

Dissolved arsenic determination in natural waters

This is an optimized colorimetric method based from Johnson and Pilson [1] to determine arsenic (As) concentrations (<0.03-5.3 μM) in natural waters (e.g., groundwater, seawater) containing dissolved phosphate (2-30 μM) [2]. The basis of this method 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 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(V)) and another sample aliquot pre-treated to reduce As(V) (absorbance from P only).

Reagents

Hydrochloric acid (0.55 M)

Prepare a 250 mL solution by mixing 11.4 mL of concentrated hydrochloric acid (HCl) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C.

Oxidizing solution

Potassium iodate solution (2 mM)

Prepare a 100 mL solution by dissolving 0.0428 g of potassium iodate (KIO_3) in 2 wt.% HCl (~4.6 mL con'c HCl). Prepare fresh for each use.

Reducing solution

Sodium metabisulfite (0.736 M)

Prepare a 50 mL solution by dissolving 6.9960 g of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) in Milli-Q water. Prepare fresh for each use.

Sodium thiosulfate (0.089 M)

Prepare a 50 mL solution by dissolving 0.7036 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) in Milli-Q water. Prepare fresh for each use.

Sulfuric acid (1.8 M)

Prepare a 100 mL solution by mixing 36 mL of 5 M sulfuric acid (H_2SO_4) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C.

Mixing procedure:

Mix together 5 mL of sodium metabisulfite solution, 5 mL of sodium thiosulfate solution and 2.5 mL of 1.8 M H_2SO_4 solution. This mixed reducing solution is stable for 6 h at room temperature.

Color complexing reagent

L-ascorbic acid solution (0.613 M)

Prepare a 50 mL solution by dissolving 5.3981 g of L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) in Milli-Q water. Prepare fresh for each use.

Ammonium molybdate (0.024 M)

Prepare a 100 mL solution by dissolving 2.9661 g of ammonium molybdate ($\text{NH}_4\text{M}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C. Discard if precipitates form.

Antimonyl potassium tartrate (0.008 M)

Prepare a 100 mL solution by dissolving 0.5343 g of antimonyl potassium tartrate ($\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2\cdot 3\text{H}_2\text{O}$) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C. Discard if precipitates form.

Sulfuric acid (2.5 M)

Prepare a 100 mL solution by mixing 50 mL of 5 M sulfuric acid (HCl) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C.

Mixing procedure:

Mix together 4 mL L-ascorbic acid solution, 4 mL ammonium molybdate solution and 2 mL potassium antimonyl tartrate solution. Add 10 mL 2.5 M H₂SO₄ solution immediately to the mixed solution after the addition of potassium antimonyl tartrate to avoid generation of turbidity in the color complexing reagent. This mixed solution is stable for 6 h at room temperature.

Standards

Primary arsenate [As(III)] standard (1,000 mg/L)

Prepare a 100 mL solution by dissolving 0.1734 g sodium arsenite (NaAsO₂) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C.

Primary arsenate [As(V)] standard (1,000 mg/L)

Prepare a 100 mL solution by dissolving 0.4165 g sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O) in Milli-Q water. The solution is stable indefinitely if stored at 4 °C.

Secondary arsenate [As(III)] standard (10 mg/L)

Prepare a 50 mL solution by mixing 0.5 mL of the primary As(III) standard in Milli-Q water. The solution is stable for ~3 months if stored at 4 °C.

Secondary arsenate [As(V)] standard (10 mg/L)

Prepare a 50 mL solution by mixing 0.5 mL of the primary As(V) standard in Milli-Q water. The solution is stable for ~3 months if stored at 4 °C.

Secondary phosphate (P) standard (50 µM)

Prepare a 50 mL solution by mixing 417 µL of the primary P standard (6 mM, used in P analysis) in Milli-Q water. The solution is stable for 1 week if stored at 4 °C.

Calibration standards

Prepare standards of 10, 50, 200, 400 and 1,000 µg/L from the secondary As(III) and/or As(V) standard solutions by dilution. Take the appropriated aliquots (see below) and make up to 50 mL with Milli-Q water.

Std.	[As] (µg/L)	Vol. of 2° As standard solution (mL)	Vol. of 2° P standard solution (mL)
Blank	0	0	2
1	10	0.05	2
2	50	0.25	2
3	200	1	2
4	400	2	2
5	1,000	5	2

If P determination is also needed, prepare standards of 0.1, 0.25, 0.5, 1, 2 and 3 µM from the secondary P standard solution by dilution. Take the appropriate aliquots (see below) and make up to 50 mL with Milli-Q water. Take note that these standards are also spiked with 2 µM P to correct for absorbance dependence of As(V)

Std.	[P] (μM)	Vol. of 2° P standard solution (mL)
1	0.1	0.1
2	0.5	0.5
3	1	1
4	2	2
5	3	3

Sample analysis

1. Switch on the instrument 15 minutes before the measurements and set wavelength to 880 nm. This is to enable the bulbs in the spectrometer to warm up.
2. Prepare the spectrophotometric cuvettes, always hold them from the opaque sides. Cuvettes must be inserted in the same orientation all the time, there is a small arrow at the top to help ensure they are used the same way around.
3. Add three 1 mL aliquots of the samples into separate spectrophotometric cuvettes.
4. One aliquot is treated with 0.1 mL oxidizing solution, one with 0.1 mL reducing solution and the last one with 0.1 mL 0.55 M HCl. Wait for 10 min until the redox state of As in the pre-treated aliquots are reached (remains stable for at least 3 h).
5. After waiting for at least 10 min, add 0.1 mL of color complexing reagent to each cuvette and wait for at least 10 minutes for colour to develop in fully.
6. Do the same procedure for the blanks.
7. Measure standards and samples in the same manner and record their absorbance values. Measure as soon as possible to avoid degradation of the coloured complex.

Calculation

$[\text{As(III)}] = (\text{oxidized} - \text{untreated})$

$[\text{As(V)}] = (\text{untreated} - \text{reduced})$

$[\text{P}] = \text{reduced}$

Reference:

- [1] Johnson, et al., *Analytica Chimica Acta*, 1972, **58**, 289-299.
 [2] Dhar, et al., *Analytica Chimica Acta*, 2004, **526**, 203-209.