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Title 40—Protection of Environment
CHAPTER I—ENVIRONMENTAL
PROTECTION AGENCY

[FRL 392-7]

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Five Categories of Sources in the Phosphate Fertilizer Industry

On October 22, 1974 (39 FR 37602), under section 111 of the Clean Air Act, as amended, the Administrator proposed standards of performance for five new affected facilities within the phosphate fertilizer industry as follows: Wet-process phosphoric acid plants, superphosphoric acid plants, diammonium phosphate plants, triple superphosphate plants, and granular triple superphosphate storage facilities.

Interested parties participated in the rulemaking by sending comments to EPA. The Freedom of Information Center, Rm 202 West Tower, 401 M Street, SW., Washington, D.C. has copies of the comment letters received and a summary of the issues and Agency responses available for public inspection. In addition, copies of the issue summary and Agency responses may be obtained upon written request from the EPA Public Information Center (PM-215), 401 M Street, SW., Washington, D.C. 20460 (specify "Comment Summary: Phosphate Fertilizer Industry"). The comments have been considered and where determined by the Administrator to be appropriate, revisions have been made to the proposed standards, and the revised version of the standards of performance for five source categories within the phosphate fertilizer industry are herein promulgated. The principal revisions to the proposed standards and the Agency's responses to major comments are summarized below.

DEFINITIONS

The comment was made that the designation of affected facilities (§§ 60.200, 60.210, 60.220, 60.230, and 60.240) were confusing as written in the proposed regulations. As a result of the proposed wording, each component of an affected facility could have been considered a separate affected facility. Since this was not the intent, the affected facility designations have been reworded. In the new wording, the listing of components of an affected facility is intended for identification of those emission sources to which the standard for fluorides applies. Any sources not listed are not covered by the standard. Additionally, the definition of a "superphosphoric acid plant" has been changed to include facilities which concentrate wet-process phosphoric acid to 66 percent or greater P_2O_5 content instead of 60 percent as specified in the proposed regulations. This was the result of a comment stating that solvent extracted acids could be evaporated to greater than 60 percent P_2O_5 using conventional evaporators in the wet-process phosphoric acid plant. The revision clarifies the original intention of preventing certain wet-process phosphoric acid plants from being subject to the more

restrictive standard for superphosphoric acid plants.

One commentator was concerned that a loose interpretation of the definition of the affected facility for diammonium phosphate plants might result in certain liquid fertilizer plants becoming subject to the standards. Therefore, the word "granular" has been inserted before "diammonium phosphate plant" in the appropriate places in subpart V to clarify the intended meaning.

Under the standards for triple superphosphate plants in § 60.231(b), the term "by weight" has been added to the definition of "run-of-pile triple superphosphate." Apparently it was not clear as to whether "25 percent of which (when not caked) will pass through a 16 mesh screen" referred to percent by weight or by particle count.

OPACITY STANDARDS

Many commentators challenged the proposed opacity standards on the grounds that EPA had shown no correlation between fluoride emissions and plume opacity, and that no data were presented which showed that a violation of the proposed opacity standard would indicate simultaneous violation of the proposed fluoride standard. For the opacity standard to be used as an enforcement tool to indicate possible violation of the fluoride standard, such a correlation must be established. The Agency has reevaluated the opacity test data and determined that the correlation is insufficient to support a standard. Therefore, standards for visible emissions for diammonium phosphate plants, triple superphosphate plants, and granular triple superphosphate storage facilities have been deleted. This action, however, is not meant to set a precedent regarding promulgation of visible emission standards. The situation which necessitates this decision relates only to fluoride emissions. In the future, the Agency will continue to set opacity standards for affected facilities where such standards are desirable and warranted based on test data.

In place of the opacity standard, a provision has been added which requires an owner or operator to monitor the total pressure drop across an affected facility's scrubbing system. This requirement will provide an affected facility's scrubbing system. This requirement will provide for a record of the operating conditions of the control system, and will serve as an effective method for monitoring compliance with the fluoride standards.

REFERENCE METHODS 13A AND 13B

Reference Methods 13A and 13B, which prescribed testing and analysis procedures for fluoride emissions, were originally proposed along with standards of performance for the primary aluminum industry (39 FR 37730). However, these methods have been included with the standards of performance for the phosphate fertilizer industry and the fertilizer standards are being promulgated before the primary aluminum standards. Comments were received from

the phosphate fertilizer industry and the primary aluminum industry as the methods are applicable to both industries. The majority of the comments discussed possible changes to procedures and to equipment specifications. As a result of these comments some minor changes were made. Additionally, it has been determined that acetone causes a positive interference in the analytical procedures. Although the bases for the standard are not affected, the acetone wash has been deleted in both methods to prevent potential errors. Reference Method 13A has been revised to restrict the distillation procedure (Section 7.3.4) to 175°C instead of the proposed 180°C in order to prevent positive interferences introduced by sulfuric acid carryover in the distillate at the higher temperatures. Some commentators expressed a desire to replace the methods with totally different methods of analysis. They felt they should not be restricted to using only those methods published by the Agency. However, in response to these comments, an equivalent or alternative method may be used after approval by the Administrator according to the provisions of § 60.8(b) of the regulations (as revised in 39 FR 9308).

FLUORIDE CONTROL

Comments were received which questioned the need for Federal fluoride control because fluoride emissions are localized and ambient fluoride concentrations are very low. As discussed in the preamble to the proposed regulations, fluoride was the only pollutant other than the criteria pollutants, specifically named as requiring Federal action in the March 1970 "Report of the Secretary of Health, Education, and Welfare to the United States (91st Congress)." The report concluded that "inorganic fluorides are highly irritant and toxic gases" which, even in low ambient concentrations, have adverse effects on plants and animals. The United States Senate Committee on Public Works in its report on the Clean Air Amendments of 1970 (Senate Report No. 91-1196, September 17, 1970, page 9) included fluorides on a list of contaminants which have broad national impact and require Federal action.

One commentator questioned EPA's use of section 111 of the Clean Air Act, as amended, as a means of controlling fluoride air pollution. Again, as was mentioned in the preamble to the proposed regulations, the "Preferred Standards Path Report for Fluorides" (November 1972) concluded that the most appropriate control strategy is through section 111. A copy of this report is available for inspection during normal business hours at the Freedom of Information Center, Environmental Protection Agency, 401 M Street, SW., Washington, D.C.

Another objection was voiced concerning the preamble statement that the "phosphate fertilizer industry is a major source of fluoride air pollution." According to the "Engineering and Cost Effectiveness Study of Fluoride Emissions

Control" (Contract EHSD 71-14) published in January 1972, the phosphate fertilizer industry ranks near the top of the list of fluoride emitters in the U.S., accounting for nearly 14 percent of the total soluble fluorides emitted every year. The Agency contends that these facts justify naming the phosphate fertilizer industry a major source of fluorides.

DIAMMONIUM PHOSPHATE STANDARD

One commentator contended that the fluoride standard for diammonium phosphate plants could not be met under certain extreme conditions. During periods of high air flow rates through the scrubbing system, high ambient temperatures, and high fluoride content in scrubber liquor, the commentator suggested that the standard would not be met even by sources utilizing best demonstrated control technology. This comment was refuted for two reasons: (1) The surmised extreme conditions would not occur and (2) even if the conditions did occur, the performance of the control system would be such as to meet the standard anyway. Thus the fluoride standard for diammonium phosphate plants was not revised.

POND WATER STANDARDS

The question of the standards for pond water was raised in the comments. The commentator felt that it would have been more logical if the Agency had postponed proposal of the phosphate fertilizer regulations until standards of performance for pond water had also been decided upon, instead of EPA saying that such pond water standards might be set in the future. EPA researched pond water standards along with the other fertilizer standards, but due to the complex nature of pond chemistry and a general lack of available information, simultaneous proposal was not feasible. Rather than delay new source fluoride control regulations, possibly for several years, the Agency decided to proceed with standards for five categories of sources within the industry.

ECONOMIC IMPACT

As was indicated by the comments received, clarification of some of the Agency's statements concerning the economic impact of the standards is necessary. First, the statement that "for three of the five standards there will be no increase in power consumption over that which results from State and local standards" is misleading as written in the preamble to the proposed regulations. The statement should have been qualified in that this conclusion was based on projected construction in the industry through 1980, and was not meant to be applicable past that time. Second, some comments suggested that the cost data in the background document were out of date. Of course the time between the gathering of economic data and the proposal of regulations may be as long as a year or two because of necessary intermediate steps in the standard setting process, however, the economic data are developed with future industry growth

and financial status in mind, and therefore, the analysis should be viable at the time of standard proposal. Third, an objection was raised to the statement that "the disparity in cost between triple superphosphate and diammonium phosphate will only hasten the trend toward production of diammonium phosphate." The commentator felt that EPA should not place itself in a position of regulating fertilizer production. In response, the Agency does not set standards to regulate production. The standards are set to employ the best system of emission reduction considering cost. The standards will basically require use of a packed scrubber for compliance in each of the five phosphate fertilizer source categories. In this instance, control costs (although considered reasonable for both source categories) are higher for triple superphosphate plants than for diammonium phosphate plants. The reasons for this are that (1) larger gas volumes must be scrubbed in triple superphosphate facilities and (2) triple superphosphate storage facility emissions must also be scrubbed. However, the greater costs can be partially offset in a plant producing both granular triple superphosphate and diammonium phosphate with the same manufacturing facility and same control device. Such a facility can optimize utilization of the owner's capital by operating his phosphoric acid plant at full capacity and producing a product mix that will maximize profits. The information gathered by the Agency indicates that all new facilities equipped to manufacture diammonium phosphate will also produce granular triple superphosphate to satisfy demand for direct application materials and exports.

CONTROL OF TOTAL FLUORIDES

Most of the commentators objected to EPA's control of "total fluorides" rather than "gaseous and water soluble fluorides." The rationale for deciding to set standards for total fluorides is presented on pages 5 and 6 of volume 1 of the background document. Essentially the rationale is that some "insoluble" fluoride compounds will slowly dissolve if allowed to remain in the water-impinger section of the sample train. Since EPA did not closely control the time between capture and filtration of the fluoride samples, the change was made to insure a more accurate data base. Additional comments on this subject revealed concern that the switch to total fluorides would bring phosphate rock operations under the standards. EPA did not intend such operations to be controlled by these regulations, and did not include them in the definitions of affected facilities; however, standards for these operations are currently under development within the Agency.

MONITORING REQUIREMENTS

Several comments were received with regard to the sections requiring a flow measuring device which has an accuracy of ± 5 percent over its operating range. The commentators felt that this accuracy could not be met and that the capital and operating costs outweighed

anticipated utility. First of all, "weigh-belts" are common devices in the phosphate fertilizer industry as raw material feeds are routinely measured. EPA felt there would be no economic impact resulting from this requirement because plants would have normally installed weighing devices anyway. Second, contacts with the industry led EPA to believe that the ± 5 percent accuracy requirement would be easily met, and a search of pertinent literature showed that weighing devices with ± 1 percent accuracy are commercially available.

PERFORMANCE TEST PROCEDURES

Finally some comments specifically addressed § 60.245 (now § 60.244) of the proposed granular triple superphosphate storage facility standards. The first two remarks contended that it is impossible to tell when the storage building is filled to at least 10 percent of the building capacity without requiring an expensive engineering survey, and that it was also impossible to tell how much triple superphosphate in the building is fresh and how much is over 10 days old. EPA's experience has been that plants typically make surveys to determine the amount of triple superphosphate stored, and typically keep good records of the movement of triple superphosphate into and out of storage so that it is possible to make a good estimate of the age and amount of product. In light of data gathered during testing, the Agency disagrees with the above contentions and feels the requirements are reasonable. A third comment stated that § 60.244 (proposed § 60.245) was too restrictive, could not be met with partially filled storage facilities, and that the 10 percent requirement was not valid or practical. In response, the requirement of § 60.244(d) (1) is that "at least 10 percent of the building capacity" contain granular triple superphosphate. This means that, for a performance test, an owner or operator could have more than 10 percent of the building filled. In fact it is to his advantage to have more than 10 percent because of the likelihood of decreased emissions (in units of the standard) as calculated by the equation in § 60.244(g). The data obtained by the Agency show that the standard can be met with partially filled buildings. One commentator did not agree with the requirement in § 60.244(e) [proposed § 60.245(e)] to have at least five days maximum production of fresh granular triple superphosphate in the storage building before a performance test. The commentator felt this section was unreasonable because it dictated production schedules for triple superphosphate. However, this section applies only when the requirements of § 60.244(d) (2) [proposed § 60.245(d) (2)] are not met. In addition this requirement is not unreasonable regarding production schedules because performance tests are not required at regular intervals. A performance test is conducted after a facility begins operation; additional performance tests are conducted only when the facility is suspected of violation of the standard of performance.

Effective date. In accordance with section 111 of the Act, these regulations prescribing standards of performance for the selected stationary sources are effective on August 4, 1975, and apply to sources at which construction or modification commenced after October 22, 1974.

RUSSELL E. TRAIN,
Administrator.

JULY 25, 1975.

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

1. The table of sections is amended by adding Subparts T, U, V, W, and X and revising Appendix A to read as follows:

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Subpart T—Standards of Performance for the Phosphate Fertilizer Industry: Wet Process Phosphate Acid Plants

- 60.200 Applicability and designation of affected facility.
60.201 Definitions.
60.202 Standard for fluorides.
60.203 Monitoring of operations.
60.204 Test methods and procedures.

Subpart U—Standards of Performance for the Phosphate Fertilizer Industry: Superphosphoric Acid Plants

- 60.210 Applicability and designation of affected facility.
60.211 Definitions.
60.212 Standard for fluorides.
60.213 Monitoring of operations.
60.214 Test methods and procedures.

Subpart V—Standards of Performance for the Phosphate Fertilizer Industry: Diammonium Phosphate Plants

- 60.220 Applicability and designation of affected facility.
60.221 Definitions.
60.222 Standard for fluorides.
60.223 Monitoring of operations.
60.224 Test methods and procedures.

Subpart W—Standards of Performance for the Phosphate Fertilizer Industry: Triple Superphosphate Plants

- 60.230 Applicability and designation of affected facility.
60.231 Definitions.
60.232 Standard for fluorides.
60.233 Monitoring of operations.
60.234 Test methods and procedures.

Subpart X—Standards of Performance for the Phosphate Fertilizer Industry: Granular Triple Superphosphate Storage Facilities

- 60.240 Applicability and designation of affected facility.
60.241 Definitions.
60.242 Standard for fluorides.
60.243 Monitoring of operations.
60.244 Test methods and procedures.

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APPENDIX A—REFERENCE METHODS

- Method 1—Sample and velocity traverses for stationary sources.
Method 2—Determination of stack gas velocity and volumetric flow rate. (Type S pitot tube).
Method 3—Gas analysis for carbon dioxide, excess air, and dry molecular weight.
Method 4—Determination of moisture in stack gases.
Method 5—Determination of particulate emissions from stationary sources.
Method 6—Determination of sulfur dioxide emissions from stationary sources.
Method 7—Determination of nitrogen oxide emissions from stationary sources.

Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources.

Method 9—Visual determination of the opacity of emissions from stationary sources.

Method 10—Determination of carbon monoxide emissions from stationary sources.

Method 11—Determination of hydrogen sulfide emissions from stationary sources.

Method 12—Reserved.

Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS Zirconium Lake Method.

Method 13B—Determination of total fluoride emissions from stationary sources—Specific Ion Electrode Method.

2. Part 60 is amended by adding subparts T, U, V, W, and X as follows:

Subpart T—Standards of Performance for the Phosphate Fertilizer Industry: Wet-Process Phosphoric Acid Plants

§ 60.200 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each wet-process phosphoric acid plant. For the purpose of this subpart, the affected facility includes any combination of: reactors, filters, evaporators, and hotwells.

§ 60.201 Definitions.

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

(a) "Wet-process phosphoric acid plant" means any facility manufacturing phosphoric acid by reacting phosphate rock and acid.

(b) "Total fluorides" means elemental fluorine and all fluoride compounds as measured by reference methods specified in § 60.204, or equivalent or alternative methods.

(c) "Equivalent P₂O₅ feed" means the quantity of phosphorus, expressed as phosphorous pentoxide, fed to the process.

§ 60.202 Standard for fluorides.

(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 from any affected facility any gases which contain total fluorides in excess of 10.0 g/metric ton of equivalent P₂O₅ feed (0.020 lb/ton).

§ 60.203 Monitoring of operations.

(a) The owner or operator of any wet-process phosphoric acid plant subject to the provisions of this subpart shall install, calibrate, maintain, and operate a monitoring device which can be used to determine the mass flow of phosphorus-bearing feed material to the process. The monitoring device shall have an accuracy of ±5 percent over its operating range.

(b) The owner or operator of any wet-process phosphoric acid plant shall maintain a daily record of equivalent P₂O₅ feed by first determining the total mass rate in metric ton/hr of phosphorus bearing feed using a monitoring device for measuring mass flowrate which meets the requirements of paragraph (a) of

this section and then by proceeding according to § 60.204(d) (2).

(c) The owner or operator of any wet-process phosphoric acid subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously measures and permanently records the total pressure drop across the process scrubbing system. The monitoring device shall have an accuracy of ±5 percent over its operating range.

§ 60.204 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided in § 60.8 (b), shall be used to determine compliance with the standard prescribed in § 60.202 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and the associated moisture content;

(2) Method 1 for sample and velocity traverses;

(3) Method 2 for velocity and volumetric flow rate; and

(4) Method 3 for gas analysis.

(b) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be 0.85 dscm (30 dscf) except that shorter sampling times or smaller volumes, when necessitated by process variables or other factors, may be approved by the Administrator.

(c) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(d) Equivalent P₂O₅ feed shall be determined as follows:

(1) Determine the total mass rate in metric ton/hr of phosphorus-bearing feed during each run using a flow monitoring device meeting the requirements of § 60.203 (a).

(2) Calculate the equivalent P₂O₅ feed by multiplying the percentage P₂O₅ content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass rate of phosphorus-bearing feed. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11-12. Other methods may be approved by the Administrator.

(e) For each run, emissions expressed in g/metric ton of equivalent P₂O₅ feed shall be determined using the following equation:

$$E = \frac{(C_s Q_s) 10^{-3}}{M_{P_2O_5}}$$

where:

E = Emissions of total fluorides in g/metric ton of equivalent P₂O₅ feed.

C_s = Concentration of total fluorides in mg/dscm as determined by Method 13A or 13B.

Q_s = Volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2.

10⁻³ = Conversion factor for mg to g.

M_{P₂O₅} = Equivalent P₂O₅ feed in metric ton/hr as determined by § 60.204(d).

Subpart U—Standards of Performance for the Phosphate Fertilizer Industry: Superphosphoric Acid Plants

§ 60.210 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each superphosphoric acid plant. For the purpose of this subpart, the affected facility includes any combination of: evaporators, hotwells, acid sumps, and cooling tanks.

§ 60.211 Definitions.

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

(a) "Superphosphoric acid plant" means any facility which concentrates wet-process phosphoric acid to 66 percent or greater P₂O₅ content by weight for eventual consumption as a fertilizer.

(b) "Total fluorides" means elemental fluorine and all fluoride compounds as measured by reference methods specified in § 60.214, or equivalent or alternative methods.

(c) "Equivalent P₂O₅ feed" means the quantity of phosphorus, expressed as phosphorous pentoxide, fed to the process.

§ 60.212 Standard for fluorides.

(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 from any affected facility any gases which contain total fluorides in excess of 5.0 g/metric ton of equivalent P₂O₅ feed (0.010 lb/ton).

§ 60.213 Monitoring of operations.

(a) The owner or operator of any superphosphoric acid plant subject to the provisions of this subpart shall install, calibrate, maintain, and operate a flow monitoring device which can be used to determine the mass flow of phosphorus-bearing feed material to the process. The flow monitoring device shall have an accuracy of ± 5 percent over its operating range.

(b) The owner or operator of any superphosphoric acid plant shall maintain a daily record of equivalent P₂O₅ feed by first determining the total mass rate in metric ton/hr of phosphorus-bearing feed using a flow monitoring device meeting the requirements of paragraph (a) of this section and then by proceeding according to § 60.214(d) (2).

(c) The owner or operator of any superphosphoric acid plant subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously measures and permanently records the total pressure drop across the process scrubbing system. The monitoring device shall have an accuracy of ± 5 percent over its operating range.

§ 60.214 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided in § 60.8(b), shall be used to determine

compliance with the standard prescribed in § 60.212 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and the associated moisture content.

(2) Method 1 for sample and velocity traverses,

(3) Method 2 for velocity and volumetric flow rate, and

(4) Method 3 for gas analysis.

(b) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be at least 0.85 dscm (30 dscf) except that shorter sampling times or smaller volumes, when necessitated by process variables or other factors, may be approved by the Administrator.

(c) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(d) Equivalent P₂O₅ feed shall be determined as follows:

(1) Determine the total mass rate in metric ton/hr of phosphorus-bearing feed during each run using a flow monitoring device meeting the requirements of § 60.213(a).

(2) Calculate the equivalent P₂O₅ feed by multiplying the percentage P₂O₅ content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass rate of phosphorus-bearing feed. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11-12. Other methods may be approved by the Administrator.

(e) For each run, emissions expressed in g/metric ton of equivalent P₂O₅ feed, shall be determined using the following equation:

$$E = \frac{(C_t Q_t) 10^{-3}}{M_{P_2O_5}}$$

where:

E = Emissions of total fluorides in g/metric ton of equivalent P₂O₅ feed.

C_t = Concentration of total fluorides in mg/dscm as determined by Method 13A or 13B.

Q_t = Volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2.

10⁻³ = Conversion factor for mg to g.

M_{P₂O₅} = Equivalent P₂O₅ feed in metric ton/hr as determined by § 60.214(d).

Subpart V—Standards of Performance for the Phosphate Fertilizer Industry: Diammonium Phosphate Plants

§ 60.220 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each granular diammonium phosphate plant. For the purpose of this subpart, the affected facility includes any combination of: reactors, granulators, dryers, coolers, screens and mills.

§ 60.221 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning

given them in the Act and in subpart A of this part.

(a) "Granular diammonium phosphate plant" means any plant manufacturing granular diammonium phosphate by reacting phosphoric acid with ammonia.

(b) "Total fluorides" means elemental fluorine and all fluoride compounds as measured by reference methods specified in § 60.224, or equivalent or alternative methods.

(c) "Equivalent P₂O₅ feed" means the quantity of phosphorus, expressed as phosphorous pentoxide, fed to the process.

§ 60.222 Standard for fluorides.

(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 from any affected facility any gases which contain total fluorides in excess of 30 g/metric ton of equivalent P₂O₅ feed (0.060 lb/ton).

§ 60.223 Monitoring of operations.

(a) The owner or operator of any granular diammonium phosphate plant subject to the provisions of this subpart shall install, calibrate, maintain, and operate a flow monitoring device which can be used to determine the mass flow of phosphorus-bearing feed material to the process. The flow monitoring device shall have an accuracy of ± 5 percent over its operating range.

(b) The owner or operator of any granular diammonium phosphate plant shall maintain a daily record of equivalent P₂O₅ feed by first determining the total mass rate in metric ton/hr of phosphorus-bearing feed using a flow monitoring device meeting the requirements of paragraph (a) of this section and then by proceeding according to § 60.224(d) (2).

(c) The owner or operator of any granular diammonium phosphate plant subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously measures and permanently records the total pressure drop across the scrubbing system. The monitoring device shall have an accuracy of ± 5 percent over its operating range.

§ 60.224 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided for in § 60.8(b), shall be used to determine compliance with the standard prescribed in § 60.222 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and the associated moisture content,

(2) Method 1 for sample and velocity traverses,

(3) Method 2 for velocity and volumetric flow rate, and

(4) Method 3 for gas analysis.

(b) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be at least 0.85 dscm (30 dscf) except that shorter sampling

times or smaller volumes when necessitated by process variables or other factors, may be approved by the Administrator.

(c) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(d) Equivalent P_2O_5 feed shall be determined as follows:

(1) Determine the total mass rate in metric ton/hr of phosphorus-bearing feed during each run using a flow monitoring device meeting the requirements of § 60.223(a).

(2) Calculate the equivalent P_2O_5 feed by multiplying the percentage P_2O_5 content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass rate of phosphorus-bearing feed. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11-12. Other methods may be approved by the Administrator.

(e) For each run, emissions expressed in g/metric ton of equivalent P_2O_5 feed shall be determined using the following equation:

$$E = \frac{(C_e Q_e) 10^{-3}}{M_{P_2O_5}}$$

where:

E = Emissions of total fluorides in g/metric ton of equivalent P_2O_5 .

C_e = Concentration of total fluorides in mg/dscm as determined by Method 13A or 13B.

Q_e = Volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2.

10^{-3} = Conversion factor for mg to g.

$M_{P_2O_5}$ = Equivalent P_2O_5 feed in metric ton/hr as determined by § 60.224(d).

Subpart W—Standards of Performance for the Phosphate Fertilizer Industry: Triple Superphosphate Plants

§ 60.230 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each triple superphosphate plant. For the purpose of this subpart, the affected facility includes any combination of: Mixers, curing belts (dens), reactors, granulators, dryers, cookers, screens, mills and facilities which store run-of-pile triple superphosphate.

§ 60.231 Definitions.

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

(a) "Triple superphosphate plant" means any facility manufacturing triple superphosphate by reacting phosphate rock with phosphoric acid. A rule-of-pile triple superphosphate plant includes curing and storing.

(b) "Run-of-pile triple superphosphate" means any triple superphosphate that has not been processed in a granulator and is composed of particles at

least 25 percent by weight of which (when not caked) will pass through a 16 mesh screen.

(c) "Total fluorides" means elemental fluorine and all fluoride compounds as measured by reference methods specified in § 60.234, or equivalent or alternative methods.

(d) "Equivalent P_2O_5 feed" means the quantity of phosphorus, expressed as phosphorus pentoxide, fed to the process.

§ 60.232 Standard for fluorides.

(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 from any affected facility any gases which contain total fluorides in excess of 100 g/metric ton of equivalent P_2O_5 feed (0.20 lb/ton).

§ 60.233 Monitoring of operations.

(a) The owner or operator of any triple superphosphate plant subject to the provisions of this subpart shall install, calibrate, maintain, and operate a flow monitoring device which can be used to determine the mass flow of phosphorus-bearing feed material to the process. The flow monitoring device shall have an accuracy of ± 5 percent over its operating range.

(b) The owner or operator of any triple superphosphate plant shall maintain a daily record of equivalent P_2O_5 feed by first determining the total mass rate in metric ton/hr of phosphorus-bearing feed using a flow monitoring device meeting the requirements of paragraph (a) of this section and then by proceeding according to § 60.234(d) (2).

(c) The owner or operator of any triple superphosphate plant subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously measures and permanently records the total pressure drop across the process scrubbing system. The monitoring device shall have an accuracy of ± 5 percent over its operating range.

§ 60.234 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided for in § 60.8(b), shall be used to determine compliance with the standard prescribed in § 60.232 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and the associated moisture content,

(2) Method 1 for sample and velocity traverses,

(3) Method 2 for velocity and volumetric flow rate, and

(4) Method 3 for gas analysis.

(b) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be at least 0.85 dscm (30 dscf) except that shorter sampling times or smaller volumes, when necessitated by process variables or other factors, may be approved by the Administrator.

(c) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates

and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(d) Equivalent P_2O_5 feed shall be determined as follows:

(1) Determine the total mass rate in metric ton/hr of phosphorus-bearing feed during each run using a flow monitoring device meeting the requirements of § 60.233(a).

(2) Calculate the equivalent P_2O_5 feed by multiplying the percentage P_2O_5 content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass rate of phosphorus-bearing feed. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11-12. Other methods may be approved by the Administrator.

(e) For each run, emissions expressed in g/metric ton of equivalent P_2O_5 feed shall be determined using the following equation:

$$E = \frac{(C_e Q_e) 10^{-3}}{M_{P_2O_5}}$$

where:

E = Emissions of total fluorides in g/metric ton of equivalent P_2O_5 feed.

C_e = Concentration of total fluorides in mg/dscm as determined by Method 13A or 13B.

Q_e = Volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2.

10^{-3} = Conversion factor for mg to g.

$M_{P_2O_5}$ = Equivalent P_2O_5 feed in metric ton/hr as determined by § 60.224(d).

Subpart X—Standards of Performance for the Phosphate Fertilizer Industry: Granular Triple Superphosphate Storage Facilities

§ 60.240 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each granular triple superphosphate storage facility. For the purpose of this subpart, the affected facility includes any combination of: storage or curing piles, conveyors, elevators, screens and mills.

§ 60.241 Definitions.

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

(a) "Granular triple superphosphate storage facility" means any facility curing or storing granular triple superphosphate.

(b) "Total fluorides" means elemental fluorine and all fluoride compounds as measured by reference methods specified in § 60.244, or equivalent or alternative methods.

(c) "Equivalent P_2O_5 stored" means the quantity of phosphorus, expressed as phosphorus pentoxide, being cured or stored in the affected facility.

(d) "Fresh granular triple superphosphate" means granular triple superphosphate produced no more than 10 days prior to the date of the performance test.

§ 60.242 Standard for fluorides.

(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 from any affected facility any gases which contain total fluorides in excess of 0.25 g/hr/metric ton of equivalent P₂O₅ stored (5.0 x 10⁻⁴ lb/hr/ton of equivalent P₂O₅ stored).

§ 60.243 Monitoring of operations.

(a) The owner or operator of any granular triple superphosphate storage facility subject to the provisions of this subpart shall maintain an accurate account of triple superphosphate in storage to permit the determination of the amount of equivalent P₂O₅ stored.

(b) The owner or operator of any granular triple superphosphate storage facility shall maintain a daily record of total equivalent P₂O₅ stored by multiplying the percentage P₂O₅ content, as determined by § 60.244(f) (2), times the total mass of granular triple superphosphate stored.

(c) The owner or operator of any granular triple superphosphate storage facility subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously measures and permanently records the total pressure drop across the process scrubbing system. The monitoring device shall have an accuracy of ±5 percent over its operating range.

§ 60.244 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided for in § 60.8(b), shall be used to determine compliance with the standard prescribed in § 60.242 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and the associated moisture content,

(2) Method 1 for sample and velocity traverses,

(3) Method 2 for velocity and volumetric flow rate, and

(4) Method 3 for gas analysis.

(b) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be at least 0.85 dscm (30 dscf) except that shorter sampling times or smaller volumes, when necessitated by process variables or other factors, may be approved by the Administrator.

(c) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(d) Except as provided under paragraph (e) of this section, all performance tests on granular triple superphosphate storage facilities shall be conducted only when the following quantities of product are being cured or stored in the facility:

(1) Total granular triple superphosphate—at least 10 percent of the building capacity.

(2) Fresh granular triple superphosphate—at least 20 percent of the amount of triple superphosphate in the building.

(e) If the provisions set forth in paragraph (d) (2) of this section exceed production capabilities for fresh granular triple superphosphate, the owner or operator shall have at least five days maximum production of fresh granular triple superphosphate in the building during a performance test.

(f) Equivalent P₂O₅ stored shall be determined as follows:

(1) Determine the total mass stored during each run using an accountability system meeting the requirements of § 60.243(a).

(2) Calculate the equivalent P₂O₅ stored by multiplying the percentage P₂O₅ content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass stored. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11-12. Other methods may be approved by the Administrator.

(g) For each run, emissions expressed in g/hr/metric ton of equivalent P₂O₅ stored shall be determined using the following equation:

$$E = \frac{(C_e Q_e) 10^{-3}}{M_{P_2O_5}}$$

where:

E = Emissions of total fluorides in g/hr/metric ton of equivalent P₂O₅ stored.

C_e = Concentration of total fluorides in mg/dscm as determined by Method 13A or 13B.

Q_e = Volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2.

10⁻³ = Conversion factor for mg to g.

M_{P₂O₅} = Equivalent P₂O₅ fed in metric tons as measured by § 60.244(d).

3. Part 60 is amended by adding Reference Methods 13A and 13B to Appendix A as follows:

METHOD 13—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES—SPADNS ZIRCONIUM LAKE METHOD

1. Principle and Applicability.

1.1 Principle. Gaseous and particulate fluorides are withdrawn isokinetically from the source using a sampling train. The fluorides are collected in the impinger water and on the filter of the sampling train. The weight of total fluorides in the train is determined by the SPADNS Zirconium Lake colorimetric method.

1.2 Applicability. This method is applicable for the determination of fluoride emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. Fluorocarbons, such as Freons, are not quantitatively collected or measured by this procedure.

2. Range and Sensitivity.

The SPADNS Zirconium Lake analytical method covers the range from 0-1.4 µg/ml fluoride. Sensitivity has not been determined.

3. Interferences.

During the laboratory analysis, aluminum in excess of 300 mg/liter and silicon dioxide in excess of 300 µg/liter will prevent complete recovery of fluoride. Chloride will distill over and interfere with the SPADNS Zirconium

lake color reaction. If chloride ion is present, use of Specific Ion Electrode (Method 13B) is recommended; otherwise a chloride determination is required and 5 mg of silver sulfate (see section 7.3.6) must be added for each mg of chloride to prevent chloride interference. If sulfuric acid is carried over in the distillation, it will cause a positive interference. To avoid sulfuric acid carryover, it is important to stop distillation at 175°C.

4. Precision, Accuracy and Stability.

4.1 Analysis. A relative standard deviation of 3 percent was obtained from twenty replicate intralaboratory determinations on stack emission samples with a concentration range of 39 to 369 mg/l. A phosphate rock standard which was analyzed by this procedure contained a certified value of 3.84 percent. The average of five determinations was 3.88 percent fluoride.

4.2 Stability. The color obtained when the sample and colorimetric reagent are mixed is stable for approximately two hours. After formation of the color, the absorbances of the sample and standard solutions should be measured at the same temperature. A 3°C temperature difference between sample and standard solutions will produce an error of approximately 0.005 mg F/liter.

5. Apparatus.

5.1 Sample train. See Figure 13A-1; it is similar to the Method 5 train except for the interchangeability of the position of the filter. Commercial models of this train are available. However, if one desires to build his own, complete construction details are described in APTD-0581; for changes from the APTD-0581 document and for allowable modifications to Figure 13A-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576. 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.

5.1.1 Probe nozzle—Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤30° 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. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 cm (1/8 in.) up to 1.27 cm (1/2 in.) (or larger if higher volume sampling trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/8 in.). Each nozzle shall be calibrated according to the procedures outlined in the calibration section.

5.1.2 Probe liner—Borosilicate glass or stainless steel (316). When the filter is located immediately after the probe, a probe heating system may be used to prevent filter plugging resulting from moisture condensation. The temperature in the probe shall not exceed 120 ± 14°C (248 ± 25°F).

5.1.3 Pitot tube—Type S, or other device approved by the Administrator, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other, not necessarily on the same plane, during sampling. The free space between the nozzle and

pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge—Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micro-manometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micro-manometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Administrator may be used when conditions warrant.

5.1.5 Filter holder—Borosilicate glass with a glass frit filter support and a silicone rubber gasket. Other materials of construction may be used with approval from the Administrator, e.g., if probe liner is stainless steel, then filter holder may be stainless steel. The holder design shall provide a positive seal against leakage from the outside or around the filter.

5.1.6 Filter heating system—When moisture condensation is a problem, any heating system capable of maintaining a temperature around the filter holder during sampling of no greater than $120 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$). A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that when the filter heater is used, the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

5.1.7 Impingers—Four impingers connected as shown in Figure 13A-1 with ground glass (or equivalent), vacuum tight fittings. The first, third, and fourth impingers are of the Greensburg-Smith design, modified by replacing the tip with a $1\frac{1}{4}$ cm ($\frac{1}{2}$ in.) inside diameter glass tube extending to $\frac{1}{4}$ cm ($\frac{1}{8}$ in.) from the bottom of the flask. The second impinger is of the Greensburg-Smith design with the standard tip.

5.1.8 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C ($\sim 5^\circ\text{F}$), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.9 Barometer—Mercury, aneroid, or other barometers 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 weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

5.2 Sample recovery.

5.2.1 Probe liner and probe nozzle brushes—Nylon bristles with stainless steel wire handles. The probe brush shall have extensions, at least as long as the probe, of stainless steel, teflon, or similarly inert material. Both brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

5.2.2 Glass wash bottles—Two.

5.2.3 Sample storage containers—Wide mouth, high density polyethylene bottles, 1 liter.

5.2.4 Plastic storage containers—Air tight containers of sufficient volume to store silica gel.

5.2.5 Graduated cylinder—250 ml.

5.2.6 Funnel and rubber policeman—to aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.3 Analytcs.

5.3.1 Distillation apparatus—Glass distillation apparatus assembled as shown in Figure 13A-2.

5.3.2 Hot plate—Capable of heating to 500°C .

5.3.3 Electric muffle furnace—Capable of heating to 600°C .

5.3.4 Crucibles—Nickel, 75 to 100 ml capacity.

5.3.5 Beaker, 1600 ml.

5.3.6 Volumetric flask—50 ml.

5.3.7 Erlenmeyer flask or plastic bottle—500 ml.

5.3.8 Constant temperature bath—Capable of maintaining a constant temperature of $\pm 1.0^\circ\text{C}$ in the range of room temperature.

5.3.9 Balance—300 g capacity to measure to ± 0.5 g.

5.3.10 Spectrophotometer—Instrument capable of measuring absorbance at 570 nm and providing at least a 1 cm light path.

5.3.11 Spectrophotometer cells—1 cm.

6. Reagents

6.1 Sampling.

6.1.1 Filters—Whatman No. 1 filters, or equivalent, sized to fit filter holder.

6.1.2 Silica gel—Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

6.1.3 Water—Distilled.

6.1.4 Crushed ice.

6.1.5 Stopcock grease—Acetone insoluble, heat stable silicone grease. This is not necessary if screw-on connectors with teflon sleeves, or similar, are used.

6.2 Sample recovery.

6.2.1 Water—Distilled from same container as 6.1.3.

6.3 Analytcs.

6.3.1 Calcium oxide (CaO)—Certified grade containing 0.005 percent fluoride or less.

6.3.2 Phenolphthalein Indicator—0.1 percent in 1:1 ethanol-water mixture.

6.3.3 Silver sulfate (Ag₂SO₄)—ACS reagent grade, or equivalent.

6.3.4 Sodium hydroxide (NaOH)—Pellets, ACS reagent grade, or equivalent.

6.3.5 Sulfuric acid (H₂SO₄)—Concentrated, ACS reagent grade, or equivalent.

6.3.6 Filters—Whatman No. 541, or equivalent.

6.3.7 Hydrochloric acid (HCl)—Concentrated, ACS reagent grade, or equivalent.

6.3.8 Water—Distilled, from same container as 6.1.3.

6.3.9 Sodium fluoride—Standard solution. Dissolve 0.2210 g of sodium fluoride in 1 liter of distilled water. Dilute 100 ml of this solution to 1 liter with distilled water. One milliliter of the solution contains 0.01 mg of fluoride.

6.3.10 SPADNS solution—[4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene - disulfonic acid trisodium salt]. Dissolve 0.960 \pm 0.010 g of SPADNS reagent in 500 ml distilled water. This solution is stable for at least one month, if stored in a well-sealed bottle protected from sunlight.

6.3.11 Reference solution—Add 10 ml of SPADNS solution (6.3.10) to 100 ml distilled water and acidify with a solution prepared by diluting 7 ml of concentrated HCl to 10 ml with distilled water. This solution is used to set the spectrophotometer zero point and should be prepared daily.

6.3.12 SPADNS Mixed Reagent—Dissolve 0.135 \pm 0.005 g of zirconyl chloride octahydrate (ZrOCl₂·8H₂O), in 25 ml distilled water. Add 350 ml of concentrated HCl and dilute to 500 ml with distilled water. Mix equal volumes of this solution and SPADNS solution

to form a single reagent. This reagent is stable for at least two months.

7. Procedure.

NOTE: The fusion and distillation steps of this procedure will not be required, if it can be shown to the satisfaction of the Administrator that the samples contain only water-soluble fluorides.

7.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure.

7.1.1 Pretest preparation. All train components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh approximately 200-300 g of silica gel in air tight containers to the nearest 0.5 g. Record the total weight, both silica gel and container, on the container. More silica gel may be used but care should be taken during sampling that it is not entrained and carried out from the impinger. As an alternative, the silica gel may be weighed directly in the impinger or its sampling holder just prior to the train assembly.

7.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

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 differential pressure gauge is capable of measuring the minimum velocity head value to within 10%, or as specified by the Administrator.

Select a suitable probe liner and probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks 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 the sampling time per point is not less than 3 min, or select some greater time interval as specified by the Administrator, and such that the sample volume that will be taken will exceed the required minimum total gas sample volume specified in the test procedures for the specific industry. The latter is based on an approximate average sampling rate. Note also that the minimum total sample volume is corrected to standard conditions.

It is recommended that a half-integral or integral number of minutes be sampled at each point 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.

7.1.3 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.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and place approximately 200-300 g or more, if necessary, of preweighed silica gel in the fourth impinger. Record the weight of the silica gel and container on the data sheet. Place the empty container in a clean place for later use in the sample recovery.

Place a filter in the filter holder. Be sure that the filter is properly centered and the

gasket properly placed so as to not allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed.

When glass liners are used, install selected nozzle using a Viton A O-ring; the Viton A O-ring is installed as a seal where the nozzle is connected to a glass liner. See APTD-0576 for details. When metal liners are used, install the nozzle as above or by a leak free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor extends beyond the probe tip and does not touch any metal. Its position should be about 1.9 to 2.54 cm (0.75 to 1 in.) from the pitot tube and probe nozzle to avoid interference with the gas flow.

Assemble the train as shown in Figure 13A-1 with the filter between the third and fourth impingers. Alternatively, the filter may be placed between the probe and the first impinger. A filter heating system may be used to prevent moisture condensation, but the temperature around the filter holder shall not exceed $120 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$). [(Note: Whatman No. 1 filter decomposes at 150°C (300°F)).] Record filter location on the data sheet.

Place crushed ice around the impingers.

7.14 Leak check procedure—After the sampling train has been assembled, turn on and set (if applicable) the probe and filter heating system(s) to reach a temperature sufficient to avoid condensation in the probe. Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate or $0.00057 \text{ m}^3/\text{min}$. (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 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of by-pass valve. This will cause water to back up into the filter holder. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as described below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe or filter holder and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder (if placed before the impingers) and silica gel from being entrained backward into the third impinger.

Leak checks shall be conducted as described whenever the train is disengaged, e.g. for silica gel or filter changes during the test, prior to each test run, and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

7.1.5 Particulate train operation—During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Administrator, of true isokinetic shall be maintained.

For each run, record the data required on the example data sheet shown in Figure 13A-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, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Be sure to level and zero the manometer.

Clean the portholes prior to the test run to minimize chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify (if applicable) that the probe heater is working and filter heater is up to temperature, and that the pitot tube and probe 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 for sampling trains using type S pitot tubes with 0.85 ± 0.02 coefficients (C_p), and when sampling in air or a stack gas with equivalent density (molecular weight, M_a , equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. APTD-0576 details the procedure for using these nomographs. If C_p and M_a are outside the above stated ranges, do not use the nomograph unless appropriate steps 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 into the stack to avoid water backing into the filter holder. 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 through the portholes to minimize chance of extracting deposited material.

During the test run, make periodic adjustments to keep the probe and (if applicable) filter temperatures at their proper values. Add more ice and, if necessary, salt to the ice bath, to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes high enough to make isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. After the new filter or filter assembly is installed conduct a leak check. The final emission results shall be based on the summation of all filter catches.

A single train shall be used for the entire sample run, except for filter and silica gel changes. However, if approved by the Administrator, two or more trains may be used for a single test run when there are two or more ducts or sampling ports. The final emission results shall be based on the total of all sampling train catches.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check.¹ Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to course con-

ditions, consult with the Administrator for possible variance on the isokinetic rates.

7.3 Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to keep from losing part of the sample. 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, thus drawing water from the impingers into the filter.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate, if present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Ground glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly 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.

Inspect the train prior to and during disassembly and note any abnormal conditions. Using a graduated cylinder, measure and record the volume of the water in the first three impingers, to the nearest ml; any condensate in the probe should be included in this determination. Treat the samples as follows:

7.2.1 Container No. 1. Transfer the impinger water from the graduated cylinder to this container. Add the filter to this container. Wash all sample exposed surfaces, including the probe tip, probe, first three impingers, impinger connectors, filter holder, and graduated cylinder thoroughly with distilled water. Wash each component three separate times with water and clean the probe and nozzle with brushes. A maximum wash of 500 ml is used, and the washings are added to the sample container which must be made of polyethylene.

7.2.2 Container No. 2. Transfer the silica gel from the fourth impinger to this container and seal.

7.3 Analysis. Treat the contents of each sample container as described below.

7.3.1 Container No. 1.

7.3.1.1 Filter this container's contents, including the Whatman No. 1 filter, through Whatman No. 541 filter paper, or equivalent into a 1500 ml beaker. Note: If filtrate volume exceeds 800 ml make filtrate basic with NaOH to phenolphthalein and evaporate to less than 900 ml.

7.3.1.2 Place the Whatman No. 541 filter containing the insoluble matter (including the Whatman No. 1 filter) in a nickel crucible, add a few ml of water and macerate the filter with a glass rod.

Add 100 mg CaO to the crucible and mix the contents thoroughly to form a slurry. Add a couple of drops of phenolphthalein indicator. The indicator will turn red in a basic medium. The slurry should remain basic during the evaporation of the water or fluoride ion will be lost. If the indicator turns colorless during the evaporation, an acidic condition is indicated. If this happens add CaO until the color turns red again.

Place the crucible in a hood under infrared lamps or on a hot plate at low heat. Evaporate the water completely.

After evaporation of the water, place the crucible on a hot plate under a hood and slowly increase the temperature until the paper chars. It may take several hours for complete charring of the filter to occur.

¹ With acceptability of the test run to be based on the same criterion as in 7.1.4.

Place the crucible in a cold muffle furnace and gradually (to prevent smoking) increase the temperature to 600°C, and maintain until the contents are reduced to an ash. Remove the crucible from the furnace and allow it to cool.

7.3.1.3 Add approximately 4 g of crushed NaOH to the crucible and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 600°C.

Remove the sample from the furnace and cool to ambient temperature. Using several rinsings of warm distilled water transfer the contents of the crucible to the beaker containing the filtrate from container No. 1 (7.3.1). To assure complete sample removal, rinse finally with two 20 ml portions of 25 percent (v/v) sulfuric acid and carefully add to the beaker. Mix well and transfer a one-liter volumetric flask. Dilute to volume with distilled water and mix thoroughly. Allow any undissolved solids to settle.

7.3.2 Container No. 2. Weigh the spent silica gel and report to the nearest 0.5 g.

7.3.3 Adjustment of acid/water ratio in distillation flask—(Utilize a protective shield when carrying out this procedure.) Place 400 ml of distilled water in the distilling flask and add 200 ml of concentrated H₂SO₄. Caution: Observe standard precautions when mixing the H₂SO₄ by slowly adding the acid to the flask with constant swirling. Add some soft glass beads and several small pieces of broken glass tubing and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175°C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

7.3.4 Distillation—Cool the contents of the distillation flask to below 80°C. Pipette an aliquot of sample containing less than 0.6 mg F directly into the distilling flask and add distilled water to make a total volume of 220 ml added to the distilling flask. [For an estimate of what size aliquot does not exceed 0.6 mg F, select an aliquot of the solution and treat as described in Section 7.3.6. This will give an approximation of the fluoride content, but only an approximation since interfering ions have not been removed by the distillation step.]

Place a 250 ml volumetric flask at the condenser exit. Now begin distillation and gradually increase the heat and collect all the distillation up to 175°C. Caution: Heating the solution above 175°C will cause sulfuric acid to distill over.

The acid in the distilling flask can be used until there is carryover of interferences or poor fluoride recovery. An occasional check of fluoride recovery with standard solutions is advised. The acid should be changed whenever there is less than 90 percent recovery or blank values are higher than 0.1 µg/ml. Note: If the sample contains chloride, add 5 mg Ag₂SO₄ to the flask for every mg of chloride. Gradually increase the heat and collect at the distillate up to 175°C. Do not exceed 175°C.

7.3.5 Determination of Concentration—Bring the distillate in the 250 ml volumetric flask to the mark with distilled water and mix thoroughly. Pipette a suitable aliquot from the distillate (containing 10 µg to 40 µg fluoride) and dilute to 50 ml with distilled water. Add 10 ml of SPADNS Mixed Reagent (see Section 6.3.12) and mix thoroughly.

After mixing, place the sample in a constant temperature bath containing the standard solution for thirty minutes before reading the absorbance with the spectrophotometer.

Set the spectrophotometer to zero absorbance at 570 nm with reference solution (6.3.11), and check the spectrophotometer

calibration with the standard solution. Determine the absorbance of the samples and determine the concentration from the calibration curve. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.

8. Calibration.

Maintain a laboratory log of all calibrations.

8.1 Sampling Train.

8.1.1 Probe nozzle—Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make 3 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.

8.1.2 Pitot tube—The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter. Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with by-pass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m³/min. (0.2 cfm) with the by-pass valve fully opened and then with it fully closed. If there is more than ±2 percent difference in flow rates when compared to the fully closed position of the by-pass valve, the system is not designed properly and must be corrected.

8.1.4 Probe heater calibration—The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.1.5 Temperature gauges—Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples need not be calibrated. For other devices, check with the Administrator.

8.2 Analytical Apparatus. Spectrophotometer. Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of distilled water. Accurately prepare a series of standards from the standard fluoride solution (see Section 6.3.9) by diluting 2, 4, 6, 8, 10, 12, and 14 ml volumes to 100 ml with distilled water. Pipette 50 ml from each solution and transfer to a 100 ml beaker. Then add 10 ml of SPADNS mixed reagent to each. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 µg of fluoride (0—1.4 µg/ml) respectively.

After mixing, place the reference standards and reference solution in a constant temperature bath for thirty minutes before reading the absorbance with the spectrophotometer. All samples should be adjusted to this same temperature before analyzing. Since a 3°C temperature difference between samples and standards will produce an error of approximately 0.005 mg F/liter, care must be taken to see that samples and standards are at nearly identical temperatures when absorbances are recorded.

With the spectrophotometer at 570 nm, use the reference solution (see section 6.3.11) to set the absorbance to zero.

Determine the absorbance of the standards. Prepare a calibration curve by plotting µg F/50 ml versus absorbance on linear graph paper. A standard curve should be prepared initially and thereafter whenever the SPADNS mixed reagent is newly made. Also, a calibration standard should be run with

each set of samples and if it differs from the calibration curve by ±2 percent, a new standard curve should be prepared.

9. Calculations.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

9.1 Nomenclature.

A_s=Aliquot of distillate taken for color development, ml.

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

A_t=Aliquot of total sample added to still, ml.

B₀=Water vapor in the gas stream, proportion by volume.

C_s=Concentration of fluoride in stack gas, mg/m³, corrected to standard conditions of 20° C, 760 mm Hg (68° F, 29.92 in. Hg) on dry basis.

F_t=Total weight of fluoride in sample, mg.

µGF=Concentration from the calibration curve, µg.

I=Percent of isokinetic sampling.

m_n=Total amount of particulate matter collected, mg.

M_w=Molecular weight of water, 18 g/g-mole (18 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 (21.83 in. Hg-ft³/°R-lb-mole).

T_a=Absolute average dry gas meter temperature (see fig. 13A-3), °K (°R).

T_s=Absolute average stack gas temperature (see fig. 13A-3), °K (°R).

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

V₀=Volume of acetone blank, ml.

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

V_c=Volume of distillate collected, ml.

V_l=Total volume of liquid collected in impingers and silica gel, ml. Volume of water in silica gel equals silica gel weight increase in grams times 1 ml/gram. Volume of liquid collected in impinger equals final volume minus initial volume.

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

V_{n(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_t=Total volume of sample, ml.

v_s=Stack gas velocity, calculated by Method 2, Equation 2-7 using data obtained from Method 5, m/sec (ft/sec).

W_a=Weight of residue in acetone wash, mg.

ΔH=Average pressure differential across the orifice (see fig. 13A-3), meter, mm H₂O (in. H₂O).

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

ρ_w=Density of water, 1 g/ml (0.00220 lb/ml).

θ=Total sampling time, min.

13.6=Specific gravity of mercury.

60=Sec/min.

100=Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (fig. 13A-3).

9.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions [20° C, 760 mm Hg (68° F, 29.92 inches Hg)] by using equation 13A-1.

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] = K V_m \frac{P_{bar} + \Delta H/13.6}{T_m}$$

equation 13A-1

where:
 K=0.3855 °K/mm Hg for metric units.
 =17.65 °R/in. Hg for English units.
 9.4 Volume of water vapor.

$$V_{w(std)} = V_{tc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K V_{tc}$$

equation 13A-2

where:
 K=0.00134 m³/ml for metric units.
 =0.0472 ft³/ml for English units.
 9.5 Moisture content.

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

equation 13A-3

If the liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

9.6 Concentration.
 9.6.1 Calculate the amount of fluoride in the sample according to Equation 13A-4.

$$F_t = K \frac{V_t V_d}{A_t A_d} (\mu g F)$$

equation 13A-4

where:
 K=10⁻³ mg/μg.
 9.6.2 Concentration of fluoride in stack gas. Determine the concentration of fluoride in the stack gas according to Equation 13A-5.

$$C_s = K \frac{F_t}{V_{m(std)}}$$

equation 13A-5

where:
 K=35.31 ft³/m³.
 9.7 Isokinetic variation.
 9.7.1 Calculations from raw data.

$$I = \frac{100 T_s [K V_{tc} + (V_m/T_m) (P_{bar} + \Delta H/13.6)]}{60 \theta v_s P_s A_n}$$

equation 13A-6

where:
 K=0.00346 mm Hg-m³/ml-°K for metric units.
 =0.00267 in. Hg-ft³/ml-°R for English units.
 9.7.2 Calculations from intermediate values.

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

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

equation 13A-7

where:
 K=4.323 for metric units.
 =0.0944 for English units.
 9.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:
 If 90 percent <I< 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results. Use reference 7.4 to make judgments. Otherwise, reject the results and repeat the test.

10. References.
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Fluoride Determination in Stack Emission Samples," *Analytical Chemistry* 45: 1272-1273 (1973).
 Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.
 1973 *Annual Book of ASTM Standards*, Part 23, Designation: D 1179-72.
 Rom, Jerome J., "Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0576.
Standard Methods for the Examination of Water and Waste Water, published jointly by American Public Health Association, American Water Works Association and Water Pollution Control Federation, 13th Edition (1971).

RULES AND REGULATIONS

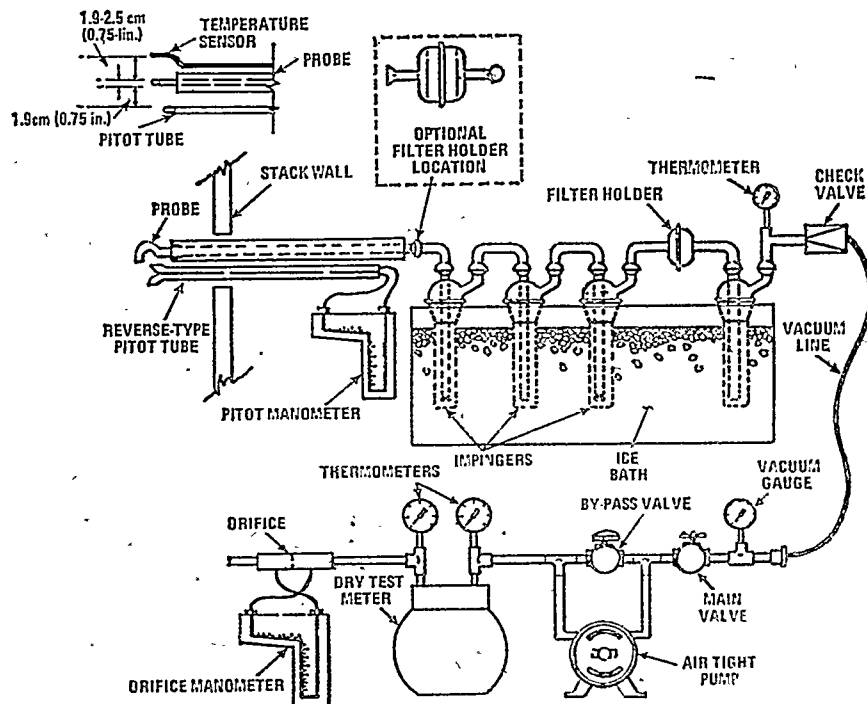


Figure 13A 1. Fluoride sampling train.

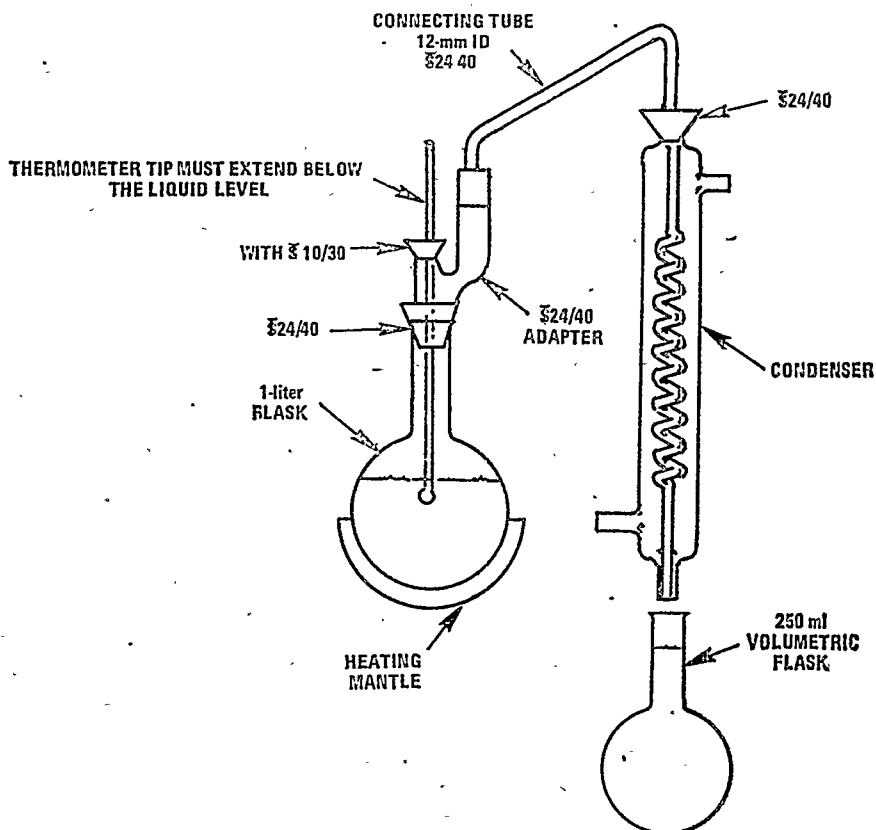


Figure 13A-2. Fluoride Distillation Apparatus.

5.3 Analysis.

5.3.1 Distillation apparatus—Glass distillation apparatus assembled as shown in Figure 13A-2 (Method 13A).

5.3.2 Hot plate—Capable of heating to 500°C.

5.3.3 Electric muffle furnace—Capable of heating to 600°C.

5.3.4 Crucibles—Nickel, 75 to 100 ml capacity.

5.3.5 Beaker—1500 ml.

5.3.6 Volumetric flask—50 ml.

5.3.7 Erlenmeyer flask or plastic bottle—500 ml.

5.3.8 Constant temperature bath—Capable of maintaining a constant temperature of $\pm 1.0^\circ\text{C}$ in the range of room temperature.

5.3.9 Trip balance—300 g capacity to measure to ± 0.5 g.

5.3.10 Fluoride ion activity sensing electrode.

5.3.11 Reference electrode—Single junction; sleeve type. (A combination-type electrode having the reference electrode and the fluoride-ion sensing electrode built into one unit may also be used).

5.3.12 Electrometer—A pH meter with millivolt scale capable of ± 0.1 mv resolution, or a specific ion meter made specifically for specific ion use.

5.3.13 Magnetic stirrer and TFE fluorocarbon coated stripping bars.

6. Reagents.

6.1 Sampling.

6.1.1 Filters—Whatman No. 1 filters, or equivalent, sized to fit filter holder.

6.1.2 Silica gel—Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

6.1.3 Water—Distilled.

6.1.4 Crushed ice.

6.1.5 Stopcock grease—Acetone insoluble, heat stable silicone grease. This is not necessary if screw-on connectors with teflon sleeves, or similar, are used.

6.2 Sample recovery.

6.2.1 Water—Distilled from same container as 6.1.3.

6.3 Analysis.

6.3.1 Calcium oxide (CaO)—Certified grade containing 0.005 percent fluoride or less.

6.3.2 Phenolphthalein Indicator—0.1 percent in 1:1 ethanol water mixture.

6.3.3 Sodium hydroxide (NaOH)—Pellets, ACS reagent grade or equivalent.

6.3.4 Sulfuric acid (H_2SO_4)—Concentrated, ACS reagent grade or equivalent.

6.3.5 Filters—Whatman No. 541, or equivalent.

6.3.6 Water—Distilled, from same container as 6.1.3.

6.3.7 Total Ionic Strength Adjustment Buffer (TISAB)—Place approximately 500 ml of distilled water in a 1-liter beaker. Add 57 ml glacial acetic acid, 58 g sodium chloride, and 4 g CDTA (Cyclohexylene dimethyl tetraacetic acid). Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-liter flask and dilute to volume with distilled water. Commercially prepared TISAB buffer may be substituted for the above.

6.3.8 Fluoride Standard Solution—0.1 M fluoride reference solution. Add 4.20 grams of reagent grade sodium fluoride (NaF) to a 1-liter volumetric flask and add enough distilled water to dissolve. Dilute to volume with distilled water.

7. Procedure.

NOTE: The fusion and distillation steps of this procedure will not be required, if it can be shown to the satisfaction of the Administrator that the samples contain only water-soluble fluorides.

7.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure.

7.1.1 Pretest preparation. All train components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh approximately 200-300 g of silica gel in air tight containers to the nearest 0.5 g. Record the total weight, both silica gel and container, on the container. More silica gel may be used but care should be taken during sampling that it is not entrained and carried out from the impinger. As an alternative, the silica gel may be weighed directly in the impinger or its sampling holder just prior to the train assembly.

7.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

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 differential pressure gauge is capable of measuring the minimum velocity head value to within 10 percent, or as specified by the Administrator.

Select a suitable probe liner and probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks 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 the sampling time per point is not less than 2 min. or select some greater time interval as specified by the Administrator, and such that the sample volume that will be taken will exceed the required minimum total gas sample volume specified in the test procedures for the specific industry. The latter is based on an approximate average sampling rate. Note also that the minimum total sample volume is corrected to standard conditions.

It is recommended that a half-integral or integral number of minutes be sampled at each point 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.

7.13 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.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and place approximately 200-300 g or more, if necessary, of preweighed silica gel in the fourth impinger. Record the weight of the silica gel and container on the data sheet. Place the empty container in a clean place for later use in the sample recovery.

Place a filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to not allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed.

When glass liners are used, install selected nozzle using a Viton A O-ring; the Viton A O-ring is installed as a seal where the nozzle

is connected to a glass liner. See APTD-0576 for details. When metal liners are used, install the nozzle as above or by a leak free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor extends beyond the probe tip and does not touch any metal. Its position should be about 1.9 to 2.54 cm (0.75 to 1 in.) from the pitot tube and probe nozzle to avoid interference with the gas flow.

Assemble the train as shown in Figure 13A-1 (Method 13A) with the filter between the third and fourth impingers. Alternatively, the filter may be placed between the probe and first impinger. A filter heating system may be used to prevent moisture condensation, but the temperature around the filter holder shall not exceed $1200 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$). [(Note: Whatman No. 1 filter decomposes at 150°C (300°F)).] Record filter location on the data sheet.

Place crushed ice around the impingers.

7.1.4 Leak check procedure—After the sampling train has been assembled, turn on and set (if applicable) the probe and filter heating system(s) to reach a temperature sufficient to avoid condensation in the probe. Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate of $0.0057 \text{ m}^3/\text{min}$. (0.02 cfm), whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0570 and APTD-0581 may be helpful. Turn 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 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of by-pass valve. This will cause water to back up into the filter holder. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as described below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe or filter holder and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder (if placed before the impingers) and silica gel from being entrained backward into the third impinger.

Leak checks shall be conducted as described whenever the train is disengaged, e.g. for silica gel or filter changes during the test, prior to each test run, and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

7.1.5 Particulate train operation—During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Administrator, of true isokinetic shall be maintained.

For each run, record the data required on the example data sheet shown in Figure 13A-3 (Method 13A). 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, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) neces-

sitate additional adjustments in flow rate. Be sure to level and zero the manometer.

Clean the portholes prior to the test run to minimize chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify (if applicable) that the probe heater is working and filter heater is up to temperature, and that the pitot tube and probe 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 for sampling trains using type S pitot tubes with 0.85 ± 0.02 (coefficients (C_p), and when sampling in air or a stack gas with equivalent density (molecular weight, M_a , equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. APTD-0576 details the procedure for using these nomographs. If C_p and M_a are outside the above stated ranges, do not use the nomograph unless appropriate steps 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 into the stack to avoid water backing into the filter holder. 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 through the portholes to minimize chance of extracting deposited material.

During the test run, make periodic adjustments to keep the probe and (if applicable) filter temperatures at their proper values. Add more ice and, if necessary, salt to the ice bath, to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes high enough to make isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. After the new filter or filter assembly is installed, conduct a leak check. The final emission results shall be based on the summation of all filter catches.

A single train shall be used for the entire sample run, except for filter and silica gel changes. However, if approved by the Administrator, two or more trains may be used for a single test run when there are two or more ducts or sampling ports. The final emission results shall be based on the total of all sampling train catches.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check.¹ Calculate percent isokinetic (see calculation section) 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.

¹ With acceptability of the test run to be based on the same criterion as in 7.1.4.

7.2 Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to keep from losing part of the sample. 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, thus drawing water from the impingers into the filter.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate, if present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Ground glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly 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.

Inspect the train prior to and during disassembly and note any abnormal conditions. Using a graduated cylinder, measure and record the volume of the water in the first three impingers, to the nearest ml; any condensate in the probe should be included in this determination. Treat the samples as follows:

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7.2.1 Container No. 1. Transfer the impinger water from the graduated cylinder to this container. Add the filter to this container. Wash all sample exposed surfaces, including the probe tip, probe, first three impingers, impinger connectors, filter holder, and graduated cylinder thoroughly with distilled water. Wash each component three separate times with water and clean the probe and nozzle with brushes. A maximum wash of 500 ml is used, and the washings are added to the sample container which must be made of polyethylene.

7.2.2 Container No. 2. Transfer the silica gel from the fourth impinger to this container and seal.

7.3 Analysis. Treat the contents of each sample container as described below.

7.3.1 Container No. 1.

7.3.1.1 Filter this container's contents, including the Whatman No 1 filter, through Whatman No. 541 filter paper, or equivalent into a 1500 ml beaker. Note: If filtrate volume exceeds 900 ml make filtrate basic with NaOH to phenolphthalein and evaporate to less than 900 ml.

7.3.1.2 Place the Whatman No. 541 filter containing the insoluble matter (including the Whatman No. 1 filter) in a nickel crucible, add a few ml of water and macerate the filter with a glass rod.

Add 100 mg CaO to the crucible and mix the contents thoroughly to form a slurry. Add a couple of drops of phenolphthalein indicator. The indicator will turn red in a basic medium. The slurry should remain basic during the evaporation of the water or fluoride ion will be lost. If the indicator turns colorless during the evaporation, an acidic condition is indicated. If this happens add CaO until the color turns red again.

Place the crucible in a hood under infrared lamps or on a hot plate at low heat. Evaporate the water completely.

After evaporation of the water, place the crucible on a hot plate under a hood and slowly increase the temperature until the paper chars. It may take several hours for complete charring of the filter to occur.

Place the crucible in a cold muffle furnace and gradually (to prevent smoking) increase the temperature to 600°C , and maintain until the contents are reduced to an ash. Remove the crucible from the furnace and allow it to cool.

7.3.1.3 Add approximately 4 g of crushed NaOH to the crucible and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 690°C .

Remove the sample from the furnace and cool to ambient temperature. Using several rinsings of warm distilled water transfer the contents of the crucible to the beaker containing the filtrate from container No. 1 (7.3.1). To assure complete sample removal, rinse finally with two 20 ml portions of 25 percent (v/v) sulfuric acid and carefully add to the beaker. Mix well and transfer to a one-liter volumetric flask. Dilute to volume with distilled water and mix thoroughly. Allow any undissolved solids to settle.

7.3.2 Container No. 2. Weigh the spent silica gel and report to the nearest 0.5 g.

7.3.3 Adjustment of acid/water ratio in distillation flask—(Utilize a protective shield when carrying out this procedure). Place 400 ml of distilled water in the distilling flask and add 200 ml of concentrated H_2SO_4 . Caution: Observe standard precautions when mixing the H_2SO_4 , by slowly adding the acid to the flask with constant swirling. Add some soft glass beads and several small pieces of broken glass tubing and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175°C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

7.3.4 Distillation—Cool the contents of the distillation flask to below 80°C . Pipette an aliquot of sample containing less than 0.6 mg F directly into the distilling flask and add distilled water to make a total volume of 220 ml added to the distilling flask. [For an estimate of what size aliquot does not exceed 0.6 mg F, select an aliquot of the solution and treat as described in Section 7.3.6. This will give an approximation of the fluoride content, but only an approximation since interfering ions have not been removed by the distillation step.]

Place a 250 ml volumetric flask at the condenser exit. Now begin distillation and gradually increase the heat and collect all the distillate up to 175°C . Caution: Heating the solution above 175°C will cause sulfuric acid to distill over.

The acid in the distilling flask can be used until there is carryover of interferences or poor fluoride recovery. An occasional check of fluoride recovery with standard solutions is advised. The acid should be changed whenever there is less than 90 percent recovery or blank values are higher than 0.1 $\mu\text{g}/\text{ml}$.

7.3.5 Determination of concentration—Bring the distillate in the 250 ml volumetric flask to the mark with distilled water and mix thoroughly. Pipette a 25 ml aliquot from the distillate. Add an equal volume of TISAB and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient lab temperature fluctuates more than $\pm 2^\circ\text{C}$ from the temperature at which the calibration standards were measured, condition samples and standards in a constant temperature bath measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response

time. If the stirrer generates enough heat to change solution temperature, place a piece of insulating material such as cork between the stirrer and the beaker. Dilute samples (below 10^{-4} M fluoride ion content) should be held in polyethylene or polypropylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, soak the fluoride sensing electrode in distilled water for 30 seconds and then remove and blot dry.

8. Calibration.

Maintain a laboratory log of all calibrations.

8.1 Sampling Train.

8.1.1 Probe nozzle—Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make 3 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.

8.1.2 Pitot tube—The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter. Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with by-pass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m³/min. (0.2 cfm) with the by-pass valve fully opened and then with it fully closed. If there is more than ± 2 percent difference in flow rates when compared to the fully closed position of the by-pass valve, the system is not designed properly and must be corrected.

8.1.4 Probe heater calibration—The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.1.5 Temperature gauges—Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples need not be calibrated. For other devices, check with the Administrator.

8.2 Analytical Apparatus.

8.2.1 Fluoride Electrode—Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M NaF into a 100 ml volumetric flask and make up to the mark with distilled water for a 10^{-2} M standard solution. Use 10 ml of 10^{-2} M solution to make a 10^{-3} M solution in the same manner. Repeat 10^{-4} and 10^{-5} M solutions.

Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semi-log graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, e.g., when 50 ml of

10^{-2} M standard is diluted with 50 ml TISAB, the concentration is still designated " 10^{-2} M".

Between measurements soak the fluoride sensing electrode in distilled water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10^2 , 10^1 , 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} , 10^{-8} , 10^{-9} fluoride molarity on the log axis plotted versus electrode potential (in millivolts) on the linear scale.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily of 10^{-2} M or less. Store fluoride standardizing solutions in polyethylene or polypropylene containers. (Note: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over narrow concentration ranges. Calibrate the meter according to manufacturer's instructions.)

9. Calculations.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

9.1 Nomenclature.

A_n = Cross sectional area of nozzle, m² (ft²).
 A_t = Aliquot of total sample added to still, ml.

B_w = Water vapor in the gas stream, proportion by volume.

C_s = Concentration of fluoride in stack gas, mg/m³, corrected to standard conditions of 20° C, 760 mm Hg (68° F, 29.92 in. Hg) on dry basis.

F_t = Total weight of fluoride in sample, mg.

I = Percent of isokinetic sampling.

M = Concentration of fluoride from calibration curve, molarity.

m_n = Total amount of particulate matter collected, mg.

M_w = Molecular weight of water, 18 g/g-mole (18 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 (21.83 in. Hg-ft³/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see fig. 13A-3), °K (°R).

T_s = Absolute average stack gas temperature (see fig. 13A-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_d = Volume of distillate collected, ml.

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml. Volume of water in silica gel equals silica gel weight increase in grams times 1 ml/gram. Volume of liquid collected in impinger equals final volume minus initial volume.

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_t = Total volume of sample, ml.

v_s = Stack gas velocity, calculated by Method 2, Equation 2-7 using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.
 ΔH = Average pressure differential across the orifice (see fig. 13A-3), meter, mm H₂O (in. H₂O).

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

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 13A-3 of Method 13A).

9.3 Dry gas volume. Use Section 9.3 of Method 13A.

9.4 Volume of Water Vapor. Use Section 9.4 of Method 13A.

9.5 Moisture Content. Use Section 9.5 of Method 13A.

9.6 Concentration

9.6.1 Calculate the amount of fluoride in the sample according to equation 13B-1.

$$F_t = K \frac{V_t}{A_t} (M)$$

where:

K = 19 mg/ml.

9.6.2 Concentration of fluoride in stack gas. Use Section 9.6.2 of Method 13A.

9.7 Isokinetic variation. Use Section 9.7 of Method 13A.

9.8 Acceptable results. Use Section 9.8 of Method 13A.

10. References.

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(Sections 111 and 114 of the Clean Air Act, as amended by section 4(a) of Pub. L. 91-604, 84 Stat. 1678 (42 U.S.C. 1857 c-6, c-9))

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