Arsenic, atomic absorption spectrometric, hydride, automated

Parameters and Codes:
Arsenic, dissolved, I-2062-85 (µg/L as As): 01000
Arsenic, total, I-4062-85 (µg/L as As): 01002
Arsenic, suspended total, I-7062-85 (µg/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-6062-85 (µg/g as As): 01003

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 1 µg/L of arsenic. Samples containing more than 20 µg/L need to be diluted.

1.2 Suspended total arsenic is calculated by subtracting dissolved arsenic from total arsenic.

1.3 This method may be used to analyze bottom material containing at least 1 µg/g of arsenic (NOTE 1). For samples containing more than 20 µg/g, use less sediment.
NOTE 1. Do not use more than 100 mg sediment, because erratic results and large blanks will occur.

1.4 Bottom material may be analyzed by this procedure after it has been prepared as directed in method P-0520.

1.5 Total arsenic in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable portion has been rapidly withdrawn from the mixture (NOTE 2).
NOTE 2. Do not use a sample containing more than 1 g/L sediment. Concentrations greater than 1 g/L cause erratic results.

1.6 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the acid-persulfate digestion or the ultraviolet radiation.

2. Summary of method

2.1 Organic arsenic-containing compounds are decomposed either by sulfuric acid-potassium persulfate digestion or by ultraviolet radiation. The arsenic so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsine with sodium borohydride. The arsine is stripped from the solution with the aid of nitrogen and is then decomposed in a tube furnace placed in the optical path of an atomic absorption spectrometer.

2.2 For additional information on the determination of arsenic in water, see Pierce and others (1976), and Fishman and Spencer (1977).

3. Interferences

3.1 Since the arsine is freed from the original sample matrix, interferences are minimized.

3.2 A detailed inorganic-interferences study showed that most trace elements at concentration levels of less than 300 µg/L do not interfere (Pierce and Brown, 1976).

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to manufacturer's manual to optimize instrument for the following:
Grating ---------------------- Ultraviolet
Wavelength ------------------ 193.7 nm
Source (electrodeless-
    discharge lamp) --------- Arsenic

4.3 *Autotransformer, variable:* Superior Power-stat type 3 PN 1010 or equivalent.

4.4 *Pyrometer,* portable, 0°C to 1,200°C. Thermolyne Model PM-20700 or equivalent.

4.5 *Stripping-condensing column,* Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 1). Cooling of the condensing column is not required. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approximately 200 mL/min has been found satisfactory.
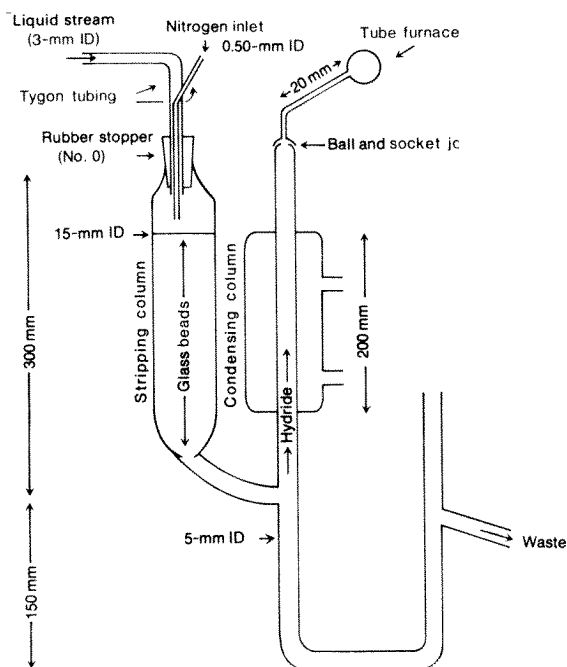
Figure 1. - Stripping-condensing column and quartz-tube furnace

4.6 *Tube furnace,* quartz, 10-mm ID×100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge, nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.7 *Technicon AutoAnalyzer II,* consisting of sampler with stirrer, manifold, ultraviolet digestor (optional, NOTE 3), proportioning pump, and heating bath (optional, NOTE 4).

    Heating-bath temperature ------ 95 °C.

NOTE 3. The ultraviolet digestor can be used only when determining dissolved arsenic; it cannot be used when analyzing water-suspended sediment or bottom material.

NOTE 4. The heating bath is used only in the acid-persulfate digestion procedure.

5. Reagents

5.1 *Arsenic standard solution I,* 1.00 mL= 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic standard solution II,* 1.00 mL= 10.0 µg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic standard solution III,* 1.00 mL= 0.10 µg As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated HNO_3 to 500.0 mL with demineralized water. Prepare fresh weekly.

5.4 *Arsenic working standards:* Prepare daily a blank and 100 mL each of a series of arsenic working standards containing 0.15 mL concentrated HNO_3 by appropriate dilution of arsenic standard solution III.

Arsenic standard solution III (mL)	Arsenic concentration (µg/L)
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15
20.0	20

5.5 *Hydrochloric acid, 6M:* Add 500 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.6 *Potassium iodide solution,* 100 g/L: Dissolve 100 g KI in demineralized water and dilute to 1 L.

5.7 *Potassium persulfate solution,* 50 g/L: Dissolve 50 g $K_2S_2O_8$ in demineralized water with warming and dilute to 1 L after the solution has cooled.

5.8 *Sodium borohydride solution,* 5 g/L: Dissolve 5 g $NaBH_4$ and 40 g NaOH in demineralized water and dilute to 1 L.

5.9 *Sodium hydroxide solution, 10M Cautiously* dissolve 400 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid solution, 3M: Cautiously,* add, with constant stirring and cooling, 167 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Set up manifold-acid persulfate (fig. 2) or ultraviolet radiation (fig. 3). See NOTE 2.

6.2 Apply a voltage of 47 volts or more (variable autotransformer) as necessary to the tube furnace to maintain a constant temperature of 800°C. Monitor the tube-furnace temperature
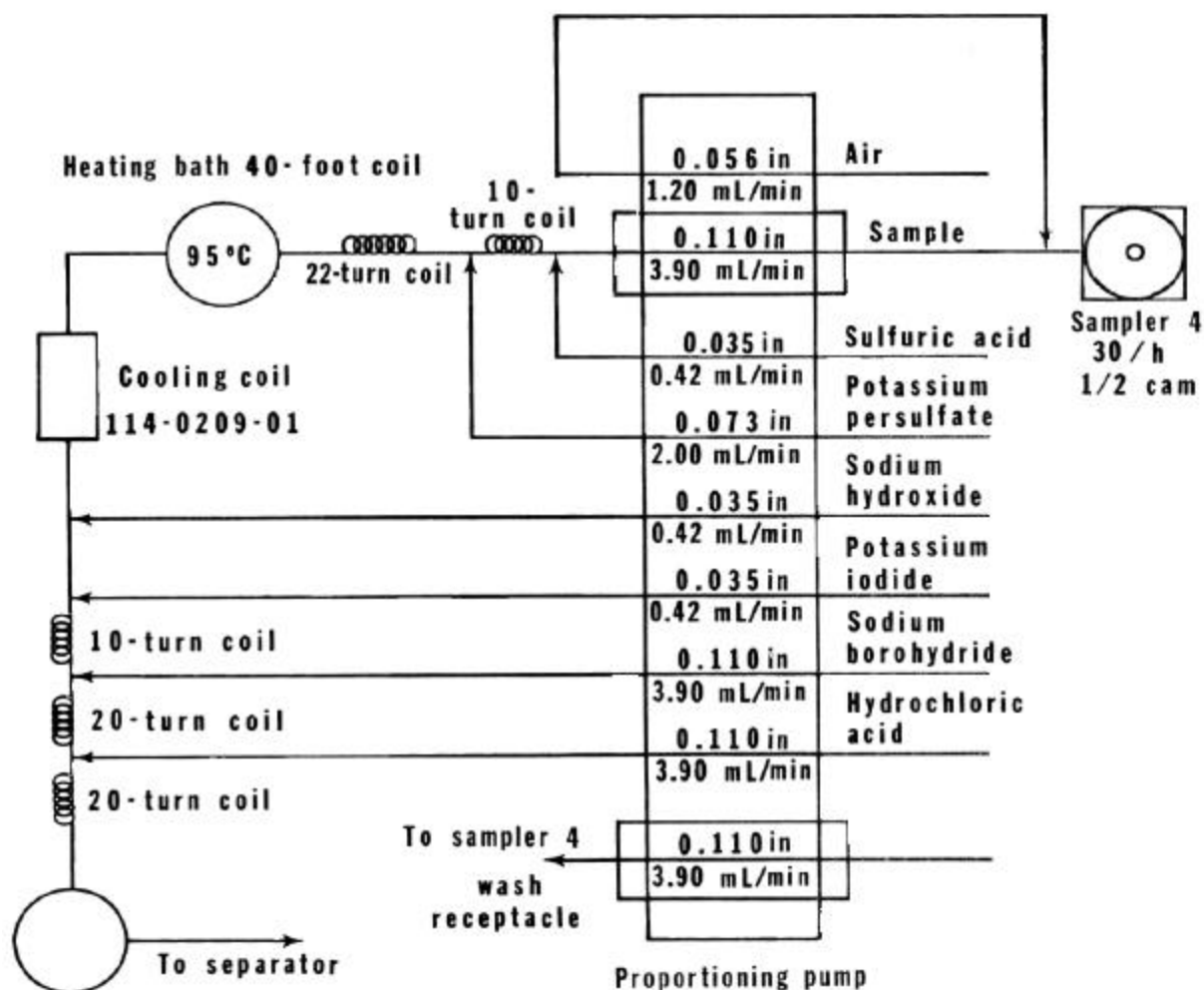
0.056 in	Air	Heating bath 40-foot coil
1.20 mL/min		10-turn coil
0.110 in	Sample	22-turn coil
3.90 mL/min		
0.035 in	Sulfuric acid	Sampler 4
0.42 mL/min	Potassium	30/h
0.073 in	persulfate	1/2 cam
2.00 mL/min	Sodium	
0.035 in	hydroxide	
0.42 mL/min	Potassium	
0.035 in	iodide	
0.42 mL/min	Sodium	
0.110 in	borohydride	
3.90 mL/min	Hydrochloric	
0.110 in	acid	
3.90 mL/min		
0.110 in		To sampler 4
3.90 mL/min		wash receptacle

95°C
Cooling coil 114-0209-01
10-turn coil
20-turn coil
20-turn coil
To separator
Proportioning pump

Figure 2. - Arsenic, acid-persulfate manifold

using portable pyrometer with the thermo-couple placed in the middle of the tube.

6.3 If bottom-material samples are being analyzed, weigh 100 mg or less of bottom-material sample (2.0 µg As max), transfer to a 100-mL volumetric flask, and dilute to volume with demineralized water. Sample as directed for water and water-suspended sediment samples in paragraph 6.5 (NOTE 5).

NOTE 5. Bottom material may be manually digested using method I-5062 (arsenic, atomic absorption spectrometric) if standards and blank are treated identically. Adjust pH of digested solutions to between 2 and 3 before proceeding to paragraph 6.5.

6.4 Feed all reagents through the system, using demineralized water in the sample line, Allow the heating bath to warm to 95°C.

6.5 Beginning with the most concentrated standard (NOTE 6), place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays. Fill remainder of each sample tray with unknown samples (well mixed).

NOTE 6. It is best to place two or three samples of the most concentrated standard at the beginning, since the first peak is usually low.
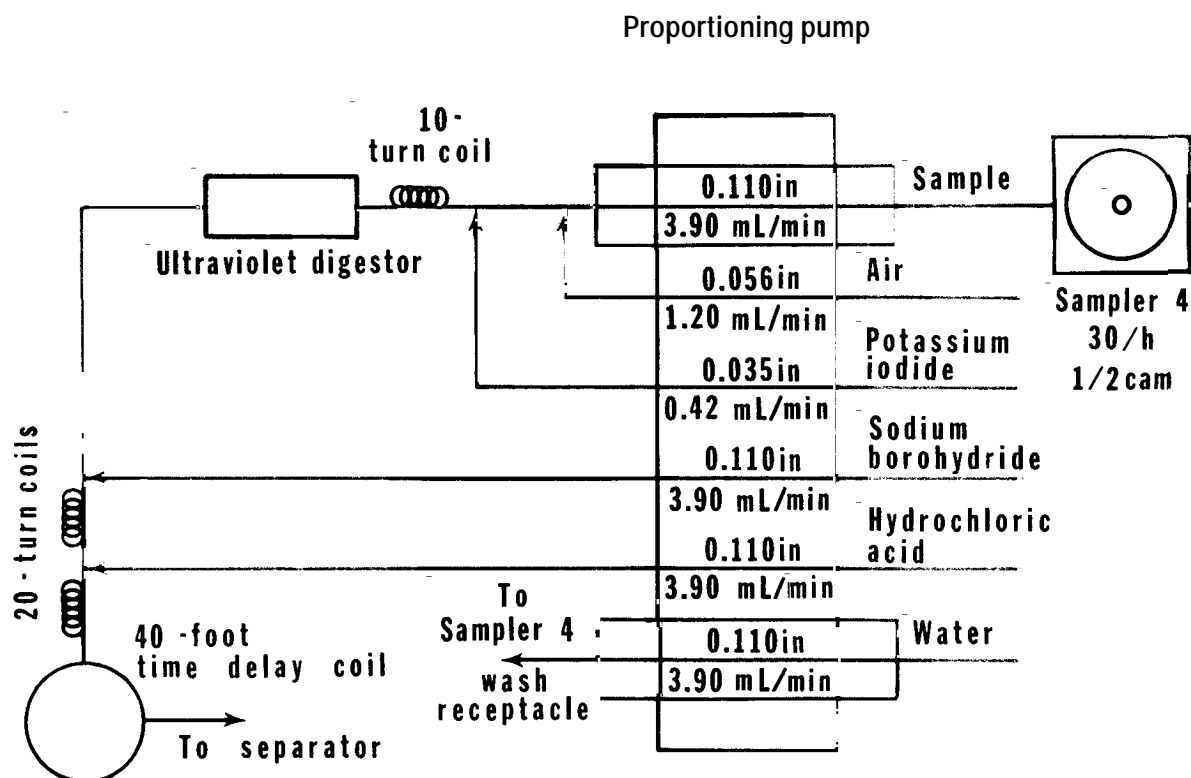
Proportioning pump

Figure 3. - Arsenic, ultraviolet radiation manifold

The first standard should not be used in any of the calculations.

6.6 Remove the sample line from the demineralized-water wash solution when the baseline stabilizes and begin the analyses (NOTE 7).

NOTE 7. When the analyses are complete, the tubes in the manifold and the separator-condensor column should be cleaned if any sediment is present.

6.7 With 10 mV recorder, 20 µg/L of arsenic will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace or treat the cell by one of the following methods:

6.7.1 Soak the tube furnace for 30 min in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

6.7.2 Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-in. chuck on a slowly revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto-valve-grinding compound. Using a standard speed drill and an aluminum oxide-grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of

water, begin grinding cell with a steady movement from inside to outside of cell. Grind one half of cell at a time and regrind if necessary to achieve an even frosting.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective arsenic concentration.

7.2 Determine the concentration of dissolved or total arsenic in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 To determine the concentration of suspended total arsenic, subtract dissolved-arsenic concentration from total-arsenic concentration.

7.4 To determine the concentration of arsenic in bottom-material samples, first determine the micrograms per liter of arsenic in each sample as in paragraph 7.2, then

$$\text{As } (\mu g/g) = \frac{\mu g/L \text{ As} \times 0.1}{\text{wt of sample (g)}}$$

8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 µg/L, nearest microgram per liter; 10 µg/L and above, two significant figures.

8.2 Report arsenic, total-in-bottom-material (01003), concentrations as follows: less than 10 µg/g, nearest microgram per gram; 10 µg/g and above, two significant figures.

9. Precision

9.1 Acid-persulfate digestion: Precision, for dissolved arsenic for replicate analysis by one operator expressed in terms of percent relative standard deviation, is as follows:

Mean (µg/L)	Relative standard deviation (percent)
5.8	5
10.4	5
15.5	5

9.2 Ultraviolet radiation: Precision for dissolved arsenic for replicate analysis by one operator expressed in terms of percent relative standard deviation is as follows:

Mean (µg//L)	Relative standard deviation (percent)
5.0	10
10.4	10
13.8	4

9.3 It is estimated that the percent relative standard deviation for total and suspended arsenic and for arsenic in bottom material will be greater than that reported for dissolved arsenic.

References

Fishman, M. J., Spencer, R. R., 1977, Automated atomic absorption spectrometric determination of total arsenic in water and streambed materials: Analytical Chemistry, v. 49, p. 1599-1602.

Pierce, F. D., Lamoreaux, T. C., Brown, H. R., and Fraser, R. S., 1976, An automated technique for the sub-microgram determination of selenium and arsenic in surface waters by atomic absorption spectroscopy: Applied Spectroscopy, v. 30, p. 38-42.

Pierce, F. D., and Brown, H. R., 1976, Inorganic interference study of automated arsenic and selenium determination with atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 693-695.