



## **Chapter M**

# **Mercury in water, geologic, and plant materials by continuous flow-cold vapor-atomic absorption spectrometry**

*By Zoe Ann Brown, Richard M. O'Leary, Philip L. Hageman, and James G. Crock*

**U.S. Geological Survey Open File Report 02-223-M**

**Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey**

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Codes: A091  
T12

Accepted: 9/23/93  
Revised: 1/15/02

## Principle

To determine mercury in geologic and plant materials, samples are digested with nitric acid and sodium dichromate in a disposable test tube. After digestion, samples are diluted with water to 12 mL. To determine mercury in water, samples must be preserved with a 1 percent sodium dichromate/nitric acid solution. All samples are then mixed with air and a sodium chloride-hydroxylamine hydrochloride-sulfuric acid solution and Hg (II) is reduced to Hg<sup>0</sup> with stannous chloride in a continuous flow manifold. The mercury vapor is separated and measured using continuous-flow cold vapor-atomic absorption spectrometry (CV-AAS). This method is a variation of Kennedy and Crock (1987).

## Interferences

Samples containing high concentrations of Ag, Au, Pt, Te, and Se may diminish the extraction efficiency of the Hg in geologic samples (Bartha and Ikrenyi, 1982 and Suddendorf, 1981). Of these, only selenium poses a significant problem for nonmineralized geologic materials. Although a 1 ppm solution of the other elements causes greater than a 90 percent suppression of a 0.01 ppm Hg solution, these elements either will not be dissolved (Au, Pt) or are normally present at low concentrations (Ag, Te). Silver does not become a problem until its concentration exceeds 12 ppm in sample. Samples containing silver above 12 ppm need to be diluted. Concentrations above 25 ppm Se suppress recovery of Hg and should be diluted.

## Scope

The method offers a lower reporting limit of 0.02 ppm mercury in solid-phase samples. Samples exceeding the working range of 0.02-1.8 ppm mercury require dilution. For water samples, the method offers a lower reporting limit of 0.1 ppb. Samples exceeding the working range of 0.1-1.5 ppb mercury must be diluted. Approximately 40 samples can be analyzed per person-day.

## Apparatus

- Perkin-Elmer 3030B Spectrophotometer
- Perkin-Elmer 56 Strip Chart Recorder
- Technicon AAI Autosampler, modified by replacing the metal sampling probe with a glass sampling probe
- Gilson Medical Electronic (Middleton, Wisconsin) Model Minipulse 2, eight channel, variable-speed peristaltic pump equipped with standard tygon pump tubing
- Standard laboratory hot plate with a 30x60-cm heating surface
- General Electric Chill Chaser Deluxe Infrared Heat Lamp. Position around the flow-through cell and the phase separator

- 7.5-cm-thick x 33-cm-wide x 43-cm-long aluminum heating block, with 18-mm holes drilled through in a 10 by 10 matrix

See figures 1 and 2 for the flow-through cell and phase separator used in this method. These have been described by Skougstad and others (1979). Mixing coils are available from Bran + Luebbe, Inc., Buffalo Grove, IL.

## Reagents

Unless otherwise noted, chemicals are reagent grade and water is deionized (DI).

*1 percent (w/v) sodium dichromate-nitric acid solution:* Dissolve 10 g  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  in 1.0 L conc 'INSTRA-ANALYZED' grade  $\text{HNO}_3$ .

*30 percent (w/v) potassium hydroxide solution:* Dissolve 30 g KOH in DI water and dilute to 100 mL.

*25 percent (w/v) sodium dichromate solution:* Dissolve 500 g reagent grade  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  in sufficient DI water to bring the volume to 2 L.

*Nitric acid wash:* Dilute 40 mL 'INSTRA-ANALYZED' grade  $\text{HNO}_3$  (16 M) to 4 L with DI water.

*Stannous chloride solution:* Dissolve 100.0 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (suitable for Hg determination grade) in 100 mL conc (12 M) 'INSTRA-ANALYZED' grade HCl. Let the solution stand for 20 to 30 min until the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  totally dissolves. Dilute to 1 L with DI water. This solution is stable for about 1 week with refrigeration at 5°C.

*Complex-reducing solution:* Dissolve 30.0 g hydroxylamine hydrochloride and 30.0 g NaCl in about 500 mL DI water. While mixing, slowly add 100 mL conc (18 M)  $\text{H}_2\text{SO}_4$ , 'INSTRA-ANALYZED' grade. When the solution is cool, dilute to 1 L with DI water.

*Stock solution:* SRM 1641c (1.47 ppm mercury in DI water) available from the National Institute of Standards and Technology.

*Mercury calibration standards:* 1.47 ppb, 7.35 ppb, and 14.7 ppb: Prepare by diluting with DI water, 0.5 and 2.5, and 5.0 mL of 1.47 ppm mercury solution (SRM 1641c) in three 500 mL volumetric flasks containing 100 mL conc  $\text{HNO}_3$  and 10 mL 25 percent sodium dichromate solution.

## Safety precautions

Normal laboratory safety procedures should be observed, including the use of protective eyewear, laboratory coat, and gloves. All chemical digestion activities should be performed in a chemical hood. See the *CHP and MSDS* for further information concerning first-aid treatment and disposal procedures etc. for chemical products used in this method. The atomic absorption spectrophotometer should be located under a vent exhaust hood to evacuate the acid gases and mercury vapors that are generated by the continuous flow-cold vapor system.

## Procedure for geologic and plant samples

1. Weigh 0.100 g sample into 16x100-mm disposable test tube.
2. Add 2.0 mL 16 M HNO<sub>3</sub>, and 0.50 mL 25 percent sodium dichromate solution to the sample. Vortex the solution to wet the entire sample.
3. Place test tube in the aluminum heating block for 2 hours at 110°C. Remove from the heating block and allow to cool completely. (Overnight cooling is acceptable.)
4. Dilute sample solution to 12 mL with DI water, cap and shake for 2 min.
5. If the sample is mineralized or it contains more than 25 ppm Se, 10 ppm Au, 10 ppm Ag; transfer 0.6 mL to a second test tube, add 2 mL HNO<sub>3</sub>, 0.5 mL 25 percent dichromate solution, and dilute to 12 mL with DI water.
6. Aqueous standards of 1.47, 7.35, and 14.7 ppb Hg are used for the calibration curve with each day's analysis.
7. Using the manifold illustrated in figure 3, the digested geochemical materials are analyzed along with aqueous calibration standards. The modifications to the manifold include changes to reagent and sample flow rates and reagent composition. These were made to maximize the absorbance signal of a 0.01 ppm Hg solution, and to allow the high dichromate concentration in the sample digest. Samples with Hg concentration greater than the highest standard (14.7 ppb in solution or 1.8 ppm in the sample) must be diluted and reanalyzed. Any sample following a sample that exceeds the concentration of the upper standard, should be reanalyzed due to potential Hg carry over from the previous sample.
8. The calibration curve is checked at the beginning and end of every job (approximately 40 samples).

## Procedure for water samples

Water samples should arrive at laboratory preserved with a 1 percent sodium dichromate/conc HNO<sub>3</sub> solution in a ratio of 1:19 (one part sodium dichromate/HNO<sub>3</sub> solution to 19 parts DI water sample).

1. Upon arrival at laboratory, water samples are shaken and transferred into 16 x 100 mm disposable test tubes.
2. Aqueous calibration standards of 0.37, 0.74, and 1.47 ppb are used for water analysis. They are obtained by dilution of the calibration standards used for geologic and plant samples, using the dilution technique previously described.
3. Water samples are then analyzed using the same reagents and equipment used for geologic and plant samples with the exception of increasing sensitivity of the strip chart recorder from 5mV to 2mV. Any sample exceeding the working range (0.20-1.47 ppb) must be diluted and reanalyzed.
4. The calibration curve is checked at the beginning and end of every job.

## Standardization of Instrument

Instrument settings used for a Perkin-Elmer 3030B AAS Spectrometer and a Perkin-Elmer 56 Recorder are outlined in table 1.

**Table 1.—Operating conditions for determination of Hg by CV-AAS**

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|                        |   |
|------------------------|---|
| Lamp.....              | Hg hollow cathode, 4 mA   |
| Slit.....              | 0.7 nm  |
| Wavelength.....        | 253.7 nm, no background correction                                    |
| Recorder.....          | 5 mV full-scale response, 5 mm/min; 2mV for water samples             |
| 1.47 µg/L.....         | 0.025 absorbance units  |
| Flow-Through Cell..... | Maximum allowable absorbance of static cell is 0.250 absorbance units |

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## Calculation

Measure peak height to the nearest division and calculate the mercury concentration in the sample with the following formula:

$$\text{Hg (ppm)} = \frac{\text{standard conc } (\mu\text{g / mL})}{\text{recorder reading of standard (divisions or mm)}} \times \frac{\text{total sample solution volume (mL)}}{\text{sample wt (g)}} \times \text{recorder reading of sample (divisions or mm)}$$

## Assignment of Uncertainty

The reporting limit can be lowered by using a larger sample (up to 0.5 g) or a smaller dilution volume (minimum of 8.0 mL due to the requirements of the manifold). Table 2 shows the analytical results of selected reference materials, duplicate samples, and method blanks obtained by this method.

**Table 2.—Analytical performance summary for Hg by CV-AAS (water samples in ppb, solid phase samples in ppm)**

[A=Erdmann, 1994; B=National Institute of Standards and Technology (NIST), 1993; C=National Bureau of Standards, 1983; D=Govindaraju, 1989; E=NIST, 1992; remaining *pv* from Potts and others, 1992]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

| <i>Reference</i> | <i>Description</i> | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>pv</i> |   | <i>% RSD</i> | <i>% R</i> |
|------------------|--------------------|----------|-------------|----------|-----------|---|--------------|------------|
| HG 5             | water              | 9        | 0.23        | 0.01     | 0.30      | A | 6            | 77         |
| HG 4             | water              | 9        | 0.58        | 0.04     | 0.60      | A | 6            | 97         |
| HG 1             | water              | 9        | 0.92        | 0.03     | 0.98      | A | 3            | 94         |

| <i>Reference</i> | <i>Description</i>  | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>pv</i>    |             | <i>% RSD</i> | <i>% R</i> |
|------------------|---------------------|----------|-------------|----------|--------------|-------------|--------------|------------|
| SRM 1515         | apple leaves        | 9        | 0.04        | 0.01     | <b>0.044</b> | B <i>cv</i> | 27           | 83         |
| G-2              | granite             | 10       | 0.07        | 0.01     | 0.049        |             | 13           | 135        |
| GSD-12           | stream sediment     | 68       | 0.10        | 0.04     | 0.056        |             | 40           | 179        |
| SRM 1572         | citrus leaves       | 9        | 0.07        | 0.02     | 0.08         | C <i>cv</i> | 26           | 88         |
| SRM 1575         | pine needles        | 9        | 0.14        | 0.01     | 0.15         | B <i>cv</i> | 7            | 95         |
| GXR-5            | soil                | 77       | 0.19        | 0.02     | 0.167        |             | 10           | 112        |
| MESS-1           | marine sediment     | 10       | 0.22        | 0.01     | 0.171        | D           | 6            | 131        |
| SGR-1            | shale               | 20       | 0.18        | 0.01     | 0.254        |             | 8            | 69         |
| GXR-3            | hot springs deposit | 63       | 0.32        | 0.02     | 0.33         |             | 5            | 97         |
| SRM 2709         | soil                | 28       | 1.4         | 0.1      | <b>1.40</b>  | E <i>cv</i> | 6            | 99         |
| GXR-2            | soil                | 145      | 3.1         | 0.2      | 2.9          |             | 8            | 107        |
| GXR-1            | jasperoid           | 10       | 4.0         | 0.3      | 3.9          |             | 8            | 103        |
| SRM 2711         | soil                | 11       | 5.9         | 0.5      | <b>6.25</b>  | E <i>cv</i> | 8            | 94         |

**Table 2.—Continued—Duplicate samples results**

| <i>Duplicate samples</i>  | <i>k</i> | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>% RSD</i> | <i>Concentration range</i> | <i>No. of &lt; (total)</i> | <i>No. of &lt; (pairs)</i> |
|---|----------|----------|-------------|----------|--------------|----------------------------|----------------------------|----------------------------|
| Solid phase   | 46       | 2        | 0.06        | 0.01     | 15           | 0.02 to 0.18               | 82                         | 36                         |
| <i>No duplicate data available for water samples at this time</i> |          |          |             |          |              |                            |                            |                            |

**Table 2.—Continued--Method blank results** 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

| <i>Method blank</i> | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>3s</i> | <i>5s</i> |
|---------------------|----------|-------------|----------|-----------|-----------|
| Water               | 15       | 0.01        | 0.02     | 0.04      | 0.08      |
| Solid phase         | 15       | 0.001       | 0.001    | 0.004     | 0.006     |

Each daily run of samples is preceded by three aqueous calibration standards, a reference sample taken through the digestion procedure, and a digested reagent blank. The three aqueous standards establish the sensitivity; the reference sample is a check of digestion and the blank establishes the level of contamination. Low values for the aqueous standards and/or high values for the reference sample suggest the apparatus needs to be disassembled and cleaned. Heating with 30% KOH removes any residual mercury or organic carbon buildup.

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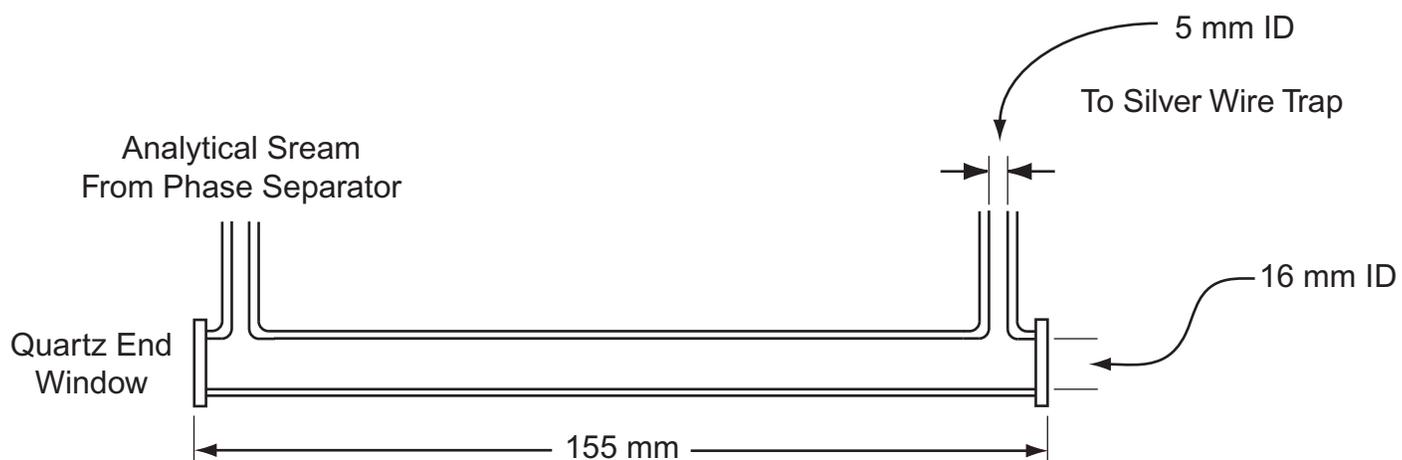


Figure 1. The flow-through cell used for the determination of mercury. The two 16-mm end windows of this cell are quartz and the remainder of the cell is Pyrex glass. J.G. Crock and others, 1987, U.S. Geological Survey Open-File Report 87-84, p. 16

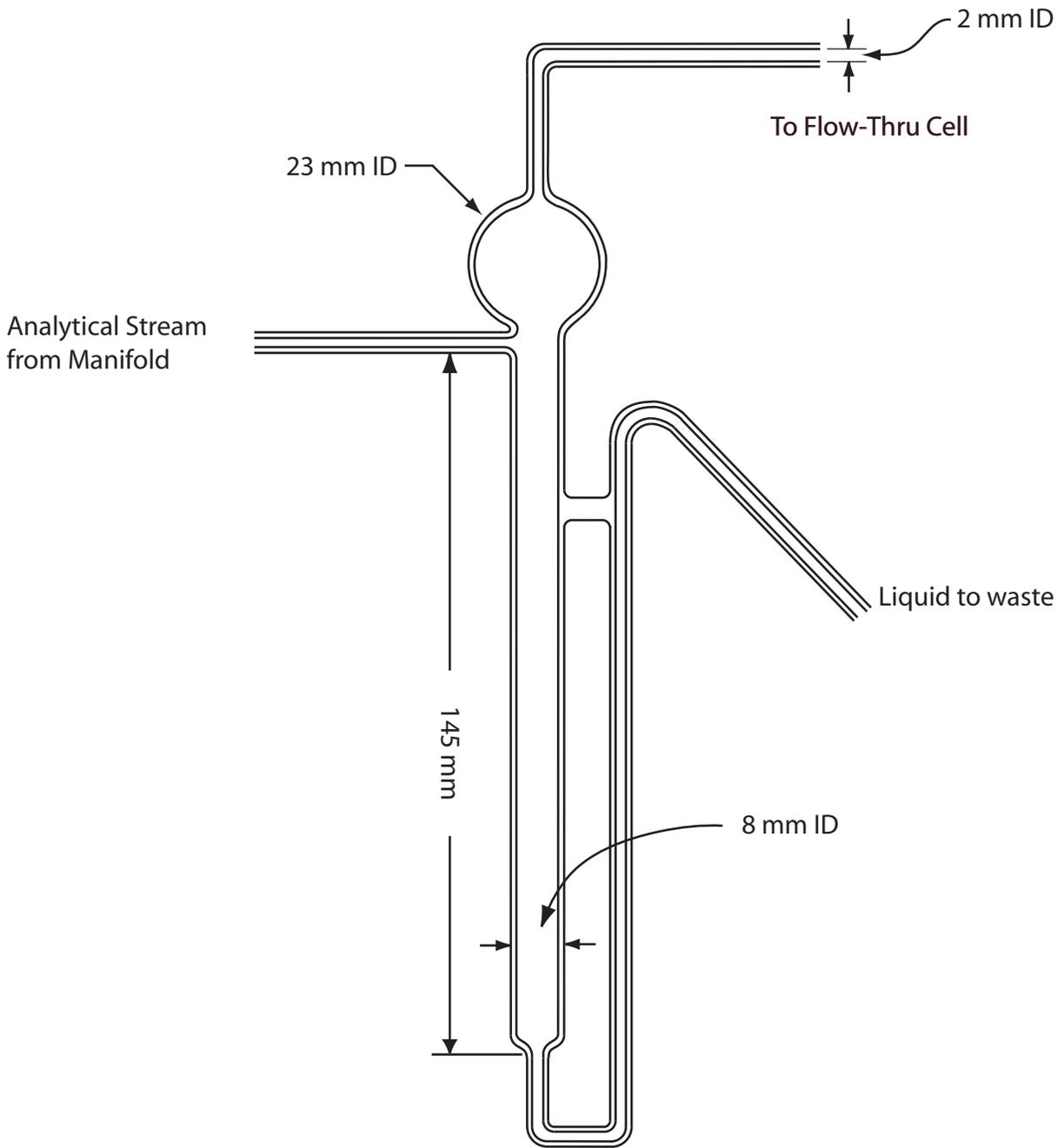


Figure 2. Phase separator used in the determination of mercury .  
 The separator is made from Pyrex glass. J.G. Crock and  
 others, 1987, U.S. Geological Survey Open-File Report  
 87-84, p. 17.

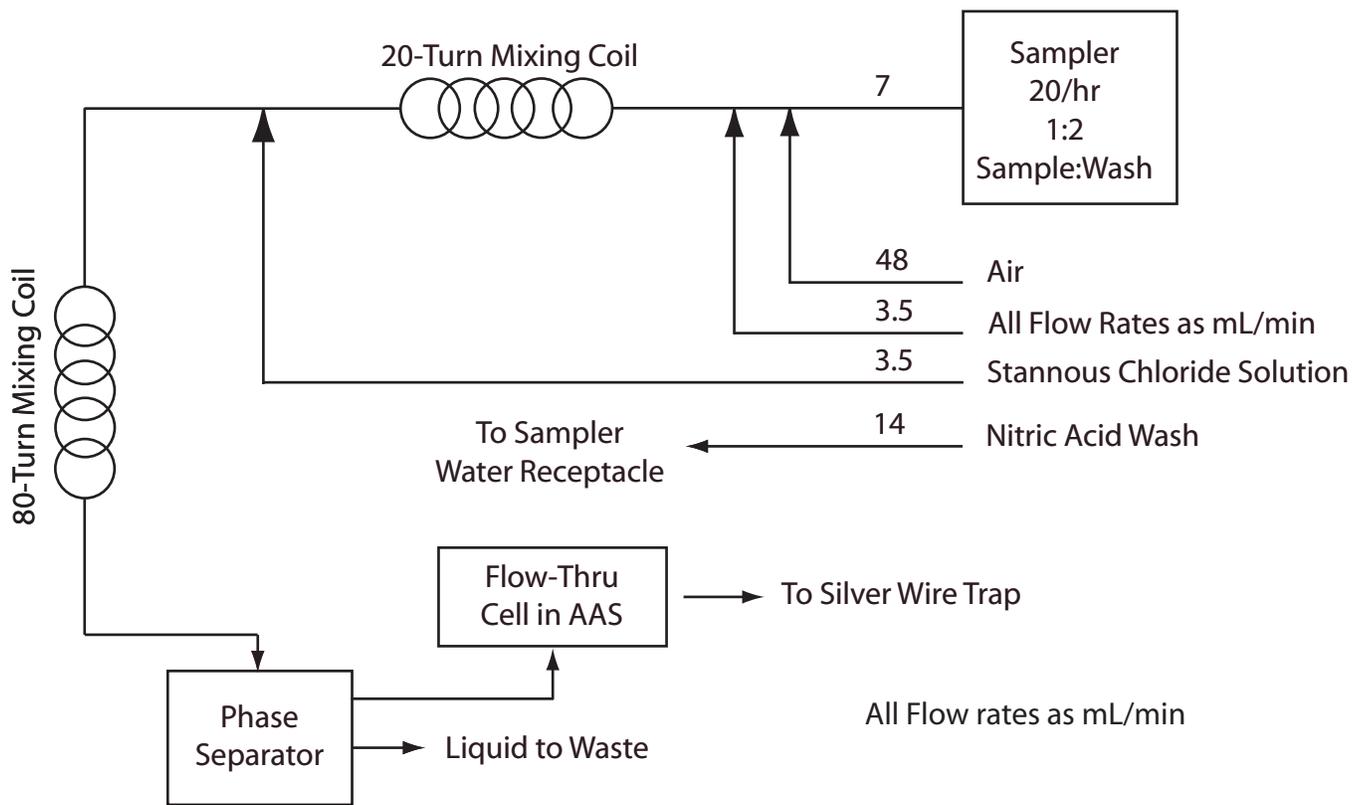


Figure 3. Manifold used for the automated generation of mercury vapor.  
 J.G. Crock and others, 1987, U.S. Geological Survey  
 Open-File Report 87-84, p. 19.