

# Direct Determination of Arsenic in Sea-water by Continuous-flow Hydride Generation Atomic Fluorescence Spectrometry

JORGE MOREDA-PIÑEIRO<sup>a</sup>, M. LUISA CERVERA<sup>b</sup> AND MIGUEL DE LA GUARDIA<sup>\*b</sup>

<sup>a</sup>Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, Av. de Las Ciencias, s/n 15706-Santiago de Compostela, Spain

<sup>b</sup>Department of Analytical Chemistry, Faculty of Chemistry, University of Valencia, Dr. Moliner 50, 96100-Burjassot, Valencia, Spain

A highly sensitive and simple procedure was developed for the direct determination of total As in sea-water samples by hydride generation atomic fluorescence spectrometry. The method involves the generation of arsenic hydride from sea-water samples, diluted with HCl to a final HCl concentration of 2 mol l<sup>-1</sup>, which were merged with a reducing solution, *viz.*, 3% m/v NaBH<sub>4</sub>. The sample and NaBH<sub>4</sub> were pumped at flow rates of 6.0 and 1.3 ml min<sup>-1</sup>, respectively, and allowed to react in a 200 cm × 0.8 mm id reaction coil. The evolved arsenic hydride was removed using an argon flow rate of 400 ml min<sup>-1</sup> and passed to a hydrogen diffusion flame where the atomic fluorescence of As was measured at 193.7 nm. With the proposed procedure a detection limit of 5.0 ng l<sup>-1</sup> was achieved. The repeatability of the determination varied between 1.5 and 4.0%. The accuracy was confirmed by the analysis of two sea-water reference materials (NASS-4 and CRM-403) and by recovery studies on natural samples spiked with known concentrations of As<sup>III</sup> and As<sup>V</sup>. The proposed method was successfully applied to the determination of As in several sea-water samples. The number of samples that can be analysed is 40 per hour.

**Keywords:** Arsenic; sea-water; hydride generation; atomic fluorescence

Electrothermal atomic absorption spectrometry (ETAAS) has been extensively used for As determination in several samples owing to its sensitivity and accuracy. However, for complex samples with a high saline content, such as sea-water, several problems occur owing to the important interference effects from NaCl and K<sub>2</sub>SO<sub>4</sub>.<sup>1,2</sup> In addition, the As concentration in sea-water<sup>3</sup> samples is below the detection limit of this technique, around 1.1–1.9 µg l<sup>-1</sup>. These levels are reduced considerably for unpolluted areas. Thus, the use of different preconcentration procedures is necessary, methods being unavailable for routine analysis.

The main advantage of analytical methodology based on covalent hydride generation (HG) is that it allows the separation of the matrix and affords increased sensitivity as compared with ETAAS, while also offering automation facilities and the possibility of speciation.<sup>4</sup>

Hence, HG combined with atomic absorption spectrometry (AAS and ETAAS) as the detection system has been used for the direct determination of As in several samples. The application of this technique is well documented and has recently been reviewed by Fang *et al.*<sup>5</sup> and Dedina.<sup>6</sup> However, the sensitivity achieved using HGAAS is often inadequate for non-contaminated sea-water samples, making previous preconcentration steps necessary. Thus, different preconcentration procedures such as liquid–liquid extraction,<sup>7</sup> flotation,<sup>8,9</sup> preconcentration on solid resins<sup>10</sup> and cryogenic trapping<sup>11</sup> have been used, increasing the sensitivity but also the analysis time.

The use of *in situ* trapping of the generated hydride vapour in a hot coated graphite furnace (HG-ETAAS) presents higher sensitivity than HGAAS owing to the avoidance of hydride dilution in the Ar flow and the use of atomization temperatures higher than 1000 °C. Thus, this technique has been recognized as the most sensitive detection system for trace metal determination.<sup>6</sup> However, the main disadvantages of this technique are the necessity of using porous graphite structures to obtain adequate hydride trapping and the reduced possibility of routine monitoring.

The use of atomic fluorescence presents a sensitivity comparable to the highest sensitivity offered by HG-ETAAS with a reduced cost because graphite tubes are unnecessary, thus offering an attractive detection system for the direct determination of As in liquid samples at trace levels. The literature concerning As determination in natural waters and geological and biological samples by HGAAS is extensive;<sup>12–25</sup> however, only a single paper concerning As determination in sea-water samples by HGAAS was found in the literature,<sup>26</sup> which used non-dispersive AFS and radiofrequency-excited electrodeless discharge lamps.

The purpose of this paper was the development of a highly sensitive and accurate method for the direct determination of trace amounts of As in sea-water samples using HGAAS. The method should be applicable to routine analysis and monitoring studies.

## EXPERIMENTAL

### Apparatus

A Unicam VP-90 continuous-flow vapour system equipped with a B-type gas–liquid separator (Cambridge, UK) and a Perma pure drier tube (PS Analytical, Sevenoaks, Kent, UK) was used. An Excalibur atomic fluorescence detector (PSA 10033; PS Analytical), equipped with a boosted discharge hollow cathode lamp (BDHCL) (Superlamp; Photon, Victoria, Australia) for As as the excitation source, a hydrogen diffusion flame as the atom cell, a series of lenses to collect and focus useful radiation, and a specific filter to achieve isolation and reduction of flame emission in conjunction with a solar blind photomultiplier, was used. Measurements were carried out at the resonance wavelength of As (193.7 nm).

### Reagents

All solutions were prepared from analytical-reagent grade chemicals using ultrapure water, with a resistivity of 18 MΩ cm, which was obtained from a Milli-Q water-purification system (Millipore, Bedford, MA, USA). An As<sup>III</sup> stock standard solution (1.000 g l<sup>-1</sup>) was prepared by dissolving 1.320 g of As<sub>2</sub>O<sub>3</sub> (Riedel-de Haën, Hannover, Germany) in 25 ml of 20% m/v KOH solution, neutralizing with 20% v/v H<sub>2</sub>SO<sub>4</sub> and diluting

to 1 l with 1% v/v  $\text{H}_2\text{SO}_4$ . The  $\text{As}^{\text{V}}$  stock standard solution (Titrisol;  $1.000 \text{ g l}^{-1}$ ) was obtained from Merck (Darmstadt, Germany). Sodium tetrahydroborate (Fluka, Buchs, Switzerland) dissolved in 0.5% m/v NaOH (Carlo-Erba, Milan, Italy) was used as the reducing solution. This solution was prepared daily and filtered before use. Hydrochloric acid solution was prepared from 37% HCl (Merck). NASS-4 Open Ocean Seawater Reference Material for Trace Metals (National Research Council of Canada) and CRM-403 Sea Water, supplied by the Commission of the European Communities, were used to evaluate the accuracy of the developed procedure.

Argon C-45 (purity 99.995%) was used as the carrier gas for the atomizer and as the internal purge gas and was obtained from Carburios Metalicos (Barcelona, Spain). Synthetic air (Carburios Metalicos) was used to dry the generated vapour phase in the Perma pure drier tube.

### Procedure for Sample Collection

Sea-water samples were collected from coastal surface water of the Mediterranean Sea near to Valencia in 100 ml polyethylene bottles. The samples were immediately acidified with 100  $\mu\text{l}$  of concentrated  $\text{HNO}_3$ , which provided a pH lower than 2, to avoid the adsorption of As onto the polyethylene bottle walls.

### Procedure for Measurement

The method involves the continuous generation of arsenic hydride from sea-water samples diluted with HCl to a final HCl concentration of  $2 \text{ mol l}^{-1}$ , which were merged with a reducing solution, *viz.*, 3.0% m/v  $\text{NaBH}_4$ . The evolved arsenic hydride was transferred, using an argon flow rate of  $400 \text{ ml min}^{-1}$ , to the atomic fluorescence detector. Fluorescence measurements for samples were interpolated using the calibration line obtained with  $\text{As}^{\text{III}}$  standards. A schematic diagram of the continuous flow injection system is shown in Fig. 1. The operating conditions for HGAFS are shown in Table 1.

## RESULTS AND DISCUSSION

### Evaluation of Arsenic Hydride Generation Conditions

All experiments were performed on natural sea-water samples and aqueous standard solutions of  $1 \mu\text{g l}^{-1}$  As expressed as  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ .

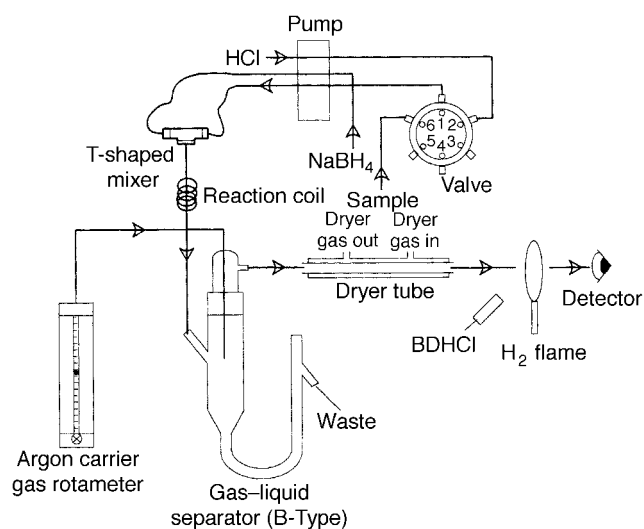


Fig. 1 Schematic diagram of the continuous-flow system used.

Table 1 Operating conditions for HGAFS

Parameter	
<i>Spectrometer operating conditions —</i>	
Resonance wavelength/nm	197.3
Bandpass/nm	0.5
Primary current/mA	27.0
Boost current/mA	35.0
Gain	$\times 10$
<i>Hydride generation conditions —</i>	
[HCl]/ $\text{mol l}^{-1}$	2.0
[ $\text{NaBH}_4$ ] (% m/v)	3.0
Reaction coil length/cm	200
Sample/HCl flow rate/ $\text{ml min}^{-1}$	6.0
$\text{NaBH}_4$ flow rate/ $\text{ml min}^{-1}$	1.3
Ar flow rate/ $\text{ml min}^{-1}$	400
<i>Atomic fluorescence measurement —</i>	
Delay time/s	15
Rinse time/s	30
Measurement time/s	40
Memory time/s	30
Measurement mode	Peak height

### Hydrochloric acid concentration

The effect of varying the HCl concentration on the atomic fluorescence from  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  is shown in Fig. 2. As can be seen, the signals related to  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  increase up to a concentration of  $2 \text{ mol l}^{-1}$  HCl. In addition, the response obtained from  $\text{As}^{\text{V}}$  is around 30% lower than that obtained from  $\text{As}^{\text{III}}$ . This is due to the poor efficiency of arsine generation obtained using a low  $\text{NaBH}_4$  concentration (1.5%) and the short length of the reaction coil employed (11 cm), as will be seen in the following sections.

### Reaction coil

The variation of the efficiency of arsenic hydride generation from  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  was evaluated using reaction coils of different lengths (11, 100, 200 and 300 cm). Results (Fig. 3) show that a reaction coil longer than 200 cm is necessary to obtain complete volatilization of  $\text{As}^{\text{V}}$ . For  $\text{As}^{\text{III}}$  no variation of the hydride generation efficiency with the length of the reaction coil was observed. Thus, a reaction loop of 200 cm was selected for further experiments.

### Sodium tetrahydroborate concentration

The  $\text{NaBH}_4$  concentration is an important parameter for arsine generation because arsenic hydride is formed in the presence

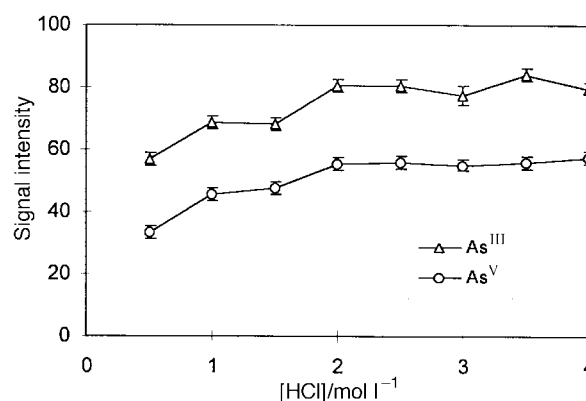
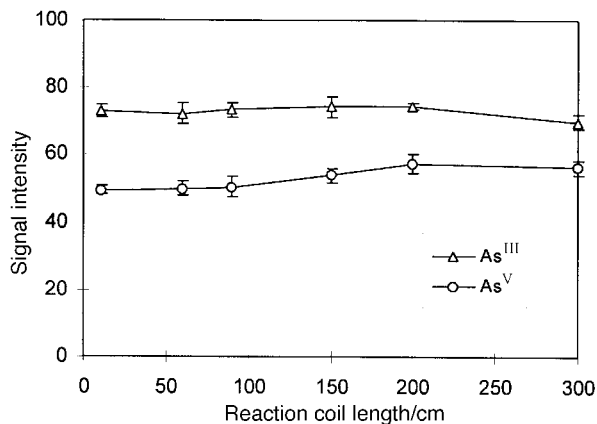


Fig. 2 Effect of HCl concentration on arsine generation from  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  solutions. The concentration of  $\text{NaBH}_4$  and reaction coil length were 1.5% m/v and 11 cm, respectively. The  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  concentrations were  $1.0 \mu\text{g l}^{-1}$ . Error bars indicate the variability of fluorescence measurement as  $\pm$  the standard deviation of three independent measurements.



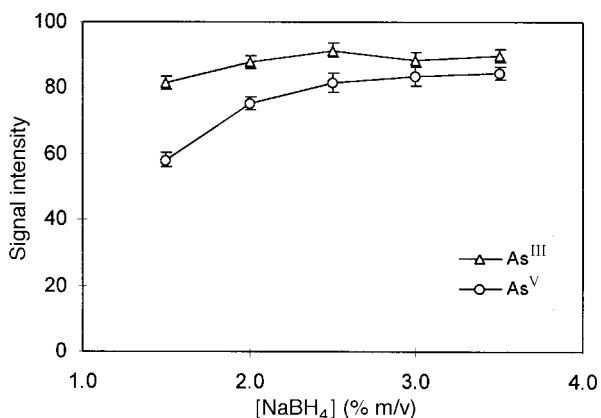
**Fig. 3** Effect of the reaction coil length on the integrated signal of As<sup>III</sup> and As<sup>V</sup> solutions. The concentrations of HCl and NaBH<sub>4</sub> were 2.0 mol l<sup>-1</sup> and 1.5% m/v, respectively. The As<sup>III</sup> and As<sup>V</sup> concentrations were 1.0 µg l<sup>-1</sup>.

of hydrogen generated by NaBH<sub>4</sub> in an acidic medium and because the flame in which the generated hydride is atomized is maintained by the excess of hydrogen produced in this reaction. As can be seen in Fig. 4, an NaBH<sub>4</sub> concentration higher than 3.0% m/v is required to obtain complete arsenic hydride generation from both As<sup>III</sup> and As<sup>V</sup>. For NaBH<sub>4</sub> concentrations lower than 1.5% m/v, the flame is extinguished, while for NaBH<sub>4</sub> concentrations higher than 3.5% the instability in the flame caused by the excess of hydrogen gives a poor reproducibility and sensitivity of the fluorescence measurements. Thus, an NaBH<sub>4</sub> concentration of 3.0% m/v was selected in order to obtain the best analytical performance.

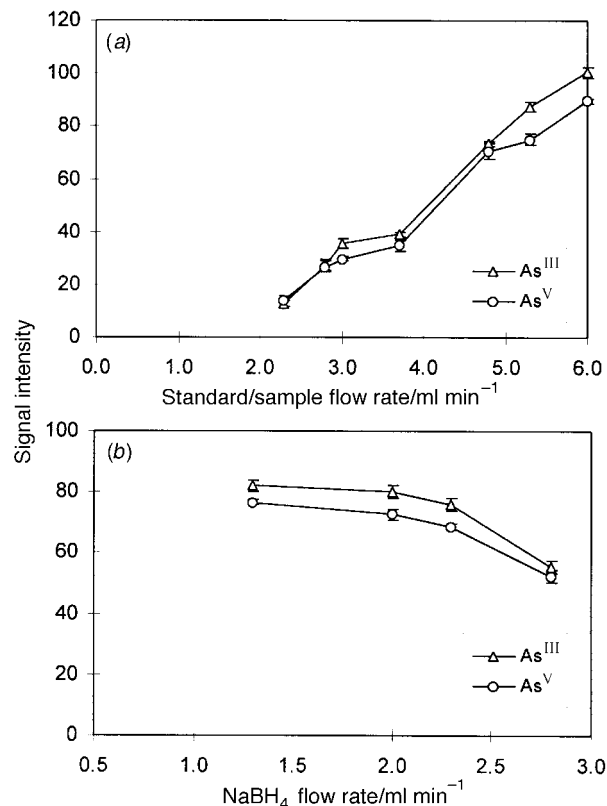
As can be seen, the hydride generation from As<sup>V</sup> exhibits slow kinetics compared with As<sup>III</sup>, making it necessary to increase the NaBH<sub>4</sub> and HCl concentrations to obtain a good comparability between the results found for both species.<sup>27,28</sup>

#### Flow rate parameters for standard/sample and NaBH<sub>4</sub>

The efficiency of the arsenic hydride generation was studied for different flow rates of standard/sample in 2.0 mol l<sup>-1</sup> HCl and NaBH<sub>4</sub>. Results shown in Fig. 5(a) indicate an increase in the As fluorescence signals with an increase in standard/sample flow rate up to 6.0 ml min<sup>-1</sup>. However, a decrease in the hydride generation efficiency was obtained for an NaBH<sub>4</sub> flow rate higher than 2.0 ml min<sup>-1</sup> [see Fig. 5(b)], for the reasons



**Fig. 4** Effect of NaBH<sub>4</sub> concentration on arsine generation from As<sup>III</sup> and As<sup>V</sup> solutions. The concentration of HCl and reaction coil length were 2.0 mol l<sup>-1</sup> and 200 cm, respectively. The As<sup>III</sup> and As<sup>V</sup> concentrations were 1.0 µg l<sup>-1</sup>.



**Fig. 5** Effect of the standard/sample (a) and NaBH<sub>4</sub> (b) flow rates on the fluorescence of As<sup>III</sup> and As<sup>V</sup> solutions. The HCl and NaBH<sub>4</sub> concentrations were 2 mol l<sup>-1</sup> and 1.5% m/v, respectively; the reaction coil length was 200 cm. The As<sup>III</sup> and As<sup>V</sup> concentrations were 1.0 µg l<sup>-1</sup>.

mentioned earlier. For an NaBH<sub>4</sub> flow rate lower than 1.0 ml min<sup>-1</sup> the flame is extinguished owing to the low hydrogen concentration obtained. Therefore, a sample flow rate of 6 ml min<sup>-1</sup> and an NaBH<sub>4</sub> flow rate of 1.3 ml min<sup>-1</sup> were selected for further experiments.

#### Argon flow rate

An increase in the Ar flow rate produces an increase in the atomic fluorescence up to an Ar flow rate of 400 ml min<sup>-1</sup>. However, for Ar flows higher than this value, samples were diluted and fluorescence signals reduced. Hence, a 400 ml min<sup>-1</sup> Ar flow was selected as the most convenient.

#### Analytical Figures of Merit

The calibration and standard additions equations obtained for aqueous standard solutions and natural sea-water samples spiked with As<sup>III</sup> and As<sup>V</sup> are shown in Table 2. As can be seen, no matrix effect was observed; in addition, the slopes obtained for the As<sup>III</sup> and As<sup>V</sup> calibration and standard additions equations are similar. The calibration and standard additions graphs

**Table 2** Calibration and standard additions graphs\*

	As <sup>III</sup>	As <sup>V</sup>
Calibration	$I = 1.5 + 86.9[\text{As}]$ $r = 0.9999$	$I = 1.7 + 79.7[\text{As}]$ $r = 0.9999$
Standard additions (natural sea-water)	$I = 85.7 + 88.9[\text{As}]$ $r = 0.9987$	$I = 84.3 + 82.2[\text{As}]$ $r = 0.9999$

\* [As] expressed as µg l<sup>-1</sup>.

obtained were linear up to a concentration of  $1.25 \mu\text{g l}^{-1}$  for which a signal intensity lower than 200 was obtained. For samples with a high As concentration, the use of a low gain was selected to obtain an atomic fluorescence intensity below 200.

The detection and quantification limits, defined as  $3s_b/m$  and  $10s_b/m$ , where  $s_b$  is the standard deviation of 11 measurements of a blank and  $m$  is the slope of the calibration graphs, were 5.0 and  $17 \text{ ng l}^{-1}$ , respectively. As can be observed, the sensitivity achieved is adequate for As determination in non-polluted sea-water samples and in open ocean sea-water samples. The sensitivity achieved by using this direct procedure for As determination is considerably improved with respect to published literature values concerning the use of HG-ETAAS. Hence, Tsalev *et al.*<sup>29</sup> reported characteristic masses of 31–35 pg for inorganic and organic As species using Ir–Zr-coated graphite tubes. Ding and Sturgeon<sup>30</sup> reported a detection limit of  $84 \text{ ng l}^{-1}$  using Ir- and Pd-coated graphite tubes and electrochemical hydride generation. Willie<sup>31</sup> reported a detection limit of  $140 \text{ ng l}^{-1}$  using an Ir-coated graphite tube, corresponding to a characteristic mass of 41 pg.

As compared with the previously reported procedures for the simultaneous determination of As, Se, Sn and Hg by non-dispersive atomic fluorescence,<sup>21</sup> the procedure developed here is simpler, because it does not require the use of expensive radiofrequency-excited discharge lamps. Additionally, the detection limit found by us is four times lower than that reported for a 5 ml sample volume.

The repeatability (relative standard deviation for seven replicate measurements of the same sample spiked at different concentration levels) [RSD (%)] obtained was lower than 4.0% for all concentrations tested, as can be seen in Table 3.

Analytical recovery values close to 100% were obtained for experiments carried out using sea-water samples spiked with  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ . The values obtained, shown in Table 4, were calculated using the slope of the calibration graph for  $\text{As}^{\text{III}}$ . As can be seen,  $\text{As}^{\text{V}}$  is reduced efficiently using the selected experimental conditions.

The accuracy of the method was evaluated by analysing different reference materials: NASS-4, with a certified inorganic As concentration of  $1.26 \pm 0.04 \mu\text{g l}^{-1}$ , and CRM-403, with an

indicative value of  $1.461 \mu\text{g kg}^{-1}$ . Results obtained were  $1.28 \pm 0.03 \mu\text{g l}^{-1}$  and  $1.51 \pm 0.02 \mu\text{g kg}^{-1}$ , respectively. These results are in good agreement with the certified values.

## Application

The proposed method was applied to the determination of As in different samples from the Mediterranean Sea. Results ranged from 1.1 to  $1.6 \mu\text{g l}^{-1}$ , with RSDs from 0.5 to 1.7%. Hence, the developed procedure is suitable for the direct determination of As in natural sea-water samples with good precision.

## CONCLUSION

The use of HGAFS provides adequate sensitivity and accuracy for the direct determination of As in coastal and open ocean sea-water samples, avoiding the tedious preconcentration procedures required by using other AAS techniques. The number of samples that can be analysed is 40 per hour, making the method suitable for routine analysis and monitoring studies.

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**Table 3** Analytical recovery studies\*

[As] added/ $\mu\text{g l}^{-1}$	Analytical recovery (%)	
	$\text{As}^{\text{III}}$	$\text{As}^{\text{V}}$
0.25	$101 \pm 1$	$103 \pm 3$
0.5	$107 \pm 3$	$102 \pm 2$
0.75	$100 \pm 4$	$108 \pm 2$
1.0	$101 \pm 1$	$100 \pm 1$
1.25	$99 \pm 2$	$104 \pm 2$

\* Natural sea-water samples were spiked with different concentrations of  $\text{As}^{\text{III}}$  or  $\text{As}^{\text{V}}$  and analysed by the proposed procedure using  $\text{As}^{\text{III}}$  standards for calibration.

**Table 4** Repeatability of As determination by HGAFS\*

$\text{As}^{\text{III}}$ concentration/ $\mu\text{g l}^{-1}$	RSD (%)
0	3.1
0.25	2.1
0.5	3.2
0.75	4.0
1.0	1.5
1.25	1.7

\* Values reported were found for seven independent measurements of each solution.