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Title 40—Protection of the Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER C—AIR PROGRAMS

[FRL 833-1]

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Kraft Pulp Mills

AGENCY: Environmental Protection Agency.

ACTION: Final rule.

SUMMARY: The standards limit emissions of total reduced sulfur (TRS) and particulate matter from new, modified, and reconstructed kraft pulp mills. The standards implement the Clean Air Act and are based on the Administrator's determination that emissions from kraft pulp mills contribute significantly to air pollution. The intended effect of these standards is to require new, modified, and reconstructed kraft pulp mills to use the best demonstrated system of continuous emission reduction.

EFFECTIVE DATE: February 23, 1978.

ADDRESSES: The Standards Support and Environmental Impact Statement (SSEIS) may be obtained from the U.S. EPA Library (MD-35), Research Triangle Park, N.C. 27711 (specify "Standards Support and Environmental Impact Statement, Volume 2: Promulgated Standards of Performance for Kraft Pulp Mills" (EPA-450/2-76-014b)). Copies of all comment letters received from interested persons participating in this rulemaking are available for inspection and copying during normal business hours at EPA's Public Information Reference Unit, Room 2922 (EPA Library), 401 M Street SW., Washington, D.C.

FOR FURTHER INFORMATION CONTACT:

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SUPPLEMENTARY INFORMATION: On September 24, 1976 (41 FR 42012), standards of performance were proposed for new, modified, and reconstructed kraft pulp mills under section 111 of the Clean Air Act, as amended. The significant comments that were received during the public comment period have been carefully reviewed and considered and, where determined by the Administrator to be appropriate, changes have been included in this notice of final rulemaking.

THE STANDARDS

The standards limit emissions of particulate matter from three affected facilities at kraft pulp mills. The limits are: 0.10 gram per dry standard cubic meter (g/dscm) at 8 percent oxygen for recovery furnaces, 0.10 gram per kilogram of black liquor solids (dry weight) (g/kg BLS) for smelt dissolving tanks, 0.15 g/dscm at 10 percent oxygen for lime kilns when burning gas, and 0.30 g/dscm at 10 percent oxygen for lime kilns when burning oil. Visible emissions from recovery furnaces are limited to 35 percent opacity.

The standards also limit emissions of TRS from eight affected facilities at kraft pulp mills. The limits are: 5 parts per million (ppm) by volume at 10 percent oxygen from the digester systems, multiple-effect evaporator systems, brown stock washer systems, black liquor oxidation systems, and condensate stripper systems; 5 ppm by volume at 8 percent oxygen from straight kraft recovery furnaces, 8 ppm by volume at 10 percent oxygen from lime kilns; and 25 ppm by volume at 8 percent oxygen from cross recovery furnaces, which are defined as furnaces burning at least 7 percent neutral sulfite semi-chemical (NSSC) liquor and having a green liquor sulfidity of at least 28 percent. In addition, TRS emissions from smelt dissolving tanks are limited to 0.0084 g/kg BLS.

The proposed TRS standard for the lime kiln has been changed, a separate TRS standard for cross recovery furnaces has been developed, and the proposed format of the standards for smelt dissolving tanks, digesters, multiple-effect evaporators, brown stock washers, black liquor oxidation and condensate strippers have been changed. The TRS, particulate matter and opacity standards for the other facilities, however, are essentially the same as those proposed.

It should be noted that standards of performance for new sources established under section 111 of the Clean Air Act reflect emission limits achievable with the best adequately demonstrated technological system of continuous emission reduction considering the cost of achieving such emission reductions and any nonair quality health, environmental, and energy impacts. State implementation plans (SIP's) approved or promulgated under section 110 of the Act, on the other hand, must provide for the attainment and maintenance of national ambient air quality standards (NAAQS) designed to protect public health and welfare. For that purpose SIP's must in some cases require greater emission reductions than those required by standards of performance for new sources. Section 173(2) of the Clean Air Act, as amended in 1977, requires, among other things, that a new

or modified source constructed in an area which exceeds the NAAQS must reduce emissions to the level which reflects the "lowest achievable emission rate" for such category of source, unless the owner or operator demonstrates that the source cannot achieve such an emission rate. In no event can the emission rate exceed any applicable standard of performance.

A similar situation may arise when a major emitting facility is to be constructed in a geographic area which falls under the prevention of significant deterioration of air quality provisions of the Act (Part C). These provisions require, among other things, that major emitting facilities to be constructed in such areas are to be subject to best available control technology. The term "best available control technology" (BACT) means "an emission limitation based on the maximum degree of reduction of each pollutant subject to regulation under this Act emitted from or which results from any major emitting facility, which the permitting authority, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines it achievable for such facility through application of production processes and available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of each such pollutant. In no event shall application of 'best available control technology' result in emissions of any pollutants which will exceed the emissions allowed by any applicable standard established pursuant to section 111 or 112 of this Act."

Standards of performance should not be viewed as the ultimate in achievable emission control and should not preclude the imposition of a more stringent emission standard, where appropriate. For example, cost of achivement may be an important factor in determining standards of performance applicable to all areas of the country (clean as well as dirty). Costs must be accorded far less weight in determining the "lowest achievable emission rate" for new or modified sources locating in areas violating statutorily-mandated health and welfare standards. Although there may be emission control technology available that can reduce emissions below those levels required to comply with standards of performance, this technology might not be selected as the basis of standards of performance due to costs associated with its use. This in no way should preclude its use in situations where cost is a lesser consideration, such as determination of the "lowest achievable emission rate."

In addition, States are free under section 116 of the Act to establish even more stringent emission limits than

those established under section 111 or those necessary to attain or maintain the NAAQS under section 110. Thus, new sources may in some cases be subject to limitations more stringent than standards of performance under section 111, and prospective owners and operators of new sources should be aware of this possibility in planning for such facilities.

ENVIRONMENTAL AND ECONOMIC IMPACT

The promulgated standards will reduce particulate emissions about 50 percent below requirements of the average existing State regulations. TRS emissions will be reduced by about 80 percent below requirements of the average existing State regulations, and this reduction will prevent odor problems from arising at most new kraft pulp mills. The secondary environmental impacts of the promulgated standard will be slight increases in water demand and wastewater treatment requirements. The energy impact of the promulgated standards will be small, increasing national energy consumption in 1980 by the equivalent of only 1.4 million barrels per year of No. 6 oil. The economic impact will be small with fifth-year annualized costs being estimated at $33 million.

PUBLIC PARTICIPATION

Prior to proposal of the standards, interested parties were advised by public notice in the FEDERAL REGISTER of a meeting of the National Air Pollution Control Techniques Advisory Committee. In addition, copies of the proposed standards and the Standards Support and Environmental Impact Statement (SSEIS) were distributed to members of the kraft pulp industry and several environmental groups at the time of proposal. The public comment period extended from September 24, 1976, to March 14, 1977, and resulted in 42 comment letters with 28 of these letters coming from the industry, 12 from various regulatory agencies, and two from U.S. citizens. Several comments resulted in changes to the proposed standards. A detailed discussion of the comments and changes which resulted is presented in Volume 2 of the SSEIS. A summary is presented here.

SIGNIFICANT COMMENTS AND CHANGES MADE IN THE PROPOSED REGULATIONS

Most of the comment letters received contained multiple comments. The most significant comments and changes made to the proposed regulations are discussed below.

IMPACTS OF THE PROPOSED STANDARDS

Several commenters expressed concern about the increased energy consumption which would result from compliance with proposed standards. These commenters felt that this would conflict with the Department of Energy's goal to reduce total energy consumption in the pulp and paper industry by 14 percent. This factor was considered in the analysis of the energy impact associated with the standards and is discussed in the SSEIS. Although the standards will increase the difficulty of attaining this energy reduction goal, the 4.3 percent increase in energy usage that will be required by new, modified, or reconstructed by kraft pulp mills to comply with the standards is considered reasonable in comparison to the benefits which will result from the corresponding reduction in TRS and particulate matter emissions.

EMISSION CONTROL TECHNOLOGY

Most of the comments received regarding emission control technology concerned the application of this technology to either lime kilns or recovery furnaces. A few comments, however, expressed concern with the use of the oxygen correction factor included in the proposed standards for both lime kilns and recovery furnaces. These commenters pointed out that adjusting the concentration of particulate matter and TRS emissions to 10 percent oxygen for lime kilns and 8 percent oxygen for recovery furnaces only when the oxygen concentration exceeded these values effectively placed more stringent standards on the most energy-efficient operators. To ensure that the standard is equitable for all operators, these commenters suggested that the measured particulate matter and TRS concentrations should always be adjusted to 10 percent oxygen for the lime kiln and 8 percent oxygen for the recovery furnace.

These comments are valid. Requiring a lime kiln or recovery furnace with a low oxygen concentration to meet the same emission concentration as a lime kiln or recovery furnace with a high oxygen concentration would effectively place a more stringent emission limit on the kiln or furnace with the low oxygen concentration. Consequently, the promulgated standards require correction of particulate matter and TRS concentrations to 10 percent or 8 percent oxygen, as appropriate, in all cases.

Lime Kilns. Numerous comments were received on the emission control technology for lime kilns. The main points questioned by the commenters were: (a) Whether caustic scrubbing is effective in reducing TRS emissions from lime kilns; (b) whether an overdesign of the mud washing facilities at lime kiln E was responsible for the lower TRS emissions observed at this lime kiln; and (c) the adequacy of the data base used in developing the TRS standard.

The effectiveness of caustic scrubbing is substantiated by comparison of TRS emissions during brief periods when caustic was not being added to the scrubber at lime kiln E, with TRS emissions during normal operation at lime kiln E when caustic is being added to the scrubber. These observations clearly indicate that TRS emissions would be higher if caustic was not used in the scrubber. The ability of caustic scrubbing to reduce TRS emissions is also substantiated by the experience at another kraft pulp mill which was able to reduce TRS emissions from its lime kiln from 40–50 ppm to about 20 ppm merely by adding caustic to the scrubber. These factors, coupled with the emission data showing higher TRS emissions from those lime kilns which employed only efficient mud washing and good lime kiln process control, clearly show that caustic scrubbing reduces TRS emissions.

The mud washing facilities at lime kiln E are larger than those at other kraft pulp mills of equivalent pulp capacity. This "overdesign" resulted from initial plans of the company to process lime mud from waste water treatment. These waste water treatment plans were later abandoned. Since the quality or efficiency of mud washing has been shown to be a significant factor in reducing TRS emissions from lime kilns, the larger mud washing facilities at lime kiln E undoubtedly contributed to the low TRS emissions observed at this kiln. With the data available, however, it is not possible to separate the relative contribution of these mud washing facilities to the low TRS emissions observed from the relative contributions of good process operation of the lime kiln and caustic scrubbing.

Comments questioning the adequacy of the data base used in developing the standards for lime kilns were mainly directed toward the following points: the TRS standard was based on only one lime kiln; sampling losses which may have occurred during testing were not taken into account; and no lime kiln met both the TRS standard and the particulate standard.

As mentioned above, the TRS standard is based upon the emission control system installed at lime kiln E (i.e., efficient mud washing, good lime kiln process operation, and caustic scrubbing). While it is true that no other lime kiln in the United States is currently achieving the TRS emission levels observed at lime kiln E, there is no other lime kiln in the United States which is using the same emission control system that is employed at this facility. As discussed in the SSEIS, an analysis of the various parameters influencing TRS emissions from lime kilns indicates that this system of emission reduction could be applied to

all new, modified, or reconstructed lime kilns and achieve the same reduction in emissions as observed at lime kiln E. Section 111 of the Clean Air Act requires that "standards of performance reflect the degree of emission reduction achievable through the application of the best system of continuous emission reduction which (taking into consideration the cost of achieving such emission reduction, and any nonair quality health and environmental impact and energy requirements) the Administrator determines has been adequately demonstrated for that category of sources." Litigation of standards of performance has resulted in clarification of the term "adequately demonstrated." In Portland Cement Association v. Ruckelshaus (486 F. 2d 375, D.C. Circuit, 1973), the standards of performance were viewed by the Court as "technology-forcing." Thus, while a system of emission reduction must be available for use to be considered adequately demonstrated, it does not have to be in routine use. However, in order to ensure that the numerical emission limit selected was consistent with proper operation and maintenance of the emission control system on lime kiln E, continuous monitoring data was examined. This analysis indicated that an emission source test of lime kiln E would have found TRS emission above 5 ppm greater than 5 percent of the time. This analysis also indicated, however, that it was very unlikely that an emission source test of lime kiln E would have found TRS emissions above 8 ppm. Thus, it appeared that the 5 ppm TRS numerical emission limit included in the proposed standard for lime kilns was too stringent. Accordingly, the numerical emission limit included in the promulgated TRS standard for lime kilns has been revised to 8 ppm. As discussed later in this preamble, consistent with this change in the numerical emission limit, the excess emissions allowance included within the emission monitoring requirements has been eliminated.

This does not reflect a change in the basis for the standard. The standard is still based on the best system of emission reduction, considering costs, for controlling TRS emissions from lime kilns (i.e., efficient mud washing, good lime kiln process operation, and caustic scrubbing). This system, or one equivalent to it, will still be required to comply with the standard.

Since proposal of the standards, sample losses of up to 20 percent during emission source testing have been confirmed. Although these losses were not considered in selecting the numerical emission limit included in the proposed TRS emission standard, they have been considered in selecting the numerical emission limit included in the promulgated standard. Also, since the amount of sample loss that occurs within the TRS emission measurement system during source testing can be determined, procedures have been added to Reference Method 16 requiring determination of these losses during each source test and adjustment of the emission data obtained to take these losses into account.

With regard to the ability of a lime kiln to comply with both the TRS emission standard and the particulate emission standard simultaneously, caustic scrubbing will tend to increase particulate emissions due to release of sodium fume from the scrubbing liquor. Compared to the concentration of particulate matter permitted in the gases discharged to the atmosphere, however, the potential contribution of sodium fume from caustic scrubbing is quite small. Consequently, with proper operation and maintenance, sodium fume due to caustic scrubbing will not cause particulate emissions from a lime kiln to exceed the numerical emission limit included in the promulgated standard.

Recovery Furnace. A number of comments were received regarding both the proposed TRS emission standard and the proposed particulate emission standard for recovery furnaces. Basically, the major issue was whether a cross recovery furnace could comply with the 5 ppm TRS standard or whether a separate standard was necessary.

. Review of the data and information submitted with these comments indicates that the operation of cross recovery furnaces is substantially different from that of straight kraft recovery furnaces. The sulfidity of the black liquor burned in cross recovery furnaces and the heat content of the liquor, both of which are significant factors influencing TRS emissions, are considerably different from the levels found in straight kraft recovery furnaces.

Analysis of the data indicated that TRS emissions were generally less than 25 ppm, with only occasional excursions exceeding this level. Consequently, the promulgated TRS emission standard has been revised to include a separate TRS numerical emission limit of 25 ppm for cross recovery furnaces.

Smelt Dissolving Tank. Numerous comments were received concerning the format of the proposed TRS and particulate emission standards for smelt dissolving tanks. These. comments pointed out that standards in terms of emissions per unit of air-dried pulp were inequitable for kraft pulp mills which produced low-yield pulps since both TRS and particulate emissions from the smelt dissolving tanks are proportional to the tons of black liquor solids fed into the tanks. The black liquor solids produced per ton of air-dried pulp, however, can vary substantially from mill to mill. A standard in terms of emissions per unit of air-dried pulp, therefore, requires greater control of emissions at kraft pulp mills which use low-yield pulps (higher solids-to-pulp ratio).

Review of these comments does indeed indicate that the format of the proposed standards was inequitable. The format of the promulgated standards, therefore, has been revised to emissions per unit of black liquor solids fed to the smelt dissolving tanks. Since the percent solids and black liquor flow rate to the recovery furnace is routinely monitored at kraft pulp mills, the weight of black liquor solids corresponding to a particular emissions period will be easy to determine.

Brown Stock Washers. Several comments expressed concern about combustion of the high volume-low TRS concentration gases discharged from brown stock washers and black liquor oxidation facilities in recovery furnaces without facing a serious risk of explosions. As discussed in the SSEIS, information obtained from two kraft pulp mill operators indicates that this practice is both safe and reliable when it is accompanied by careful engineering and operating practices. Danger of an explosion occurring is essentially eliminated by introducing the gases high in the furnace. Since some older furnaces do not have the capability to accept large volumes of gases at higher combustion ports, this practice may not be safe for some existing furnaces. In addition, the costs associated with altering these furnaces to accept these gases are frequently prohibitive. Consequently, the promulgated standards include an exemption for new, modified, or reconstructed brown stock washers and black liquor oxidation facilities within existing kraft pulp mills where combustion of these gases in an existing facility is not feasible from a safety or economic standpoint.

CONTINUOUS MONITORING

Numerous comments were received concerning the proposed continuous monitoring requirements. Generally, these comments questioned the requirement to install TRS monitors in light of the absence of performance specifications for these monitors.

At the time of proposal of the standards, both EPA and the kraft pulp mill industry were engaged in developing performance specifications for TRS continuous emission monitoring systems. It was expected that this work would lead to performance specifications for these monitoring systems by the time the standards of performance were promulgated. Unfortunately, this is not the case. In a joint EPA/industry effort, the compatibility of various TRS emission monitoring

methods with Reference Method 16, which is the performance test method to determine TRS emissions, is still under study. There is little doubt but that these TRS emission monitoring systems will be shown to be compatible with Reference Method 16, and that performance specifications for these systems will be developed. Consequently, the promulgated standards include TRS continuous emission monitoring requirements. These requirements, however, will not become effective until performance specifications for TRS continuous emission monitoring systems have been developed. To accommodate this situation, not only for the promulgated standards for kraft pulp mills, but also for standards of performance that may be developed in the future that may also face this situation, section 60.13 of the General Provisions for subpart 60 is amended to provide that continuous monitoring systems need not be installed until performance specifications for these systems are promulgated under Appendix B to subpart 60. This will ensure that all facilities which are covered by standards of performance will eventually install continuous emission monitoring systems where required.

EXCESS EMISSIONS

Numerous comments were received which were concerned with the excess emission allowances and the reporting requirements for excess emissions. In general, these comments reflected a lack of understanding with regard to the concept of excess emissions. Consequently, a brief review of this concept is appropriate.

Standards of performance have two major objectives. The first is installation of the best system of emission reduction, considering costs; and the second is continued proper operation and maintenance of the system throughout its useful life. Since the numerical emission limit included in standards of performance is selected to reflect the performance of the best system of emission reduction under conditions of proper operation and maintenance, the performance test, under 40 CFR 60.8 represents the ability of the source to meet these objectives. Performance tests, however, are often time consuming and complex. As a result, while the performance test is an excellent mechanism for achieving these objectives, it is rather cumbersome and inconvenient for routinely achieving these objectives. Therefore, the Agency believes that continuous monitors must play an important role in meeting these objectives.

Excess emissions are defined as emissions exceeding the numerical emission limit included in a standard of performance. Continuous emission monitoring, therefore, identifies periods of excess emissions and when com-

bined with the requirement that these periods be reported to EPA, it provides the Agency with a useful mechanism for achieving the previously mentioned objectives.

Continuous emission monitoring, however, will identify all periods of excess emissions, including those which are not the result of improper operation and maintenance. Excess emissions due to start-ups, shutdowns, and malfunctions, for example, are unavoidable or beyond the control of an owner or operator and cannot be attributed to improper operation and maintenance. Similarly, excess emissions as a result of some inherent variability or fluctuation within a process which influences emissions cannot be attributed to improper operation and maintenance, unless these fluctuations could be controlled by more carefully attending to those process operating parameters during routine operation which have little effect on operation of the process, but which may have a significant effect on emissions.

To quantify the potential for excess emissions due to inherent variability in a process, continuous monitoring data are used whenever possible to calculate an excess emission allowance. For TRS emissions at kraft pulp mills, this allowance is defined as follows. If a calendar quarter is divided into discrete contiguous 12-hour time periods, the excess emission allowance is expressed as the percentage of these time periods. Excess emissions may occur as the result of unavoidable variability within the kraft pulping process. Thus, the excess emissions allowance represents the potential for excess emissions under conditions of proper operation and maintenance in the absence of start-ups, shutdowns and malfunctions, and is used as a guideline or screening mechanism for interpreting the data generated by the excess emission reporting requirements.

Although the excess emission reporting requirements provide a mechanism for achieving the objective of proper operation and maintenance of the best system of emission reduction, this mechanism is not necessarily a direct indicator of improper operation and maintenance. Consequently, excess emission reports must be reviewed and interpreted for proper decisionmaking.

In general, the comments received concerning the excess emission reporting requirements questioned: (1) The adequacy of the TRS excess emission allowance for lime kilns and (2) the lack of a TRS excess emission allowance for recovery furnaces.

With regard to the adequacy of the TRS excess emissions allowance for lime kilns, a reevaluation of the TRS emission data from lime kiln E led the Agency to the conclusion that, for a TRS emission limit of 5 ppm, an

excess emission allowance of 6 percent was appropriate. However, a similar analysis also indicates that an excess emission allowance is not appropriate at a TRS emission level of 8 ppm. Accordingly, the excess emission reporting requirements included in the promulgated standard for lime kilns contains no excess emission allowance. This does not represent a change in the basis of the standard. The standard will still require installation of the best system of emission reduction, considering costs (i.e., efficient mud washing, good lime kiln process operation, and caustic scrubbing; or an alternative system equivalent to the performance of this system).

With regard to the lack of a TRS excess emission allowance for recovery furnaces, at the time of proposal of the standards, no TRS continuous emission monitoring data were available from a well-controlled and well operated recovery furnace which could be used to determine an excess emission allowance. Several months of TRS continuous emission monitoring data, however, were submitted with the comments received from the operator of recovery furnace D concerning this point.

A review of the data indicates that, while some of the excursions of TRS emissions above 5 ppm reflected either improper operation and maintenance, or start-ups, shutdowns, or malfunctions, most of these excursions reflected unavoidable normal variability in the operation of a kraft pulp mill recovery furnace. Discounting those excursions in emissions from the data which were due to improper operation and maintenance, or start-ups, shutdowns, or malfunctions indicates that an excess emission allowance of 1 percent is appropriate for all recovery furnaces.

Including an excess emissions allowance in the promulgated standards for recovery furnaces, but not for lime kilns, is a reversal of the proposed requirements. Including such an allowance for recovery furnaces but not for lime kilns, however, is consistent with the nature of the different emission control systems which were selected as the bases for these standards. The emission control system upon which the TRS standard for recovery furnaces is based consists of black liquor oxidation and good process operation of the recovery furnace for direct recovery furnaces, and good process operation alone for indirect recovery furnaces. Neither of these emission control systems are particularly well suited to controlling fluctuations in the kraft pulping process. Thus, fluctuations in the process tend to pass through the emission control system and show up as fluctuations in TRS emissions.

The emission control system upon which the TRS standard for lime kilns

is based consists of efficient mud washing, good process operation of the lime kiln, and caustic scrubbing of the gases discharged from the lime kiln. As with the emission control system upon which the standard for recovery furnaces is based, the first two emission control techniques (i.e., mud washing and good process operation) are not particularly well suited to controlling fluctuations in the kraft pulping process. The third emission control technique, however, caustic scrubbing, is an "add-on" emission control technique that can be designed to accommodate fluctuations in TRS emissions and minimize or essentially eliminate these fluctuations.

EMISSION TESTING

A few comments were received which questioned the validity of the results obtained by Reference Method 16, due to sample losses and sulfur dioxide (SO₂) interference.

With regard to the validity of the results obtained by Reference Method 16, as mentioned earlier, during the emission testing program, it was not widely known that sample losses could occur within the TRS emission measurement system. Since proposal of the standards, however, sample losses of up to 20 percent during emission source testing have been confirmed. Although these losses were not considered in selecting the numerical emission limits included in the proposed TRS emission standards, they have been considered in selecting the numerical emission limit included in the promulgated standards. Also, since the amount of sample loss that occurs within the TRS emission measurement system during source testing can be determined, procedures have been added to Reference Method 16 requiring determination of these losses during each source test and adjustment of the emission data obtained to take these losses into account. This will ensure that the TRS emission data obtained during a performance test are accurate.

It has also been confirmed that high concentrations of SO₂ will interfere with the determination of TRS emissions to some extent. At this point, however, it is not known what SO₂ concentration levels will result in a significant loss of accuracy in determining TRS emissions. The ability of a citrate scrubber to selectively remove SO₂ prior to measurement of TRS emissions is now being tested. In addition, various chromatographic columns might exist which would effectively resolve this problem. As soon as an appropriate technique is developed to overcome this problem, Reference Method 16 will be amended. This problem of SO₂ interference will not present major difficulties to the use of Reference Method 16. Rela-

tively high SO₂ concentration levels were observed in only one EPA emission source test. Accordingly, high SO₂ concentration levels are probably not a frequent occurrence within kraft pulp mills. More importantly, however, high SO₂ concentrations only interfere with the determination of methyl mercaptan in the emission measurement system outlined in Reference Method 16. Since methyl mercaptan is usually only a small contributor to total TRS emissions, neglecting methyl mercaptan where this interference occurs should not seriously affect the determination of TRS emissions. Consequently, Reference Method 16 can be used to enforce the promulgated standards without major difficulties.

Miscellaneous: The effective date of this regulation is February 24, 1976. Section 111(b)(1)(B) of the Clean Air Act provides that standards of performance or revisions of them become effective upon promulgation and apply to affected facilities, construction or modification of which was commenced after the date of proposal (September 24, 1976).

NOTE.—An economic assessment has been prepared as required under section 317 of the Act. This also satisfies the requirements of Executive Orders 11821 and OMB Circular A-107.

Dated: February 10, 1978.

BARBARA BLUM,
Acting Administrator.

Part 60 of Chapter I, Title 40 of the Code of Federal Regulations is amended as follows:

Subpart A—General Provisions

1. Section 60.13 is amended to clarify the provisions in paragraph (a) by revising paragraph (a) to read as follows:

§ 60.13 Monitoring requirements.

(a) For the purposes of this section, all continuous monitoring systems required under applicable subparts shall be subject to the provisions of this section upon promulgation of performance specifications for continuous monitoring system under Appendix B to this part, unless:

(1) The continuous monitoring system is subject to the provisions of paragraphs (c)(2) and (c)(3) of this section, or

(2) otherwise specified in an applicable subpart or by the Administrator.

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2. Part 60 is amended by adding subpart BB as follows:

Subpart BB—Standards of Performance for Kraft Pulp Mills

Sec.
60.280 Applicability and designation of affected facility.
60.281 Definitions.

60.282 Standard for particulate matter.
60.283 Standard for total reduced sulfur (TRS).
60.284 Monitoring of emissions and operations.
60.285 Test methods and procedures.

AUTHORITY: Secs. 111, 301(a) of the Clean Air Act, as amended [42 U.S.C. 7411, 7601(a)], and additional authority as noted below.

Subpart BB—Standards of Performance for Kraft Pulp Mills

60.280 Applicability and designation of affected facility.

(a) The provisions of this subpart are applicable to the following affected facilities in kraft pulp mills: digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, recovery furnace, smelt dissolving tank, lime kiln, and condensate stripper system. In pulp mills where kraft pulping is combined with neutral sulfite semichemical pulping, the provisions of this subpart are applicable when any portion of the material charged to an affected facility is produced by the kraft pulping operation.

(b) Any facility under paragraph (a) of this section that commences construction or modification after September 24, 1976, is subject to the requirements of this subpart.

§ 60.281 Definitions.

As used in this subpart, all terms not defined herein shall have the same meaning given them in the Act and in Subpart A.

(a) "Kraft pulp mill" means any stationary source which produces pulp from wood by cooking (digesting) wood chips in a water solution of sodium hydroxide and sodium sulfide (white liquor) at high temperature and pressure. Regeneration of the cooking chemicals through a recovery process is also considered part of the kraft pulp mill.

(b) "Neutral sulfite semichemical pulping operation" means any operation in which pulp is produced from wood by cooking (digesting) wood chips in a solution of sodium sulfite and sodium bicarbonate, followed by mechanical defibrating (grinding).

(c) "Total reduced sulfur (TRS)" means the sum of the sulfur compounds hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, that are released during the kraft pulping operation and measured by Reference Method 16.

(d) "Digester system" means each continuous digester or each batch digester used for the cooking of wood in white liquor, and associated flash tank(s), below tank(s), chip steamer(s), and condenser(s).

(e) "Brown stock washer system" means brown stock washers and associated knotters, vacuum pumps, and fil-

trate tanks used to wash the pulp following the digester system.

(f) "Multiple-effect evaporator system" means the multiple-effect evaporators and associated condenser(s) and hotwell(s) used to concentrate the spent cooking liquid that is separated from the pulp (black liquor).

(g) "Black liquor oxidation system" means the vessels used to oxidize, with air or oxygen, the black liquor, and associated storage tank(s).

(h) "Recovery furnace" means either a straight kraft recovery furnace or a cross recovery furnace, and includes the direct-contact evaporator for a direct-contact furnace.

(i) "Straight kraft recovery furnace" means a furnace used to recover chemicals consisting primarily of sodium and sulfur compounds by burning black liquor which on a quarterly basis contains 7 weight percent or less of the total pulp solids from the neutral sulfite semichemical process or has green liquor sulfidity of 28 percent or less.

(j) "Cross recovery furnace" means a furnace used to recover chemicals consisting primarily of sodium and sulfur compounds by burning black liquor which on a quarterly basis contains more than 7 weight percent of the total pulp solids from the neutral sulfite semichemical process and has a green liquor sulfidity of more than 28 percent.

(k) "Black liquor solids" means the dry weight of the solids which enter the recovery furnace in the black liquor.

(l) "Green liquor sulfidity" means the sulfidity of the liquor which leaves the smelt dissolving tank.

(m) "Smelt dissolving tank" means a vessel used for dissolving the smelt collected from the recovery furnace.

(n) "Lime kiln" means a unit used to calcine lime mud, which consists primarily of calcium carbonate, into quicklime, which is calcium oxide.

(o) "Condensate stripper system" means a column, and associated condensers, used to strip, with air or steam, TRS compounds from condensate streams from various processes within a kraft pulp mill.

§ 60.282 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere:

(1) From any recovery furnace any gases which:

(i) Contain particulate matter in excess of 0.10 g/dscm (0.044 gr/dscf) corrected to 8 percent oxygen.

(ii) Exhibit 35 percent opacity or greater.

(2) From any smelt dissolving tank any gases which contain particulate

matter in excess of 0.1 g/kg black liquor solids (dry weight)[0.2 lb/ton black liquor solids (dry weight)].

(3) From any lime kiln any gases which contain particulate matter in excess of:

(i) 0.15 g/dscm (0.067 gr/dscf) corrected to 10 percent oxygen, when gaseous fossil fuel is burned.

(ii) 0.30 g/dscm (0.13 gr/dscf) corrected to 10 percent oxygen, when liquid fossil fuel is burned.

§ 60.283 Standard for total reduced sulfur (TRS).

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere:

(1) From any digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system any gases which contain TRS in excess of 5 ppm by volume on a dry basis, corrected to 10 percent oxygen, unless the following conditions are met:

(i) The gases are combusted in a lime kiln subject to the provisions of paragraph (a)(5) of this section; or

(ii) The gases are combusted in a recovery furnace subject to the provisions of paragraphs (a)(2) or (a)(3) of this section; or

(iii) The gases are combusted with other waste gases in an incinerator or other device, or combusted in a lime kiln or recovery furnace not subject to the provisions of this subpart, and are subjected to a minimum temperature of 1200° F. for at least 0.5 second; or

(iv) It has been demonstrated to the Administrator's satisfaction by the owner or operator that incinerating the exhaust gases from a new, modified, or reconstructed black liquor oxidation system or brown stock washer system in an existing facility is technologically or economically not feasible. Any exempt system will become subject to the provisions of this subpart if the facility is changed so that the gases can be incinerated.

(2) From any straight kraft recovery furnace any gases which contain TRS in excess of 5 ppm by volume on a dry basis, corrected to 8 percent oxygen.

(3) From any cross recovery furnace any gases which contain TRS in excess of 25 ppm by volume on a dry basis, corrected to 8 percent oxygen.

(4) From any smelt dissolving tank any gases which contain TRS in excess of 0.0084 g/kg black liquor solids (dry weight) [0.0168 lb/ton liquor solids (dry weight)].

(5) From any lime kiln any gases which contain TRS in excess of 8 ppm by volume on a dry basis, corrected to 10 percent oxygen.

§ 60.284 Monitoring of emissions and operations.

(a) Any owner or operator subject to the provisions of this subpart shall install, calibrate, maintain, and operate the following continuous monitoring systems:

(1) A continuous monitoring system to monitor and record the opacity of the gases discharged into the atmosphere from any recovery furnace. The span of this system shall be set at 70 percent opacity.

(2) Continuous monitoring systems to monitor and record the concentration of TRS emissions on a dry basis and the percent of oxygen by volume on a dry basis in the gases discharged into the atmosphere from any lime kiln, recovery furnace, digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system, except where the provisions of § 60.283(a)(1) (iii) or (iv) apply. These systems shall be located downstream of the control device(s) and the span(s) of these continuous monitoring system(s) shall be set:

(i) At a TRS concentration of 30 ppm for the TRS continuous monitoring system, except that for any cross recovery furnace the span shall be set at 50 ppm.

(ii) At 20 percent oxygen for the continuous oxygen monitoring system.

(b) Any owner or operator subject to the provisions of this subpart shall install, calibrate, maintain, and operate the following continuous monitoring devices:

(1) A monitoring device which measures the combustion temperature at the point of incineration of effluent gases which are emitted from any digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system where the provisions of § 60.283(a)(1)(iii) apply. The monitoring device is to be certified by the manufacturer to be accurate within ±1 percent of the temperature being measured.

(2) For any lime kiln or smelt dissolving tank using a scrubber emission control device:

(i) A monitoring device for the continuous measurement of the pressure loss of the gas stream through the control equipment. The monitoring device is to be certified by the manufacturer to be accurate within a gage pressure of ±500 pascals (ca. ±2 inches water gage pressure).

(ii) A monitoring device for the continuous measurement of the scrubbing liquid supply pressure to the control equipment. The monitoring device is to be certified by the manufacturer to be accurate within ±15 percent of design scrubbing liquid supply pressure. The pressure sensor or tap is to

be located close to the scrubber liquid discharge point. The Administrator may be consulted for approval of alternative locations.

(c) Any owner or operator subject to the provisions of this subpart shall, except where the provisions of § 60.283(a)(1)(iv) or § 60.283(a)(4) apply.

(1) Calculate and record on a daily basis 12-hour average TRS concentrations for the two consecutive periods of each operating day. Each 12-hour average shall be determined as the arithmetic mean of the appropriate 12 contiguous 1-hour average total reduced sulfur concentrations provided by each continuous monitoring system installed under paragraph (a)(2) of this section.

(2) Calculate and record on a daily basis 12-hour average oxygen concentrations for the two consecutive periods of each operating day for the recovery furnace and lime kiln. These 12-hour averages shall correspond to the 12-hour average TRS concentrations under paragraph (c)(1) of this section and shall be determined as an arithmetic mean of the appropriate 12 contiguous 1-hour average oxygen concentrations provided by each continuous monitoring system installed under paragraph (a)(2) of this section.

(3) Correct all 12-hour average TRS concentrations to 10 volume percent oxygen, except that all 12-hour average TRS concentration from a recovery furnace shall be corrected to 8 volume percent using the following equation:

$$C_{corr} = C_{meas} \times (21-X/21-Y)$$

where:

C_{corr} = the concentration corrected for oxygen.

C_{meas} = the concentration uncorrected for oxygen.

X = the volumetric oxygen concentration in percentage to be corrected to (8 percent for recovery furnaces and 10 percent for lime kilns, incinerators, or other devices).

Y = the measured 12-hour average volumetric oxygen concentration.

(d) For the purpose of reports required under § 60.7(c), any owner or operator subject to the provisions of this subpart shall report periods of excess emissions as follows:

(1) For emissions from any recovery furnace periods of excess emissions are:

(i) All 12-hour averages of TRS concentrations above 5 ppm by volume for straight kraft recovery furnaces and above 25 ppm by volume for cross recovery furnaces.

(ii) All 6-minute average opacities that exceed 35 percent.

(2) For emissions from any lime kiln, periods of excess emissions are all 12-hour average TRS concentration above 8 ppm by volume.

(3) For emissions from any digester system, brown stock washer system,

multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system periods of excess emissions are:

(i) All 12-hour average TRS concentrations above 5 ppm by volume unless the provisions of § 60.283(a)(1) (i), (ii), or (iv) apply; or

(ii) All periods in excess of 5 minutes and their duration during which the combustion temperature at the point of incineration is less than 1200° F. where the provisions of § 60.283(a)(1)(ii) apply.

(e) The Administrator will not consider periods of excess emissions reported under paragraph (d) of this section to be indicative of a violation of § 60.11(d) provided that:

(1) The percent of the total number of possible contiguous periods of excess emissions in a quarter (excluding periods of startup, shutdown, or malfunction and periods when the facility is not operating) during which excess emissions occur does not exceed:

(i) One percent for TRS emissions from recovery furnaces.

(ii) Six percent for average opacities from recovery furnaces.

(2) The Administrator determines that the affected facility, including air pollution control equipment, is maintained and operated in a manner which is consistent with good air pollution control practice for minimizing emissions during periods of excess emissions.

§ 60.285 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided under § 60.8(b), shall be used to determine compliance with § 60.282(a) as follows:

(1) Method 5 for the concentration of particulate matter and the associated moisture content,

(2) Method 1 for sample and velocity traverses,

(3) When determining compliance with § 60.282(a)(2), Method 2 for velocity and volumetric flow rate,

(4) Method 3 for gas analysis, and

(5) Method 9 for visible emissions.

(b) For Method 5, the sampling time for each run shall be at least 60 minutes and the sampling rate shall be at least 0.85 dscm/hr (0.53 dscf/min) except that shorter sampling times, when necessitated by process variables or other factors, may be approved by the Administrator. Water shall be used as the cleanup solvent instead of acetone in the sample recovery procedure outlined in Method 5.

(c) Method 17 (in-stack filtration) may be used as an alternate method for Method 5 for determining compliance with § 60.282(a)(1)(i): *Provided,* That a constant value of 0.009 g/dscm (0.004 gr/dscf) is added to the results of Method 17 and the stack tempera-

ture is no greater than 205° C (ca. 400° F). Water shall be used as the cleanup solvent instead of acetone in the sample recovery procedure outlined in Method 17.

(d) For the purpose of determining compliance with § 60.283(a) (1), (2), (3), (4), and (5), the following reference methods shall be used:

(1) Method 16 for the concentration of TRS,

(2) Method 3 for gas analysis, and

(3) When determining compliance with § 60.283(a)(4), use the results of Method 2, Method 16, and the black liquor solids feed rate in the following equation to determine the TRS emission rate.

$$E = (C_{H2S}F_{H2S} + C_{MeSH}F_{MeSH} + C_{DMS}F_{DMS} + C_{DMDS}F_{DMDS}) (Q_{sd})/BLS$$

Where:

E = mass of TRS emitted per unity of black liquor solids (g/kg) (lb/ton)

C_{H2S} = average concentration of hydrogen sulfide (H_2S) during the test period, PPM.

C_{MeSH} = average concentration of methyl mercaptan (MeSH) during the test period, PPM.

C_{DMS} = average concentration of dimethyl sulfide (DMS) during the test period, PPM.

C_{DMDS} = average concentration of dimethyl disulfide (DMDS) during the test period, PPM.

F_{H2S} = 0.001417 g/m³ PPM for metric units = 0.08844 lb/ft³ PPM for English units

F_{MeSH} = 0.00200 g/m³ PPM for metric units = 0.1248 lb/ft³ PPM for English units

F_{DMS} = 0.002583 g/m³ PPM for metric units = 0.1612 lb/ft³ PPM for English units

F_{DMDS} = 0.003917 g/m³ PPM for metric units = 0.2445 lb/ft³ PPM for English units

Q_{sd} = dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr)

BLS = black liquor solids feed rate, kg/hr (lb/hr)

(4) When determining whether a furnace is straight kraft recovery furnace or a cross recovery furnace, TAPPI Method T.624 shall be used to determine sodium sulfide, sodium hydroxide and sodium carbonate. These determinations shall be made three times daily from the green liquor and the daily average values shall be converted to sodium oxide (Na_2O) and substituted into the following equation to determine the green liquor sulfidity:

$$GLS = 100 \quad C_{Na2S}/C_{Na2S} + C_{NaOH} + C_{Na2CO3}$$

Where:

GLS = percent green liquor sulfidity

C_{Na2S} = average concentration of Na_2S expressed as Na_2O (mg/1)

C_{NaOH} = average concentration of NaOH expressed as Na_2O (mg/1)

C_{Na2CO3} = average concentration of Na_2CO_3 expressed as Na_2O (mg/1)

(e) All concentrations of particulate matter and TRS required to be measured by this section from lime kilns or incinerators shall be corrected 10 volume percent oxygen and those concentrations from recovery furnaces

shall be corrected to 8 volume percent oxygen. These corrections shall be made in the manner specified in § 60.284(c)(3).

APPENDIX A—REFERENCE METHODS

(3) Method 16 and Method 17 are added to Appendix A as follows:

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METHOD 16. SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

Introduction

The method described below uses the principle of gas chromatographic separation and flame photometric detection. Since there are many systems or sets of operating conditions that represent usable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the criteria set below are met.

1. *Principle and Applicability.*

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are known collectively as total reduced sulfur (TRS).

1.2 Applicability. This method is applicable for determination of TRS compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills.

2. *Range and Sensitivity.*

2.1 Range. Coupled with a gas chromatographic system utilizing a ten milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 1 ppm. This limit is expanded by dilution of the sample gas before analysis. Kraft mill gas samples are normally diluted tenfold (9:1), resulting in an upper-limit of about 10 ppm for each compound.

For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size to 1 milliliter.

2.2 Using the sample size, the minimum detectable concentration is approximately 50 ppb.

3. *Interferences.*

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effect on the flame photometric detector even after 9:1 dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromato-

graphs should show agreement within the precision limits of Section 4.1.

3.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference must be eliminated by use of a probe filter.

3.4 Sulfur Dioxide. SO_2 is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from other compounds of interest. The procedure must be designed to eliminate this problem either by the choice of separation columns or by removal of SO_2 from the sample.

Compliance with this section can be demonstrated by submitting chromatographs of calibration gases with SO_2 present in the same quantities expected from the emission source to be tested. Acceptable systems shall show baseline separation with the amplifier attenuation set so that the reduced sulfur compound of concern is at least 50 percent of full scale. Base line separation is defined as a return to zero ± percent in the interval between peaks.

4. *Precision and Accuracy.*

4.1 GC/FPD and Dilution System Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than ±3 percent from the mean of the three injections.

4.2 GC/FPD and Dilution System Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period shall not exceed ± percent.

4.3 System Calibration Accuracy. The complete system must quantitatively transport and analyze with an accuracy of 20 percent. A correction factor is developed to adjust calibration accuracy to 100 percent.

5. *Apparatus* (See Figure 16-1).

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.2 Sample Line. The sample line must be made of Teflon,[1] no greater than 1.3 cm (½) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120° C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120° C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert materials (e.g., stainless steel or Teflon). It must be heated to 120° C. and be capable of approximately a 9:1 dilution of the sample.

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1° C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1° C.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

5.3.4 Flame Photometric Detector.

5.3.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.3.4.2 Power Supply. Capable of delivering up to 750 volts.

5.3.4.3 Recorder. Compatible with the output voltage range of the electrometer.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capble of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences.

To demonstrate that adequate resolution has been achieved, the tester must submit a chromatograph of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined in Section 3.4. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5. Calibration System. The calibration system must contain the following components.

5.5.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

5.5.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±0.1° C.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1° C.

6. *Reagents.*

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons. This gas must be heated prior to mixing with the sample to avoid water condensation at the point of contact.

6.5 Calibration Gases. Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, agravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7. *Pretest Procedures.* The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. In any component, or if the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8. *Calibration.* Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in Section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires a understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components; particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within ±0.1° C. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of Section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K\frac{P_r}{ML}$$

Equation 16-1

where:

C=Concentration of permeant produced in ppm.

P_r=Permeation rate of the tube in μg/min.

M=Molecular weight of the permeant (g/g-mole).

L=Flow rate, 1/min, of air over permeant @ 20° C, 760 mm Hg.

K=Gas constant at 20° C and 760 mm Hg=24.04 1/g mole.

8.3 Calibration of analysis system. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in Section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data.

8.5 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in Section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H₂S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of Section 4.1 are still applicable.

9. *Sampling and Analysis Procedure.*

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximtely 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. *Post-Test Procedures.*

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to insure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is unacceptable. Sampling losses of 0-20 percent must be corrected for by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 8. Only H₂S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. *Calculations.*

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least square line.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each anaylsis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$TRS = \Sigma(H_2S, MeSH, DMS, 2DMDS)d$$

Equation 16-2

where:

TRS=Total reduced sulfur in ppm, wet basis.

H₂S=Hydrogen sulfide, ppm.

MeSH=Methyl mercaptan, ppm.

DMS=Dimethyl sulfide, ppm.

DMDS=Dimethyl disulfide, ppm.

d=Dilution factor, dimensionless.

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Average TRS} = \frac{\sum\limits_{i=1}^{N} \text{TRS}_i}{N(1-B_{wo})}$$

Average TRS=Average total reduced sulfur in ppm, dry basis.

TRS_i=Total reduced sulfur in ppm as determined by Equation 16-2.

N=Number of samples.

B_{wo}=Fraction of volume of water vapor in the gas stream as determined by method 4—Determination of Moisture in Stack Gases (36 FR 24887).

11.4 Average concentration of individual reduced sulfur compounds.

$$C = \frac{\sum\limits_{i=1}^{N} S_i}{N}$$

Equation 16-3

where:

S_i=Concentration of any reduced sulfur compound from the ith sample injection, ppm.

C=Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N=Number of injections in any run period.

12. *Example System.* Described below is a system utilized by EPA in gathering NSPS data. This system does not now reflect all the latest developments in equipment and column technology, but it does represent one system that has been demonstrated to work.

12.1 Apparatus.

12.1.1 Sampling System.

12.1.1.1 Probe. Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. the probe is designed with the deflector shield placed between the sample and the gas inlet holes and the glass wool plugs to reduce clogging of the filter and possible adsorption of sample gas. The exposed portion of the probe between the sampling port and the sample line is heated with heating tape.

12.1.1.2 Sample Line ⅜₆ inch inside diameter Teflon tubing, heated to 120° C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120° C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 16-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120° C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Teflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by com-

bining 150 cc of sample with 1,350 cc of clean dry air as shown in Figure 16-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120° C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min ±1 percent per dilution stage.

12.1.3 Gas Chromatograph Columns. Two types of columns are used for separation of low and high molecular weight sulfur compounds:

12.1.3.1 Low Molecular Weight Sulfur Compounds Column (GC/FPD-1).

12.1.3.1 Separation Column. 11 m by 2.16 mm (36 ft by 0.085 in) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 5 percent polyphenyl ether and 0.05 percent orthophosphoric acid, or equivalent (see Figure 16-3).

12.1.3.1.2 Stripper or Precolumn. 0.6 m by 2.16 mm (2 ft by 0.085 in) inside diameter Teflon tubing packed as in 5.3.1.

12.1.3.1.3 Sample Valve. Teflon 10-port gas sampling valve, equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.3.1.4 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100° C, constant within ±1° C.

12.1.3.1.5 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1° C.

12.1.3.1.6 Flow System. Gas metering system to measure sample flow, hydrogen flow, and oxygen flow (and nitrogen carrier gas flow).

12.1.3.1.7 Detector. Flame photometric detector.

12.1.3.1.8 Electrometer. Capable of full scale amplification of linear ranges of 10⁻⁹ to 10⁻⁴ amperes full scale.

12.1.3.1.9 Power Supply. Capable of delivering up to 750 volts.

12.1.3.1.10 Recorder. Compatible with the output voltage range of the electrometer.

12.1.3.2 High Molecular Weight Compounds Column (GC/FPD-11).

12.1.3.2.1. Separation Column. 3.05 m by 2.16 mm (10 ft by 0.0885 in) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 10 percent Triton X-305, or equivalent.

12.1.3.2.2 Sample Valve. Teflon 6-port gas sampling valve equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.3.2.3 Other Components. All components same as in 12.1.3.1.4 to 12.1.3.1.10.

12.1.4 Calibration. Permeation tube system (figure 16-4).

12.1.4.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.4.2 Mass Flowmeters. Two mass flowmeters in the range 0-3 l/min. and 0-10 l/min. to measure air flow over permeation tubes at ±2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration

gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter, at least once each year.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30° C. within ±0.1° C.

12.2 Reagents

12.2.1 Fuel. Hydrogen (H₂) prepurified grade or better.

12.2.2. Combustion Gas. Oxygen (O₂) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N₂) prepurified grade or better.

12.2.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in Section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibrated Gases. Permeation tubes gravimetrically calibrated and certified at 30.0° C.

12.3 Operating Parameters.

12.3.1 Low-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system used for low molecular weight compounds are as follows: nitrogen carrier gas flow rate of 50 cc/min, exhaust temperature of 110° C, detector temperature of 105° C, oven temperature of 40° C, hydrogen flow rate of 80 cc/min, oxygen flow rate of 20 cc/min, and sample flow rate between 20 and 80 cc/min.

12.3.2 High-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system for high molecular weight compounds are the same as in 12.3.1 except: oven temperature of 70° C, and nitrogen carrier gas flow of 100 cc/min.

12.4 Analysis Procedure.

12.4.1 Analysis. Aliquots of diluted sample are injected simultaneously into both GC/FPD analyzers for analysis. GC/FPD-I is used to measure the low-molecular weight reduced sulfur compounds. The low molecular weight compounds include hydrogen sulfide, methyl mercaptan, and dimethyl sulfide. GC/FPD-II is used to resolve the high-molecular weight compound. The high-molecular weight compound is dimethyl disulfide.

12.4.1.1 Analysis of Low-Molecular Weight Sulfur Compounds. The sample valve is actuated for 3 minutes in which time an aliquot of diluted sample is injected into the stripper column and analytical column. The valve is then deactivated for approximately 12 minutes in which time, the analytical column continues to be foreflushed, the stripper column is backflushed, and the sample loop is refilled. Monitor the responses. The elution time for each compound will be determined during calibration.

12.4.1.2 Analysis of High-Molecular Weight Sulfur Compounds. The procedure is essentially the same as above except that no stripper column is needed.

13. *Bibliography.*

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sis." Analytical Chemical Journal, 38,760 (1966).

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13.3 Mulick, J. D., R. K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6-8, 1971.

13.4 Devonald, R. H., R. S. Serenius, and A. D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." Pulp and Paper Magazine of Canada, 73,3 (March, 1972).

13.5 Grimley, K. W., W. S. Smith, and R. M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting in St. Louis, Mo. June 14-19, 1970.

13.6 General Reference. Standard Methods of Chemical Analysis Volume III A and B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.
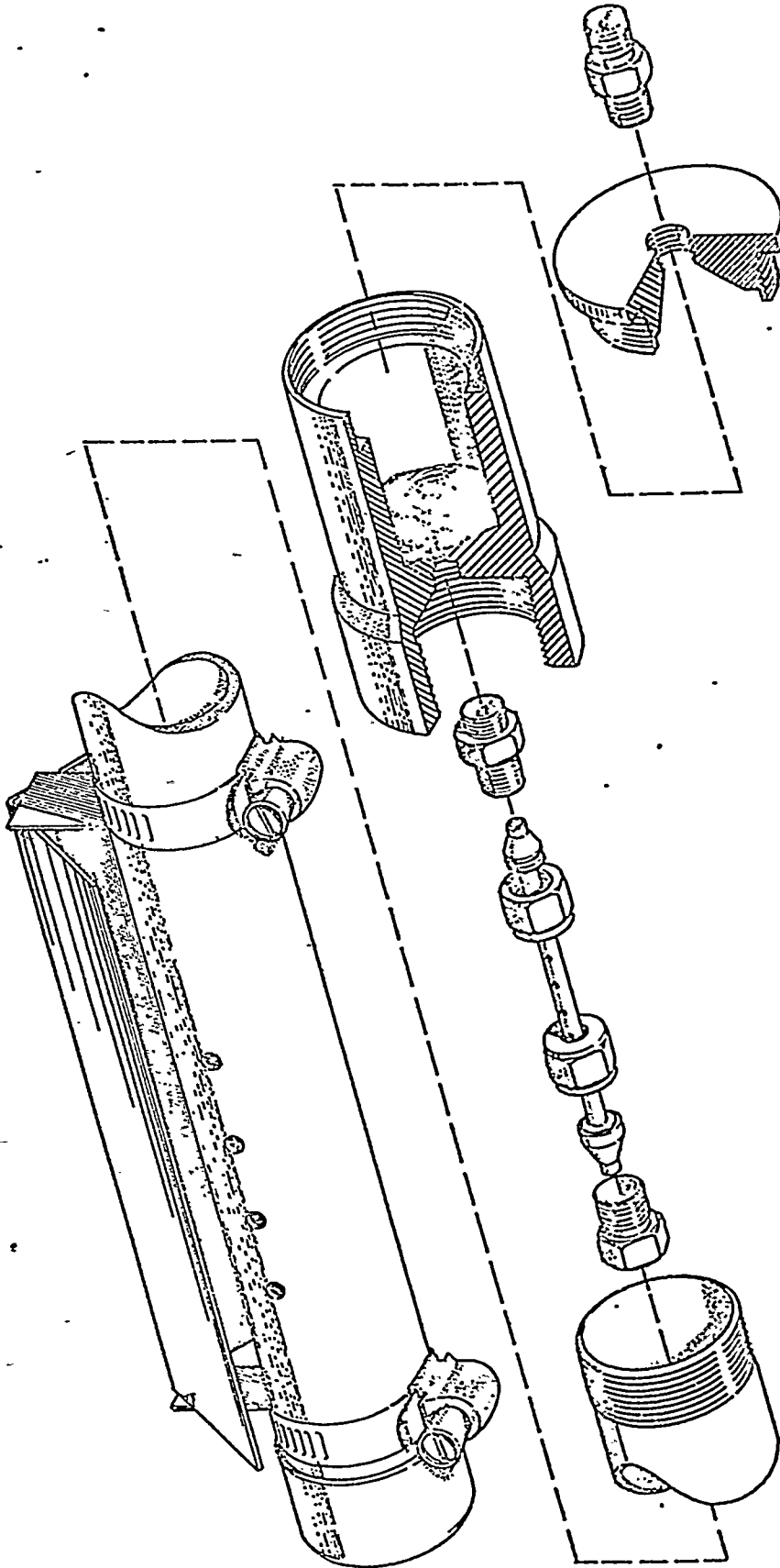
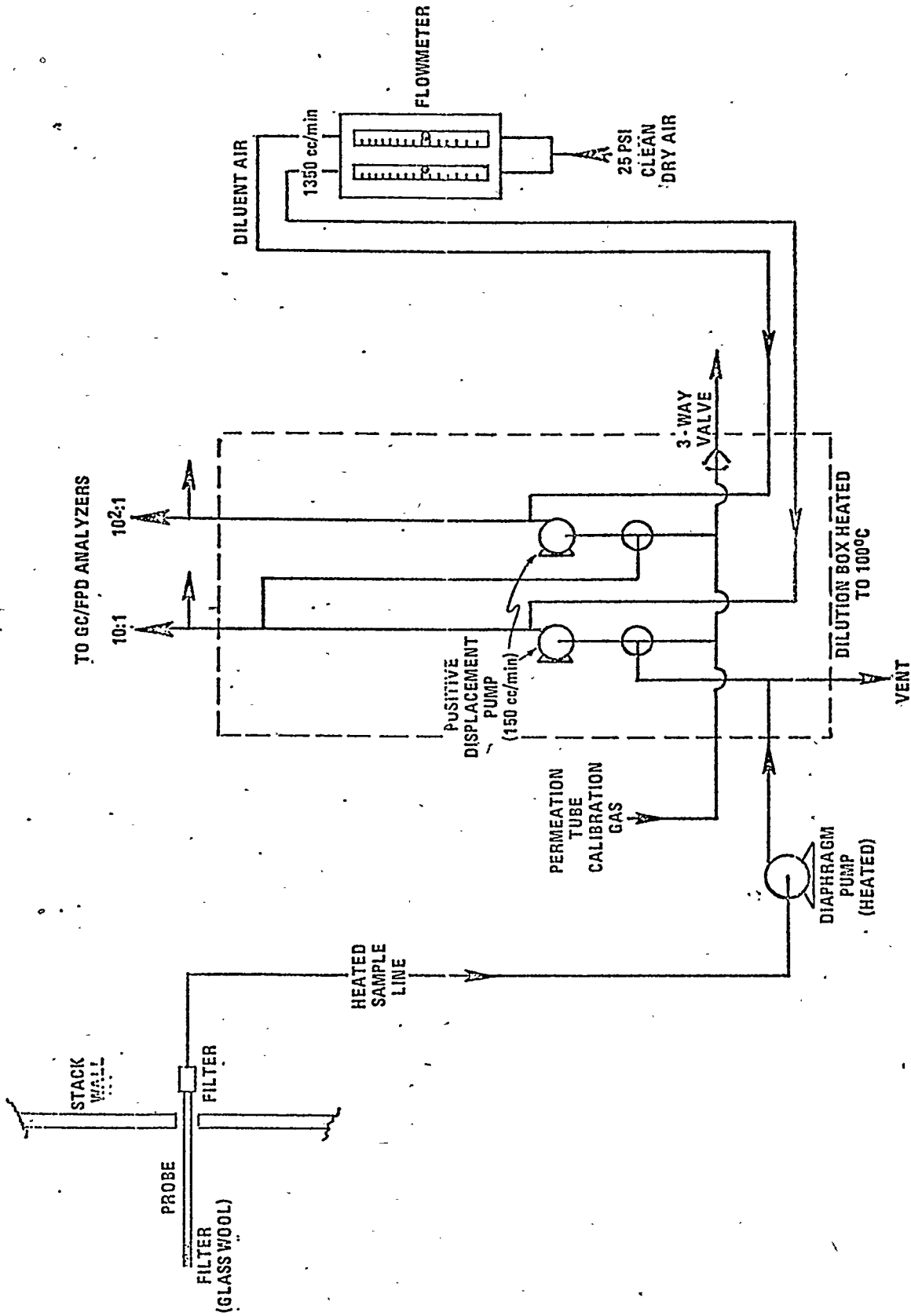Figure 16-1. Probe used for sample gas containing high particulate loadings.

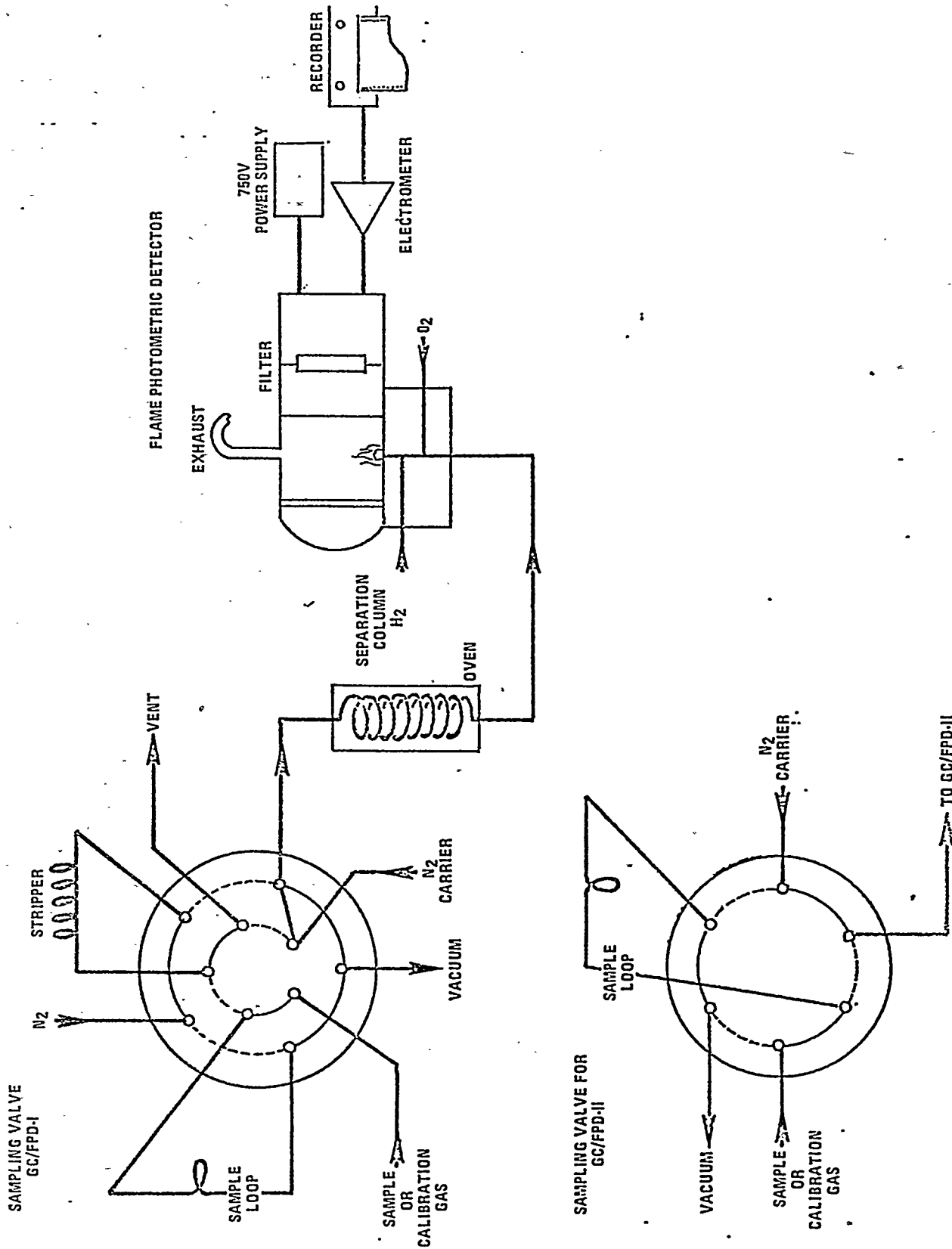Figure 16-2. Sampling and dilution apparatus.

Figure 16-3. Gas chromatographic-flame photometric analyzers.
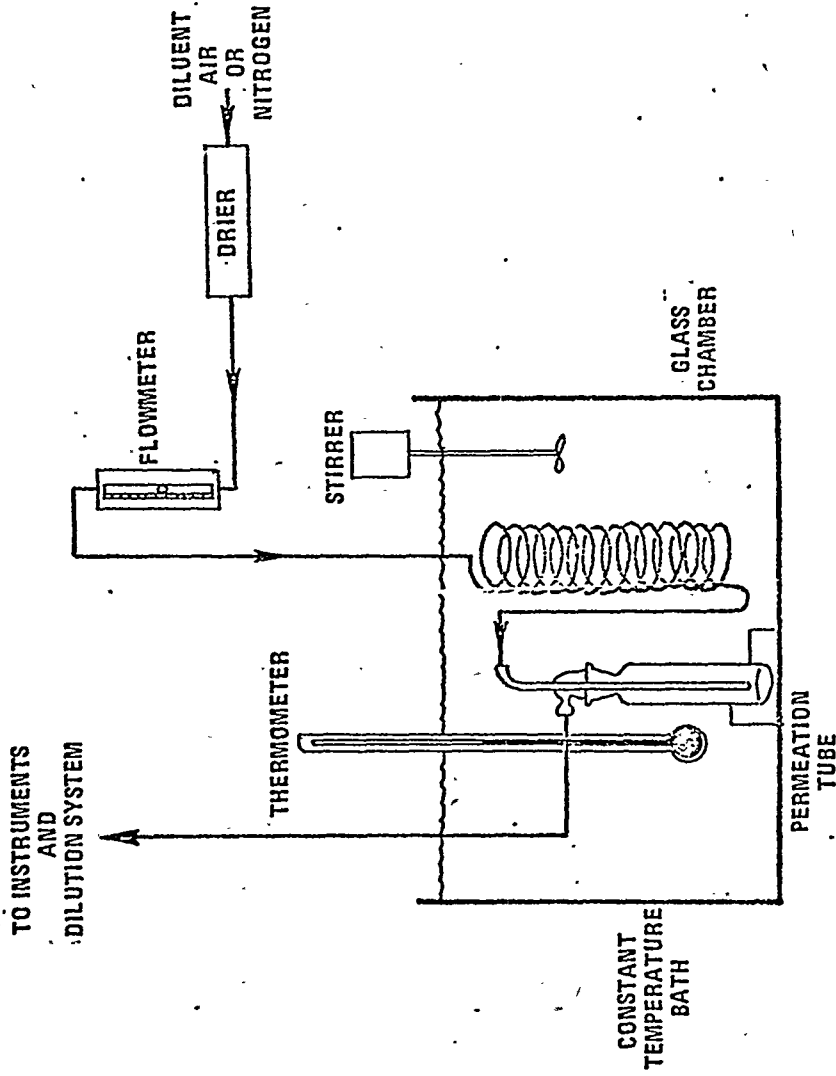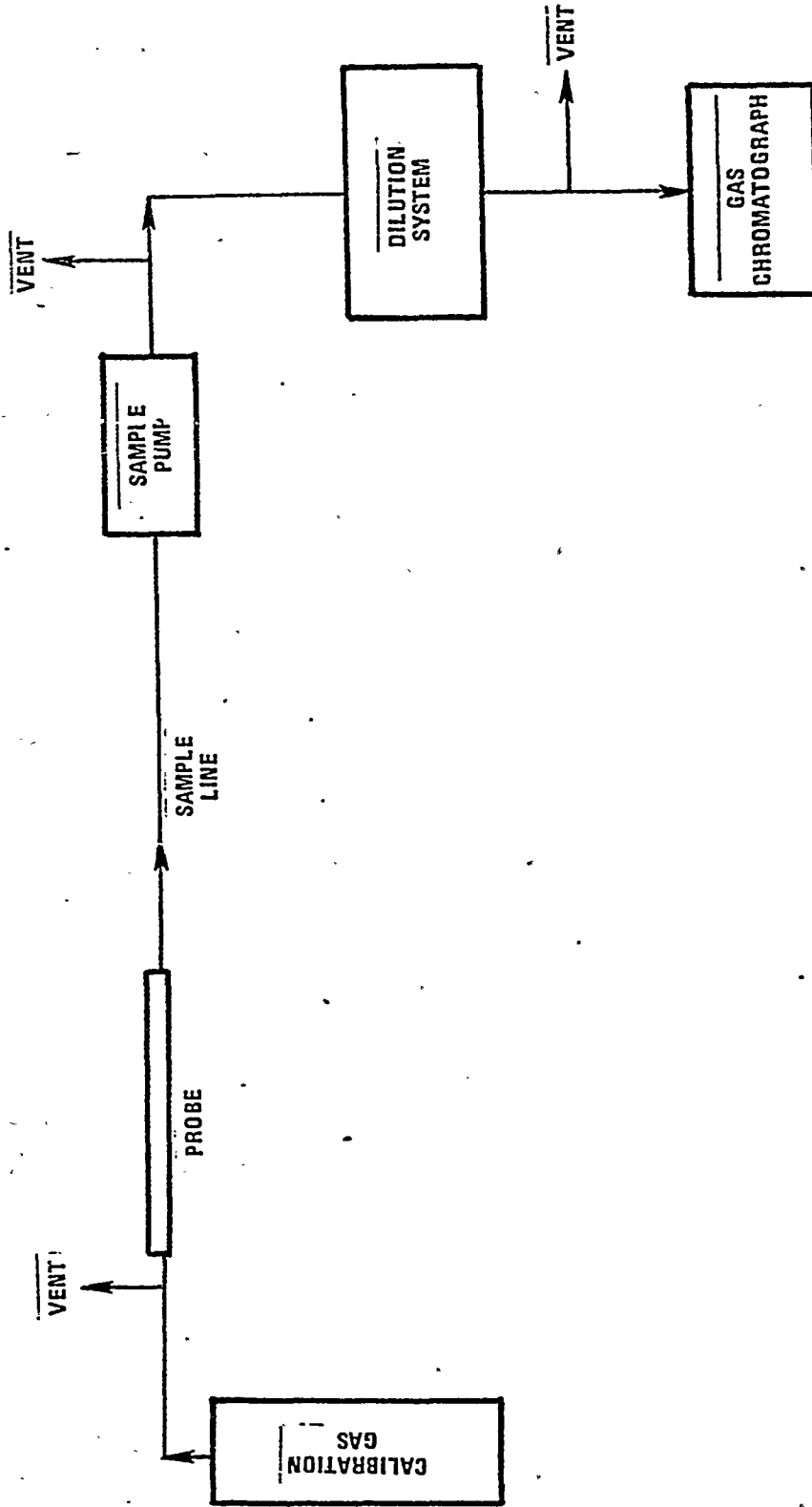
Figure 16-4. Apparatus for field calibration.

Figure 16- 5. Determination of sample line loss.

METHOD 17. DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES (IN-STACK FILTRATION METHOD)

Introduction

Particulate matter is not an absolute quantity; rather, it is a function of temperature and pressure. Therefore, to prevent variability in particulate matter emission regulations and/or associated test methods, the temperature and pressure at which particulate matter is to be measured must be carefully defined. Of the two variables (i.e., temperature and pressure), temperature has the greater effect upon the amount of particulate matter in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible.

In method 5, 250° F is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standards, particulate matter is defined with respect to temperature. In order to maintain a collection temperature of 250° F, Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where particulate matter concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and heating systems, and sample at stack temperature.

This method describes an in-stack sampling system and sampling procedures for use in such cases. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator.

1. *Principle and Applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The particulate mass is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method applies to the determination of particulate emissions from stationary sources for determining compliance with new source performance standards, only when specifically provided for in an applicable subpart of the standards. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see Section 4.1.2).

2. *Apparatus.*

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17-1. Construction details for many, but not all, of the train components are given in APTD-0581 (Citation 2 in Section 7); for changes from the APTD-0581 document and for allowable modifications to Figure 17-1, consult with the Administrator.

Figure 17-1. Particulate-Sampling Train, Equipped with In-Stack Filter.

The operating and maintenance procedures for many of the sampling train components are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass, with sharp, tapered leading edge. The angle of taper shall be 030° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used subject to the approval of the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (⅛ to ½ in)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm (¹⁄₁₆ in). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1.

2.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or quartz glass, or stainless steel; if a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used subject to approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

2.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

2.1.4 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator; the pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity (see Figure 17-1). The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane during sampling (see Method 2, Figure 2-6b). It is recommended: (1) that the pitot tube have a known baseline coefficient, determined as outlined in Section 4 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17-1). Note that the 1.9 cm (0.75 in) free-space between the nozzle and pitot tube shown in Figure 17-1, is based on a 1.3 cm (0.5 in) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (0.75 in) with the largest sized nozzle in place.

Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17-1 (or the equivalent of these requirements, e.g., Figure 2-7 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

2.1.5 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.6 Condenser. It is recommended that the impinger system described in Method 5 be used to determine the moisture content of the stack gas. Alternatively, any system that allows measurement of both the water condensed and the moisture leaving the condenser, each to within 1 ml or 1 g, may be used. The moisture leaving the condenser can be measured either by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a silica gel trap with exit gases kept below 20° C (68° F) and determining the weight gain.

Flexible tubing may be used between the probe extension and condenser. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.7 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 17-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.8 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.9 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3.

The temperature sensor shall be attached to either the pitot tube or to the probe extension, in a fixed configuration. If the temperature sensor is attached in the field; the sensor shall be placed in an interference-free arrangement with respect to the Type S pitot tube openings (as shown in Figure 17-1 or in Figure 2-7 of Method 2). Alternatively, the temperature sensor need not be attached to either the probe extension or pitot tube during sampling, provided that a difference of not more than 1 percent in the average velocity measurement is introduced. This alternative is subject to the approval of the Administrator.

2.2 Sample Recovery.

2.2.1 Probe Nozzle Brush. Nylon bristle brush with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.3 Analysis.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 mg.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

3. Reagents.

3.1 Sampling.

3.1.1 Filters. The in-stack filters shall be glass mats or thimble fiber filters, without organic binders, and shall exhibit at least 99.95 percent efficiency (00.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency tests shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Crushed Ice.

3.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Sample Recovery. Acetone, reagent grade, 00.001 percent residue, in glass bottles. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers. Thus, acetone blanks shall be run prior to field use and only acetone with low blank

values (00.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis.

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

4. *Procedure.*

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.
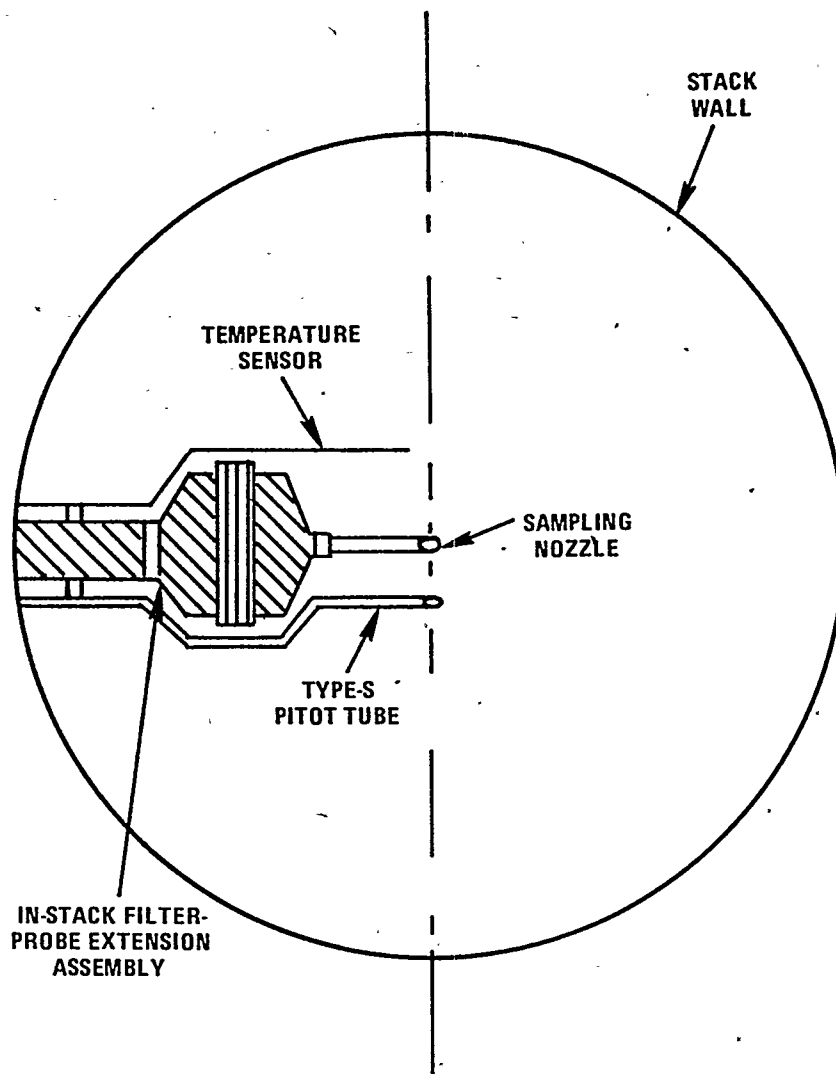
Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper size on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 00.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17-2. Calculate the estimated cross-section blockage, as shown in Figure 17-2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Citation 10 in Section 7). Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particular sample run.

STACK
WALL

TEMPERATURE
SENSOR

SAMPLING
NOZZLE

TYPE-S
PITOT TUBE

IN-STACK FILTER-
PROBE EXTENSION
ASSEMBLY

$$\text{ESTIMATED BLOCKAGE (\%)} = \left[\frac{\text{SHADED AREA}}{\text{DUCT AREA}}\right] \times 100$$

Figure 17-2. Projected-area model of cross-section blockage (approximate average for a sample traverse) caused by an in-stack filter holder-probe extension assembly.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval if specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

If impingers are used to condense stack gas moisture, prepare them as follows: place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

If some means other than impingers is used to condense moisture, prepare the condenser (and, if appropriate, silica gel for condenser outlet) for use.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 17-1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

4.1.4 Leak Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream. Turn on the pump and draw a vacuum of at least 380 mm Hg (15 in. Hg); note that a lower vacuum may be used, provided that it is not exceeded during the test. Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m³/min. (0.02 cfm), whichever is less, is unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse direction of by-pass valve. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain a sampling rate such that sampling is within 10 percent of true isokinetic, unless otherwise specified by the Administrator.

For each run, record the data required on the example data sheet shown in Figure 17-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 17-3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

PLANT _____
LOCATION _____
OPERATOR _____
DATE _____
RUN NO. _____
SAMPLE BOX NO. _____
METER BOX NO. _____
METER ΔH@ _____
C FACTOR _____
PITOT TUBE COEFFICIENT, Cp _____

BAROMETRIC PRESSURE _____
ASSUMED MOISTURE, % _____
PROBE EXTENSION LENGTH, m(ft.) _____
NOZZLE IDENTIFICATION NO. _____
AVERAGE CALIBRATED NOZZLE DIAMETER. cm (in.) _____
FILTER NO. _____
LEAK RATE, m3/min, (cfm) _____
STATIC PRESSURE, mm Hg (in. Hg) _____

SCHEMATIC OF STACK CROSS SECTION

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S), °C (°F)	VELOCITY HEAD (ΔP_S), mm H2O (in. H2O)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER, mm H2O (in. H2O)	GAS SAMPLE VOLUME, m3 (ft3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER — INLET °C (°F)	GAS SAMPLE TEMPERATURE AT DRY GAS METER — OUTLET °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
TOTAL							Avg	Avg	
AVERAGE							Avg		

Figure 17-3. Particulate field data.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment to the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85±0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29±4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Citation 7 in Section 7) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes, to minimize chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain a temperature of less than 20° C (68° F) at the condenser outlet; this will prevent excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter holder assembly be used rather than attempting to change the filter itself. Before a new filter holder is installed, conduct a leak check, as outlined in Section 4.1.4.2. The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator. Note that when two or more trains are used, a separate analysis of the collected particulate from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the particulate catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Section 3.1 of Method 2; the lines must pass this leak-

check, in order to validate the velocity head data.

. 4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Section 6.11) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe nozzle or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, fitting, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the fitting in a similar way until no visible particles remain. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Rinse the brush with acetone and quantitatively collect these washings in the sample container. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease (if applicable), clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make final rinse of the brush and filter holder. After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. If silica gel is used in the condenser system for moisture content determination, note the color of the gel to determine if it has been completely spent; make a notation of its condition. Transfer the silica gel back to its original container and seal. A funnel may make it easier to pour the silica gel without spilling, and a rubber policeman may be used as an aid in removing the silica gel. It is not necessary to remove the small amount of dust particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 under "Analysis."

Condenser Water. Treat the condenser or impinger water as follows: make a notation of any color or film in the liquid catch. Measure the liquid volume to within ±1 ml by using a graduated cylinder or, if a balance is available, determine the liquid weight to within ±0.5 g. Record the total volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight.

4.3 Analysis. Record the data required on the example sheet shown in Figure 17-4. Handle each sample container as follows:

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at the average stack temperature or

105° C (220° F), whichever is less, for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise speci- fied by the Administrator. The tester may also opt to oven dry the sample at the aver- age stack temperature or 105° C (220° F), whichever is less, for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Plant _____

Date _____

Run No. _____

Filter No. _____

Amount liquid lost during transport _____

Acetone blank volume, ml _____

Acetone wash volume, ml _____

Acetone black concentration, mg/mg (equation 17-4) _____

Acetone wash blank, mg (equation 17-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
Less acetone blank			
Weight of particulate matter			

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

* CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{INCREASE, g}{1\ g/ml} = VOLUME\ WATER,\ ml$$

Figure 17-4. Analytical data.

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE.—At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

5. *Calibration.* Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. If the pitot tube is placed in an interference-free arrangement with respect to the other probe assembly components, its baseline (isolated tube) coefficient shall be determined as outlined in Section 4 of Method 2. If the probe assembly is not interference-free, the pitot tube assembly coefficient shall be determined by calibration, using methods subject to the approval of the Administrator.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values.

Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

NOTE.—If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.5 Leak Check of Metering System Shown in Figure 17-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 17-5). Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.
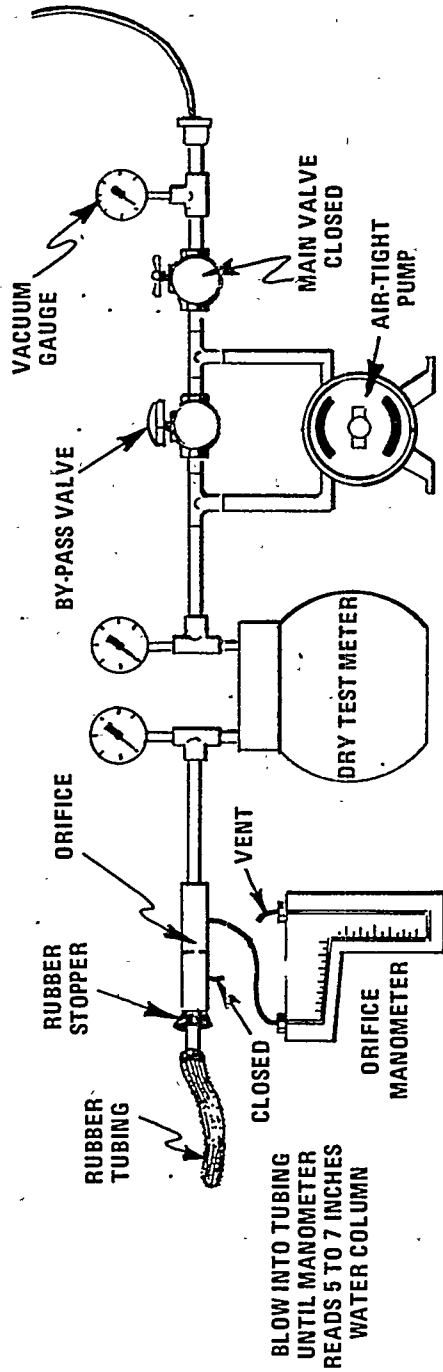
Figure 17-5. Leak check of meter box.

5.6 Barometer. Calibrate against a mercury barometer.

6. *Calculations.* Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature.

A_n=Cross-sectional area of nozzle, m² (ft²).

B_{ws}=Water vapor in the gas stream, proportion by volume.

C_a=Acetone blank residue concentration, mg/g.

c_s=Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I=Percent of isokinetic sampling.

L_a=Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i=Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i=1, 2, 3 . . . n), m³/min (cfm).

L_p=Leakage rate observed during the post-test leak check, m³/min (cfm).

m_n=Total amount of particulate matter collected, mg.

M_w=Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

m_a=Mass of residue of acetone after evaporation, mg.

P_{bar}=Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s=Absolute stack gas pressure, mm Hg (in. Hg).

P_{std}=Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R=Ideal gas constant, 0.06236 mm Hg-m³/ °K-g-mole (21.85 in. Hg-ft³/°R-lb-mole).

T_m=Absolute average dry gas meter temperature (see Figure 17-3), °K(°R).

T_s=Absolute average stack gas temperature (see Figure 17-3), °K (°R).

T_{std}=Standard absolute temperature, 293°K (528°R).

V_a=Volume of acetone blank, ml.

V_{aw}=Volume of acetone used in wash, ml.

V_{lc}=Total volume of liquid collected in impingers and silica gel (see Figure 17-4), ml.

V_m=Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$=Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$=Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s=Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 17, m/sec (ft/sec).

W_a=Weight of residue in acetone wash, mg.

Y=Dry gas meter calibration coefficient.

ΔH=Average pressure differential across the orifice meter (see Figure 17-3), mm H₂O (in. H₂O).

$ρ_a$=Density of acetone, mg/ml (see label on bottle).

$ρ_w$=Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ=Total sampling time, min.

$θ_1$=Sampling time interval, from the beginning of a run until the first component change, min.

$θ_i$=Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

$θ_p$=Sampling time interval, from the final (nth) component change until the end of the sampling run, min.

13.6=Specific gravity of mercury.

60=Sec/min.

100=Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 17-3).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 17-1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right) \left[\frac{P_{bar} + \frac{ΔH}{13.6}}{P_{std}}\right]$$

$$= K_1 V_m Y \frac{P_{bar} + (ΔH/13.6)}{T_m}$$

Equation 17-1

where:

K_1=0.3858° K/mm Hg for metric units; 17.64° R/in. Hg for English units.

Note.—Equation 17-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 17-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 17-1 with the expression:

$$[V_m-(L_p-L_a)θ]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 17-1 by the expression:

$$\{V_m - (L_1 - L_a) θ_1 - \sum_{i=2}^{n} (L_i - L_a) θ_i$$
$$- (L_p - L_a) θ_p\}$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

6.4 Volume of water vapor.

$$V_{w(std)} = V_{lc} \left(\frac{ρ_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right) = K_2 V_{lc}$$

Equation 17-2

where:

K_2=0.001333 m³/ml for metric units; 0.04707 ft³/ml for English units.

6.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

Equation 17-3

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a ρ_a}$$

Equation 17-4

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} ρ_a$$

Equation 17-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 17-4).

Note.—Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$c_s=(0.001 g/mg) (m_n/V_{m(std)})$$

Equation 17-6

6.10 Conversion Factors:

From	To	Multiply by
scf	m³	0.02832
g/ft³	gr/ft³	15.43
g/ft³	lb/ft³	2.205×10⁻³
g/ft³	g/m³	35.31

6.11 Isokinetic Variation.
6.11.1 Calculation from Raw Data.

$$I = \frac{100 T_s [K_3 V_{lc} + (V_m Y/T_m) (P_{bar} + ΔH/13.6)]}{60 θ v_s P_s A_n}$$

Equation 17-7

where:

K_3=0.003454 mm Hg-m³/ml-°K for metric units; 0.002669 in. Hg-ft³/ml-°R for English units.

6.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s θ A_n P_s 60 (1-B_{ws})}$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s v_s A_n θ (1-B_{ws})}$$

Equation 17-8

where:

K_4=4.320 for metric units; 0.09450 for English units.

6.12 Acceptable Results. If 90 percent 010110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 in Section 7 to make judgments. Otherwise, reject the results and repeat the test.

7. *Bibliography.*

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