



Project Summary

Collection Efficiency Evaluation of Mercury-Trapping Media for the SASS Train Impinger System

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This report reviews results of a project that involved generation of mercury atmospheres of known and stable concentrations and evaluation of the efficiency of mercury collection using the following trapping media:

- 10 percent hydrogen peroxide.
- 0.2M ammonium persulfate.
- 0.2M ammonium persulfate + 0.025M silver nitrate.
- 1.5 percent potassium permanganate in 10 percent sulfuric acid.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

For purposes of monitoring and development of control technology, it is important that accurate and precise methods for sampling and analysis of source emissions of mercury be available. The primary focus of this project has been the evaluation of such sampling methods.

Commonly used sampling methods for determination of mercury emissions from stationary sources include the use of the Source Assessment Sampling System (SASS), the EPA Method 5 train, or similar sampling devices. In all such

mercury collection devices, impingers containing chemical solution effective in collecting and retaining mercury and other volatiles are used. Other mercury collecting procedures utilize solid materials for collection. In general, collection media considerations have been reagent purity, possible interferences during quantification, collection efficiency at high volume sampling, reagent stability, cost, and compatibility with other impingers in the sampling train.

In spite of a number of available collection media consisting of metals, sorbants, and absorbing solutions, poor collection efficiencies have been reported during the stationary source sampling. The methodology for evaluating the collection efficiency of these various media has been given less attention in the past—in particular, analytical accuracy of standard "sources" of mercury. Subsequently, this work was undertaken (1) to develop an accurate standard mercury source, and (2) using this source, to test several of the popularly used mercury collection media.

Experimental

Description of Mercury Test Atmosphere Generation System

Figure 1 shows the mercury generator schematically. It is essentially based on a saturation technique reported by E. P. Scheide et al. in 1979, with some modifications. A stream of carrier gas (nitrogen) is passed through a dryer and a 60 μ m filter to remove impurities. The nitro-

gen stream then passes through a flow meter and a regulating valve before it is split into two streams. One stream goes through a regulating valve and a high flow rotameter and then to a dilution flask (Dilution Stage I in Figure 1). The other nitrogen stream flows through a regulating valve, through a low flow rotameter and into the generator which consists of:

- Mercury reservoir/vaporizer. A specially designed flask which contains a pool of liquid mercury (30-50 g) that is electrically heated and temperature controlled.
- Condensers. Two Graham condensers wrapped in insulating material and connected in series, through which cold water is continuously circulated. The temperature of the condensers is controlled to at least $\pm 0.1^\circ\text{C}$ by connecting them to a water source from a constant temperature bath capable of maintaining temperature down to -5°C . The temperature of the exit gas containing mercury is monitored with a thermometer at the top of the second condenser.

- After leaving the condensers, the gas stream containing mercury passes into a 1000 ml flask where it is mixed with additional nitrogen to produce the desired levels of airborne mercury.
- The gas stream exiting from the dilution flask may be passed through a quartz cell placed in the light path of an atomic absorption spectrometer (AAS). This arrangement allows a direct measurement of generated mercury vapor concentrations (following calibration of the AAS system). The exhaust gases from the quartz absorption cell are passed into an absolute mercury trap which contains a mixture of activated charcoal and Hopcalite.

Generator Performance Evaluation

Initial experimental work with the generator included evaluation of its capability to produce stable atmospheres of mercury. For this, the output from the dilution flask was passed directly through the quartz cell placed in the light path of the atomic absorption spectrometer (AAS) which provided readings in absorbance

units. These absorbance readings were monitored as a measure of the stability of the mercury atmosphere generation. Through repeated attempts for steady mercury atmosphere generation, the following observations were made:

- It is not necessary to heat the mercury reservoir for generation of mercury atmospheres in the range of 10 to 100 $\mu\text{g}/\text{m}^3$, which is the estimated range of source emissions.
- A steady (± 5 percent) low flow of nitrogen through the mercury reservoir is required (range 0.25 to 1.85 L/min) for the desired mercury concentration ranges.
- Maintenance of a precise temperature of $2^\circ\text{C} \pm 0.1^\circ\text{C}$ at the condensers is found to be essential for stable mercury atmosphere generation.

Using the above conditions, test mercury atmospheres were generated and monitored using the on-line AAS. Figure 2 shows the steady generation of mercury for more than a 5-hour period, as monitored using a strip chart recorder.

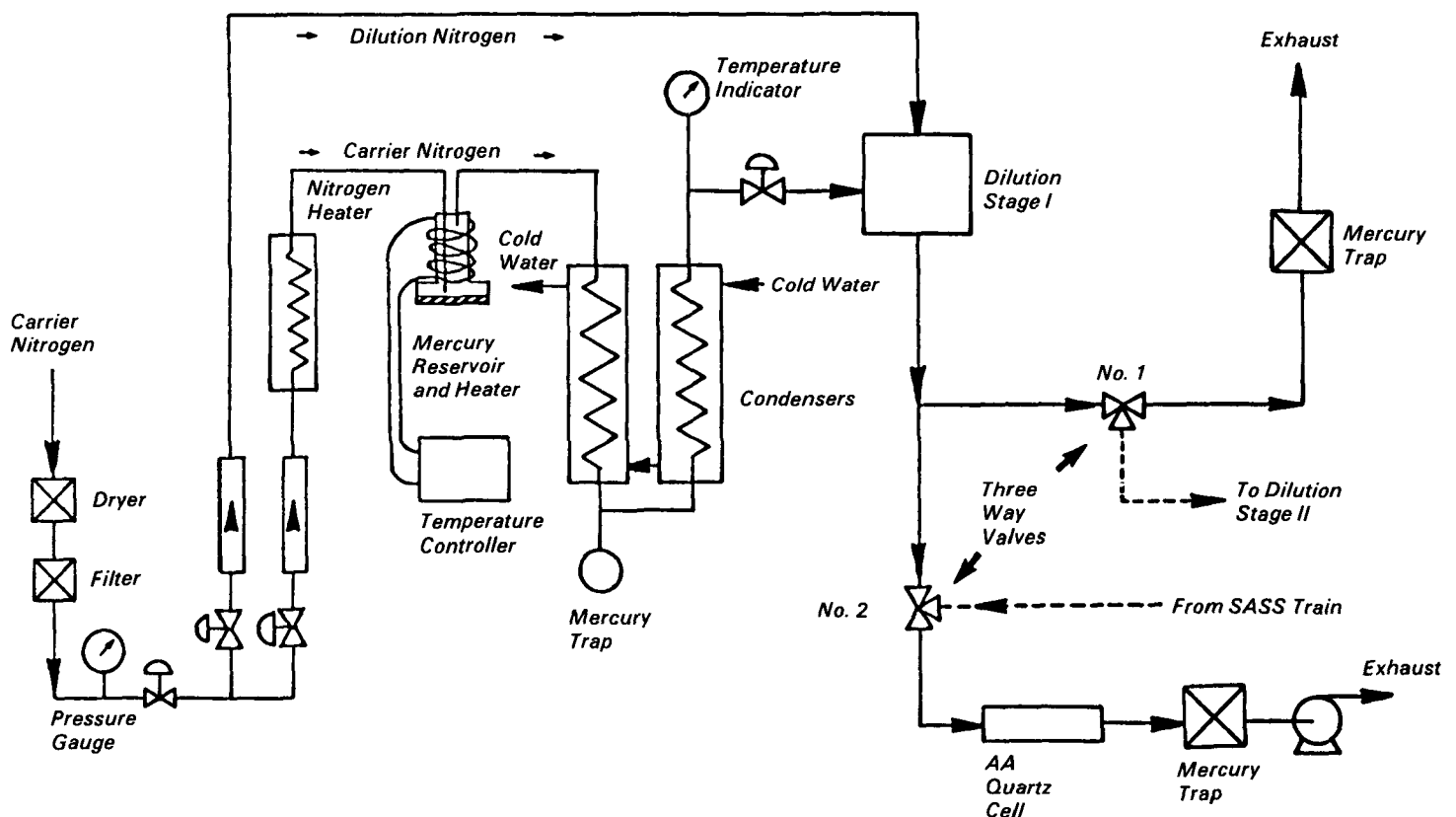


Figure 1. Schematic of mercury generation system.

Quantification of Mercury Levels in the Test Atmospheres

To determine concentrations of mercury in the generated test atmospheres, the system connections and tubing after the dilution flask were modified by incorporating two three-way valves, one after the dilution flask and one before the quartz absorption cell. With these changes the test atmospheres containing mercury could be passed through the quartz cell or, when required for concentration determinations and/or collection efficiency evaluations, through a series of impingers. The exit gas from the last impinger could be directed to the quartz cell via a moisture trap and a second three-way valve.

The mercury vapor concentrations were experimentally determined by collecting vapor for a known period of time in two impingers in series and then analyzing the impinger solutions. The collection media was 1.5 percent potassium permanganate in 10 percent (v/v) sulfuric acid; 50 mL of this media was contained in each 75-mL capacity impinger. The sampling rate was 980 cc/min. The exit gas from the second impinger was fed into the quartz absorption cell during the sampling process via a moisture trap which contained magnesium perchlorate.

The mercury in the impinger solutions was determined using the procedure in EPA-600/7-78-201. This procedure involves chemical conversion of all mercury present in solution to the elemental form and sweeping this Hg⁰ into the quartz cell of the spectrometer with a stream of nitrogen. Standards were prepared by spiking collection media with known quantities of mercury ion. Quantification was performed through comparison of absorption peak areas obtained with the impinger and standard solutions. All samples from the second impingers were found to contain mercury levels below the detection limits of the method which was 0.05 µg of mercury.

Further experimental work included generation of test atmospheres which contained varying levels of mercury. This was achieved by increasing and/or decreasing the dilution ratio. Samples were collected and analyzed to establish a relationship between experimentally determined mercury concentrations in the test atmospheres and absorbances of the test atmospheres. Figure 3 shows an approximately linear relationship between experimentally determined mercury concentrations and AAS absorbance readings for mercury concentration below 600 µg/m³.

Results and Discussion

With the successful generation of known and stable mercury atmospheres, evaluation of its collection efficiency at high volume sampling rates became the objective of the project work. For this experimental work some changes were made, including:

- Addition of a second 1000 mL dilution flask, following the first dilution flask (see Figure 1), through which filtered compressed air was passed at a high volume rate, 3-6 cfm (85-170 L/min).
- Use of three SASS train impingers in series, replacing impingers in the sampling system discussed earlier.
- Incorporation of a high volume calibrated sampling pump.
- Incorporation of one additional three-way valve after the second dilution flask so that test atmospheres with or without mercury could be passed through the impingers and then into the quartz cell via a moisture trap.

With the changes made in the system for sampling at SASS sample collection rates, the following media were tested for mercury collection efficiency:

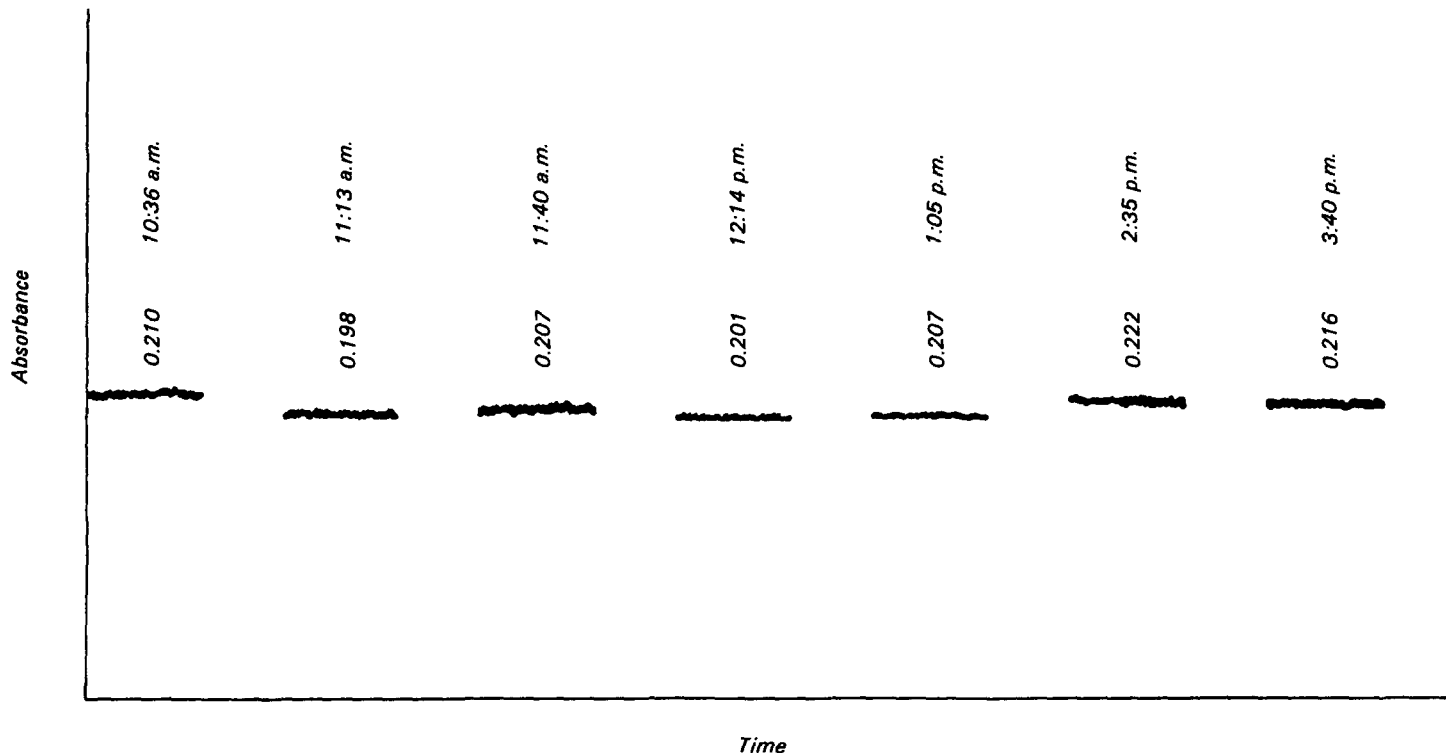


Figure 2. Absorbance level measured at various times with mercury vapor generator operating continuously.

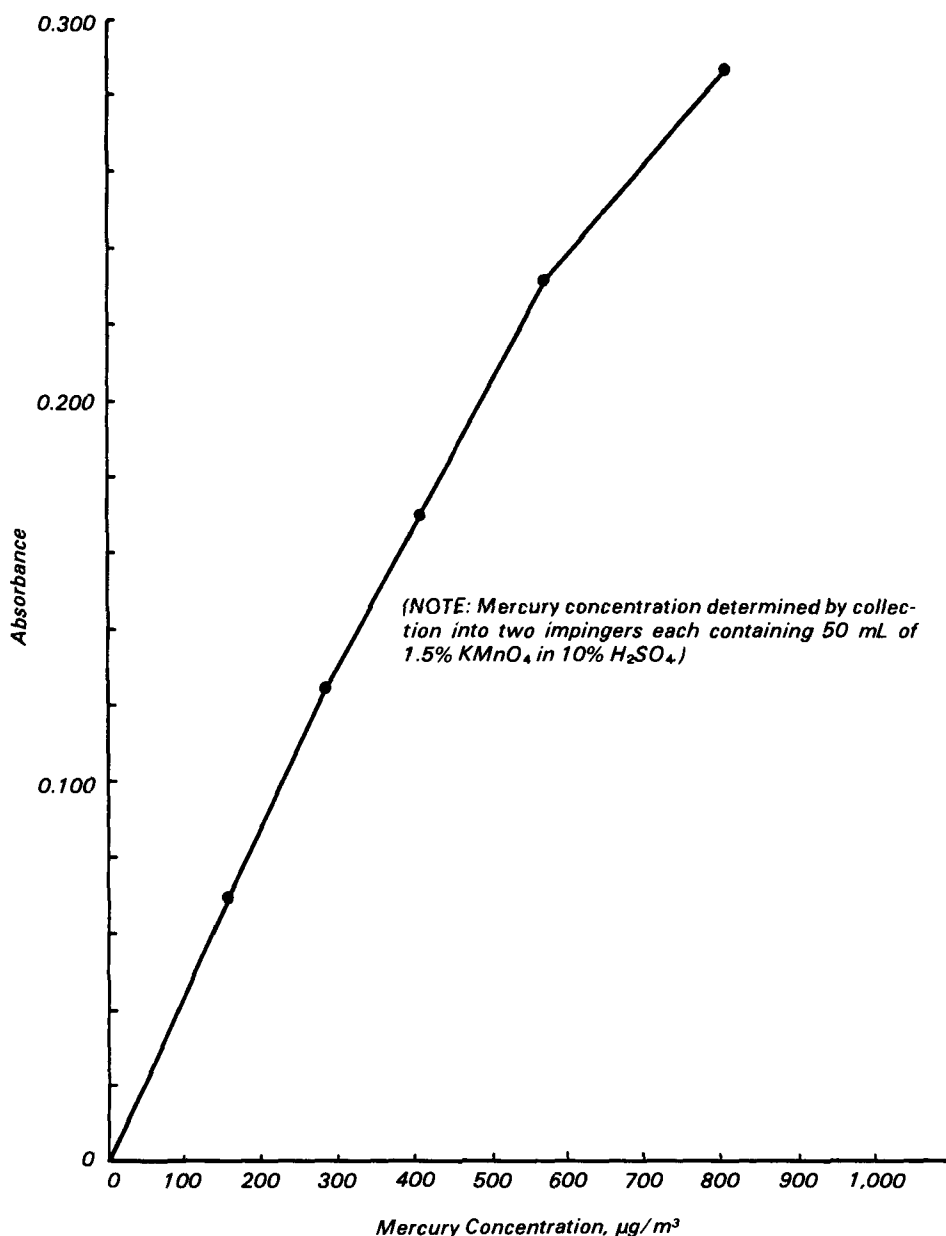


Figure 3. Absorbance vs. generated mercury concentration.

- (1) 10 percent hydrogen peroxide (v/v).
- (2) 10 percent hydrogen peroxide in 10 percent sulfuric acid.
- (3) 0.2M ammonium persulfate (w/v).
- (4) Freshly prepared solution of 0.2M ammonium persulfate + 0.025M silver nitrate (w/v).
- (5) Aged (48 hours) solution of 0.2M ammonium persulfate + 0.025M silver nitrate.
- (6) 1.5 percent potassium permanganate in 10 percent sulfuric acid.

Figure 4 depicts typical sampling and medium collection efficiency events as recorded on the strip chart recorder when using 1.5 percent KMnO_4 in 10 percent H_2SO_4 . Sampling time was 1 hour, and each impinger had 250 mL of trapping medium.

Collection Efficiency Measurements

Utilizing the mercury atmosphere generation system and the sampling approach described, the collection efficien-

cies of the above mentioned media were investigated. Data obtained are summarized in Table 1.

10 Percent Hydrogen Peroxide

Three SASS impingers in series, each containing 250 mL of 10 percent hydrogen peroxide solution, were used for collection efficiency evaluations. Three sampling runs were made at test atmosphere mercury concentrations of $70 \mu\text{g}/\text{m}^3$, and one run was made at a mercury concentration of $10 \mu\text{g}/\text{m}^3$. The collection efficiency of the medium was poor; i.e., only about 20 percent. Further experiments at low mercury levels with acidification of the hydrogen peroxide with 10 percent sulfuric acid did not improve its collection efficiency, which remained about 20 percent.

During this effort, the procedure given in EPA-600/7-78-201 was followed for analysis of the hydrogen peroxide medium. This involved taking a 10 mL aliquot of the hydrogen peroxide solution and adding 5 percent acidified permanganate solution to destroy excess peroxide. Experience indicates that a considerable volume of permanganate solution needs to be added to destroy the excess peroxide; this point should be emphasized in EPA-600/7-78-201, the EPA Level 1 manual.

Although inefficient, the collection of about 20 percent of the mercury vapor by the hydrogen peroxide impingers must be considered significant in terms of mercury distribution in the SASS train impinger system. Generally, hydrogen peroxide impingers in the SASS train or EPA Method 5 train precede mercury collection impingers. This project work indicates that these hydrogen peroxide impingers also need to be analyzed to get true concentrations of mercury emitted from a stationary source.

0.2M Ammonium Persulfate

The collection efficiency in this medium at the high mercury concentration was 29* percent and at the low mercury concentration was 25* percent.

0.2M Ammonium Persulfate with 0.025M Silver Nitrate

Duplicate sampling runs at both mercury levels showed better than 99 percent collection efficiency with the three-impinger SASS sampling system. However, one impinger showed only 74* percent collection efficiency. This means that, for

*Estimated coefficient of variation is 10 percent.

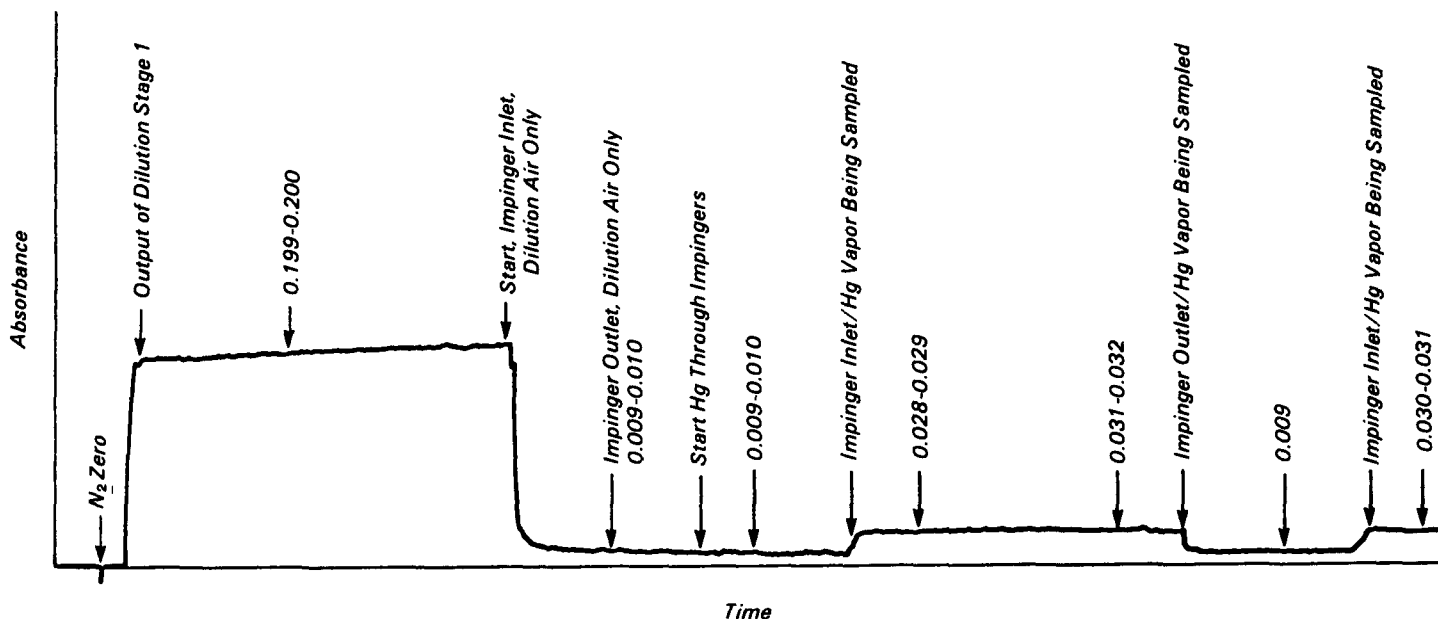


Figure 4. Recording of absorbance vs. time at various points in the mercury vapor generation/sampling system.

better than 98 percent collection efficiency, three impingers of this medium are required.

Further collection efficiency evaluation work included aging of the 0.2M ammonium persulfate/0.025M silver nitrate solution for 48 hours in a refrigerator and then using it in the three impingers. The collection efficiency of the medium at high mercury concentration was found to have gone down to 82* percent and for low concentration was 79* percent.

1.5 Percent $KMnO_4$ with 10% H_2SO_4

Three SASS impingers, each containing 250 mL of this medium at high ($70 \mu g/m^3$) and low ($10 \mu g/m^3$) mercury levels in test atmospheres, were tested. For both concentrations, the collection efficiency was found to be better than 99 percent with the three-impinger sampling system. One impinger alone, containing 250 mL of acidified potassium permanganate, was found to collect 94* percent of mercury from the test atmospheres containing high levels of mercury; this two-impinger system appears adequate for optimum collection efficiency.

*Estimated coefficient of variation is 10 percent.

Table 1. Summary of Mercury Collection Efficiency of Various Media^a

Medium	Number of Runs	Average Sampling Rate cfm	Average Collection Efficiency, %
10% hydrogen peroxide	4 ^b	4.25	20.9
Acidified 10% hydrogen peroxide	1	3.93	18.2
0.2M ammonium persulfate	2 ^b	3.75	26.8
Freshly prepared 0.2M ammonium persulfate + 0.025M silver nitrate	4 ^c	4.00	>99.0
Freshly prepared 0.2M ammonium persulfate + 0.025M silver nitrate	1 ^d	4.33	73.3
Aged 0.2M ammonium persulfate + 0.025M silver nitrate ^e	2 ^b	3.75	80.1
1.5% potassium permanganate in 10% sulfuric acid ^f	2 ^b	4.67	>99.0
1.5% potassium permanganate in 10% sulfuric acid	1 ^d	5.24	94.4

^aThree-impinger system was used unless otherwise specified. Sampling times in most cases were 60 minutes; exceptions are mentioned in the text. Room temperature was in the range of 20-25°C, and data on efficiency are based on relative absorbance readings at the inlet and outlet of the impingers.

^bIncludes one run at low mercury levels.

^cIncludes two runs at low mercury levels.

^dOnly one impinger containing 250 mL of medium was used.

^eAged for 48 hours in the refrigerator.

^fSampling times less than 60 minutes. See details in text.

The collection efficiency calculations are based only on the relative absorbance readings of the AAS taken at the inlet and outlet of the impingers. This method of calculating collection efficiency is considered valid in view of the fact that a linear relationship between AAS absorbance readings and mercury concentrations in the test atmospheres was established.

Conclusions and Recommendations

In conclusion, a simple mercury generator, capable of producing known and stable mercury-containing test atmospheres, was constructed and operated successfully. Incorporating an on-line atomic absorption spectrometer with a quartz absorption cell provided a method for continuously monitoring the performance of the mercury vapor generator and also a method for direct measurement of collection efficiencies. Of the mercury collection media investigated, the 1.5 percent KMnO_4 in 10 percent H_2SO_4 appeared promising when tested under laboratory conditions. The collection efficiency of the 1.5 percent acidified KMnO_4 solution needs to be verified through field testing. Similarly, collection efficiency needs to be verified by performing material balance; i.e., by analyzing individual impinger solutions. Although acidified KMnO_4 appears to be an efficient medium for mercury collection, it has stability and storage problems; these need to be fully investigated before the method can be considered for field use.

Hydrogen peroxide was tested as a collection medium following EPA Level 1 procedures. Although collection efficiency was low, two relevant observations were made: (1) a considerable volume of permanganate solution was necessary to destroy the excess peroxide; and (2) since hydrogen peroxide results in some mercury collection, hydrogen peroxide impingers (which normally precede mercury collecting impingers in the SASS or EPA Method 5 trains) should be analyzed for mercury.

Finally, other mercury collection media (e.g., iodized charcoal, Hopcalite, iodine monochloride, and acidified potassium dichromate) need to be studied.

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Frank E. Briden is the EPA Project Officer (see below).

The complete report, entitled "Collection Efficiency Evaluation of Mercury-Trapping Media for the SASS Train Impinger System," (Order No. PB 84-243 112; Cost: \$8.50, subject to change) will be available only from:

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