lower concentration solutions, 2.36 mg L<sup>-1</sup> (20.0 µM) HDT were prepared from the stock solutions by serial dilution. The crystal was immersed in 20.0 µM HDT solution for 1 h before measurements were made.

Before each experiment, the crystal was immersed into 10 mL “piranha” solution (a 3 + 1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide) for 3 min followed by rinsing with deionized water. Finally, the crystal was dried with nitrogen gas.

For arsenite measurements, the crystal holder was completely immersed in 50 mL of 20.0 µM DTT solution and the frequency change from that in air to the stable value in solution recorded for approximately 5 minutes until the signal stabilized. Arsenite solution (1.50 mg L<sup>-1</sup>) was added 50 µL at a time and the stable frequency recorded after each addition. The additions were continued until the final arsenite concentration was 50.0 µg L<sup>-1</sup> (0.670 µM). For the measurement of arsenate, an additional 5 min was allowed for the reduction to arsenite before recording the frequency. As the calibration curve rolled over when the arsenate concentration was above 15.0 µg L<sup>-1</sup> (0.200 µM), the measurements were stopped when the final arsenate concentration was 10.0 µg L<sup>-1</sup> (0.130 µM). Calibration curves were based on the frequency change as a function of arsenic concentration.

To study the effect of the DTT concentration, 10 µM DTT solution was used instead of 20 µM. All the other procedures were as described above.

### Interference study

To study possible interferences, a water sample was prepared with a composition similar to that of Bangladesh ground-water,<sup>19</sup> containing the potentially interfering constituents Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. These were added individually to a 6 µg L<sup>-1</sup> arsenic solution at the concentrations shown in Table 1. In initial experiments, it was found that both copper and iron interfered, and EDTA was added (as the disodium salt) as a possible masking reagent. Krug *et al.* showed<sup>20</sup> that EDTA was effective at masking the interference of copper and iron in the determination of boron as borate, H<sub>3</sub>BO<sub>3</sub> (in plant extracts) when added online in a flow injection spectrophotometric procedure. Although the reaction between EDTA and iron or copper is rapid, we found that satisfactory results were only obtained if the mixture was heated to boiling for an hour. This suggests that there is a kinetic limitation involved in the relevant reactions, but we have not investigated what this might be. It is known that some hydrated metal ions, such as chromium and aluminum, react slowly

**Table 1** Concentrations of potentially interfering ions in a Bangladesh groundwater<sup>19</sup>

Species	Concentration (mg L <sup>-1</sup> )
Na <sup>+</sup>	320
K <sup>+</sup>	15.8
Ca <sup>2+</sup>	43.3
Mg <sup>2+</sup>	24.9
Cu <sup>2+</sup>	0.090
Fe <sup>3+</sup>	0.4
Cl <sup>-</sup>	347
NO <sub>3</sub> <sup>-</sup>	5.33
SO <sub>4</sub> <sup>2-</sup>	2.56

because of the strength of the metal–water bonds. It is also known that some reactions in which the metal in an EDTA complex is exchanged are slow; for example, the reaction between NiEDTA and Fe(III) requires heating for several hours.<sup>21</sup> There is no evidence that anionic species react with EDTA, and so we do not think that there is any reaction between the arsenic species (either the original protonated arsenite or arsenate or the As–DTT species), and we consider that arsenic will react preferentially with the sulfur in the DTT rather than the oxygen or nitrogen atoms of the EDTA. It is possible that iron and copper arsenate species are formed. Insoluble compounds and minerals of both elements and arsenate are known. If these species were kinetically inert, heating would accelerate their decomposition and formation of the metal EDTA complexes.

In our study, 18.6 g L<sup>-1</sup> disodium EDTA stock solution was prepared and 5 mL of this stock solution was added to a 50 mL of water sample. Measurements were made after boiling and cooling to room temperature.

### Real water sample analysis

A number of real water samples were analyzed including rainwater, pond water (Puffers Pond Amherst, MA), river water (Connecticut River, Northampton, MA), and bottled water purchased from a local supermarket. All the samples (50 mL) were filtered through 0.45 μm filter media, and disodium EDTA stock solution was added give a concentration of 1.86 g L<sup>-1</sup> and 10 μL of 15.4 g L<sup>-1</sup> (0.100 M) DTT was added so that the final concentration of DTT was 3.09 mg L<sup>-1</sup> (20.0 μM). The crystal was first immersed into 50 mL 20.0 μM DTT solution and the baseline frequency was recorded after 5 min when the signal was stable. To determine the arsenic concentration in water samples, standard additions calibration was applied. For each addition, 100 μL of 1.50 mg L<sup>-1</sup> arsenite solution was added and the frequency was recorded once the signal was stable. Three additions were made for each sample. To evaluate the effects of the various matrices on the determination, samples were spiked with various concentrations of arsenite.

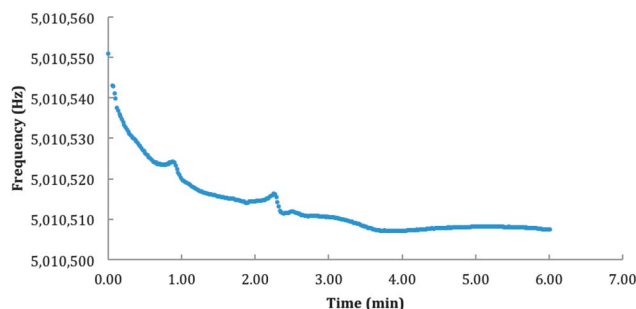
## Results and discussion

Although HDT also showed an ability to selectively bind arsenite in water, it was considered less suitable than DTT as (a) it

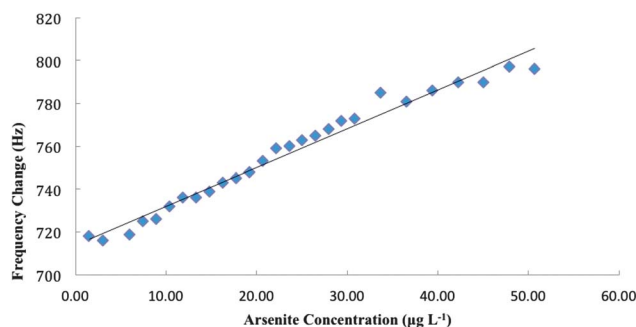
cannot be completely dissolved in water without adding ethanol and (b) the compound has an unpleasant odor.

A typical response of the QCM sensor immersed in DTT solution after adding a total of 750 μL (15 50 μL portions) of a solution containing 1.50 mg L<sup>-1</sup> of arsenite solution is shown in Fig. 1, from which it can be seen that the frequency decreased relatively rapidly in the first minute and then more slowly to reach a stable value after 4 min. The temperature coefficient of the crystal is about 8 Hz per degree,<sup>22</sup> thus the transient 3–4 Hz excursions at around 1 and 2 min could be caused by temperature fluctuations of less than half a degree.

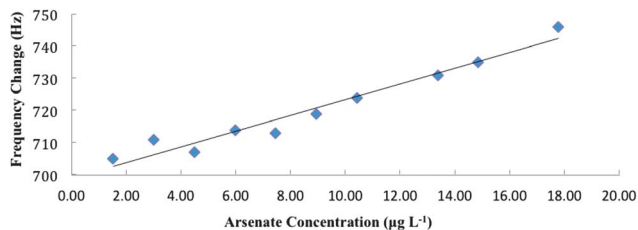
The calibration curves are shown in Fig. 2 and 3 for arsenite and arsenate, respectively. It can be seen that a usable calibration range of up to 50.0 μg L<sup>-1</sup> (0.670 μM) was achieved in the case of arsenite, and up to 15.0 μg L<sup>-1</sup> (0.200 μM) in the case of arsenate. The equations for the best fit lines are  $\Delta F = 1.81C + 714$  for arsenite and  $\Delta F = 2.44C + 699$  for arsenate, where  $\Delta F$  is the frequency change in Hz and  $C$  is the concentration in solution in μg L<sup>-1</sup>. The same experimental procedure was also applied for a lower DTT concentration. As shown in Fig. 4, the linear range was only up to 10.0 μg L<sup>-1</sup> (0.130 μM) of arsenite when using the 1.54 mg L<sup>-1</sup> (10.0 μM) DTT solution. The equation for the best fit line is  $\Delta F = 10.0C + 708$ . The detection limit for arsenic, as arsenite, is 0.6 μg L<sup>-1</sup>, which was calculated from the standard deviation of the frequency changes over 5 min when measuring a blank.



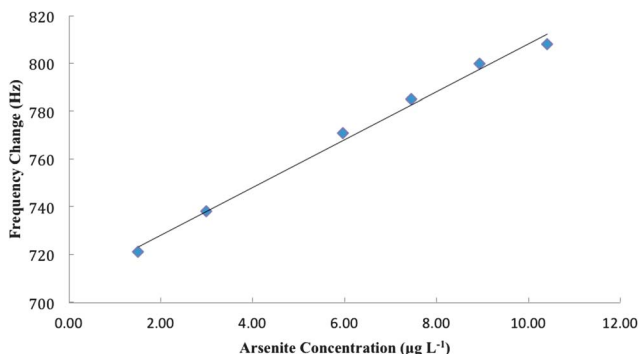
**Fig. 1** Frequency response of the DTT-coated QCM sensor, immersed in 50 mL, as a function of time following the addition of 15 50 μL portions of a solution containing 1.5 mg L<sup>-1</sup> arsenic as arsenite.



**Fig. 2** Frequency change as a function of arsenite concentration. The concentration of DTT was 3.08 mg L<sup>-1</sup>. The straight line is the best fit by unweighted least squares regression.



**Fig. 3** Frequency change as a function of arsenate concentration dependence of the frequency change. The concentration of DTT was  $3.08 \text{ mg L}^{-1}$ . The straight line is the best fit by unweighted least squares regression.



**Fig. 4** Frequency change as a function of arsenite concentration. The concentration of DTT was  $1.54 \text{ mg L}^{-1}$ . The straight line is the best fit by unweighted least squares regression.

It is assumed that when the crystal is first immersed in the DTT solution, DTT binds to the surface in a self-assembled monolayer, as this behaviour is well known for alkanethiols at gold.<sup>23</sup> When arsenite is then added, there are two possible reactions: (1) arsenite reacts with DTT in solution, exchanging up to three OH groups for one S of DTT, and (2) arsenite reacts with the exposed thiol groups of the DTT bound to the crystal surface. If reaction 1 predominates, then it is considered that a second reaction occurs in which the arsenic–DTT species are exchanged for surface-bound DTT molecules. As the system responds to arsenate, it is deduced that reaction between solution arsenate species and DTT occurs to reduce arsenate to arsenite and that this reaction is followed by whatever processes are responsible for the binding of an arsenite species to the electrode surface.

The 40 Hz decrease in frequency seen in Fig. 1 corresponds to a mass loading of  $0.97 \text{ µg}$  on the basis of the simple response model of  $\Delta F = -C_f \Delta m$ , where  $\Delta F$  is the frequency change,  $C_f$  is the sensitivity factor and  $\Delta m$  is the change in mass. For the 5 MHz AT-cut crystals used in this study,  $C_f$  is  $56.6 \text{ Hz cm}^2 \text{ µg}^{-1}$ .<sup>22</sup>

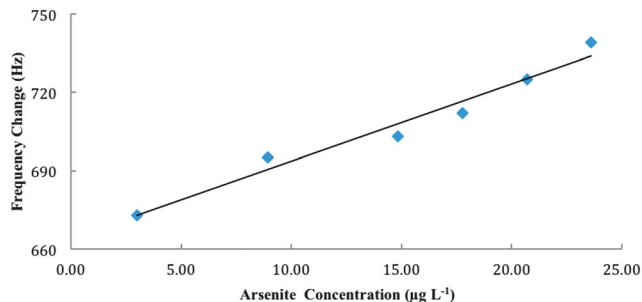
Gold has a surface coverage potential of approximately  $10^{-9} \text{ mol cm}^{-2}$  for alkanethiols,<sup>22</sup> and if the arsenic-containing species that binds to each DTT tethered to the surface is  $\text{As}(\text{DTT})_2$  then complete coverage would correspond to an additional  $0.52 \text{ µg}$ . As this is somewhat less than the  $0.97 \text{ µg}$  needed for a 40 Hz change, we suggest that multilayers are formed. If all the arsenic in the  $750 \text{ µL}$  could be attached to the surface, and each atom of arsenic was associated with two

molecules of DTT, the total mass on the surface would be  $5.7 \text{ µg}$ , well above that needed to produce a 40 Hz change in frequency. The experiments were performed in a 50 mL container and thus each  $\text{µg L}^{-1}$  change in concentration corresponds to 50 ng of arsenic, which in turn corresponds to  $0.254 \text{ µg}$  of  $\text{As}(\text{DTT})_2$ . If this were all bound to the surface, the slope of the calibration would be  $10.5 \text{ Hz (per µg L}^{-1}\text{)}$ . As the slopes for the arsenite and arsenate calibrations are 1.81 and  $2.44 \text{ Hz (per µg L}^{-1}\text{)}$ , we deduce that not all of the arsenic is bound. This is consistent with an equilibrium model, in which the arsenic species partition between the solution phase and the phase bound to the quartz surface.

It is noted that the slope of the calibration for arsenate is higher than that for arsenite, but that the linear range is shorter. It is proposed that the arsenic-containing species bound to the electrode surface responsible for the change in vibrational frequency is heavier in the case of arsenate than that bound in the case of arsenite, and this suggests that the reduction of arsenate by DTT does not lead to exactly the same species as are formed when arsenite and DTT are present in the solution. It might be expected that the product of the redox reaction with arsenate would be a dithiane ring (cyclic disulfide),<sup>24</sup> which, in turn, could react with the arsenite in solution, but would not be available to assist with the binding of an arsenic-species to the surface. It is noted that the response to arsenite continues into a region in which there are more arsenite molecules than DTT molecules, suggesting that a more complex mechanism is responsible for the frequency than simple binding *via* DTT to the surface. For arsenite, the working linear range can be improved by increasing the concentration of DTT solution.

### Interference study

Among the ions investigated, only Cu(II) and Fe(III) interfered when the Cu(II) concentration was higher than  $90 \text{ µg L}^{-1}$  and the Fe(III) concentration was higher than  $0.4 \text{ mg L}^{-1}$ . The response to arsenite in the presence of  $90.0 \text{ µg L}^{-1}$  of  $\text{Cu}^{2+}$ ,  $0.400 \text{ mg L}^{-1}$  of  $\text{Fe}^{3+}$  and  $1.86 \text{ g L}^{-1}$  of disodium EDTA is shown in Fig. 5. The equation for the best fit line is  $\Delta F = 2.97C + 664$ . It is clear that after adding EDTA, copper and iron interferences were successfully eliminated.



**Fig. 5** Frequency change as a function of arsenite concentration in the presence of EDTA as masking reagent. The concentration of DTT was  $3.08 \text{ mg L}^{-1}$ , of  $\text{Cu}^{2+}$  was  $90.0 \text{ µg L}^{-1}$ , of  $\text{Fe}^{3+}$  was  $0.400 \text{ mg L}^{-1}$  and of EDTA was  $1.86 \text{ g L}^{-1}$ . The straight line is the best fit by unweighted least squares regression.

**Table 2** Recoveries of arsenite in the analysis of water samples

Sample	Spike concentration ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Mean $\pm$ std dev of recoveries (%)
Puffers pond	0	Not detected		$95 \pm 10$ $n = 4$
	6.00	5.53	91.7	
	7.00	7.65	110	
	8.00	7.04	88.0	
	9.00	8.19	91.0	
Connecticut river	0	Not detected		$106 \pm 5$ $n = 5$
	6.00	6.27	105	
	7.00	7.46	107	
	8.00	9.10	114	
	9.00	8.96	99.5	
Rain water	10.0	10.4	104	$101 \pm 10$ $n = 5$
	0	Not detected		
	5.00	5.05	101	
	6.00	5.71	95.2	
	7.00	6.09	87.1	
Fuji brand bottled water	6.00	6.51	109	$104 \pm 18$ $n = 10$
	7.00	7.89	113	
	0	$7.6 \pm 1.4$ ( $n = 3$ )		
	2.00	$9.32 \pm 0.62$	84.8	
	3.00	$10.7 \pm 0.4$	103	
	4.00	12.8	129	
	5.00	$13.4 \pm 0.5$	116	
	6.00	15.8	136	
	7.00	$15.3 \pm 0.3$	111	
	8.00	$15.0 \pm 1.3$	92.4	
	9.00	$15.6 \pm 0.3$	88.4	
10.0	$16.1 \pm 0.6$	85.2		
11.0	$17.6 \pm 0.6$	90.6		

### Determination of total arsenic in real water samples

The results for the analysis of the water samples (rain, pond, river and bottled) are shown in Table 2. The table also shows the results for the analysis of the spiked water samples. Only the bottled water contained a measurable concentration of arsenic, but with recoveries of spikes at single-digit  $\mu\text{g L}^{-1}$  concentrations ranging from 85% to 129%, it is considered that the method is suitable for the determination of arsenic in real water samples. It was observed that the slope of the calibration varied each time a new DTT layer was formed on the gold electrode surface. Because of this variability, the method of standard additions is recommended for real water analysis.

### Conclusions

It is concluded that a viable analytical procedure for the determination of inorganic arsenic species in solution can be developed in which arsenite is sensed by binding to the surface of the gold electrode of the oscillating quartz crystal with DTT causing a decrease in the oscillation frequency. Although it is known that the oscillation frequency is dependent on both temperature and viscosity, effects due to changes in these parameters were minimized by calibration by the method of standard additions and the procedure was successfully applied to the analysis of several real water samples. Interferences from Cu(II) and Fe(III) ions were overcome by the addition of EDTA.

Compared with performance characteristics of field test kits based on the Gutzeit reaction,<sup>25</sup> the QCM method is more sensitive, more accurate and faster (once a sample has been treated with EDTA). As the instrumentation has low power consumption and is compact, it has the potential to be used outside the laboratory.

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