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Citation: 39 Fed. Reg. 37730 1974



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ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 60]

[FRL 281-3]

STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Proposed Rule for Primary Aluminum Plants

Pursuant to section 111 of the Clean Air Act, as amended, the Administrator proposes herein standards of performance for new and modified primary aluminum plants. The Administrator also proposes to amend Appendix A, Reference Methods, in Part 60 by adding three additional reference methods which pertain to measurement of fluoride emissions.

On December 23, 1971, the first standards of performance were promulgated. Those were for affected facilities at new fossil fuel-fired steam generators, incinerators, portland cement plants, nitric acid plants, and sulfuric acid plants. Since that time, additional standards have been promulgated for other categories of sources (March 8, 1974, 39 FR 9308) and several other publications in the FEDERAL REGISTER have amended the standards.

As prescribed by section 111, proposal of standards for primary aluminum plants was preceded by the Administrator's determination that these plants contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare. Notice of this determination appears elsewhere in this issue of the FEDERAL REGISTER (39 FR 37668).

Primary aluminum plants are a major source of fluoride air pollution. 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. This report concluded that "inorganic fluorides are highly irritant and toxic gases" which, in low ambient concentrations, damage plants and animals. The U.S. Senate Committee on Public Works in its report on the Clean Air Amendments of 1970 (Senate Report No. 91-1196, September 17, 1970, p. 9) included fluorides on a list of contaminants which have broad national impact and require Federal action.

Even though present evidence indicates that fluorides in the range of ambient concentrations encountered under worst conditions do not damage human health through inhalation, they do present a serious threat to public welfare. Extensive documented evidence is available describing the injurious effects of fluorides on vegetation and herbivorous animals which have consumed vegetation containing high fluoride levels. Public welfare is affected not only through the aesthetic impact of fluoride on vegetation, but also through a decrease in the economic value of sensitive crops which are overtly damaged by exposure to high ambient fluoride concentrations.

With the need for control of fluoride so obvious, an evaluation was made of available alternative avenues of regulatory control. The "Preferred Standards Path Report for Fluorides" (November 1972) concluded that the most appropriate strategy is through the authority of section 111 of the Act. This, in turn, invokes section 111(d) which provides for a regulatory mechanism to assure a nationwide strategy for control of any air pollutants which are not on lists published pursuant to section 108(a) or 112(b) (1) (A) of the Act. Fluoride has not been named on either list. Specifically, section 111(d) requires that the Administrator prescribe a procedure to assure the subsequent development, implementation, and enforcement of emission standards for existing sources that would be subject to the standard of performance if they were new sources.

As a consequence of the provisions of section 111(d), final promulgation of this standard of performance for new sources will require that the States develop emission standards for existing primary aluminum plants.

The problem of controlling air pollution emissions from primary aluminum plants has historically been one of containment. The configuration of the electrolytic cell in which the product aluminum is made and the labor activity which the cell requires have made it difficult to prevent dispersion of the emissions at the source (the reduction cell) within the building or "potroom" which houses it. As a consequence, although the control device which removes fluoride from the primary exhaust gases may be very efficient, a large portion of these gases escape containment and are never exposed to the cleaning action of the control device. These vagrant or "secondary" emissions depart from the potroom through the ventilation openings in the roof. Some plant operators have attempted to control these vagrant emissions with a "secondary" control device mounted within and below the roof of the building. Unfortunately, existing systems of this type have poor efficiency (only 20 to 50 percent) because of the severe dilution of the fluoride concentration by ventilation air.

The standards of performance herein proposed, by not differentiating between primary and secondary emissions, will encourage owners of new plants to obtain maximum containment of the gaseous emissions at the cell. Those plants which successfully contain these emissions within the primary control system should find no need to install the low efficiency secondary control system.

The standard will result in the use of either of two types of primary control devices: Wet gas scrubbers in series with an electrostatic precipitator; or dry fabric filters which use alumina as an adsorbant. The latter will likely be preferred because it generates no waste stream. All entrapped pollutants are recycled to the production process. The value of the fluoride recovered in this manner partially offsets the cost of the air pollution control equipment.

The standard of performance will require an approximate 25 percent increase in energy consumption over that required by State Implementation Plans for operation of air pollution control equipment. Based on the expected annual growth in new and modified primary aluminum plant facilities, this incremental increase in energy usage amounts to 15 million kilowatt hours per year; an insignificant amount in comparison to the total energy consumed by these facilities for the production of aluminum metal.

Two methods may be used for reducing fluoride emissions from the anode bake plant. Some significant improvement can be achieved by properly cleaning residual fluoride-bearing cryolite from the anode remnants before they are recycled. Where further reduction in fluoride emissions must be achieved, wet scrubbers may be required in conjunction with the wet electrostatic precipitators now commonly used. Electrostatic precipitators will continue to be essential for achieving the opacity limitation.

One consequence of not requiring a secondary control system is that the secondary emissions will probably exit the potroom through ventilation ports. Quantification by manual methods of the rate of such emissions would be laborious and expensive. Method 14 in Appendix A—Reference Methods, which describes a manifold system and sampling procedure, is an acceptable method of measuring roof monitor fluoride emissions at many locations. However, the building roof configuration may be different from that for which Method 14 is applicable and other variations of Method 14 or other methods may be appropriate; particularly at existing sources where the consideration of measuring secondary emissions was not a factor when the building roof was designed. Alternate methods subject to approval by the Administrator will probably be required for many affected facilities. Provisions for granting such approvals are contained in § 60.8 of this part.

Visible emission standards are proposed for the potroom and the anode bake plant. The effluent gases from these processes include particulate matter (both fluoride and non-fluorine), as well as gaseous fluoride. The control systems that must be installed to comply with the proposed standard for fluorides remove particulate matter along with gaseous fluorides. Improper operation and maintenance of such control systems result in an increase in emissions of total fluorides as well as particulate matter, the increase in particulate matter resulting in an increase in the opacity of the gas stream. Available information indicates that a control system which meets the proposed limit for total fluorides will easily meet the proposed limit for opacity. However, a control system which does not meet the proposed limit for opacity will clearly not meet the proposed limit for total fluorides.

Also included are proposed amendments to Appendix A—Reference Methods. These amendments provide addi-

tional reference methods for sampling emissions from primary aluminum plants and analyzing the samples for total fluoride content.

The bases for the proposed standards include the results of measurements of emissions conducted by industry, the Environmental Protection Agency and local agencies; data derived from available technical literature; information gathered during visits to pollution control agencies and plants in the United States and abroad; and comments and suggestions solicited from experts. The proposed standard reflects the degree of emission limitation achievable through the application of the best system of emission reduction which, taking into account the cost of achieving such reduction, the Administrator has determined to have been adequately demonstrated. Background information which presents the results of emission measurements and other factors considered in arriving at the proposed standards, including the types of control system and their costs, is available free of charge from the Emission Standards and Engineering Division, Environmental Protection Agency, Research Triangle Park, North Carolina 27711, attention: Mr. Don R. Goodwin.

It is emphasized that the costs are considered reasonable for new and modified sources. It is not implied that the same costs apply to the retrofitting of existing sources. Retrofitting to achieve the proposed emission limitations would in some cases cost much more.

In accordance with section 117(f) of the Act, publication of these proposed amendments to 40 CFR was preceded by consultation with appropriate advisory committees, independent experts, and Federal departments and agencies. The possible adverse environmental impact resulting from the proposed standards has been considered and determined to be negligible. The so-called "dry scrubbing system" permits all recovered materials to be recycled directly back to the process obviating any concern for water or solid waste pollution. If an operator should choose to install a water-based system of control, however, he must provide for treatment of the water in accordance with requirements specified by the Environmental Protection Agency in 39 FR 12822 dated April 8, 1974.

The economic impact of the proposed standards for the primary aluminum industry is judged to not be unduly severe. There will be no adverse impact upon future growth in the domestic industry. The major impact of the proposed standard will be acceleration of the current trend in the industry toward the prebake process and away from the Soderberg process.

Standards of performance for new stationary sources sometimes result in a more severe economic impact for smaller firms than larger ones. This is primarily because economies of scale generally favor larger installations. Based on the Small Business Administration (SBA) guidelines, a small primary aluminum business is one that employs less than

1,000 people. Using this definition, there are no firms in the primary aluminum industry that would be classified as small businesses. Furthermore, capital requirements to construct a primary aluminum smelter are so large, it is quite doubtful that any firm able to gain entry could fall within the SBA definition. Therefore, the standard of performance for primary aluminum smelters is unlikely to have any adverse impact upon small businesses.

The proper management of solid wastes resulting from air pollution control systems should be practiced. Air pollution control technologies generate many different amounts and types of solid wastes and liquid concentrates through the removal of pollutants from air emissions. These substances vary greatly in their chemical and physical composition. A variety of techniques may be employed to dispose of these substances depending on the degree of hazard.

If thermal processing is the choice for disposal, provisions must be made to ensure no re-entry of the pollutants into the atmosphere. Consideration should also be given to the recovery of materials of value in the wastes.

If land disposal is selected, practices similar to proper sanitary landfill technology must be followed. The principles set forth in the EPA's Land Disposal of Solid Wastes Guidelines (CFR Title 40, Chapter 1, Part 241) may be used as guidance for acceptable land disposal techniques.

The proper use of and test methods for opacity standards are presently being reconsidered by the Agency in response to remands from the U.S. Court of Appeals for the District of Columbia Circuit in *Portland Cement Association v. Ruckelshaus*, 486 F. 2d 375 (1973), and *Essex Chemical Corp. v. Ruckelshaus*, 486 F. 2d 427 (1973). The response to the remand in the *Portland Cement* case should be completed shortly. At that time, the Agency will promulgate or propose such revisions of its opacity standards or test methods as it deems necessary or desirable. In accordance with section 117(f) of the Act, publication of these proposed amendments to 40 CFR was preceded by consultation with appropriate advisory committees, independent experts and Federal departments and agencies. In the course of these consultations, the Department of Commerce has questioned the establishment of visible emissions (opacity) standards. The Department of Commerce believes that opacity limits have not been satisfactorily correlated to give rates of particulate concentration emissions or mass emissions to establish opacity as a standard. Further, Commerce has questioned whether such standards would be subject to accurate visual determination. Commerce, therefore, recommended that opacity limits not be adopted as a standard where a particulate concentration or mass emissions standard is established. Commerce believes such opacity limits should only be used in those cases to create a re-

buttable presumption of a violation of the particulate or mass emissions standards. Commerce believes such presumption could, for example, be rebutted by providing a continuous opacity monitor record showing a visual opacity observation to be in error; and/or by a showing that the particulate concentration or mass emissions standards was not exceeded at the time the opacity limit was exceeded. Commerce believes such a showing could be made by a performance test. If the owner or operator wished to use such test to show that he was not in violation of the mass or concentration standard at the time the opacity limit was exceeded, he must be able to establish the critical plant and control operating parameters that existed at the time of the observed opacity violation by a system of continuous monitoring and recording of such data so that such conditions can be duplicated at the time of the test.

EPA does not support the approach suggested by the Department of Commerce and is proposing opacity standards in the regulation. EPA believes that the opacity concept is both technically sound and the most practical and inexpensive way to insure that control equipment is adequately maintained and operated between performance tests. A performance test conducted after a source was observed to be in violation of the opacity standard would not in EPA's opinion necessarily resolve the question whether, at the time of the observed violation, the source was meeting the concentration standard. During the period between the observed violation of the opacity standard and the time of the performance test, the owner or operator in some cases could take remedial action to bring a non-complying source into compliance. EPA's opinion is that the only way to resolve this problem would be through use of a continuous monitoring system or through performance tests conducted at such frequent intervals as to yield similar results. EPA believes the approach suggested by the Department of Commerce is not a realistic or practical alternative in the absence of an appropriate continuous monitoring system. However at the request of the Department of Commerce, EPA is submitting for public comment that agency's recommendation and will consider any comments of State officials, industrial representatives, environmentalists, and the general public on this or any other alternative approach.

Interested persons may participate in this rulemaking by submitting written comments (in triplicate) to the Emission Standards and Engineering Division, Environmental Protection Agency, Research Triangle Park, North Carolina 27711, attention: Mr. Don R. Goodwin. The Administrator will welcome comments on all aspects of the proposed regulations, including economic and technological issues. All comments received not later than 45 days from the date of this proposal will be considered. Comments received will be available for public inspection.

tion at the Office of Public Affairs, 401 M Street, SW, Washington, D.C. 20460.

This notice of proposed rulemaking is issued under the authority of sections 111 and 114 of the Clean Air Act, as amended (42 U.S.C. 1857c-6 and 9).

Dated: October 11, 1974.

JOHN QUARLES,
Acting Administrator.

It is proposed to amend Part 60 of Chapter I, Title 40 of the Code of Federal Regulations, as follows:

1. Subpart S is added as follows:

Subpart S—Standards of Performance for Primary Aluminum Reduction Plants

60.190 Applicability and designation of affected facility.

60.191 Definitions.

60.192 Standard for fluorides.

60.193 Standard for particulate matter.

60.194 Monitoring of operations.

60.195 Test methods and procedures.

AUTHORITY: Secs. 111, 114, Pub. L. 91-604 (42 U.S.C. 1857c-6, 1857c-9).

Subpart S—Standards of Performance for Primary Aluminum Reduction Plants

§ 60.190 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each primary aluminum reduction plant. For the purpose of this subpart, the affected facility includes all potrooms and anode bake plants on contiguous properties of the owner or operator.

§ 60.191 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) "Primary aluminum reduction plant" means any facility manufacturing aluminum by electrolytic reduction.

(b) "Anode bake plant" means a facility which produces carbon anodes for use in a primary aluminum reduction plant.

(c) "Potroom" means the building unit which houses a group of electrolytic cells in which aluminum is produced.

(d) "Aluminum equivalent" means the equivalent amount of aluminum which can be produced from a ton of anodes.

(e) "Primary control system" means an air pollution control system designed to remove gaseous and particulate fluorides from exhaust gases which are captured at the cell.

(f) "Roof monitor" means that portion of the roof of the potroom where gases not captured at the cell exit from the potroom.

(g) "Total fluorides" means elemental fluoride and all fluoride compounds as measured by reference methods specified in § 60.195.

(h) "Secondary control system" means an air pollution control system designed to remove both gaseous and particulate fluorides from gases which escape capture by the primary control system.

§ 60.192 Standard for fluorides.

On and after the date on which the performance test required to be con-

ducted 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 1 kg/metric ton (2 lb/ton) of aluminum produced and aluminum equivalents as determined by § 60.195(f).

§ 60.193 Standard for particulate matter.

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 the potroom any gases which exhibit 10 percent opacity or greater or from the anode bake plant any gases which exhibit 20 percent opacity or greater.

§ 60.194 Monitoring of operations.

(a) The owner or operator of any affected facility subject to the provisions of this subpart shall install, calibrate, maintain, and operate weighing devices which can be used to determine daily the weight of aluminum and anode produced. The weighing devices shall have an accuracy of ± 5 percent over their operating range.

(b) The owner or operator of any affected facility shall maintain a record of daily production rates of aluminum and anodes, raw material feed rates, and cell or potline voltages.

§ 60.195 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 standards prescribed in § 60.192 as follows:

(1) For sampling emissions from stacks:

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

(ii) Method 1 for sample and velocity traverses,

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

(iv) Method 3 for gas analysis.

(2) For sampling emissions from roof monitors not employing stacks:

(i) Method 14 for the concentration of total fluorides and associated moisture content,

(ii) Method 1 for sample and velocity traverses,

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

(iv) Method 3 for gas analysis.

(b) For Method 13A or 13B, the sampling time for each run shall be at least 8 hours for any sample from the potroom and 4 hours for the anode bake plant, and the minimum sample volume shall be 6.8 dscm (240 dscf) for the potroom and 3.4 dscm (120 dscf) for the anode bake plant 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 each affected facility must be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined using applicable methods specified under paragraph (a) of this section.

(d) The rate of aluminum produced shall be determined as follows:

(1) Determine the weight of aluminum in metric tons produced during a period from the last tap before a run starts until the first tap after the run ends using a weighing device which meets the requirements of § 60.194(a).

(2) Divide the weight of aluminum produced by the length of the period in hours.

(e) For anode bake plants, the aluminum equivalents for anodes produced shall be determined as follows:

(1) Determine the average weight (metric tons) of anode produced in the anode bake plant(s) during an average oven cycle using a weighing device which meets the requirements of § 60.194(a).

(2) Determine the average rate of anode produced by dividing the total weight of anodes produced during an average oven cycle by the length of the average oven cycle in hours.

(f) For each run, emissions expressed in kg/metric ton of aluminum and aluminum equivalents shall be determined using the following equation:

$$E = \frac{(C_1 Q_1) 10^{-6}}{M} + \frac{(C_2 Q_2) 10^{-6}}{M} + \frac{(C_3 Q_3) 10^{-6}}{KM}$$

where:

E = emissions of total fluorides in kg/metric ton of aluminum and aluminum equivalents.

C_1 = concentration of total fluorides in mg/dscm as determined by Method 13A or 13B.

Q_1 = volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2 or Method 14.

10^{-6} = conversion factor from mg to kg,

M = aluminum produced in metric ton/hr as determined by § 60.195(d).

M_1 = anode produced by anode bake plants in metric ton/hr as determined by § 60.195(e).

K = 2, a factor representing the ratio of the equivalent tons of aluminum produced to the tons of anode consumed. An owner or operator who

elects to submit production records of the tons of aluminum produced and the concurrent tons of anode consumed by potrooms may establish other values for K .

(Q_1) = value of the parameters for measurements on the primary control system effluent gas streams.

(Q_2) = value of the parameters for measurements on the secondary control system or roof monitor effluent gas streams.

(Q_3) = value of the parameters for measurements on the anode bake plant effluent gas streams.

2. Appendix A—Reference Methods is amended by adding Reference Methods 13A, 13B, and 14 as follows:

METHOD 13A—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.

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 360 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 *Sampling train.* See Figure 13A-1. Many of the design specifications of this sampling train are described in APTD-0581.

5.1.1 *Nozzle.*—Stainless steel (316) with sharp, tapered leading edge.

5.1.2 *Probe.*—Borosilicate¹ glass or stainless steel (316) with a heating system capable of maintaining a gas temperature of about 121° C (250° F) at the probe when required to prevent condensation in the probe.

5.1.3 *Pitot tube.*—Type S, or equivalent, attached to probe to monitor stack gas velocity.

5.1.4 *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.

¹ Pyrex has been found suitable for this purpose. Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

5.1.5 *Filter heating system.*—Capable of maintaining the filter holder enclosure at about 121° C (250° F). The filter heating system is required only when the filter is located downstream of the impingers, or for sampling saturated gases when the filter is upstream of the impingers.

5.1.6 *Impingers.*—Four impingers connected as shown in Figure 13A-1 with ground glass, vacuum tight fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a 1¼ cm (½ in.) inside diameter glass tube extending to 1¼ cm (½ in.) from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip.

5.1.7 *Metering system.*—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (~5° 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.

5.1.8 *Barometer.*—To measure atmospheric pressure to ±2.5 mm Hg (0.1 in.).

5.2 Sample recovery.

5.2.1 *Probe brush.*—At least as long as probe.

5.2.2 *Glass wash bottle.*—Two.

5.2.3 *Sample storage containers.*—Wide mouth polypropylene bottles with Teflon liner, polyethylene not acceptable, 1 liter.

5.2.4 *Sample storage containers.*—Glass, 1 liter.

5.2.5 *Graduated cylinder.*—250 ml.

5.3 Analysis.

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.

5.3.4.1 *Beaker,* 1,500 ml.

5.3.5 *Volumetric flask.*—50 ml.

5.3.6 *Erlenmeyer flask or plastic bottle.*—500 ml.

5.3.7 *Constant temperature bath.*—Capable of maintaining a constant temperature of ±1.0°C in the range of room temperature.

5.3.8 *Trip balance.*—300 g capacity to measure to ±0.5 g.

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

5.3.10 *Spectrophotometer cells.*—1 cm.

6. Reagents.

6.1 Sampling.

6.1.1 *Filters.*—Whatman No. 1 filter or equivalent to fit filter holder.

6.1.2 *Silica gel.*—Indicating type, 6-16 mesh, dried at 175° C (350° F) for 2 hours.

6.1.3 *Water.*—Distilled.

6.1.4 *Crushed ice.*

6.2 Sample recovery.

6.2.1 *Water.*—Distilled, from same container as 6.1.3.

6.2.2 *Acetone.*—ACS reagent grade or equivalent.

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 *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-sulphophenylazo)-2,7-naphthalene-disulfonic acid trisodium salt]. Dissolve 0.960 ± .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 (6.3.9) 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 ± 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.

7.1 Sampling.

7.1.1 Select the sampling site and the minimum number of sampling points; determine the stack pressure, temperature, moisture and range of velocity head as described in Methods 1, 2, 3, and 4 (FEDERAL REGISTER, Volume 36, Number 247, Thursday, December 23, 1971).

7.1.2 *Preparation of collection train.*—Place Whatman No. 1 filter into filter holder. Weigh approximately 200 g of silica gel to the nearest gram. Place 100 ml of distilled water in each of the first two impingers, leave the third impinger empty, and place the preweighed silica gel in the fourth impinger. Assemble the train without the probe as shown in Figure 13A-1 with the filter between the third and fourth impingers. Alternately, for sampling dry sources, the filter may be placed between the probe and first impinger. This alternate configuration may be used only for sampling stacks with low moisture content, or when probe and filter heating is used. In the latter case, maintain the filter and probe heating systems at about 121° C (250° F) throughout the run to prevent moisture condensation. Record filter location on the data sheet. Leak check the sampling train at the sampling site by plugging the inlet to the train and pulling a 380 mm (15 in.) Hg vacuum, or the maximum vacuum that is expected to occur during the test run, whichever is greater. A leakage rate not in excess of 0.00057 m³/min. (0.02 cfm) at a vacuum of 380 mm (15 in.) Hg is acceptable. Attach the probe and adjust the probe heater to provide a gas temperature of about 121° C (250° F) at the probe outlet. (NOTE: Whatman No. 1 filter decomposes at 150° C (300° F)). Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 21° C (70° F) or less.

7.1.3 *Train operation.*—For each run, record the data required on the example sheet shown in Figure 13A-3. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, 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. Sample for the same

amount of time at each traverse point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack.

7.2 Sample recovery—Move the impinger train to the clean-up area. Measure the volume of water in the first three impingers. Place the samples in containers as follows:

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

7.2.2 Container No. 2—With reagent grade acetone in a manner analogous to 7.2.1 wash all sample exposed surfaces. If visible material remains, rinse or clean with a brush until the surface is clean. Add these washings to this container which must be made of glass.

7.2.3 Container No. 3—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 1,500 ml beaker. Note: If filtrate volume exceeds 900 ml make filtrate basic 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.

7.3.2 Container No. 2.

7.3.2.1 Add 100 mg of CaO to the acetone washings, mix well, and evaporate the acetone to about 20 ml with ambient air in a forced draft hood, and transfer the residue to the nickel crucible containing the insoluble

materials from container No. 1 (7.3.1). Acetone wash the container into the crucible, and evaporate the crucible contents to dryness with ambient air in a forced draft hood.

7.3.2.2 Add approximately 4 g of crushed NaOH to the crucible and mix thoroughly. Return the crucible to the muffle furnace, and fuse the sample for 10 min. 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 to a one-liter volumetric flask. Dilute to volume with distilled water and mix thoroughly. Allow any undissolved solids to settle.

7.3.3 Container No. 3. Weigh the spent silica gel and report to the nearest gram.

7.3.4 Adjustment of acid/water ratio in distillation flask—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 boiling stones and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 180°C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

7.3.5 Distillation—Cool the contents of the distillation flask to below 100°C. Pipette an aliquot of sample containing less than 0.6 mg fluoride and dilute to 300 ml with distilled water. (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.) Carefully add this to the distillation flask. Note: If the sample contains chloride, add 5 mg Ag₂SO₄ to the flask for every mg of chloride. Gradually increase the heat and collect all the distillate up to 180°C. The carryover of sulfate, an interference in the colorimetric analysis, becomes excessive above 180°C.

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 using standard solutions is advised.

7.3.6 Determination of Concentration—Record the volumes of distillate from each distillation. 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 6.3.11) and mix thoroughly.

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

Set the spectrophotometer to zero absorbance at 570 nm with reference solution, and calibrate the spectrophotometer with standard solutions. (See section 6.3.10.) 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.

8.1 Sampling Train. Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, and dry gas meter.

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 6.3.8) 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 6.3.10) 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 new standard curve should be prepared with each set of samples.

9. Calculations.

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

9.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions [21.1°C, 760 mm Hg (70°F, 29.92 inches Hg)] by using equation 13A-1.

$$V_{std} = V_m \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}$$

Equation 13A-1

where:

V_{std} = Volume of gas sample through the dry gas meter (standard conditions), liter (cu. ft.).

V_m = Volume of gas sample through the dry gas meter (meter conditions), liter (cu. ft.).

T_{std} = Absolute temperature at standard conditions, 294°K (530°R).

T_m = Average dry gas meter temperature, °K(°R).

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

ΔH = Average pressure drop across the orifice meter, mm H₂O (in. H₂O).

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 760 mm Hg (29.92 in. Hg.).

9.3 Volume of water vapor,

$$V_{w,td} = V_{i,c} \frac{\rho_{H_2O} R}{M_{H_2O} P_{std}} \quad \text{Equation 13A-2}$$

where:

- $V_{w,td}$ = Volume of water vapor in the gas sample (standard conditions), liter (cu. ft.).
- $V_{i,c}$ = 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.
- ρ_{H_2O} = Density of water, 1 g/ml. (0.0022 lb/ml).
- M_{H_2O} = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole).
- R = Ideal gas constant, 62.36 mm Hg-liter/g mole-°K (21.83 in. Hg-cu. ft/lb mole-°R).
- T_{std} = Absolute temperature at standard conditions, 294°K (530°R).
- P_{std} = Absolute pressure at standard conditions, 760 mm Hg (29.92 in. Hg.).

9.4 Moisture content.

$$B_{w,o} = \frac{V_{w,td}}{V_{w,td} + V_{g,td}} \quad \text{Equation 13A-3}$$

where:

- $B_{w,o}$ = Proportion by volume of water vapor in the gas stream, dimensionless.
- $V_{w,td}$ = Volume of water in the gas sample (standard conditions), liter (cu. ft.).
- $V_{g,td}$ = Volume of gas sample through the dry gas meter (standard conditions), liter (cu. ft.).

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.

9.5 Concentration

9.5.1 Calculate the amount of fluoride in the sample according to Equation 13A-4.

$$F_t = \frac{V_t V_d}{A_t A_d} \mu\text{g } F \frac{1 \text{ mg}}{1000 \text{ g}} \quad \text{Equation 13A-4}$$

where:

- F_t = Amount of fluoride in total sample, mg.
- V_t = Total volume of sample, ml.
- A_t = Aliquot of total sample added to still, ml.
- V_d = Volume of distillate collected, ml.
- A_d = Aliquot of distillate taken for color development, ml.
- $\mu\text{g } F$ = Concentration from the calibration curve, g.

9.5.2 Concentration of fluoride in stack gas. Determine the concentration of fluoride in the stack gas according to Equation 13A-5.

$$C_s = \frac{F_t}{V_{w,td}} \frac{35.31 \text{ cu. ft.}}{\text{m}^3} \quad \text{Equation 13A-5}$$

where:

- C_s = Concentration of fluoride in stack gas, mg/m³, corrected to standard conditions of 21.1°C, 760 mm Hg (70°F, 29.92 in. Hg.) on dry basis.
- F_t = Total weight of fluoride in sample, mg from Section 9.5.1.
- $V_{w,td}$ = Volume of gas sample through the dry meter (standard conditions), cu. ft. from equation 13A-1.

9.6 Isokinetic variation.

$$I = \frac{T_s \frac{V_{i,c}(\rho_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m} (P_{s,r} + \frac{\Delta H}{13.6})}{\theta V_s P_s A_n} \times 100. \quad \text{Equation 13A-6}$$

English Units:

$$I = \frac{(1.667 \frac{\text{min.}}{\text{sec.}}) \left[\left(0.00267 \frac{\text{in. Hg-cu. ft.}}{\text{ml-}^\circ\text{R}} \right) V_{i,c} + \frac{V_m}{T_m} (P_{s,r} + \frac{\Delta H}{13.6}) \right] T_s}{\theta V_s P_s A_n}$$

Metric Units:

$$I = \frac{(1.667 \frac{\text{min.}}{\text{sec.}}) \left[0.00346 \frac{\text{mm Hg-m}^3}{\text{ml-}^\circ\text{K}} V_{i,c} + \frac{V_m}{T_m} (P_{s,r} + \frac{\Delta H}{13.6}) \right] T_s}{\theta V_s P_s A_n}$$

Where:

- I = Percent of isokinetic sampling.
- $V_{i,c}$ = 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 impingers is final volume minus initial volume.

H_2O = Density of water, 1 g/ml.

R = Ideal gas constant, 62.36 mm Hg—liter/g mole—°K (21.83 in. Hg—cu. ft./lb mole—°R).

M_{H_2O} = Molecular weight of water, 18 g/g mole (18 lb/lb—mole).

V_m = Volume of gas sample through the dry gas meter (meter conditions), m³ (cu. ft.).

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

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

ΔH = Average pressure drop across the orifice (see Figure 13A-3), mm H₂O (in. H₂O).

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

t = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, (*Federal Register*, Volume 36, Number 247, December 23, 1971), m/sec (ft/sec).

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

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

9.7 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 100\%$, the results are acceptable, otherwise, reject the results and repeat the test.

10. References.

Bellack, Ervin, "Simplified Fluoride Distillation Method," *Journal of the American Water Works Association* # 50: 530-6 (1958).
MacLeod, Kathryn E., and Howard L. Crist, "Comparison of the SPADNS-Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples," *Analytical Chemistry* 45: 1272-1273 (1973).

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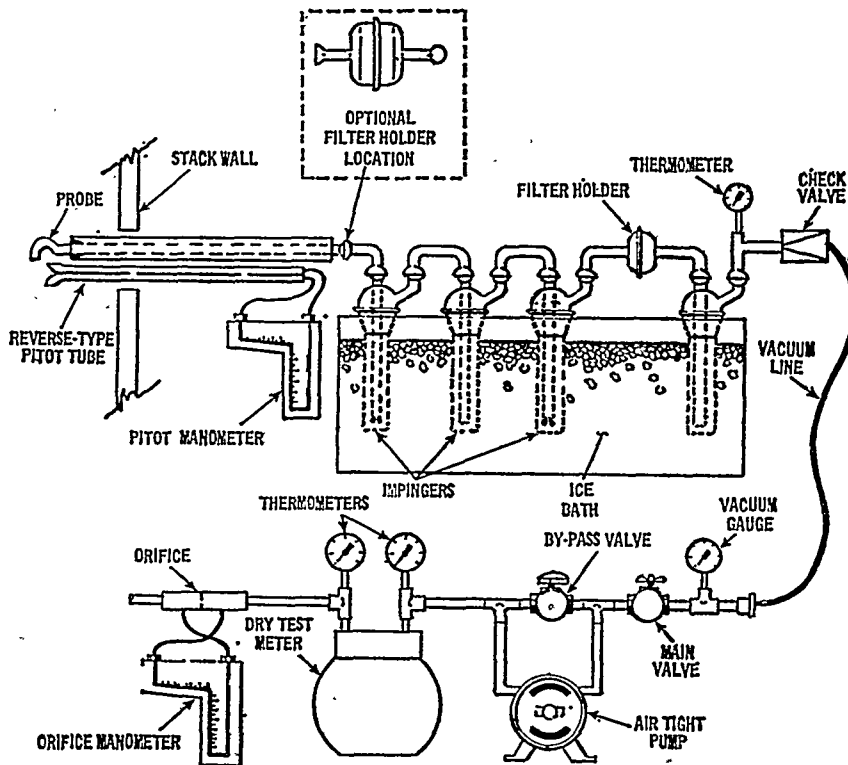


Figure 13A-1. Fluoride Sampling Train

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

5.3.4 Crucibles—Nickel, 75 to 100 ml capacity.

5.3.4.1 Beaker—1500 ml.

5.3.5 Volumetric flask—50 ml.

5.3.6 Erlenmeyer flask or plastic bottle—500 ml.

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

5.3.8 Trip balance—300 g capacity to measure to $\pm 0.05\text{ g}$.

5.3.9 Fluoride ion activity sensing electrode.

5.3.10 Reference electrode—Silver/silver chloride electrode, saturated Calomel electrode or equivalent, suitable for use with the fluoride electrode and electrometer used. A large area liquid junction is preferable to a fiber-type liquid junction.

5.3.11 Electrometer—A pH meter with millivolt scale capable of $\pm 0.5\text{ mv}$ resolution, or a specific ion meter made specifically for specific ion use.

5.3.12 Magnetic stirrer and TFE fluorocarbon coated stirring bars.

6. Reagents.

6.1 Sampling.

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

6.1.2 Silica gel—Indicating type, 6–16 mesh, dried at 175° C. (350° F) for 2 hours.

6.1.3 Water—Distilled.

6.1.4 Crushed ice.

6.2 Sample recovery.

6.2.1 Water—Distilled, from same container as 6.1.3.

6.2.2 Acetone—ACS reagent grade or equivalent.

6.3 Analysis.

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

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

6.3.3 Silver sulfate (Ag_2SO_4)—ACS reagent grade or equivalent.

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

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

6.3.6 Filters—Whatman No. 541, or equivalent.

6.3.7 Water—Distilled, from same container as 6.1.3.

6.3.8 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.

6.3.9 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.

7.1 Sampling.

7.1.1 Select the sampling site and the minimum number of sampling points; determine the stack pressure, temperature, moisture and range of velocity head as described in Methods 1, 2, 3, and 4 (FEDERAL REGISTER Volume 36, Number 247, Thursday, December 23, 1971).

7.1.2 Preparation of collection train—Place Whatman No. 1 filter into filter holder. Weigh approximately 200 g of silica gel to the nearest gram. Place 100 ml of distilled water in each of the first two impingers, leave the third impinger empty, and place the pre-

weighed silica gel in the fourth impinger. Assemble the train without the probe as shown in Figure 13A-1 (Method 13A) with the filter between the third and fourth impingers. Alternately, for sampling dry sources, the filter may be placed between the probe and first impinger. This alternate configuration may be used only for sampling stacks with low moisture content, or when probe and filter heating is used. In the latter case, maintain the filter and probe heating systems at about 121° C (250° F) throughout the run to prevent moisture condensation. Record filter location on the data sheet. Leak check the sampling train at the sampling site by plugging the inlet to the train and pulling a 380 mm (15 in.) Hg vacuum, or the maximum vacuum that is expected to occur during the test run, whichever is greater. A leakage rate not in excess of 0.00057 $\text{m}^3\text{ min.}$ (0.02 cfm) at a vacuum of 380 mm (15 in.) Hg is acceptable. Attach the probe and adjust the probe heater to provide a gas temperature of about 121° C (250° F) at the probe outlet. (Note: Whatman No. 1 filter decomposes at 150° C (300° F).) Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 21° C (–70° F) or less.

7.1.3 Train operation. For each run, record the data required on the example sheet shown in Figure 13A-3 (Method 13A). Take readings at each sampling point at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, 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. Sample for the same amount of time at each traverse point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and seal for transport.

7.2 Sample recovery. Move the impinger train to the clean-up area. Measure the volume of water in the first three impingers. Place the samples in containers as follows:

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

7.2.2 Container No. 2. With reagent grade acetone in a manner analogous to 7.2.1 wash all sample exposed surfaces. If visible material remains, rinse or clean with a brush until the surface is clean. Add these washings to this container which must be made of glass.

7.2.3 Container No. 3. 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 #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 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 two 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.

7.3.2 Container No. 2.

7.3.2.1 Add 100 mg of CaO to the acetone washings, mix well, and evaporate the acetone to about 20 ml with ambient air in a forced draft hood, and transfer the residue to the nickel crucible containing the insoluble materials from container No. 1 (7.3.1). Acetone wash the container into the crucible, and evaporate the crucible contents to dryness with ambient air in a forced draft hood.

7.3.2.2 Add approximately 4 g of crushed NaOH to the crucible and mix thoroughly. Return the crucible to the muffle furnace, and fuse the sample for 10 min. 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 to a one-liter volumetric flask. Dilute to volume with distilled water and mix thoroughly. Allow any undissolved solids to settle.

7.3.3 Container No. 3. Weigh the spent silica gel and report to the nearest gram.

7.3.4 Adjustment of acid/water ratio in distillation flask—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 boiling stones and assemble the apparatus as shown in Figure 13A-2 (Method 13A). Heat the flask until it reaches a temperature of 180° C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

7.3.5 Distillation—Cool the contents of the distillation flask to below 100° C. Pipette an aliquot of sample containing less than 0.6 mg fluoride and dilute to 300 ml with distilled water. (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 7.3.5. This will give an approximation of the fluoride content, but only an approximation since interfering ions have not been removed by the distillation step.) Carefully add this to the distillation flask. Gradually increase the heat and collect all the distillate up to 180° C.

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.

7.3.6 Determination of concentration—Record the volume of the distillate from each distillation. Pipet a suitable aliquot (prefer-

ably 25 ml or greater) 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 before 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 temperature 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, rinse the electrode with distilled water.

8. Calibration.

8.1 Sampling Train. Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, and dry gas meter.

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".

Rinse and blot the electrodes and repeat, going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} 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.

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

9.2 Dry gas volume. Use Section 9.2 of Method 13A.

9.3 Volume of water vapor. Use Section 9.3 of Method 13A.

9.4 Moisture content. Use Section 9.4 of Method 13A.

9.5 Concentration.

9.5.1 Calculate the amount of fluoride in the sample according to Equation 13B-1.

$$F_t = \frac{V_1}{A_1} (V_2) (M) 10 \frac{\text{mg}}{\text{ml}}$$

Equation 13B-1

where:

F_t = Amount of fluoride in total sample, mg.

V_1 = Total volume of sample, ml.

A_1 = Aliquot of total sample added to still, ml.

V_2 = Volume of distillate collected, ml.

M = Concentration of fluoride from calibration curve, molarity.

9.5.2 Concentration of fluoride in stack gas. Use Section 9.5.2 of Method 13A.

9.6 Isokinetic variation. Use Section 9.6 of Method 13A.

9.7 Acceptable results. Use Section 0.7 of Method 13A.

10. References.

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METHOD 14—DETERMINATION OF FLUORIDE EMISSIONS FROM POT ROOM ROOF MONITORS OF PRIMARY ALUMINUM PLANTS

1. Principle and Applicability.

1.1 Principle. Gaseous and particulate fluoride roof monitor emissions are drawn into a permanent sampling manifold through several large nozzles. The sample is transported from the sampling manifold to ground level through a duct. The gas in the duct is sampled using Method 13A or 13B—Determination of Total Fluoride Emissions From Stationary Sources Effluent velocity and volumetric flow rate are determined with anemometers permanently located in the roof monitor.

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.

2. Apparatus.

2.1 Velocity Measurement Apparatus.

2.1.1 Anemometers.—Vane or propeller anemometers with a velocity measuring threshold as low as 15 meters/minute and a range up to at least 600 meters/minute. Each anemometer must generate an electrical signal which can be calibrated to the velocity measured by the anemometer. Anemometers must be able to withstand dusty and corrosive atmospheres.

There must be one anemometer installed for every 85 meters of roof monitor length. If the roof monitor length divided by 85 meters is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. Use one anemometer for any roof monitor less than 85 meters long. Permanently mount the anemometers at the center of each equal

length along the roof monitor. One anemometer shall be installed in the same section of the roof monitor that contains the sampling manifold (see Section 5.2.1). Make a velocity traverse of the width of the roof monitor at each point along the roof monitor where an anemometer is to be placed. This traverse can be made with any suitable low velocity measuring device, and must be made during normal process operating conditions. Install the anemometer at a point of average velocity along this traverse.

2.1.2 Recorders.—Recorders equipped with signal transducers for converting the electrical signal from each anemometer to a continuous recording of air flow velocity, or to an integrated measure of volumetric flow. For the purpose of recording velocity, "continuous" shall mean one readout per 15-minute or shorter time interval. A constant amount of time shall elapse between readings. Volumetric flow rate may be determined by an electrical count of anemometer revolutions. The recorders or counters shall permit identification of the velocities, or flow rate measured by each individual anemometer.

2.2 Roof Monitor Air Sampling System.

2.2.1 Sampling Ductwork.—The manifold system and connecting duct shall be permanently installed to draw an air sample from the roof monitor to ground level. A typical installation of duct for drawing a sample from a roof monitor to ground level is shown in Figure 14-1. A plan of the manifold system that is located in the roof monitor is shown in Figure 14-2. These drawings represent a typical installation for a generalized roof monitor. The dimensions on these figures may be altered slightly to make the manifold system fit into a particular roof monitor, but the general configuration must be adhered to. There must be eight nozzles, each having a diameter of 0.40 to 0.50 meters. The length of the manifold system from the first nozzle to the eighth must be 35 meters or 8 percent of the length of the roof monitor, whichever is greater. The duct leading from the roof monitor manifold must be round with a diameter of 0.30 to 0.40-meters. As shown in Figure 14-2, each of the sample legs of the manifold must have a device, such as a blast gate or valve, to enable adjustment of flow into each sample nozzle.

Locate the manifold along the length of the roof monitor so that it lies near the midsection of the roof monitor. If the design of a particular roof monitor makes this impossible, the manifold may be located elsewhere along the roof monitor, but avoid locating the manifold near the ends of the roof monitor or in a section where the aluminum reduction pot arrangement is not typical of the rest of the pot room. Center the sample nozzles in the throat of the roof monitor. (See Figure 14-1.) Construct all sample-exposed surfaces within the nozzles, manifold and sample duct of 316 stainless steel. All connections in the ductwork must be leak free.

Locate two sample ports in a vertical section of the duct between the roof monitor and exhaust fan. The sample ports must be at least ten duct diameters downstream and two diameters upstream from any flow disturbance such as a bend or contraction. The

two sample ports shall be situated 90° apart. One of the sample ports must be situated so that the duct can be traversed in the plane of the nearest upstream duct bend.

2.2.2 Exhaust Fan—An industrial fan or blower to be attached to the sample duct at ground level. (See Figure 14-1.) This exhaust fan must have a maximum capacity such that a large enough volume of air can be pulled through the ductwork so that an isokinetic sampling rate can be maintained in all the sample nozzles for all flow rates normally encountered in the roof monitor.

The exhaust fan volumetric flow rate must be adjustable so that the roof monitor air can be drawn isokinetically into the sample nozzles. This control of flow can be achieved by a damper on the inlet to the exhaustor or by any other workable method.

2.3 Temperature Measurement Apparatus

2.3.1 Thermocouple—Installed in the roof monitor near the sample duct.

2.3.2 Signal Transducer—Transducer to change the thermocouple voltage output to a temperature readout.

2.3.3 Thermocouple wire—To reach from roof monitor to signal transducer and recorder.

2.3.4 Sampling Train—Use the train described in Methods 13A or 13B—Determination of Total Fluoride Emissions From Stationary Sources.

3. Reagents.

3.1 Sampling and Analysis. Use reagents described in Method 13A or 13B—Determination of Total Fluoride Emissions From Stationary Sources.

4. Calibration.

4.1 Propeller Anemometer. Calibrate the anemometers so that their electrical signal output corresponds to the velocity or volumetric flow they are measuring. Calibrate according to manufacturer's instructions.

4.2 Manifold Intake Nozzles. Adjust the exhaust fan to draw a volumetric flow rate (refer to Equation 14-1) such that the entrance velocity into each manifold nozzle approximates the average effluent velocity in the roof monitor. Measure the velocity of the air entering each nozzle by inserting an S type pitot tube into a 2.5 cm or less diameter hole (see Figure 14-2) which is located in the manifold between each blast gate (or valve) and nozzle. The pitot tube tip should be extended into the center of the manifold. Take care to insure that there is no leakage around the pitot probe which could affect the indicated velocity in the manifold leg. If the velocity of air being drawn into each nozzle is not the same, open or close each blast gate (or valve) until the velocity in each nozzle is the same. Fasten each blast gate (or valve) so that it will remain in this position and close the pitot port holes. This calibration shall be performed when the manifold system is installed. It is recommended that this calibration be repeated at least one a year.

5. Procedure.

5.1 Roof Monitor Velocity Determination.

5.1.1 Velocity Value for Setting Isokinetic Flow—During the 24 hours preceding a test

run, determine the velocity indicated by the propeller anemometer which is in the section of roof monitor containing the sampling manifold. Velocity readings should be taken every 15 minutes or at shorter equal time intervals. Calculate the average velocity for the 24-hour period.

5.1.2 Velocity Determination During a Test Run—During the actual test run, record the velocity or volume readings of each propeller anemometer in the roof monitor. Velocity readings must be taken for each anemometer every 15 minutes or at shorter equal time intervals (or continuously).

5.2 Temperature Recording. Record the temperature of the roof monitor every two hours during the test run.

5.3 Sampling.

5.3.1 Preliminary air flow in duct—During the 24 hours preceding the test, turn on the exhaust fan and draw roof monitor air through the manifold duct to condition

the ductwork. Adjust the fan to draw a volumetric flow through the duct such that the velocity of gas entering the manifold nozzles is about 75 meters/minute.

5.3.2 Isokinetic Sample Rate Adjustment—Adjust the fan so that the volumetric flow rate in the duct is such that air enters into the manifold sample nozzles at a velocity equal to the 24-hour average velocity determined under 5.1.1. Equation 14-1 gives the correct stream velocity which is needed in the duct at the sample ports in order for sample gas to be drawn isokinetically into the manifold nozzles. Perform a pitot traverse of the duct at the sample ports to determine if the correct average velocity in the duct has been achieved. Perform the pitot determination according to Method 2. Make this determination before the start of a test run. The fan setting need not be changed during the run.

$$V_d = \frac{8(D_n)^2}{(D_d)^2} (V_m) \left(\frac{1 \text{ minute}}{60 \text{ sec}} \right) \quad \text{Equation 14-1}$$

where:

V_d = Desired velocity in duct at sample ports, meter/sec.

D_n = Diameter of a roof monitor manifold nozzle, meters.

D_d = Diameter of duct at sample port, meters.

V_m = Average velocity of the air stream in the roof monitor meters/minute.

5.3.3 Sample Train Operation—Sample the duct using the standard fluoride train and methods described in Methods 13A and 13B—Determination of Total Fluoride Emissions From Stationary Sources. Select sample traverse points according to Method 1. If a selected sampling point is closer than 1 inch from the stack wall, adjust the location of that point to 1 inch away from the wall.

5.3.4 Each test run shall last eight hours or more. If a question exists concerning the representativeness of an eight-hour test, then a longer test period up to 24 hours should be selected. Conduct each run during a period when all normal operations are performed underneath the sampling manifold, i.e., tapping, anode changes, maintenance, and other normal duties. The test engineer must take particular care to see that all the pots in the pot room are operated in a similar manner during the test period.

5.3.5 Sample Recovery—Same as Method 13A or 13B—Determination of Total Fluoride Emissions From Stationary Sources.

5.4 Analysis. Same as Method 13A or 13B—Determination of Total Fluoride Emissions From Stationary Sources.

6. Calculations.

6.1 Isokinetic Sampling Test. Calculate the mean velocity measured during each sampling run by the anemometer which is in the section of the roof monitor containing the sampling manifold. If the mean velocity established according to 5.3.2 does not fall within ± 10 percent of the mean velocity recorded during a respective test run, repeat the run.

6.2 Average Velocity of Roof Monitor Gases. Calculate the average roof monitor velocity using all the velocity or volumetric flow readings from Section 5.1.2.

6.3 Roof Monitor Temperature. Calculate the mean value of the temperatures recorded in Section 5.2.

6.4 Concentration of fluorides in roof monitor air in mg F/m³. This is given by Equation 13A-5 in Method 13A—Determination of Total Fluoride Emissions From Stationary Sources.

6.5 Average Volumetric Flow From Roof.

$$Q_m = \frac{V_{mi}(A)(M_d)P_m(294^\circ K)}{(T_m + 273^\circ)(760 \text{ mm Hg})} \quad \text{Equation 14-2}$$

Where:

Q_m = Average volumetric flow from roof monitor at standard conditions on a dry basis, m³/min.

A = Roof monitor open area, m².

V_{mi} = Average velocity of air in the roof monitor, meters/minute, from Section 6.2.

P_m = Atmospheric pressure, mm Hg.

T_m = Roof monitor temperature, °C, from Section 6.3.

M_d = Mole fraction of dry gas, which is given by $M_d = \frac{100 - 100(B_w)}{100}$

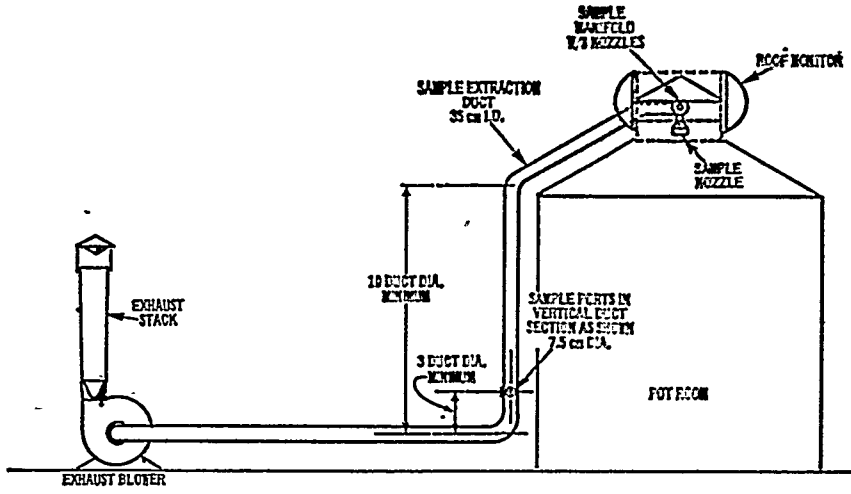


Figure 14-1. Roof Monitor Sampling System

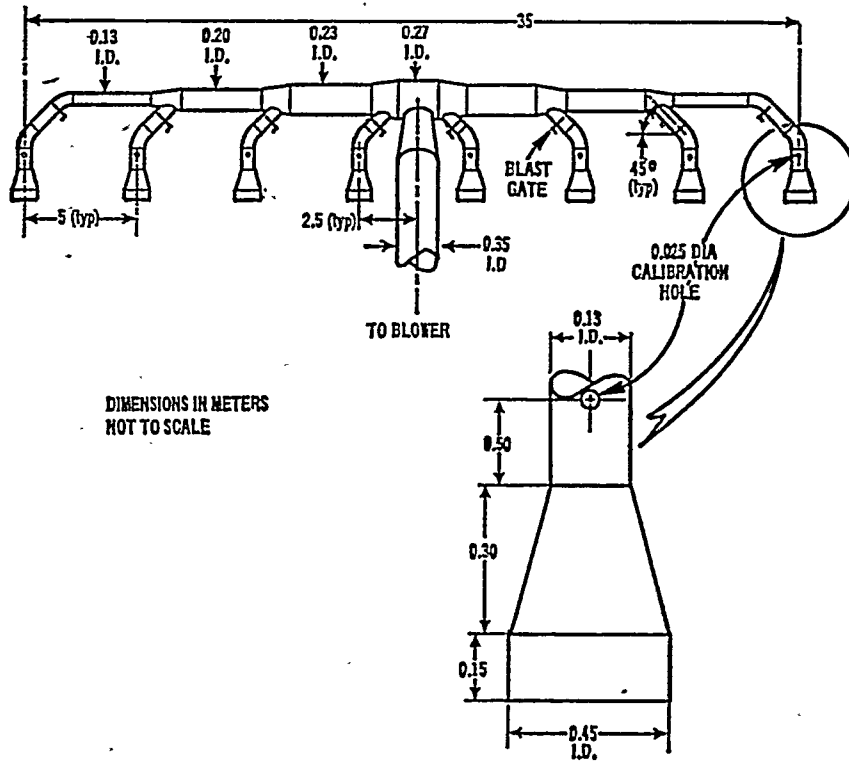


Figure 14-2. Sampling Manifold and Nozzles

B_w is the proportion by volume of water vapor in the gas stream, from Equation 13A-3, Method 13A—Determination of Total Fluoride Emissions From Stationary Sources.

[FR Doc.74-24361 Filed 10-22-74;8:45 am]