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Revisions to Methods 101, 101A, and 102 for Determination of Mercury Emissions

Summary of Comments and Responses

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Revisions to Methods 101, 101A, and 102 for Determination of Mercury Emissions (Proposed October 15, 1980, 45 FR 68514)

Summary of Comments and Responses

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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CHAPTER 1

INTRODUCTION

On October 15, 1980, the U. S. Environmental Protection Agency published in the Federal Register (45 FR 68514) revisions to Methods 101 and 102, "Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants - Air Streams," and "Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants - Hydrogen Streams," respectively, and a new Method 111, "Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators." Method 111 has been redesignated as Method 101A. These revised methods and new method were proposed under the authority of Sections 112, 114, and 301(a) of the Clean Air Act, as amended.

Public comments were solicited at the time of proposal. To provide interested persons the opportunity for oral presentation of data, views, or arguments concerning the proposed revisions and test methods, a public hearing was scheduled for November 6, 1980, at the Research Triangle Park, North Carolina, but no person desired to make an oral presentation. The public comment period was from November 6, 1980, to December 15, 1980, and was extended to February 13, 1981.

Five comment letters were received concerning issues relative to the proposed test methods. A detailed discussion of these comments and responses are summarized in this document. The summary of comments and responses serves as the basis for the revisions which have been made to the test methods between proposal and promulgation.

CHAPTER 2

SUMMARY OF CHANGES SINCE PROPOSAL

Method 101

1. Section 4.2. A performance specification has been added to allow the use of acceptable alternative equipment and procedures.

2. Section 5.3. Criteria for accepting alternative analysis apparatus are added.

3. Section 5.3.2. Asbestos insulation tape is replaced with fiberglass insulation tape.

4. Section 5.3.9. Dry, mercury-free air is included as an option for the aeration gas.

5. Section 6.2.2. It is specified that all mercury standard solutions be prepared in borosilicate glass containers.

6. Section 7.1.3. The asbestos string gasket used with the probe nozzle is replaced with a fiberglass string gasket.

7. Section 7.3.2. The first sentence has been reworded to provide technical clarity.

8. Section 8.3. The option to measure the mercury response by either peak height or peak area is added.

9. Section 9.4. $C_{Hg(AC)}$ was corrected to represent total nanograms of mercury in the aliquot analyzed as opposed to the final mercury concentration.

Method 101A

1. Section 4. A performance specification has been added to allow the use of acceptable alternative equipment and procedures.

2. Section 6.2.5. It is specified that all mercury standard solutions be prepared in borosilicate glass containers.

3. Section 7.1.1. Two runs are collected to make one sample where an excess of water condensation is encountered.

4. Section 7.2.1. The first three impingers are included in the $KMnO_4$ rinse for mercury recovery.

5. Section 8.3. The option to measure the mercury response by either peak height or peak area is added.

CHAPTER 3

SUMMARY OF PUBLIC COMMENTS AND RESPONSES

Method 101

1. D-2

Comment: Method 101A uses $KMnO_4$ as the absorbing medium. We have extensively and successfully employed $KMnO_4$ to determine Hg concentrations in gaseous and aqueous streams. We recommend that $KMnO_4$ be specified as an acceptable alternative to ICl for use in the collecting liquids for Methods 101 and 102.

Response: ICl was specified for chlor-alkali plants because the literature indicates that ICl is a better oxidizing agent for elemental Hg and a more stable reagent than $KMnO_4$. Chlor-alkali plants primarily emit elemental Hg, while sludge incinerators emit Hg compounds. Thus a strong, fast acting oxidizing reagent is needed for chlor-alkali plants but not sludge incinerators. However, this does not mean that $KMnO_4$ is unacceptable for chlor-alkali plants. If comparative data are made available to EPA, consideration will be given to the use of $KMnO_4$ for chlor-alkali plants.

2. D-4

Comment: Paragraph 7.3.2 is confusing. What is the rationale for pipetting separate flasks? We believe that separate aliquots from the same flask would be satisfactory. Also, why is it necessary at all to dilute at this point? This technique would reduce sensitivity by a factor of 100.

Response: The first two sentences in the paragraph have been corrected to read, "Pipet a 2-ml aliquot from the diluted sample (from Section 7.3.1) into a 250-ml volumetric flask. Add 10 ml of 5 percent H_2SO_4 and adjust the volume to exactly 250 ml with deionized distilled water." This dilution step is necessary to reduce the ICl concentration to a level that will not inhibit Hg reduction in the aeration cell and to bring the Hg concentration within the range of the AA.

3. D-2, D-3, D-4

Comment: Errors in the following sections should be corrected:

a. 5.1.2 Temperature should be 120 instead of 12.

b. 5.1.3 "Lead-free" should be "Leak-free."

c. 5.3.9 Omit the slash between nitrogen and cylinder.

d. 6.2.5 Reference to 7.2.5 should be changed to 7.2.3.

e. 9.4 (1) Use the calibration curve and these corrected averages, to determine the total weight of mercury in nanograms in the aeration cell for each source sample, not concentration.

(2) In Section 9.4, M_{Hg} should be m_{Hg}.

(3) Under Eq. 101-1, add: "where: $C_{Hg(AC)}$ = Total nanograms of mercury in aliquot analyzed (reagent blank subtracted)," and change D.F. = 250/2 if the source samples were diluted as described in Section 7.3.2, not 7.3.3.

(4) Eq. 101-2 uses R for emission rate and K for gas constant. The gas constant is universally designated R.

(5) V_s, $V_{m(std)}$, and $V_{w(std)}$ in Eq. 101-2 should be defined.

Response: These corrections have been made. K is not a gas constant but a numerical/dimensional constant. The terms in item (5) are defined in Sections 9.1, 9.2, and 9.3.

Method 102

4. D-2

Comment: In 2.3, add the word "mixture" after the word "explosive."

Response: This suggestion has been incorporated.

Method 101A

5. D-1

Comment: The sampling procedure as set forth by Method 101A, in general, is viewed as satisfactory.

Response: No response needed.

6. D-1

Comment: The change from ICl to $KMnO_4$ is viewed as favorable. $KMnO_4$ can be obtained in purer form than ICl, thus allowing for a lower Hg concentration in the blank.

Response: No response needed.

7. D-1

Comment: The use of $KMnO_4$ as a rinse of the probe nozzle, probe fitting, probe liner, and front half of the filter holder would be quite messy and would tend to increase the mercury in the sample if the $KMnO_4$ is contaminated. Perhaps it would be wise to consider using 8 N HCl as the rinse since it would be more effective in removing residual brown deposits and is less messy than $KMnO_4$.

Response: $KMnO_4$ is not used in the front half of the train during sampling, so no brown deposit is formed. The use of $KMnO_4$ is preferred over 8 N HCl because it is less caustic and can better oxidize and remove mercury deposits left from the previous sample. The blank would reveal whether the $KMnO_4$ was contaminated.

8. D-1

Comment: The use of a stainless steel wire screen is highly recommended as opposed to a glass frit support for the same reason as stated in the proposed revisions.

Response: No response needed.

9. D-4, D-5

Comment: The use of a stainless steel wire screen ignores the possibility of loss of mercury through amalgamation or adsorption on the wire screen.

Response: The use of a filter in this method is optional to accommodate sources with high particulate loading. At these sources, essentially all Hg emissions are in the compound form. Glass frits were found to be a source of cross contamination and are, therefore, unacceptable.

Methods 101, 101A, and 102

Analytical Alternatives

10. D-1, D-4, D-5

Comment: The EPA Method 245.1 from Methods for Chemical Analysis of Water and Wastes (EPA 600/4-79-020) should be incorporated as the preferred analytical method. This procedure is well documented and established as producing precise and accurate results. Most laboratories involved in stack testing will have the equipment and expertise to routinely perform this analysis.

Response: This method is not equivalent to the Method 101A procedure in relation to important dilutions and reagent volumes. Some deficiencies have been found in the analytical apparatus that are resolved in Method 101A (discussed in Citation 16 of Method 101). The need to condition and periodically replace the desiccant, Hg losses experienced in the BOD bottle, and the technique required to perform this procedure make it less desirable than Method 101A.

11. D-4, D-5

Comment: Section 5.3.1 specifies a Perkin-Elmer 303 AA or equivalent. Since the 303 AA is a versatile spectrophotometer, the phrase "or equivalent" eliminates the possibility of using one of the commercially available instruments specifically designed for determining Hg by flameless AA. They are equal to or superior to the 303 for the analysis of Hg and are much less expensive.

Response: Substitution of such commercially available systems is allowable as long as they meet the calibration and analytical precision and accuracy specified in the method. The following guidelines will be added to the method.

a. The reducing agent should be added after the aeration cell is closed.

b. The aeration bottle bubbler should not contain a frit.

c. Any Tygon used should be as short as possible and conditioned prior to use until blanks and standards yield linear and reproducible results.

d. If manual stirring is done before aeration, it should be done with the aeration cell closed.

e. The system must be demonstrated to have accuracy and precision equivalent to the method (done through replicate analyses of spiked samples and/or analysis of samples of known concentration obtained from a reliable source).

f. A drying tube should not be used unless it is conditioned as the Tygon above.

12. D-2

Comment: Certain other methods than atomic absorption spectrophotometry for analyzing the absorbing solution are acceptable alternatives and should be allowed. It is recommended that direct current argon plasma emission spectrometry (APES) be included in the test methods as an alternative to atomic absorption. Attached is a reprint which elaborates on the use of APES.

Response: Alternative methods are allowed on a case-by-case basis. In the case of the APES method, the level of operator skill and equipment needs are much higher than most companies will have available. It is a sophisticated technique that yields results very sensitive to operator technique and, therefore, is not readily adaptable at this time to routine, widespread use.

Variations in Equipment Specifications

13. D-2, D-4, D-5

Comments: (a) Variations in the dimensions of the optical cell should be allowed because: (1) calibration with a given cell adjusts for its peculiarities. (2) The dimensions specified do not coincide with cells in commercially available instruments. (3) The large diameter (3.81 cm) of the optical cell reduced mixing and sensitivity, both of which lead to poorer analysis. (4) The aeration flask specified is fragile and would be very difficult to clean properly. It would be a major problem in routine use. (5) Some commercially available instruments use a recirculating, rather than a flow-through system. Studies reported in the literature have shown recirculating systems to be as valid as the once through system. Since the absorbance is read when the Hg concentration reaches equlibrium, there is no need for a recorder.

(b) Alternative heating devices should be allowed because: (1) Other devices achieve the same effect. For example, infrared lamps have been used. The Agency 245.1 allows the use of a desiccant and a 60-watt incandescent lamp to prevent condensation in the optical cell.

(2) Moisture condensation is not normally a problem, and, therefore, heating the optical cell is not necessary; this may be a particular problem resulting from the proposed large diameter optical cell.

(c) The use of flexible Tygon tubing should be allowed as an alternative to glass in the aeration cell-to-optical cell conncection for the following reasons: (1) The EPA allows its use in Method 245.1 for Hg analysis of water and wastes. (2) Flexible tubing is necessary for some of the comercially available systems. (3) The standard practice of daily conditioning the system with 5 to 10 µg of Hg eliminates any problems resulting from the choice of tubing. (4) Use of flexible tubing allows for mixing by swirling the aeration flask and eliminates the need for a magnetic stirrer. Silicone tubing has been found to be completely satisfactory, too.

Response: The analytical equipment described in Methods 101, 101A, and 102 (aeration bottle, all glass tubing connection, single pass system, optical cell heating) is significantly different from that allowed in EPA 245.1. The equipment was designed to minimize imprecision and inaccuracy in the analysis. Maximum accuracy and precision is necessary because of sampling costs and the dilutions required to bring the sample concentration into the range of the flame AA. Method 101 is more accurate and precise than EPA 245.1 as can be seen by comparison of the precision and accuracy of both methods.

However, since the research on Methods 101 and 102, commercially available systems have been developed that are just as accurate and precise. Therefore, substitution of these systems will be allowed as long as they meet the guidelines stated in the response to Comment 11.

Miscellaneous

14. D-2

Comment: The proposed changes will improve the accuracy and precision of the sampling and analysis methods.

Response: No response needed.

15. D-4, D-5

Comment: The use of nitrogen is not essential. Dried, filtered, Hg-free air is adequate.

Response: We agree. Section 5.3.9 has been revised to read, "Aeration Gas Cylinder. Nitrogen or dry, Hg-free air, equipped with a single stage regulator."

16. D-4, D-5

Comment: The use of an asbestos gasket with the probe nozzle and asbestos insulation tape is inconsistent with the Agency's position relative to the use of asbestos substitute materials. Many laboratories have abandoned use of these products.

Response: Fiberglass tape may be substituted. Sections 5.3.2 and 7.1.3 have been revised to read "fiberglass tape" and "fiberglass gasket," respectively.

17. D-4, D-5

Comment: For the flow-through system, measurement of the peak area is far more precise and sensitive than the peak height. This also eliminates the need for precise control of temperature and volume.

Response: Our data showed that either peak height or area was acceptable. Either may be used. The following sentence will be added to the beginning of Section 8.3: "The mercury response may be measured by either peak height or peak area."

18. D-4

Comment: The Method of Standard Additions should be detailed in some way, perhaps as an appendix.

Response: The method is described in Citation 19 of Method 101.

19. D-3

Comment: Why is the source sample initially diluted with deionized distilled water? This only serves to decrease the sensitivity of the test. If all rinses were done with 0.1 M ICl and the total volume was then measured, a 2-ml aliquot of sample diluted to 250 ml as described in the second dilution step would yield a 0.0008 M ICl solution. If a 5-ml aliquot of this solution was pipetted into the aeration flask (containing 50 ml of deionized water), the final solution would be 0.00008 M ICl, which would not inhibit the reduction of Hg.

Response: These dilutions are needed to bring the sample concentration into the range of the spectrophotometer. In doing so, an accurate initial volume is needed. The source sample volume after recovery is approximately 550 to 600 ml. Because the density of this solution is uncertain after collection, weighing is not a suitable method of determining volume. Similarly, the graduations on a 0 to 1000 ml graduated cylinder that would be needed (if dilution in a volumetric flask is not done) would be too large for accurate measurement.

20. D-3

Comment: It would be helpful to state the minimum total ng detectable in the aeration cell. This works out to about 20 ng.

Response: This depends upon the sensitivity of the system.

21. D-4

Comment: We recommend that the mercury stock solution be stored in and pipetted into borosilicate glass bottles, and not plastic bottles.

Response: This has been incorporated into the method.

22. D-3

Comment: In cleaning glassware, the Preparation of Sampling Train Section and the Calibration and Standards Section do not agree. The procedure in the latter section of prolonged soaking with 50 percent nitric acid should be the first step in cleaning glassware.

Response: Equipment in the Preparation of Sampling Train Section is not soaked because this would be difficult for probes. Recovery studies have shown that the specified rinsing is an acceptable method for avoiding contamination. Also, the washing procedure is done after each sample while the sample recovery for the previous run is being performed.

TABLE 1. LIST OF COMMENTERS

Docket No. A-79-45

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15 SUPPLEMENTARY NOTES

16. ABSTRACT

This document addresses the public comments submitted after proposal of the mercury methods in the Federal Register. Changes made to the methods as a result of these comments are included. This document serves as the basis for the revisions which have been made to the test methods between proposal and promulgation.

17. KEY WORDS AND DOCUMENT ANALYSIS

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