



**AN UPDATE AND DISCUSSION OF THE CRITICAL ASPECTS  
OF PROPOSED EPA REFERENCE METHOD 6B**

**JULY 1982**

**Office of Air, Noise and Radiation  
Division of Stationary Source Enforcement  
Washington, D.C. 20460**

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OF PROPOSED EPA REFERENCE METHOD 6B

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## Executive Summary

The U.S. EPA has undertaken the development of Reference Method 6B, a wet-chemical method which can be used in lieu of, or as a back-up for sulfur dioxide continuous emission monitoring systems required at stationary sources of air pollution. The measurement technique for Method 6B is based upon the simultaneous determination of sulfur dioxide and carbon dioxide with emission rates, in units of  $\text{lb SO}_2/10^6 \text{ Btu}$ , computed according to the F-Factor method. Method 6B has evolved significantly since its proposal in early 1981. In this report, Method 6B, as it is currently envisioned for promulgation, is described, and in addition, the reasons for the changes to the method that have occurred since proposal are briefly discussed.

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## Introduction

Since 1971<sup>1</sup>, fossil fuel fired steam generators subject to New Source Performance Standards (NSPS) have been required to install monitors to measure emission rates of sulfur dioxide in units of lb SO<sub>2</sub>/10<sup>6</sup> Btu heat input. Two monitors are required for determining SO<sub>2</sub> emission rates: (a) an SO<sub>2</sub> monitor and (b) a diluent monitor which measures either oxygen or carbon dioxide. From the pollutant and diluent data provided by the monitors, emission rates can be computed according to the F-Factor Method.<sup>2</sup> The emission rate data supplied by these monitors, commonly termed continuous emission monitors (CEMS), may be interpreted by the Agency as being indicative of the operation and maintenance of the source's air pollution control system.

The scope of continuous emission monitoring requirements was significantly broadened when New Source Performance Standards were promulgated in 1979<sup>3</sup> for "Subpart Da - Electric Utility Steam Generating Units for Which Construction is Commenced After September 18, 1978." According to the continuous monitoring requirements of Subpart Da, the SO<sub>2</sub> emission rate data may be used as indicators of compliance with standards for emission rates and sulfur removal. Emission rates are computed on a 30-day rolling average basis, which itself is calculated from the daily average emission rates determined using continuous emission monitoring systems.

Within Subpart Da it is stated that if minimum daily SO emission rate data cannot be obtained using continuous monitoring systems, then the necessary emission rate data are to be acquired using Reference Methods 3 and 6. However, from the time of the proposal of Subpart Da<sup>4</sup>, it was recognized within the Agency that this method of data acquisition would be potentially burdensome, and consequently, work was started on the development of a sulfur dioxide emission rate measurement method which would be inexpensive, reliable, and accurate, and more importantly, which would be capable of making determinations over time periods as long as 24 hours.

The methodology considered for development was essentially based upon a simple modification of the Reference Method 6 sampling train: a carbon dioxide absorber<sup>5</sup> was placed within the sampling train following the impingers containing the hydrogen peroxide solution. This modification enabled the concurrent determination of sulfur dioxide and carbon dioxide concentrations, which could be used according to the F-Factor method to compute the SO emissions rate in units of lb SO<sub>2</sub>/10<sup>6</sup> Btu. In 1978, Whittle and Westlin<sup>6</sup> reported the results from a field evaluation of "an intermittent integrated SO<sub>2</sub>/CO<sub>2</sub> emission sampling procedure," which demonstrated the feasibility of the methodology with regard to unattended operation and acceptable precision. This methodology was formally proposed as Reference Method 6B in January 1981.<sup>7</sup> (Proposed Reference Methods 6A and 6B are contained in the Appendix.)

At this writing, the method has been sent for "red border review" and has not yet been promulgated. Collaborative testing is scheduled to begin in the Fall of 1982.<sup>8</sup>

This paper has a three-fold purpose:

- (a) to provide those individuals involved in the field of stationary source emission measurement with an understanding of Reference Method 6B as it is currently envisioned for promulgation,
- (b) to update those individuals already familiar with the method regarding developments and changes which have occurred as a consequence of the results of past and ongoing investigations, and
- (c) to provide guidance in the form of recommendations for those who are currently using the method and its variants.

In the sections which follow, a general description of the proposed method is presented first; detailed discussions are then presented which address the critical aspects of the method.



## General Description of Proposed Reference Method 6B

Using the method as proposed, the following can be determined over periods up to 24 hours:

- (a) lb SO<sub>2</sub>/10<sup>6</sup> Btu,
- (b) ppm SO<sub>2</sub> (dry and wet bases),
- (c) %CO<sub>2</sub> (dry and wet bases), and
- (d) %H<sub>2</sub>O.

The sampling train consists of the following major components:

- (a) a heated, glass, or stainless steel probe equipped with a filter (either in-stack, out-of-stack, or both);
- (b) two midjet impingers each containing 15 mL 3% (v/v) hydrogen peroxide to absorb the sulfur dioxide;
- (c) one midjet bubbler containing about 25 g Drierite<sup>®</sup> (anhydrous calcium sulfate) to remove water vapor from the effluent sample stream;
- (d) an Erlenmeyer bubbler containing a weighed amount of (around 100 g) Ascarite II<sup>®</sup> (sodium hydroxide on a vermiculite solid support) to absorb carbon dioxide; and
- (e) a pump and dry gas meter equipped with an industrial timer-switch.

These components are illustrated in Figure 1.

Samples are obtained at a flow rate of 1.0 L/min (± 10%). The timer controls the sampling duration and frequency; sampling is conducted from 2 to 4 minutes on a 2-hour repeating cycle for 24 hours. The final sample volumes should be between 20 and 40 L.

Sulfur dioxide (as sulfate ion) is determined titrimetrically according to the barium-thorin method<sup>9</sup> contained in Reference Method 6.

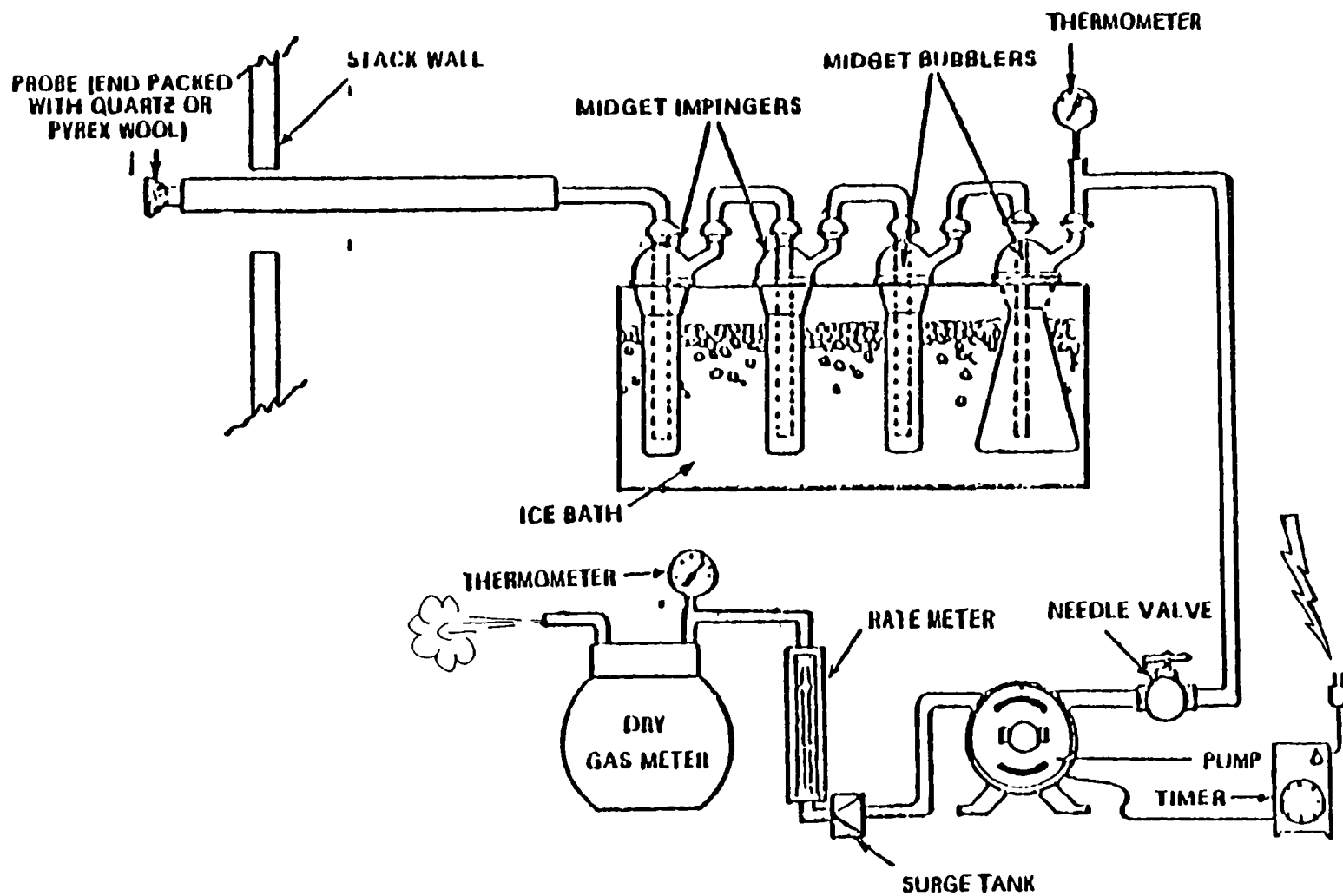


Figure 1  
Reference Method 6B Sampling Train  
(as proposed 1/26/81)

Moisture may be determined gravimetrically using the procedure of Stanley and Westlin.<sup>10</sup> The mass gained by the Ascarite II<sup>®</sup> is used to compute the concentration of carbon dioxide. Finally, the SO<sub>2</sub> emission rate is calculated according to the F-Factor method,<sup>2</sup> using the gravimetric data from the SO<sub>2</sub> and CO<sub>2</sub> determinations. (It should be noted that gravimetric data may be used in lieu of concentration data, because the sample volumes associated with the SO<sub>2</sub> and CO<sub>2</sub> concentrations are essentially equal.)

In the proposed method it is noted that continuous sampling, as distinguished from intermittent sampling, is technically feasible; brief specifications for the application of the continuous sampling mode are provided:

Note.--Sampling may be conducted continuously if a low flow-rate sample pump (> 24 ml/min) is used. Then the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 20 and 40 liters for the amounts of sampling reagents prescribed in this method.

Since proposal of Reference Method 6B, considerable attention has been directed toward placing the methodology of such continuous mode sampling on a firm technical basis, so that the ultimately promulgated Reference Method 6B will detail both sampling modes thoroughly, and therefore, consistently. In this regard emphasis has been placed on (1) evaluating the

performance of pumps and associated flow controls when applied to low sampling rates ( $< 100$  mL/min), (2) determining the quantities and concentrations of reagents necessary for large sample volumes (e.g., up to 80 L); and (3) investigating systems to separate sulfur trioxide and sulfuric acid from sulfur dioxide.

## Descriptions and Discussions of Critical Aspects of the Proposed Method

In the following paragraphs the proposed Reference Method 6B (both sampling modes) is addressed in detail. Attention is focused on those items that distinguish the proposed Reference Method 6B from Reference Method 6. In addition, recommendations which reflect the results from investigations conducted since the date of proposal are provided.

### Heated Borosilicate Glass or Stainless Steel Probe Equipped with Filter(s)

For sample acquisition, heated borosilicate glass or stainless steel probes are required. Relative to stainless steel probes, glass probes are clearly more susceptible to breakage. Glass probes, on the other hand, are insensitive to corrosive compounds in the effluent stream and are much easier to clean. These two attributes are important because of the potential for spurious reactions between probe contaminants and sulfur dioxide; such reactions could lead to low results for SO<sub>2</sub> determinations. The choice of probe material is best made on a case-by-case basis, taking into account source specific variables such as vibrations at the sampling location and particulate matter and sulfuric acid concentrations in the effluent.

Filtration is necessary in order to remove particulate matter from the effluent sample prior to impingement in the hydrogen peroxide solution. The barium-thorin titration, which is performed on the hydrogen peroxide solution, is sensitive to interference by alkali metal ions, which may occur at significant concentrations within particulate matter. In addition, particulate matter may contain water soluble sulfates which would be ultimately determined as  $\text{SO}_2$  if allowed to enter the impingers containing the hydrogen peroxide solution. An in-stack filter, e.g., a plug of borosilicate glass wool, is capable of removing this particulate matter. Nevertheless, a second filter, located out-of-stack, is currently recommended in order (1) to ensure quantitative removal of interfering particulate matter, and (2) to minimize passage of sulfuric acid aerosol (mist) which either may exist in the effluent or may form in the effluent sample after passage through the first filter.

The  $\text{SO}_2$  emission rate determination using the barium-thorin method will be biased high if sulfur oxides such as  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  are collected in the hydrogen peroxide solutions. This potential bias may be minimized through proper selection and control of the temperature of the effluent sample within the probe. The results from recent investigations<sup>8</sup> indicate that the method's precision is optimized when the sampling temperature is approximately  $20^\circ\text{F}$  above the effluent moisture (i.e., water) dewpoint -- as distinguished from the sulfuric acid dewpoint. This empirically selected temperature

reflects the necessary control of two physical processes which can affect the results of the determination. First, the temperature must be above the moisture dewpoint, because sulfur dioxide dissolves and oxidizes in liquid water; using barium-thorin titrimetry, this oxidation product cannot be distinguished from sulfuric acid. Second, the temperature should be in the range where equilibrium favors the presence of filterable sulfuric acid aerosol, rather than the other higher sulfur oxide compound, sulfur trioxide, which exists as a gas. Thus, by selecting a sampling temperature that favors the presence of an aerosol, the contribution of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  can be minimized through removal by the second, out-of-stack filter.

Nevertheless, data pertaining to the magnitude of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  biases on  $\text{SO}_2$  determinations using the proposed Reference Method 6B are currently unavailable; thus, the significance of the potential bias is unknown.

#### Absence of Impinger Containing Isopropanol Solution

As reported by Butler<sup>11</sup> and Westlin, isopropanol interferes with the collection of  $\text{CO}_2$  by Ascarite II.<sup>®</sup> Laboratory investigations have shown that during sampling, isopropanol can penetrate the impingers containing the hydrogen peroxide solution and the Drierite<sup>®</sup>. In addition, investigations have shown that masses of isopropanol less than one gram are sufficient to reduce  $\text{CO}_2$  absorption by 50 percent.<sup>8</sup> Consequently, the use of isopropanol has not been included within the procedure for either sampling mode of the method.

In Reference Method 6 the primary function of the isopropanol is to separate  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  from the  $\text{SO}_2$  sample. The critical importance of the probe temperature setting and the presence of probe filters is better understood when viewed in light of the fact that the proposed Reference Method 6B sampling train has no provisions for the removal of these potentially biasing species. This potential bias has not gone unrecognized; considerable efforts have been made to identify means of separating higher sulfur oxides from the sulfur dioxide sample. For example, drawing from the equilibrium expressions for the  $\text{SO}_2$ /water system, investigators proposed the use of acidic solutions for scrubbing  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  from the effluent sample. Of the common acids available, hydrochloric acid was judged unsuitable because of its volatility, and consequently, its potential to interfere with the barium-thorin titration method. Nitric acid was not considered because of its oxidizing properties. Sulfuric acid was investigated, but its use was found to offer no noticeable improvement over the proposed method. Investigations are in progress to identify other practical means of accomplishing the  $\text{SO}_2$  separation.

#### Two Impingers Containing Hydrogen Peroxide Solution

The proposed method calls for midget impingers, each containing 15 mL 3% hydrogen peroxide; this method of absorbing  $\text{SO}_2$  is identical to that specified within Reference Method 6.



To accomodate flow rates greater than 24 mL/min and consequently, greater sample volumes, larger impingers (e.g., Mae West) containing 75 mL of more concentrated peroxide (6% to 10% (v/v)), have been used with continuous mode sampling.

For Reference Method 6 sampling, the alternative use of 10% (v/v) hydrogen peroxide has been approved in lieu of the specified 3% (v/v) hydrogen peroxide.<sup>12</sup> While it would appear that even greater concentrations could be applied to continuous mode sampling to ensure that sufficient hydrogen peroxide is always available, concentrations greater than the approved 10% (v/v) are not recommended for use at this time. Investigators in the past<sup>13</sup> have noted a negative bias when SO<sub>2</sub> was absorbed in concentrated hydrogen peroxide; however, since quantitative data were not provided due to the limitations of analytical methods at that time, the significance of the bias is unknown. The EPA, QAD is currently investigating this potential bias through the use of ion chromatography, a methodology that only recently has been available.<sup>14</sup>

The impingers containing the hydrogen peroxide solution should be protected from direct sunlight because of the potential for photodecomposition. If a significant quantity of the hydrogen peroxide were to decompose, sulfur dioxide would not be absorbed quantitatively, and a negative bias could result for determinations of ppm SO<sub>2</sub> and lb SO<sub>2</sub>/10<sup>6</sup> Btu. Relative to Reference Method 6, photodecomposition is a greater potential problem because of the extended sampling period. It should be noted that photodecomposition does not necessarily demand

sunlight. For example, mercury vapor lights may affect photodecomposition also. For the reasons touched upon above, it is recommended that the impingers containing hydrogen peroxide be covered throughout the sampling period.

#### Bubbler (or Tube) Containing Drierite<sup>®</sup>

An accurate determination of carbon dioxide can be accomplished only if moisture has been quantitatively removed from the effluent sample prior to reaching the Ascarite II<sup>®</sup>. Drying is accomplished using indicating Drierite<sup>®</sup>, which signals loss of drying activity by changing its color from blue to pink.

For the intermittent sampling mode, approximately 25 g Drierite<sup>®</sup> is specified; for the continuous mode the specified mass is approximately 150 g. The design of the Drierite<sup>®</sup> container is not critical; however, it is imperative that the container be oriented in a manner to minimize channeling that could be aggravated as a consequence of settling. For example, if tubes are used for containing the Drierite<sup>®</sup>, these tubes must be secured in a vertical position; otherwise, channeling along the top of the tube would be likely.

#### Erlenmeyer Bubbler (or Tube) Containing Ascarite II<sup>®</sup>

Both sampling modes envisioned employ sodium hydroxide for absorbing the carbon dioxide in the effluent sample. (It should be noted that as proposed, the method specifies the use

of Ascarite<sup>®</sup>; since that time the supplier has changed the product's formulation so that vermiculite is used rather than asbestos. Ascarite II<sup>®</sup>, the approximate formulation being 96% (w/w) sodium hydroxide and 4% (w/w) vermiculite solid support, is functionally equivalent to Ascarite<sup>®</sup>.)

For intermittent mode sampling, 100 g Ascarite II<sup>®</sup> in a 250 mL Erlenmeyer bubbler is specified. Most versions of continuous mode sampling systems employ 150 g Ascarite II<sup>®</sup> contained in a glass tube.

Of all the method's operations, the Ascarite II<sup>®</sup> absorption presents the greatest potential for causing serious error. And in this regard, the specie of notable concern is water. Water's role in causing bias is best understood in light of the reaction that occurs during CO<sub>2</sub> absorption.

In the Ascarite II<sup>®</sup> container, carbon dioxide reacts with sodium hydroxide to afford anhydrous sodium carbonate and water vapor. Water vapor rather than liquid water is formed because of the (appreciable) heat of reaction. During sampling the extent of reaction is indicated by the advance of a white zone, which is the anhydrous sodium carbonate (and which is capable of reacting with water). The water vapor, on the other hand, is swept ahead into the effluent sample stream, (which then contains no carbon dioxide) and condenses on the fresh sodium hydroxide beyond the reaction zone. The greater proportion of this condensed water is visible as a wet zone, which, as previously indicated, moves ahead of the reaction. Nevertheless, not all the condensed moisture is visible.

The reaction described above must be isolated and contained within the preweighed CO<sub>2</sub> absorption container. As indicated earlier, water vapor can interfere with the method. Two interfering mechanisms are possible. First, if water vapor breaks through the Drierite<sup>®</sup>, it will react with the anhydrous sodium carbonate. This added mass can bias CO<sub>2</sub> concentration determinations high, and lb SO<sub>2</sub>/10<sup>6</sup> Btu determinations low. In addition, because the reaction products (sodium carbonate hydrates) have greater molar volumes, sample flow through the absorber may be reduced and potentially stopped altogether.

The water vapor produced by the CO<sub>2</sub> reaction is the other problem. Accordingly, the location of the wet zone is a poor breakthrough indicator, because a significant quantity of water is generally present some distance ahead of this zone. If water vapor exits the absorber, CO<sub>2</sub> determinations may be biased low, and lb SO<sub>2</sub>/10<sup>6</sup> Btu determinations, high.

Many investigators have approached the problem through use of two CO<sub>2</sub> absorbers in series. The use of a back-up ensures that a valid sample will be obtained in the event that CO<sub>2</sub> breaks through the first absorber. The unreacted sodium hydroxide in the back-up appears to possess adequate dessicating ability to handle the resultant moisture. Moisture breakthrough, however, is best prevented by including a back-up absorber that contains either Drierite<sup>®</sup>, or silica gel.<sup>5</sup>

### Dry Gas Meter

The proposed Reference Method 6B requires the use of a dry gas meter when pollutant and diluent concentrations are determined in conjunction with SO<sub>2</sub> emission rates. However, an abbreviated procedure is permitted<sup>15</sup> if only emission rate data are desired. This abbreviated procedure essentially entails omitting the dry gas meter from the sampling train. It should be recognized, however, that anomalous emission rate data may be impossible to rationalize when the associated concentration data are unavailable. The use of a dry gas meter for all applications of Reference Method 6B is currently advised because of its value for assessing quality control.

### Pump

The proposed Reference Method 6B specifies the use of a diaphragm pump for sample acquisition. Problems with pumping have been encountered during the development of the Method as applied using the continuous sampling mode. Peristaltic pumps, although capable of operating at low flow rates, were found to be unreliable, especially when applied to "negative" pressure effluent streams. Diaphragm pumps, on the other hand, exhibit reliability problems when operated at low (< 100 mL/min) flow rates. Thus, the small volumes of gas handled create what is called a dead-head condition, leading in turn to overheating, and, at the extreme, failure. This problem can be minimized by

providing the pump with sample recirculation capability. (Pump recirculation is illustrated in Figure 5-1 within Reference Method 5.)

Sample acquisition has also been accomplished using compressed air aspiration.<sup>16</sup>

#### Flow Meter

For the intermittent sampling mode, the proposed Reference Method 6B specifies the use of a flow meter and a sampling rate of 1.0 L/min ( $\pm 10\%$ ). Within the proposed method it is noted that if a constant flow sampling pump is employed for the continuous sampling mode, the flow meter may be deleted from the sampling train.

The results from field evaluations of the continuous sampling mode have shown that when sampling trains are operated unattended, constant sampling rates (i.e.,  $\pm 10\%$ ) cannot be guaranteed. The reason for this is due to the fact that the reaction product at the Ascarite II<sup>®</sup> absorber chokes the gas passages therein, causing the pressure drop across the CO<sub>2</sub> absorber to increase with sampling time. Conditions of varying sample flow rates may result in biases which would reflect the acquisition of non-representative samples. The use of critical orifices in conjunction with diaphragm pumps is being investigated as a potential means of maintaining constant sampling rates.

It is currently recognized that the proposed Method 6B train should be equipped with a flow meter.

# FOOTNOTES

<sup>1</sup> Federal Register, Vol. 36, No. 247 - Thursday, December 23, 1971.

<sup>2</sup> F-Factor methods are described within 40 CFR 60, Subpart D and within 40 CFR 60, Appendix A, Reference Method 19.

<sup>3</sup> Federal Register, Vol. 44, No. 113 - Monday, June 11, 1979.

<sup>4</sup> Federal Register, Vol. 43, No. 182 - Tuesday, September 19, 1979.

<sup>5</sup> Standard Method for Carbon and Hydrogen in the Analysis of Coal and Coke. In: Book of ASTM Standards, Part 26, ASTM Designation D 3178-73, Philadelphia, Pa., 1980.

<sup>6</sup> R. N. Whittle and P. R. Westlin, "Air Pollution Test Report: Development and Evaluation of an Intermittant Integrated SO<sub>2</sub>/CO<sub>2</sub> Emission Sampling Procedure." Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch, Research Triangle Park, North Carolina, December 1979.

<sup>7</sup> Federal Register, Vol. 46, No. 16 - Monday, January 26, 1981.

<sup>8</sup> F. E. Butler, U. S. EPA Telecon, May 19, 1982.

<sup>9</sup> J. S. Fritz and S. Yamamura, "Rapid Microtitrations of Sulfate," Anal. Chem., 27, 1461 (1955).

<sup>10</sup> J. Stanley and P. R. Westlin, "An Alternative Method for Stack Gas Moisture Determination." Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch, Research Triangle Park, North Carolina. August 1978.

<sup>11</sup> F. E. Butler, J. E. Knoll, T. J. Logan, and M. R. Midget, "Method Development for 24-Hour Analysis of Sulfur Dioxide and Carbon Dioxide at Fossil Fuel Combustion Sources (Method 6B)," presented at National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources, Raleigh, North Carolina, May 4, 1982.

<sup>12</sup> R. T. Shigehara, Environmental Protection Agency, Emission Measurement Branch, Emission Standard and Engineering Division, Memorandum, July 6, 1978.

<sup>13</sup> H. Wagner, Microchim. Acta, 19 (1957).

<sup>14</sup> John Margeson, U.S. EPA, QAD, (personal communication), June 1982.

<sup>15</sup> The abbreviated procedure is described within proposed Reference Method 6A which is cited as a procedural source with Method 6B. Proposed Reference Method 6A is contained in the Appendix.

<sup>16</sup> Joe Leslie, Virginia Electric and Power Company (Vepco), (personal communication), March 1982.



## APPENDIX

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Monday  
January 26, 1981

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**Part IX**

**Environmental  
Protection Agency**

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**Standards for Performance for New  
Stationary Sources; Revisions to General  
Provisions and Additions to Appendix A,  
and Reproposal of Revisions to  
Appendix B**

6. In Performance Specification 2, the definition of "Relative Accuracy" is incorrect. Instead of a degree of correctness, it is actually a measure of "relative error." One commenter feels that "relative accuracy" should be changed to "relative error."

7. In Section 7.3 of Performance Specification 2, the tester is allowed to reject up to three samples provided that the total number of test results used to determine the relative accuracy is greater than or equal to nine. EPA had considered using statistical techniques to reject outliers, but found that these techniques were too restrictive. One commenter feels that statistical techniques should be used. At a minimum, the commenter feels that the control agencies should be consulted before any data is rejected.

#### Miscellaneous

**Authority:** This proposed rule making is issued under the authority of sections 111, 114, and 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7414, and 7601(a)).

Dated: January 13, 1981.

Douglas M. Costle,  
Administrator.

It is proposed that §§ 60.13, 60.46, and 60.47a, Appendix A, and Appendix B of 40 CFR Part 60 be amended as follows:

1. By revising § 60.13(b), 60.13(c)(2)(ii), and 60.13(d), by removing subparagraphs (1), (2), and (3) of § 60.13(b), and by removing subparagraphs (1), (2), and (3) of § 60.13(d) as follows:

#### § 60.13 Monitoring requirements.

(b) All continuous monitoring systems and monitoring devices shall be installed and operational prior to conducting performance tests under § 60.8. Verification of operational status shall, as a minimum, include completion of the manufacturer's written requirements or recommendations for installation, operation, and calibration of the device.

(c) . . .  
(2) . . .

(ii) Continuous monitoring systems for measurement of nitrogen oxides or sulfur dioxide shall be capable of measuring emission levels within  $\pm 20$  percent with a confidence level of 95 percent. The performance tests and calculation procedures set forth in Performance Specification 2 of Appendix B shall be used for demonstrating compliance with this specification.

(d) Owners and operators of all continuous emission monitoring systems installed in accordance with the

provisions of this part shall check the zero and span drift at least once daily in accordance with the method prescribed by the manufacturer of such systems unless the manufacturer recommends adjustments at shorter intervals in which case such recommendations shall be followed. The zero and span shall, as a minimum, be adjusted whenever the 24-hour zero drift of 24-hour span drift limits of the applicable performance specifications in Appendix B are exceeded. The amount of excess zero and span drift measured at the 24-hour interval checks shall be quantified and recorded. For continuous monitoring systems measuring opacity of emissions, the optical surfaces exposed to the effluent gases shall be cleaned prior to performing the zero and span drift adjustments except that for systems using automatic zero adjustments, the optical surfaces shall be cleaned when the cumulative automatic zero compensation exceeds 4 percent opacity. Unless otherwise approved by the Administrator, the following procedures shall be followed for continuous monitoring systems measuring opacity of emissions. Minimum procedures shall include a method for producing a simulated zero opacity condition and an upscale(span) opacity condition using a certified neutral density filter or other related technique to produce a known obscuration of the light beam. Such procedures shall provide a system check of the analyzer internal optical surfaces and all electronic circuitry including the lamp and photodetector assembly.

2. By revising § 60.46(a)(4) as follows:

#### § 60.46 Test methods and procedures.

(a) . . .

(4) Method 6 for concentration of  $\text{SO}_2$ . Method 6A may be used whenever Methods 6 and 3 data are used to determine the  $\text{SO}_2$  emission rate in ng/l, and

. . . . .

3. By revising § 60.47a(b)(1) as follows:

#### § 60.47a Emission monitoring.

. . . . .

(b) . . .

(1) Reference Methods 3, 6, and 7 as applicable, are used. Method 6B may be used whenever Methods 6 and 3 data are used to determine the  $\text{SO}_2$  emission rate in ng/l. The sampling location(s) are the same as those used for the continuous monitoring system.

. . . . .

4. By adding to Appendix A of 40 CFR Part 60 two new methods, Methods 6A and Method 6B, to read as follows:

#### Appendix A—Reference Test Methods

. . . . .

#### Method 6A—Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide Emissions from Fossil Fuel Combustion Sources

##### 1. Applicability and Principle

1.1 **Applicability.** This method applies to the determination of sulfur dioxide ( $\text{SO}_2$ ) emissions from fossil fuel combustion sources in terms of concentration (mg/m<sup>3</sup>) and in terms of emission rate (ng/l) and to the determination of carbon dioxide ( $\text{CO}_2$ ) concentration (percent). Moisture, if desired, may also be determined by this method.

The minimum detectable limit, the upper limit, and the interferences of the method for the measurement of  $\text{SO}_2$  are the same as for Method 6. For a 20-liter sample, the method has a precision of 0.5 percent  $\text{CO}_2$  for concentrations between 2.5 and 25 percent  $\text{CO}_2$  and 1.0 percent moisture for moisture concentrations greater than 5 percent.

1.2 **Principle.** The principle of sample collection is the same as for Method 6 except that moisture and  $\text{CO}_2$  are collected in addition to  $\text{SO}_2$  in the same sampling train. Moisture and  $\text{CO}_2$  fractions are determined gravimetrically.

##### 2. Apparatus

2.1 **Sampling.** The sampling train is shown in Figure 6A-1, the equipment required is the same as for Method 6, except as specified below:

2.1.1 **Midget Impingers.** Two 30-ml midget impingers with a 1-mm restricted tip.

2.1.2 **Midget Bubbler.** One 30-ml midget bubbler with an unrestricted tip.

2.1.3  **$\text{CO}_2$  Absorber.** One 250-ml Erlenmeyer bubbler with an unrestricted tip, or equivalent.

2.2 **Sample Recovery and Analysis.** The equipment needed for sample recovery and analysis is the same as required for Method 6. In addition, a balance to measure within 0.05 g is needed for analysis.

##### 3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 **Sampling.** The reagents required for sampling are the same as specified in Method 6, except that 80 percent isopropanol and 10 percent potassium iodide solutions are not required. In addition, the following reagents are required:

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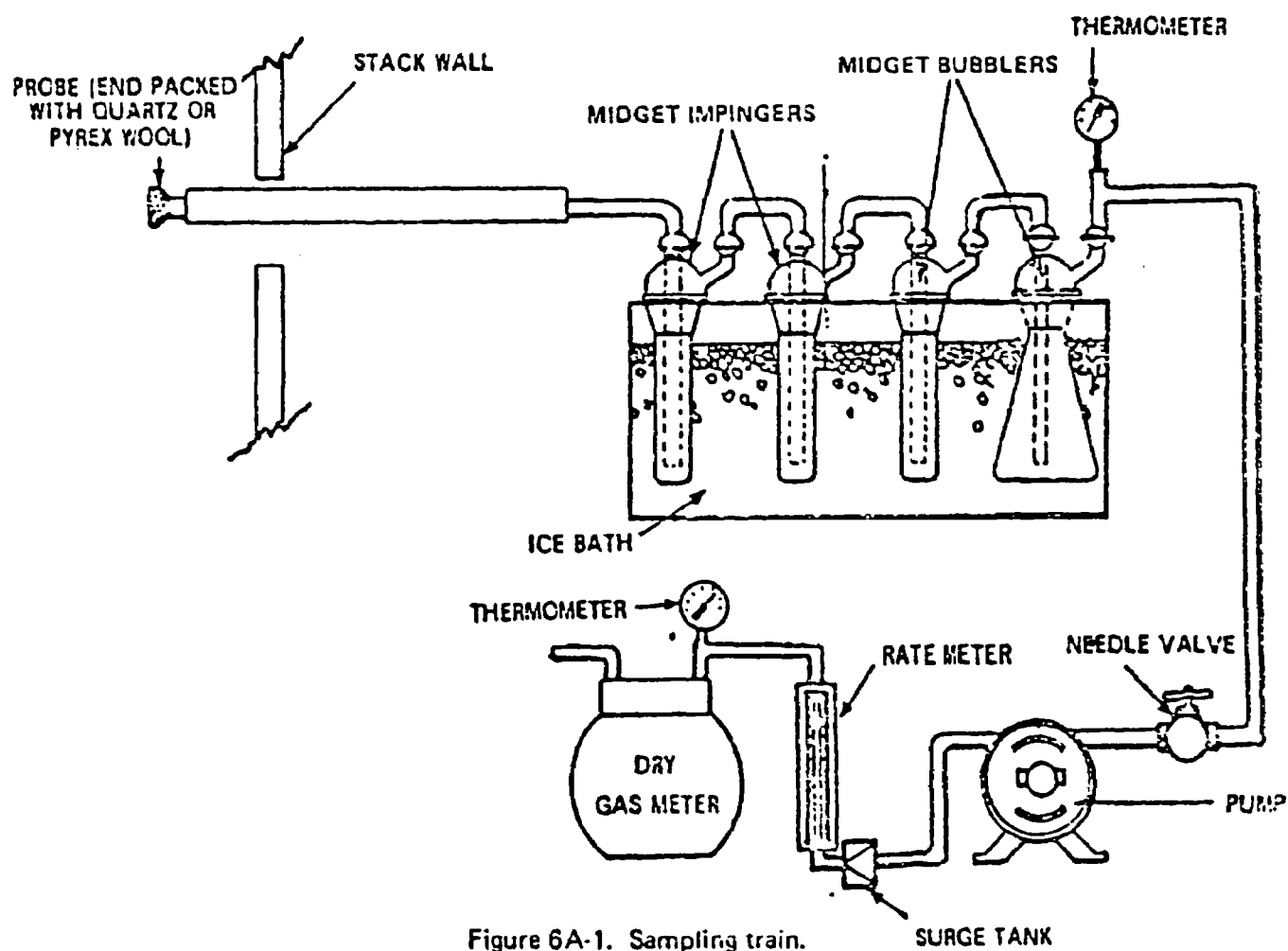


Figure 6A-1. Sampling train.

3.1.1 *Drierite.*\* Anhydrous calcium sulfate ( $\text{CaSO}_4$ ) desiccant, 3 mesh.

3.1.2 *Ascarite.* Sodium hydroxide coated asbestos for absorption of  $\text{CO}_2$ , 9 to 20 mesh.

3.2 *Sample Recovery and Analysis.* The reagents needed for sample recovery and analysis are the same as for Method 8, Sections 3.2 and 3.3, respectively.

#### 4. Procedure

##### 4.1 Sampling

##### 4.1.1 Preparation of Collection Train.

Measure 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers. Into the midget bubbler, place about 25 g of drierite. Clean the outsides of the impingers and the drierite bubbler and weigh (at room temperature,  $\sim 20^\circ\text{C}$ ) to the nearest 0.1 g. Weigh the three vessels simultaneously and record this initial mass.

Place a small amount of glass wool in the Erlenmeyer bubbler. The glass wool should cover the entire bottom of the flask and be about 1-cm thick. Place about 100 g of ascarite on top of the glass wool and carefully insert the bubbler top. Plug the bubbler exhaust leg and invert the bubbler to remove any ascarite from the bubbler tube. A wire may be useful in assuring that no ascarite remains in the tube. With the plug removed and the outside of the bubbler cleaned, weigh (at room temperature (at room temperature,  $\sim 20^\circ\text{C}$ ), to the nearest 0.1 g. Record this initial mass.

Assemble the train as shown in Figure 6A-1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers and bubblers.

Note.—For stack gas streams with high particulate loadings, an in-stack or heated out-of-stack glass fiber mat filter may be used in place of the glass wool plug in the probe.

4.1.2 *Leak-Check Procedure and Sample Collection.* The leak-check procedure and sample collection procedure are the same as specified in Method 8, Sections 4.1.2 and 4.1.3, respectively.

##### 4.2 Sample Recovery.

4.2.1 *Moisture Measurement.* Disconnect the peroxide impingers and the drierite bubbler from the sample train. Allow time (about 10 minutes) for them to reach room temperature, clean the outsides and then weigh them simultaneously in the same manner as in Section 4.1.1. Record this final mass.

4.2.2 *Peroxide Solution.* Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with deionized distilled water, and add the washings to the same storage container.

\*Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

4.2.3  *$\text{CO}_2$  Absorber.* Allow the Erlenmeyer bubbler to warm to room temperature (about 10 minutes), clean the outside, and weigh to the nearest 0.1 g in the same manner as in Section 4.1.1. Record this final mass and discard the used ascarite.

4.3 *Sample Analysis.* The sample analysis procedure for  $\text{SO}_2$  is the same as specified in Method 8, Section 4.3.

##### 5. Calibration

The calibrations and checks are the same as required in Method 8, Section 5.

##### 6. Calculations

Carry out calculations, retaining at least 1 extra decimal figure beyond that of the acquired data. Round off figures after final calculation. The calculation nomenclature and procedure are the same as specified in Method 8 with the addition of the following:

##### 6.1 Nomenclature.

$C_{\text{H}_2\text{O}}$  = Concentration of moisture, percent.

$C_{\text{CO}_2}$  = Concentration of  $\text{CO}_2$ , dry basis, percent.

$m_{\text{wi}}$  = Initial mass of peroxide impingers and drierite bubbler, g.

$m_{\text{wf}}$  = Final mass of peroxide impingers and drierite bubbler, g.

$m_{\text{di}}$  = Initial mass of ascarite bubbler, g.

$m_{\text{df}}$  = Final mass of ascarite bubbler, g.

$V_{\text{CO}_2(\text{std})}$  = Standard equivalent volume of  $\text{CO}_2$  collected, dry basis,  $\text{m}^3$ .

6.2  $\text{CO}_2$  volume collected, corrected to standard conditions.

$$V_{\text{CO}_2(\text{std})} = 5.467 \times 10^{-4} (m_{\text{di}} - m_{\text{df}}) \quad (\text{Eq. 6A-1})$$

6.3 Moisture volume collected, corrected to standard conditions.

$$V_{\text{w}(\text{std})} = 1.336 \times 10^{-3} (m_{\text{wf}} - m_{\text{wi}}) \quad (\text{Eq. 6A-2})$$

##### 6.4 $\text{SO}_2$ concentration.

$$C_{\text{SO}_2} = 32.03 \frac{(V_{\text{t}} - V_{\text{tb}}) N \left( \frac{V_{\text{soln}}}{V_{\text{a}}} \right)}{V_{\text{m}(\text{std})} + V_{\text{CO}_2(\text{std})} \quad (\text{Eq. 6A-3})$$

##### 6.5 $\text{CO}_2$ concentration.

$$C_{\text{CO}_2} = \frac{V_{\text{CO}_2(\text{std})}}{V_{\text{m}(\text{std})} + V_{\text{CO}_2(\text{std})} \times 100 \quad (\text{Eq. 6A-4})$$

##### 6.6 Moisture concentration.

$$C_{\text{H}_2\text{O}} = \frac{V_{\text{H}_2\text{O}(\text{std})}}{V_{\text{m}(\text{std})} + V_{\text{H}_2\text{O}(\text{std})} + V_{\text{CO}_2(\text{std})} \quad (\text{Eq. 6A-5})$$

#### 7 Emission Rate Procedure

If the only emission measurement desired is in terms of emission rate of  $\text{SO}_2$  (ng/l), an abbreviated procedure may be used. The differences between Method 6A and the abbreviated procedure are described below.

7.1 *Sample Train.* The sample train is the same as shown in Figure 6A-1 and as

described in Section 4, except that the dry gas meter is not needed.

7.2 *Preparation of the collection train.* Follow the same procedure as in Section 4.1.1, except that the peroxide impingers and drierite bubbler need not be weighed before or after the test run.

7.3 *Sampling.* Operate the train as described in Section 4.1.3, except that dry gas

meter readings, barometric pressure, and dry gas meter temperatures need not be recorded.

7.4 *Sample Recovery*: Follow the procedure in Section 4.2, except that the peroxide impingers and drying bubbler need not be weighed.

7.5 *Sample Analysis*. Analysis of the peroxide solution is the same as described in Section 4.3.

7.6 Calculations.

7.6.1  $\text{SO}_2$  mass collected.

$$m_{\text{SO}_2} = 32.03 (V_t - V_{\text{th}}) N \left( \frac{V_{\text{soln}}}{V_a} \right) \quad (\text{Eq. 6A-7})$$

Where:

$m_{\text{SO}_2}$  = Mass of  $\text{SO}_2$  collected, mg.

#### 7.6.2 Sulfur dioxide emission rate.

$$E_{\text{SO}_2} = F_c (1.829 \times 10^9) \frac{m_{\text{SO}_2}}{(m_{\text{af}} - m_{\text{at}})} \quad (\text{Eq. 6A-8})$$

Where:

$E_{\text{SO}_2}$  = Emission rate of  $\text{SO}_2$ , ng/j.

$F_c$  = Carbon F factor for the fuel burned,  $\text{m}^3/\text{j}$ , from Method 19.

#### 8. Bibliography

8.1 Same as for Method 6, citations 1 through 8, with the addition of the following:

8.2 Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter, Volume 3, Number 4, November 1978.

8.3 Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated  $\text{SO}_2/\text{CO}_2$  Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch, Research Triangle Park, North Carolina. December 1979. 14 pages.

#### Method 6B—Determination of Sulfur Dioxide and Carbon Dioxide Daily Average Emissions From Fossil Fuel Combustion Sources

##### 1. Applicability and Principle

1.1 *Applicability*. This method applies to the determination of sulfur dioxide ( $\text{SO}_2$ ) emissions from combustion sources in terms of concentration ( $\text{mg}/\text{M}^3$ ) and emission rate ( $\text{ng}/\text{j}$ ), and for the determination of carbon dioxide ( $\text{CO}_2$ ) concentration (percent) on a daily (24 hours) basis.

The minimum detectable limit, upper limit, and the interferences for  $\text{SO}_2$  measurements are the same as for Method 6. For a 20-liter sample, the method has a precision of 0.5 percent  $\text{CO}_2$  for concentrations between 2.5 and 25 percent  $\text{CO}_2$ .

1.2 *Principle*. A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. Sampling may also be conducted continuously if the apparatus and

procedure are modified (see the note in Section 4.1.1). The  $\text{SO}_2$  and  $\text{CO}_2$  are separated and collected in the sampling train. The  $\text{SO}_2$  fraction is measured by the barium-thorium titration method and  $\text{CO}_2$  is determined gravimetrically.

##### 2. Apparatus

The equipment required for this method is the same as specified for Method 6A, Section 2, with the addition of an industrial timer-switch designed to operate in the "on" position from 3 to 5 continuous minutes and "off" the remaining period over a repeating, 2-hour cycle.

##### 3. Reagents

All reagents for sampling and analysis are the same as described in Method 6A, Section 3.

##### 4. Procedure

###### 4.1 Sampling

###### 4.1.1 Preparation of Collection Train.

Preparation of the sample train is the same as described in Method 6A, Section 4.1.4 with the addition of the following:

Assemble the train as shown in Figure 6B-1. The probe must be heated to a temperature sufficient to prevent water condensation and must include a filter (either in-stack, out-of-stack, or both) to prevent particulate entrainment in the peroxide impingers. The electric supply for the probe heat should be continuous and separate from the timed operation of the sample pump.

Adjust the timer-switch to operate in the "on" position from 2 to 4 minutes on a 2-hour repeating cycle. Other timer sequences may be used provided there are at least 12 equal, evenly spaced periods of operation over 24 hours and the total sample volume is between 20 and 40 liters for the amounts of sampling reagents prescribed in this method.

Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

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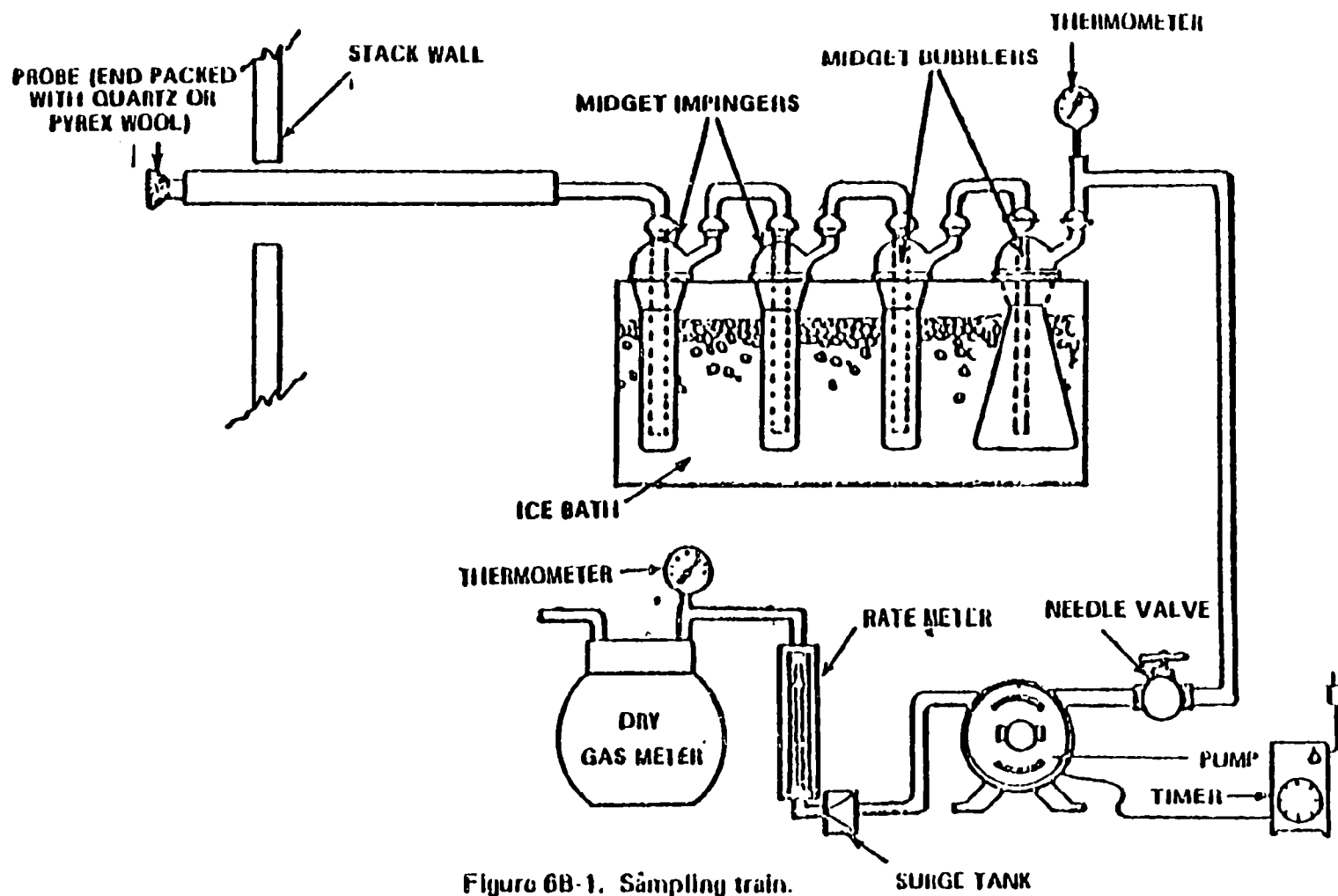


Figure 6B-1. Sampling train.

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**Note.**—Sampling may be conducted continuously if a low flow-rate sample pump (>24ml/min) is used. Then the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 20 and 40 liters for the amounts of sampling reagents prescribed in this method.

**4.1.2 Leak-Check Procedure.** The leak-check procedure is the same as described in Method 8, Section 4.1.2.

**4.1.3 Sample Collection.** Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rotameter. Assume that the timer is operating as intended, i.e., in the "on" position 3 to 5 minutes at 2-hour intervals, or other time interval specified.

During the 24-hour sampling period, record the dry gas meter temperature between 9:00 a.m. and 11:00 a.m., and the barometric pressure.

At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak check as described in Section 4.1.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in this Section (4.1.3) for successive runs.

**4.2 Sample Recovery.** The procedures for sample recovery (moisture measurement, peroxide solution, and ascante bubbler) are the same as in Method 8A, Section 4.2.

**4.3 Sample Analysis.** Analysis of the peroxide impinger solutions is the same as in Method 8, Section 4.3.

## 5. Calibration

### 5.1 Metering System.

**5.1.1 Initial Calibration.** The initial calibration for the volume metering system is the same as for Method 8, Section 5.1.1.

**5.1.2 Periodic Calibration Check.** After 30 days of operation of the test train conduct a calibration check as in Section 5.1.1 above, except for the following variations: (1) The leak check is not be conducted, (2) three or more revolutions of the dry gas meter may be used, and (3) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor determined in Section 5.1.1, then the dry gas meter volumes obtained during the test series are acceptable and use of the train can continue. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1, and for the calculations for the preceding 30 days of data, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run. Use the latest calibration factor for succeeding tests.

**5.2 Thermometers.** Calibrate against mercury-in-glass thermometers initially and at 30-day intervals.

**5.3 Rotameter.** The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

**5.4 Barometer.** Calibrate against a mercury barometer initially and at 30-day intervals.

**5.5 Barium Perchlorate Solution.** Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

## 6. Calculations

The nomenclature and calculation procedures are the same as in Method 6A with the following exceptions:

$P_{\text{bar}}$  = Initial barometric pressure for the test period, mm Hg.

$T_{\text{abs}}$  = Absolute meter temperature for the test period, °K.

## 7. Emission Rate Procedure

The emission rate procedure is the same as described in Method 8A, Section 7, except that the timer is needed and is operated as described in this method.

## 8. Bibliography

The bibliography is the same as described in Method 8A, Section 8.

5. By revising Performance 2 and Performance 3 of Appendix B of 40 CFR Part 60 to read as follows:

## Appendix B—Performance Specifications

**Performance Specification 2—Specifications and Test Procedures for SO<sub>2</sub> and NO<sub>x</sub> Continuous Emission Monitoring Systems in Stationary Sources**

### 1. Applicability and Principle

**1.1 Applicability.** This specification is to be used for evaluating the acceptability of SO<sub>2</sub> and NO<sub>x</sub> continuous emission monitoring systems (CEMS) after the initial installation and whenever specified in an applicable subpart of the regulations. The CEMS may include, for certain stationary sources, diluent (O<sub>2</sub> or CO<sub>2</sub>) monitors.

**1.2 Principle.** Installation and measurement location specifications, performance and equipment specifications, test procedures, and data reduction procedures are included in this specification. Reference method (RM) tests and calibration drift tests are conducted to determine conformance of the CEMS with the specification.

### 2. Definitions

**2.1 Continuous Emission Monitoring System (CEMS).** The total equipment required for the determination of a gas concentration or emission rate. The system consists of the following major subsystems:

**2.1.1 Sample Interface.** That portion of the CEMS that is used for one or more of the following: Sample acquisition, sample transportation, and sample conditioning, or protection of the monitor from the effects of the stack effluent.

**2.1.2 Pollutant Analyzer.** That portion of the CEMS that senses the pollutant gas and generates an output that is proportional to the gas concentration.

**2.1.3 Diluent Analyzer (if applicable).** That portion of the CEMS that senses the diluent gas (e.g., CO<sub>2</sub> or O<sub>2</sub>) and generates an

output that is proportional to the gas concentration.

**2.1.4 Data Recorder.** That portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may include automatic data reduction capabilities.

**2.2 Point CEMS.** A CEMS that measures the gas concentration either at a single point or along a path that is equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section.

**2.3 Path CEMS.** A CEMS that measures the gas concentration along a path that is greater than 10 percent of the equivalent diameter of the stack or duct cross section.

**2.4 Span Value.** The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable subpart of the regulations.

**2.5 Relative Accuracy (RA).** The absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the reference method(s) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the reference method (RM) tests or the applicable emission limit.

**2.6 Calibration Drift (CD).** The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

**2.7 Centroidal Area.** A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross-sectional area.

**2.8 Representative Results.** As defined by the RM test procedure outlined in this specification.

## 3. Installation and Measurement Location Specifications

**3.1 CEMS Installation and Measurement Location.** Install the CEMS at an accessible location where the pollutant concentration or emission rate measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility. Then select representative measurement points or paths for monitoring such that the CEMS will pass the relative accuracy (RA) test (see Section 7). If the cause of failure to meet the RA test is determined to be the measurement location, the CEMS may be required to be relocated.

Suggested measurement locations and points or paths are listed below; other locations and points or paths may be less likely to provide data that will meet the RA requirements.

**3.1.1 CEMS Location.** It is suggested that the measurement location be at least two equivalent diameters downstream from the nearest control device or other point at which a change in the pollutant concentration or emission rate may occur and at least a half equivalent diameter upstream from the effluent exhaust.

**3.1.2 Point CEMS.** It is suggested that the measurement point be (1) no less than 1.0 meter from the stack or duct wall, or (2) within or centrally located over the centroidal area of the stack or duct cross section.