
Air



Primary Aluminum

Background Information: Proposed Amendments

Primary Aluminum Background Information: Proposed Amendments

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
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1. INTRODUCTION AND SUMMARY

This document supplements information contained in the preamble for the amended Standard of Performance for Primary Aluminum Plants (40 CFR Part 60, Subpart S). The amendments are being proposed in response to arguments raised by four aluminum companies who filed petitions for review of the standard of performance.

The principal amendments to Subpart S would be as follows:

1. Following the initial performance test, performance testing would be required at least once each month during the life of a new primary aluminum plant.

2. Performance test results above the level of the current potroom standard [0.95 kg/Mg (1.9 lb/ton) for prebake plants and 1.0 kg/Mg (2.0 lb/ton) for Soderberg plants] would be allowed if an owner or operator can establish that the emission control system was properly operated and maintained at the time the excursion above the current standard occurred. Emissions above 1.25 kg/Mg (2.5 lb/ton) would not be allowed under any condition.

3. The owner or operator of a new primary aluminum plant may apply to the Administrator for an exemption from the monthly testing requirement for primary and anode bake plant emissions.

Additional information, including the amendments to Reference Method 14 - Determination of Fluoride Emissions from Potroom Roof

Monitors of Primary Aluminum Plants, may be found in the preamble and regulation for the proposed amendments in the Federal Register.

2. BACKGROUND

A standard of performance for new primary aluminum plants was promulgated on January 26, 1976 (41 FR 3826),¹ and shortly thereafter petitions for review were filed by four U. S. aluminum companies. The principal argument raised by the petitioners was that the standard was too stringent and could not be consistently complied with by modern, well-controlled facilities. (Facilities which commenced construction prior to October 23, 1974, are not affected by the standard.) Following discussions with the petitioning aluminum companies, EPA conducted an emission test program at the Anaconda Aluminum Company plant in Sebree, Kentucky. The Sebree plant is the newest primary aluminum plant in the U. S., and its emission control system conforms with what EPA has defined as the best technological system of continuous emission reduction for new facilities. The purpose of the test program was to aid EPA in its reevaluation of the standard by expanding the emission data base. The test results were available in August of 1977 and indicated that there is some probability that the result of a performance test conducted at a modern, well-controlled plant would be above the existing standard. EPA has concluded that this justifies revising the standard.

During discussions and in correspondence with the petitioners, several issues were raised. These may be summarized as follows:

1. The level of the emission standard is too stringent and cannot be consistently achieved by modern, well-controlled plants.
2. Operating practices, in particular the bath ratio, can adversely affect fluoride emissions.
3. Anode bake plant control is not cost-effective.
4. EPA Method 13 consistently understates the measured level of fluoride emissions.
5. The EPA emission test program at the Sebree plant of the Anaconda Aluminum Company yielded questionable results.
6. Dry scrubbing causes increased secondary emission rates.

EPA has determined that only the first of these issues justifies amending the regulation. This issue is discussed in the preamble for the amended standard of performance, and supplemental information is contained in Chapter 3. The remaining issues are discussed in Chapter 4.

¹For more information see:

U. S. Environmental Protection Agency. Proposed Standards of Performance for New Stationary Sources (Primary Aluminum Industry). 40 CFR Part 60, Subpart S. Washington, D. C. Federal Register (39 FR 37730). October 23, 1974.

U. S. Environmental Protection Agency. Promulgated Standards of Performance for New Stationary Sources (Primary Aluminum Industry). 40 CFR Part 60, Subpart S. Washington, D. C. Federal Register (41 FR 3826). January 26, 1976.

Background Information for Standards of Performance: Primary Aluminum Industry (Volume 1: Proposed Standards; Volume 2: Test Data Summary; and Volume 3: Supplemental Information). Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency. Research Triangle Park, North Carolina. Report number EPA 450/2-74-020(a); (b); and (c). October 1974; October 1974; and January 1976. 122, 48, and 47 pages.

3. SUPPLEMENTAL INFORMATION

Sebree Test

The results of the Sebree test program are presented in Table 1.¹ EPA personnel observed potroom operations during the test program and afterwards concluded that although operations could have been improved, the variability of emissions was largely inherent in the production process and beyond the control of plant personnel. The emission data base EPA used to establish the original standard did not reflect this variability.

Analysis of Sebree Results

A performance test is defined in 40 CFR Part 60.8(f) as the arithmetic mean of three separate runs, except in situations where a run must be discounted or cancelled and the Administrator approves using the arithmetic mean of two runs. To determine the probability that a performance test would be above the level of the current standard, EPA calculated the arithmetic mean of all 504 possible combinations of three of the nine Sebree runs; 8.3 percent of the means are above the level of the current standard of 0.95 kg/Mg (1.9 lb/ton). Thus, EPA estimates that there is about an 8 percent chance that a performance test conducted at a well-controlled plant would be above the current standard. The petitioners, using different

¹ The Sebree test program is described in:

Air Pollution Emission Test: The Anaconda Company Sebree Reduction Plant, Henderson, Kentucky. Office of Air Quality Planning and Standards. U. S. Environmental Protection Agency. Research Triangle Park, North Carolina. Report number 77-ALR-6. October, 1977. 700 pages.

Table 1. EPA TEST RESULTS AT THE ANACONDA PRIMARY ALUMINUM PLANT IN SEBREE, KENTUCKY

FLUORIDE EMISSIONS							
Test Series	Run ⁽¹⁾	Date (1977)	Primary Emissions (lb/ton)	Roof Monitor Emissions (lb/ton)		Total Potroom Emissions ⁽²⁾	
						(lb/ton)	(kg/Mg)
1	1a b	3/29	0.055	1.39 1.47	avg=1.43	1.49	0.75
1	2a b	3/30	0.033	0.84 0.86	avg=0.85	0.88	0.44
1	3a b	3/31	0.021	1.68 1.78	avg=1.73	1.75	0.88
1	4a b	4/1	0.023	2.58 2.85	avg=2.72	2.74	1.37
2	1a b	6/6-7	0.033 ⁽³⁾	1.83 1.79	avg=1.81	1.84	0.92
2	2a b	6/7-8	"	0.83 0.80	avg=0.82	0.85	0.43
2	3a b	6/8-9	"	1.17 1.12	avg=1.15	1.18	0.59
3 ⁽⁴⁾	1	6/29-30	"	1.18		1.21	0.61
3	2	6/30-7/1	"	1.44		1.47	0.74

(1) During the EPA tests, two sampling trains were run simultaneously at the roof monitor sampling site. One served as a backup to the other, in case of malfunction.

(2) Total potroom emissions were calculated by adding the primary and roof monitor emissions.

(3) Primary emissions for test series 2 and 3 are estimates based on the average of the primary emissions from the first test series.

(4) Test series 3 was performed by Anaconda using EPA test methods.

analytical methods, have estimated chances of failure ranging from 2.5 to 10 percent. (For example, see page 24 of Appendix A.)

The relatively small number of runs performed at the Sebree plant introduces some uncertainty into the method used to calculate the probability that a performance test would be above the current standard. For example, if the highest of the nine Sebree runs, 1.37 kg/Mg (2.74 lb/ton), is increased just one percent, the probability of a performance test being above the standard increases to 10.7 percent. Similarly, if 1.37 kg/Mg is decreased by one percent, the probability decreases to 5.9 percent. Thus, it is difficult to determine exactly the probability of a performance test being above the standard.

The average of the three highest Sebree runs, 1.06 kg/Mg (2.11 lb/ton), is well below the proposed never-to-be-exceeded limit of 1.25 kg/Mg (2.5 lb/ton). EPA believes it is reasonable to expect emissions from a modern, well-controlled plant to be below 1.25 kg/Mg all of the time.

Costs

The major costs incurred by the amendments are associated with the periodic emission testing requirement. Testing of the primary control system, secondary emissions, and the anode bake plant (for prebake plants) would be required at least once each month during the life of the primary aluminum plant. However, once the emission characteristics of the primary or bake plant control systems are known, the owner or operator may apply to the Administrator for an exemption from the monthly testing requirement for primary and bake plant emissions. The estimated costs of performance tests conducted by local private contractors, by nonlocal private contractors, or by plant personnel are presented in Table 2. Due to the higher costs

associated with contractor tests, the owner or operator of a new plant would probably arrange to conduct testing with plant personnel if required to test as often as once each month. Thus, the estimated costs for testing conducted by plant personnel are more representative of what actual costs would probably be.

Table 2. ESTIMATED COSTS FOR PERFORMANCE TESTING
AT NEW PRIMARY ALUMINUM PLANTS

<u>Estimated costs per performance test</u>			
<u>Optional Tester</u>	<u>Secondary Emissions</u>	<u>Primary Control</u>	<u>Bake Plant Control</u>
Plant Personnel	\$ 4,800	\$ 4,000	\$ 4,000
Local Private Contractor	7,700	6,400	6,400
Nonlocal Private Contractor	13,200	11,400	11,400

These estimated costs assume that: (1) each monthly performance test would consist of the average of three 24-hour runs; (2) testing would be performed by two crews working 13-hour shifts; (3) primary control system sampling would be performed at a single point within the stack; and (4) Sebree inhouse testing costs would be representative of average costs for other new plants. Although these assumptions may not hold for all situations, EPA believes they provide a representative estimate of what testing costs would be for new plants.

There are also costs associated with recalibration of anemometers following performance tests, as required by the revisions made to Reference Method 14. These costs, however, would be minor.

Environmental Impact

One of the proposed amendments would allow emissions to be above the current limits, but not above a higher limit of 1.25 kg/Mg (2.5 lb/ton) if the owner or operator can establish that the control system was properly operated and maintained during the excursion above the current limits. This amendment is intended to account for the inherent variability of emissions from aluminum potrooms. Since the amendment would simply make the current regulation more realistic with regard to emission rates from what EPA considers the best system of continuous emission reduction, environmental quality would not suffer. There would be no other environmental impacts associated with this amendment.

Another of the proposed amendments would require performance testing at least once each month during the life of a plant. (Under the current regulation, a performance test is only required to be performed within 60 days after achieving the maximum production rate, but not later than 180 days after initial startup of a new plant.) EPA believes that this amendment would provide an incentive to properly operate and maintain control equipment throughout the life of a plant rather than just during the initial performance test. This, in turn, would result in improved air quality in the vicinity of an aluminum reduction plant. There would be no other environmental impacts associated with this amendment.

The other amendments are basically clarifying in nature and would have no impact on the environment. Thus, the proposed amendments would have an overall beneficial impact on environmental quality.

4. OTHER ISSUES

During negotiations with the litigants, several major issues were raised. EPA has evaluated these issues and has determined that only one - the contention that the standard is unachievable - requires amending Subpart S. These amendments are discussed in the preamble to the proposed amendments and in Chapter 3. The other major issues are summarized and responded to below.

Method 13

One litigant contended that EPA Method 13 consistently understates the measured level of fluoride emissions, and thus, the data base is suspect. An EPA study was used in support of this contention.

EPA carefully examined the original data base in light of the cited EPA study and found no basis for concluding that the data base is biased. Furthermore, the litigant was misinterpreting the study since it showed a large bias only when a Whatman paper filter supported by a glass frit was used at the front of the sampling train. EPA data were not gathered using this method; rather a glass fiber filter was used. There is no evidence of bias when using a glass fiber filter. In addition, the data collected at Sebree were obtained using a sampling train with the filter holder mounted between the third and fourth impingers, a position for which no bias has been observed.

Another study submitted to EPA raised questions about the efficiency of paper filters placed in front of the Method 13 impingers. Since a significant level of inefficiency is indicated, it is EPA's intention to revise the reference method, disallowing the use of the paper filter in the front of the impingers (an option which had been originally included in Method 13 in response to industry comments) and recommending use of a more efficient glass fiber or similar filter. This revision will be made at a later date.

Additional information may be found in Appendices A and B.

Bake Plant Control

One of the litigants argued that the anode bake plant emission limit is not cost-effective and should be revised from 0.05 to 0.25 kg/Mg (0.1 to 0.5 lb/ton) aluminum equivalent.

Standards of performance are based on the degree of emission reduction achievable through the application of the best system of continuous emission reduction which (taking into consideration the cost of achieving such emission reduction) has been adequately demonstrated. In considering cost, the Agency determines if the industry can procure the necessary equipment and personnel to meet the standard at a cost which will allow it to remain a viable competitive force. The cost consideration is thus one of affordability rather than cost effectiveness. EPA has determined that the bake plant standard is affordable and represents application of the best system of continuous emission reduction. This is borne out by the fact that the litigant recently started up a new bake plant in compliance with the standard.

Operating Practices

One litigant suggested that the aluminum industry standard could not be achieved without production losses when operating a plant in a low bath ratio (high current efficiency) mode.

The proposed amendments are based on EPA's experiences at the Sebree Reduction Plant of the Anaconda Aluminum Company. The Sebree plant is the newest primary aluminum plant in the U. S. and operates with a low bath ratio. Since the Sebree plant can comply with the proposed amended standard, EPA believes that other new plants will be able to comply with the standard without production losses.

Sebree Test

It is argued that deviations from EPA's prescribed test methods in the Sebree test program caused the fluoride emission measurements to understate the true level of fluoride emissions. One of the more significant departures from Method 14, it is claimed, involved the number of anemometers used and the location of the anemometers. EPA used three anemometers rather than two as called for under Method 14.

The use of three anemometers exceeds the requirement of Method 14 which specifies that only two are needed for a roof vent of this size. (This type of variation from the reference test method is allowed under the provisions of section 60.8 of 40 CFR Part 60.) Therefore, the accuracy of the reported flow rates should be equal to or greater than the accuracy that would have been obtained by following the Method 14 requirement exactly. The contention that significantly higher emission rates would have resulted if two anemometers had been used is purely speculative, since no comparisons were made between the use of two and three anemometers. The Sebree data

show that a substantial velocity gradient existed in the roof monitor; because of this (and in the absence of data to indicate otherwise), the use of three anemometers instead of two must be considered more representative of the actual conditions in the monitor.

It is also contended that the velocity and fluoride concentration in each eight-hour test were measured for different lengths of time, and this had the effect of understating secondary emissions.

During the Sebree tests, velocity was monitored for the entire 480 minutes of each 8-hour test period. Therefore, the calculated volumetric flow rates are considered to be representative. Fluoride concentration, on the other hand, was measured only for the first 400 minutes of each 8-hour period. Since the majority of the activity in the potrooms occurs in the first half of each shift, fluoride emissions tend to be higher during this period. Consequently, measuring the fluoride concentration for only 400 of the 480 minutes would tend to bias the results toward the high side. Therefore, an emission rate calculated from the product of an average fluoride concentration measured over the first 400 minutes times an average volumetric flow rate measured over the entire 480 minutes would tend to be higher than the true rate, rather than "understating the secondary fluoride emission values," as contended.

Another argument was that EPA did not calibrate the anemometers properly, and that the back-calculating EPA did in an attempt to rectify the erroneous anemometer readings made the results highly suspect.

It is true that the velocity data from the Sebree tests were adjusted after-the-fact based upon information obtained from the anemometer manufacturer and from a series of post-test anemometer calibrations. However, these adjustments were made in order to increase the accuracy of the

reported emission rates. (It should be noted that, in general, the adjustments made in the Sebree data tended to increase the total flow and emission rates, and thus, were in the industry's favor.) The contention that industry would have no right to make similar adjustments in NSPS performance test data is unfounded. Section 60.8 provides authority for the Administrator to approve minor deviations from the reference methods if it can be shown that equivalent or or more representative data will result. Note that as a result of EPA's experience with the anemometers, EPA has proposed revising Method 14 to include the proper calibration procedure for anemometers.

EPA's use of monthly averages for determining the rate of aluminum production was questioned since Subpart S expressly provides that the actual rate of aluminum production is to be determined for the test run.

EPA considered using actual metal tapped in the calculations but decided against this in favor of using the monthly average per pot production rate, since the amount of metal tapped on any given day is not necessarily the amount of metal produced on that day. For example, it would be possible to not tap any pots on a given day in which case metal tapped would be zero, but the pots would still be producing aluminum and evolving fluorides. Alternatively, it would be to the advantage of the source to tap a larger amount of metal than the amount actually produced on the day of a compliance test, thereby reducing the calculated emission rate. Thus, EPA believes that the monthly average gives a better indication of actual metal production than amount tapped during the test. The proposed amendments would make this an explicit provision.

More information on the Sebree test issues appears Appendices A and B.

Dry Scrubber Emissions

One litigant has experienced secondary emission increases following the installation of dry scrubbers at several of its facilities and worries that emissions from new plants equipped with the scrubbers could be in violation with the standards. It is theorized that the problem of increased secondary emissions is related to the increased fines content and increased fluoride content of the recycled alumina.

The proposed amendments are based on EPA's experiences at the Sebree plant. Since the Sebree plant successfully utilizes dry scrubbers, EPA believes this is evidence that new plants which are subject to Subpart S would be able to comply with the amended standard.

APPENDIX A

12-115
12/20/77

ALUMINUM COMPANY OF AMERICA

ALCOA BUILDING • PITTSBURGH, PENNSYLVANIA 15219



1977 December 14

Mr. Don R. Goodwin
Environmental Protection Agency
Emission Standards and Engineering Division
Research Triangle Park, N. C. 27711

Dear Mr. Goodwin:

Aluminum Company of America ("Alcoa") does not agree with EPA's conclusion that the results of the fluoride emission tests conducted at The Anaconda Company's Sebree Reduction Plant demonstrate that a new aluminum prebake reduction plant " . . . which incorporates the best system of emission reduction, considering cost, and which is properly operated and maintained . . ." can achieve compliance with the New Source Performance Standards for the Primary Aluminum Industry, promulgated on January 26, 1976, 41 Fed. Reg. 3826 et seq. (See Letter dated September 2, 1977, from Don R. Goodwin (EPA) to Dr. Patrick R. Atkins (Alcoa), hereinafter referred to as the "Goodwin Letter"). To the contrary, if the Sebree Emission Test results demonstrate anything, they support Alcoa's contention that the fluoride emission limitation set forth in the New Source Performance Standards cannot be achieved on a never-to-be-exceeded basis. The following are Alcoa's comments with respect to the report published by EPA in connection with the Sebree Emission Test (EPA Emission Test Report No. 77-ALR-6).

The Sebree Emission Test Data
Clearly Show that a "New" Pre-
bake Aluminum Plant Would Exceed
the Fluoride Emission Limitation
in the New Source Performance
Standards a Significant Percent-
age of the Time

One of the most striking aspects of the Sebree Emission Test data is the variability in the secondary fluoride emissions. The 24-hour secondary fluoride emission values calculated by EPA from

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sets of three consecutive 8-hour measurements range from a low of .80 pounds of fluoride per ton of aluminum produced ("lbs. F/TAP") to a high of 2.85 lbs. F/TAP. The spread in the individual 8-hour secondary fluoride emission measurements is even more pronounced, ranging from .29 lbs. F/TAP to 3.75 lbs. F/TAP (Sebree Emission Test Report, p. 5).

The Goodwin Letter of September 2, 1977, implies that the variability of secondary emissions is a function of operation and maintenance practices in the potroom. It suggests that the higher emission values found during Phase I of the Sebree Emission Test are attributable to alleged poor operating and maintenance procedures "not conducive to low emissions;" the implication being that the emission values found during Phases II and III of the Sebree Emission Test are attributable to improvements made by Anaconda in operating and maintenance conditions. However, it must be pointed out that test runs 2a and 2b in Phase I of the Sebree Emission Test produced secondary fluoride emission values of .84 lbs. F/TAP and .86 lbs. F/TAP, while six of the eight test runs in Phases II and III, which were supposedly performed under conditions conducive to low fluoride emissions, yielded secondary fluoride emission values far in excess of .86 lbs. F/TAP. The point is that the level of secondary emissions is not a function of operation and maintenance conditions alone; rather, it is the function of a complex interaction of numerous factors which, in addition to operation and maintenance conditions, include pot evolution, meteorological conditions, wind direction and velocity, raw material quality fluctuations, etc. Consequently, the level of secondary fluoride emissions is highly variable. Furthermore, the Sebree Emission Test data clearly indicate that there are measurable sources of variation intrinsic to the fluoride sampling methods themselves.

Because of the variability of secondary fluoride emission test results, the Sebree Emission Test data must be analyzed through the application of standard statistical methods to determine whether or not it supports the never-to-be-exceeded limitation of 1.9 lbs. F/TAP in the New Source Performance Standards. Alcoa submitted the Sebree Emission Test data, along with the emission test data for Plants "B," "C," and "D" in the Background Documents published by EPA in connection with the initial promulgation of the New Source Performance Standards for the Primary Aluminum Industry (EPA 450/2-74-020a & b), to Dr. Morris DeGroot, Ph.D, Professor of Statistics and Industrial Administration at Carnegie-Mellon University in Pittsburgh, Pennsylvania, for the purpose

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of obtaining an independent statistical evaluation of the data. Dr. DeGroot's report, which is attached to these Comments as Appendix A, conclusively establishes that, based upon the emission test data cited by EPA to support the 1.9 lbs. F/TAP emission limitation in the New Source Performance Standards, a modern prebake aluminum reduction facility will exceed the emission limitation up to 10 percent of the time.

In interpreting Dr. DeGroot's Report, it should be observed that Methods I, II and V used by him to analyze Sebree Emission Test data are based on the assumption that the 8-hour test segments are independent of each other and can be mixed taking a 0:00 to 8:00 test run from one day, a 8:00 to 16:00 test run from another day and a 16:00 to 24:00 test run from a third day. In fact, that assumption is false since meteorologic, raw material quality and operating condition impacts, as well as many other factors will frequently have an effect on fluoride emissions which extend beyond an 8-hour period. The consequence is that the estimates obtained by Methods I, II and V are lower than those obtained by the other methods employed by Dr. DeGroot, which were based on 24-hour test runs.

Based upon Dr. DeGroot's analysis, Alcoa reiterates that if the emission limitation in the New Source Performance Standards is to be a never-to-be-exceeded limit, it must be increased significantly to allow for the highly variable nature of secondary fluoride emissions which occur even in the best controlled facilities. The EPA recently recognized the need for relief from a never-to-be-exceeded emission limitation in the case of highly variable emissions when it amended the New Source Performance Standards for the copper smelter industry published on November 1, 1977, in the Federal Register (42 Fed. Reg. p. 57125). In the preamble to that amendment, EPA noted that analysis showed that affected facilities under the New Source Performance Standards for the copper industry could be expected to exceed the emission limitation set forth in the Standards a certain percentage of the time. To reconcile this probability of excursions with the emission limitation, EPA amended the Standards to allow these predicted excursions.

Deviations From EPA's Prescribed Test
Methods in the Sebree Emission Test
Caused the Fluoride Emission Measure-
ments Calculated by EPA to Understate the
Level of Fluoride Emissions

Following the promulgation of the New Source Performance Standards, both Alcoa and Anaconda submitted to EPA test data which support the conclusion that the 1.9 lbs. F/TAP emission limitation set

forth in the Standards cannot be achieved on a never-to-be-exceeded basis by "affected facilities" in the primary aluminum industry. EPA refused to consider any of this data because the emission tests performed by Alcoa and Anaconda were not in strict compliance with EPA testing procedures, e.g., Method 13 and Method 14 (Goodwin Letter, pp. 1-2). The express purpose of the Sebree Emission Test was to measure emissions from a modern prebake aluminum reduction facility, utilizing EPA test methods, for the purpose of re-evaluating the achievability of the fluoride emission limitation in the New Source Performance Standards. However, in conducting the Sebree Emission Test, EPA chose not to adhere to the specifications of the prescribed test methods.

One of the more significant departures from EPA Method 14 involved the number of anemometers used and the location of the anemometers. For purposes of its test program, EPA utilized three anemometers in the area of the Sebree potroom being tested. As EPA acknowledges in the Sebree Emission Test Report (p. 27), this is one more anemometer in that area than called for under Method 14.

The data show, and EPA acknowledges in a "Trip Report" dated June 29, 1977 (Sebree Emission Test Report, Appendix 16) that the center anemometer consistently recorded higher exit velocities than the two end anemometers. In the "Trip Report", EPA concluded that the difference was not the result of the calibration error found. Furthermore, a subsequent "Trip Report" included in the Sebree Emission Test Report as Appendix 17 concludes that magnetic fields in the potroom had little or no effect on the signal characteristics of the anemometers. Therefore, it appears clear that the difference in anemometer measurements can be attributable to an actual velocity gradient in the roof monitor.

If the Sebree Emission Tests were conducted using only two anemometers located in compliance with EPA Method 14, the air volume calculation would have been significantly higher than the air volume reported in the Sebree Emission Test Report. This higher air volume determination would have resulted in a higher secondary emission level value since fluoride emissions are calculated by the direct multiplication of fluoride concentration times velocity times monitor area.

In addition to the mislocation of the anemometers, the sampling procedure employed in the Sebree Emission Test also had the effect of understating the secondary fluoride emission values measured by EPA. As explained in the Sebree Emission Test Report, a separate sampling run was conducted for each 8-hour shift at the Sebree Plant. However, in the case of the secondary emission samples, the actual sampling time for each shift was only 400 minutes out of a possible 480 minutes (Sebree Emission Test Report, p. 4). In every instance, the sampling run was

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started at the beginning of the shift and terminated approximately 80 minutes prior to the end of each shift. EPA reasoned that since the majority of the activity in the potrooms occur in the first half of each shift, fluoride emissions are potentially greater during that time (Sebree Emission Test Report, p. 4).

On the other hand, anemometer measurements of air volume were taken continuously and, therefore, covered all 480 minutes in the 8-hour shift. For purposes of calculating the fluoride emission levels, EPA determined a 24-hour average roof monitor flow rate.

The effect of this discrepancy in sampling time is to understate the level of fluoride emissions measured. This conclusion is required by the following reasoning: As EPA assumes, the majority of activity in the potrooms occurs in the first half of each shift. By the same token, higher air volume values are obtained when the pots are being worked during the first half of the shift. The average air volume per minute over the entire 480 minutes is substantially less than the average air volume per minute over the 400 minutes when fluoride samples were being collected. By including the air volume measurements taken during the last 80 minutes of the shift when virtually no work is being done, EPA has effectively reduced the air volume factor to be used in computing emission levels. Since the fluoride emission level is calculated from the direct multiplication of concentration times velocity times monitor area, the effect of lowering the velocity factor is to lower the fluoride emission level measured.

The Validity of the Sebree Emission Test is Highly Questionable

In reporting the results of his statistical analysis of EPA's emission test data, Dr. DeGroot felt constrained to conclude that there were too few data points available to enable one confidently to assess the fluoride emission behavior of modern aluminum reduction facilities (DeGroot Report, p. 2). Alcoa concurs in this conclusion. It is equally important to note that the limited data collected by EPA from the Sebree Test is so affected by deficiencies in the apparatus and test procedures employed in the emission testing that its validity must be seriously questioned.

For example, in the Sebree Emission Test Report (p. 28 and Appendices 2 and 3) EPA concedes that the anemometers used

for the testing were not calibrated properly. Anemometer values have direct impact upon the determination of the fluoride emission value; therefore, accurate calibration of the anemometers is of critical importance to the accuracy of the emission test results. It is obvious that EPA did a great deal of back-calculating in an attempt to rectify the clearly erroneous anemometer readings. Such manipulations necessarily make the results of the Sebree Emission Test highly suspect.

A second source of inaccuracy in the Sebree Emission Test is the method by which EPA determined the level of production at the Sebree Plant. Section 60.194(d) of EPA's New Source Performance Standards Regulations expressly provides that the actual rate of aluminum production is to be determined for the test run period. For purposes of the Sebree Emission Test, EPA merely used a monthly average production figure (Sebree Emission Test Report, p. 33). Obviously, since the emission limitation set forth in the New Source Performance Standards is stated in pounds of fluoride per ton of aluminum produced, an accurate determination of actual tonnage is essential. EPA's failure to adhere to its own regulations in this regard brings the accuracy of the Sebree Emission Test results into question.

The foregoing are merely two examples of instances where EPA has failed to adhere to its own methodology for determining fluoride emissions from an aluminum reduction facility. These deviations from EPA methodology have a substantial impact upon the results of the emission test. Furthermore, it is clear that industry would have no right to employ such deviations in performance tests conducted under the New Source Performance Standards.

Another way in which the conduct of these tests differed from what the owner of a source would be permitted in a performance test under the New Source Performance Standards is the alleged correction of a number of practices and conditions which were not "conducive to low emissions" (Sebree Emission Test Report, p. 7). Replacement and repair of hoods, cleaning raw materials from pot decks and special hood cover placement were performed specifically for Phases II and III of the Sebree Emission Test program; all quite beyond the possibility of any normal long-term practice in an aluminum smelter. In addition, mechanical floor sweeping was suspended and the floors were swept by hand brooms, specifically to reduce fluoride collection during the tests.

In essence, EPA required the Sebree Plant to make special changes in equipment and operating procedures prior to Phase II in order

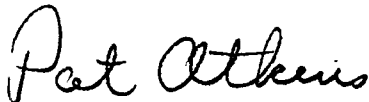
Mr. Don R. Goodwin
1977-12-14
Page Seven

to obtain lower fluoride emission measurements than would have been obtained under normal conditions.

Finally, although this comment does not pertain solely to the Sebree Emission Test, Alcoa wishes to reiterate its contention that EPA Method 13 consistently understates the measured level of fluoride emissions. Attached to these Comments as Appendix B are (1) an article entitled "Retention of Fluoride by Sintered-Glass Filter Supports" dated May, 1977 by Mitchell and Midgett and (2) a report entitled "Investigation of EPA Method 13 for Total Fluoride Determination," dated September 29, 1977, by Jerry W. Jones of Revere Copper and Brass, Inc. Both of these reports support Alcoa's position in this regard.

After you have reviewed these Comments, if you have any questions please contact me.

Sincerely,



Patrick R. Atkins, Manager
Environmental Control

PRA:smk

cc: Ronald Hausmann, Esq. - EPA

STATISTICAL ANALYSIS OF
EPA EMISSION TEST DATA

Morris H. DeGroot, Ph.D.
December 12, 1977

1. Introduction

The purpose of this report is to describe our analysis of the emission test data presented in Tables I, II, III, and IV attached to this report. Each of the four tables contains data pertaining to emissions of gaseous and particulate fluorides from different aluminum reduction plants. For each plant the analysis was carried out in order to estimate the proportion of measurements that would exceed the New Source Performance Standards for the Primary Aluminum Industry. We estimated this proportion for each plant by the probability that the arithmetic mean of three separate 24-hour emission measurements exceeded the applicable EPA standard of 1.9 lbs/ton for prebake reduction plants and 2 lbs/ton for horizontal stud Soderberg reduction plants. Several methods were used to analyze each set of data.

2. General Considerations

Before we proceed to our specific problem, we believe it is important to note that the specification of emission limitations on a "never-to-be-exceeded" basis necessarily contradicts the inherent random nature of emission measurements. The stochastic nature of these measurements implies that some proportion of measurements will exceed any given value. In particular, the lognormal distribution, which has often been used to model the random behavior of emission measurements, allows arbitrarily large observations.

Furthermore, the imposition of a penalty when the standard is exceeded, no matter how small the excess, seems inappropriate when the emissions measurements follow a continuous distribution. A penalty which is a continuous increasing function of the excess over the standard seems more appropriate.

A major obstacle to our analysis of the data in Tables I-IV was the limited number of observations. It is difficult to estimate the behavior of the average of three 24-hour measurements, as required by the EPA standard, when only a few measurements of short duration are available. In fact, for plant C there are only two observations on the primary emissions, each of duration less than 7 hours. Thus, it must be kept in mind that all the estimates derived from these data could change drastically if more measurements were available.

Our analysis takes into account the fact that there is a 24-hour production cycle in these plants. Virtually all of the measurements for plants B, C, and D were for durations of less than 24 hours. We do not know from which part of the production cycle each of these measurements was taken, and each measurement is itself a time average. Therefore, in some of our methods of analysis we have assumed that the variance of a measurement is proportional to the reciprocal of its time duration. For the Sebree plant, we utilized measurements from each of the three 8-hour shifts, thus covering the entire production cycle.

It seems to us that the EPA standard should specifically require that each test run be for the duration of the production cycle. The standard as presently written of at least 8 hours for primary control system emissions and at least 8 hours but up to 24 hours for secondary emissions is unsatisfactory because it could potentially lead to different results for different durations.

We did not seriously consider the possibility that some observations were aberrant and should be excluded from the analysis. With so few observations to begin with, we felt that we could not afford to exclude any.

3. Plant B

Plant B is a horizontal stud Soderberg-type plant for which the data can be summarized as follows:

<u>Test Time Duration</u>	<u>Total F lbs/T</u>	
	<u>Primary</u>	<u>Secondary</u>
18:25		1.10
12:15		2.01
4:05	0.410	
4:10	0.382	
10:55		2.28
3:27	0.422	
7:35		2.85

These data were analyzed by four different methods.

Method I: Our first method of analysis is to assume that the three primary measurements form a random sample from a lognormal distribution, and that the four secondary measurements form an independent random sample from some other lognormal distribution. The lognormal distribution is commonly accepted in pollution data analysis.

For any group of numbers X_1, \dots, X_n , we shall let \bar{X} and s^2 denote the sample mean and sample variance, defined as follows:

$$\bar{X} = \frac{1}{n} \sum_{i=1}^n X_i \quad \text{and} \quad s^2 = \frac{1}{n} \sum_{i=1}^n (X_i - \bar{X})^2$$

Some statisticians might use the divisor $n-1$ rather than n in the definition of s^2 in order to obtain an unbiased estimator of the variance σ^2 when the observations are normally distributed. Since this property is not directly relevant to our analysis, we have chosen to use n in our definition of s^2 which will yield maximum likelihood estimates for both normal and lognormal distributions.

We took the logarithms of the measurements in the table in order to obtain normally distributed values. For these logarithms, we computed the following values of \bar{X} and s^2 :

	\bar{X}	s^2
Primary	-.9056	.00175
Secondary	.6662	.12429

For any given values of \bar{X} and s^2 , the estimates m and v of the mean and variance of the corresponding lognormal distribution are

$$m = \exp \left(\bar{X} + \frac{1}{2} s^2 \right)$$

$$v = m^2 [\exp(s^2) - 1] .$$

The appropriate values are

	m	v
Primary	.4047	.000286
Secondary	2.0717	.5680

The total emission for a single test run will be the sum of an observation P from the primary source and an observation S from the secondary source. The EPA standard specifies that the average of three test runs shall not exceed 2 lbs/ton. This average A can be represented as

$$A = \frac{1}{3} (P_1 + S_1 + P_2 + S_2 + P_3 + S_3) .$$

The distribution of the sum of these six independent lognormal variables is not known exactly, and so we use the Central Limit Theorem to approximate this distribution. The distribution of A is approximately normal with mean 2.4764 and variance .1894.

The probability that the average of three test runs will exceed the EPA standard is $\Pr(A > 2)$. Using our approximation, we find that this is equal to the probability that a standard normal variable exceeds -1.095. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .863.

Method II: In the application of our second method, we noted that the average duration of the three primary measurements is 3 hours and 54 minutes. As discussed in Section 2, the variance of an observation will be approximately proportional to the reciprocal of the test time duration. Hence, the variance of a 24-hour primary measurement will be approximately .0000466. Similarly, the average duration of the four secondary measurements is 12 hours and 17 minutes. Hence, the variance of a 24-hour secondary measurement will be approximately .2909. From these values, we find that the distribution of A will be approximately normal with mean 2.4764 and variance .0970. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .937.

Method III: Our third method is to assume that the three primary measurements form a random sample from a normal distribution, rather than a lognormal distribution, and similarly that the secondary measurements form an independent random sample from some other normal distribution.

For these measurements, we find the following values of \bar{X} and s^2 :

	\bar{X}	s^2
Primary	.4047	.000281
Secondary	2.060	.3992

It now follows that the distribution of A is normal with mean 2.465 and variance .1331. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .899.

Method IV: Our fourth method is to assume again the primary and secondary measurements have normal distributions, and to adjust the variances as in Method II. In this way, we find that the distribution of A is normal with mean 2.465 and variance .0683. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .962.

4. Plant C

Plant C is a prebake plant for which the data can be summarized as follows:

<u>Test Time Duration</u>	<u>Total F lbs/T Al</u>	
	<u>Primary</u>	<u>Secondary</u>
9:25		1.12
6:35	0.267	
20:40		1.37
6:52	0.168	
23:03		1.23
22:54		1.10

We applied the same four methods to these data as were used for plant B.

Method I: After taking logarithms, we compute the following values of \bar{X} and s^2 :

	\bar{X}	s^2
Primary	-1.552	.05366
Secondary	.1826	.00762

The corresponding values of m and v are:

	m	v
Primary	.2176	.00261
Secondary	1.2049	.01111

The distribution of A is approximately normal with mean 1.4225 and variance .00457. For a prebake plant, the EPA standard is 1.9 lbs/ton. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be the probability that a standard normal variable exceeds 7.06. This probability is essentially zero.

Methods II, III, and IV yield the same result.

5. Plant D

Plant D is a prebake plant for which the data are as follows:

<u>Test Time Duration</u>	<u>Total F lbs/T AL</u>	
	<u>Primary</u>	<u>Secondary</u>
4:15	0.612	
24:00		0.8615
3:45	0.519	
3:40	0.504	
20:00		1.475
3:50	0.321	
3:30	0.495	
3:30	0.381	
3:30	0.438	

We applied the same four methods to these data as were used for plant B

Method I: After taking logarithms, we compute the following values of \bar{X} and s^2 :

	\bar{X}	s^2
Primary	-.7803	.03958
Secondary	.1198	.07229

The corresponding values of m and v are:

	m	v
Primary	.4674	.00882
Secondary	1.1688	.10241

The distribution of A is approximately normal with mean 1.6362 and variance .03708. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard of 1.9 lbs/ton to be .085.

Method II: The average duration of the seven primary measurements is 3 hours and 43 minutes. Hence, the variance of a 24-hour primary measurement will be approximately .00137. Similarly, the average duration of the two secondary measurements is 22 hours. Hence, the variance of a 24-hour secondary measurement will be approximately .09388. From these values, we find that the distribution of A will be approximately normal with mean 1.6362 and variance .03175. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .069.

Method III: We find the following values of \bar{X} and s^2 directly from the observations:

	\bar{X}	s^2
Primary	.4671	.00792
Secondary	1.1682	.09410

It now follows that the distribution of A is normal with mean 1.6353 and variance .03401. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .076.

Method IV: By adjusting the variances as in Method II, we find that the distribution of A is normal with mean 1.6353 and variance .02916. Hence, we estimate the probability that the average of three test runs will exceed the EPA standard to be .060.

6. The Sebree Reduction Plant

We note that the measurements of the primary emissions for both 8-hour and 24-hour periods have very small variation relative to the variation of the secondary emissions. For these reasons, we assumed throughout our analysis that the primary emissions had a constant value of .033 lbs/ton, which is the average of the twelve 8-hour measurements and also is the average of the four 24-hour measurements.

Some of the measurements of secondary emissions were made on two test trains a and b . We noted that the measurements on the two trains were not independent and that the variability between the trains was small relative to the variability within the trains. Furthermore, there were two days for which measurements were reported on only one train. For these reasons we have chosen to use the average of the measurements for the two test trains in our analysis whenever both trains are presented. It should be remarked that when measurements are made according to the performance standard only a single value will be available for each time period. The average of two measurements necessarily has a smaller variance than a single measurement of the same quantity. For this reason our estimates, based on the average of

the measurements for the two test trains, will be slightly smaller than estimates based on single measurements.

By averaging the measurements made on the a and b test trains, we obtain the following table of secondary measurements:

Total F lbs/T Al for Sebree Plant

<u>0:00-8:00</u>	<u>8:00-16:00</u>	<u>16:00-24:00</u>	<u>24-hr.</u>
.795	.770	2.980	1.430
.720	.640	1.190	.850
1.050	1.660	2.645	1.730
2.065	2.285	3.655	2.715
.970	1.525	3.555	1.810
.595	.290	1.585	.815
1.385	.915	1.180	1.145
1.000	.840	1.670	1.180
.700	1.080	2.380	1.440

These data were analyzed by six different methods. In each of the methods of analysis we have assumed that measurements made during different time periods were independent of each other. We are aware that this assumption is violated somewhat by meteorologic and other conditions that may persist for prolonged periods. Any positive dependencies between these measurements would increase their variance. For this reason our estimates, which ignore such dependencies, will be no larger than estimates which account for positive dependence of the measurements.

Method I: Our first method of analysis is to assume that the nine 8-hour measurements for the time period 0:00-8:00 form a random sample from a lognormal distribution, that the nine 8-hour measurements for the period 8:00-16:00 form an independent random sample from some other lognormal distribution, and that the nine measurements for the period 16:00-24:00 form a third independent random sample from a third lognormal distribution. After taking the logarithms of the measurements in the table, we computed the following values of \bar{X} and s^2 :

	\bar{X}	s^2
0:00- 8:00	-.04051	.13086
8:00-16:00	-.04184	.32734
16:00-24:00	.75656	.17336

The estimates m and v for the lognormal distribution corresponding to each time period are:

	m	v
0:00- 8:00	1.0252	.14695
8:00-16:00	1.1296	.49414
16:00-24:00	2.3239	1.02225

The secondary emission for a single 24-hour test run will be approximately the average of the secondary emissions from each of the three 8-hour shifts. We are aware that the actual 24-hour measurements reported in the table are not merely the averages of three successive 8-hour measurements but are based on the formula given in Table 1-1 of Appendix 1 of EPA Report No. 77-ALR-6. However, because of the cyclical nature of the production process, we believe that the average of the 8-hour measurements from the three different shifts will provide a less variable estimate of a 24-hour emission than will a single 24-hour measurement.

Therefore, the arithmetic mean B of three 24-hour test runs for the secondary emissions can be represented as the average of nine independent measurements, three from each of the three shifts. Thus,

$$B = \frac{1}{9} (J_1 + K_1 + L_1 + J_2 + K_2 + L_2 + J_3 + K_3 + L_3)$$

where J_1, J_2, J_3 are independent measurements from the lognormal distribution for the 0:00-8:00 period; K_1, K_2, K_3 are independent measurements from the lognormal distribution for the 8:00-16:00 period; and L_1, L_2, L_3 are independent measurements from the lognormal distribution for the 16:00-24:00 period. The distribution of the sum of nine independent lognormal variables is not known exactly, so we use the Central Limit Theorem to approximate this distribution. Thus, the distribution of B is approximately normal with mean 1.4929 and variance .06161.

The total of the primary and secondary emissions will be $B + .033$. Therefore, the probability that the average of three 24-hour test runs will exceed the EPA standard is $\Pr(B + .033 > 1.9)$. We estimate that this probability is .066.

Method II: Our second method is to assume that each of the 8-hour secondary measurements has a normal distribution, rather than a lognormal distribution. We compute the following values of \bar{X} and s^2 :

	\bar{X}	s^2
0:00- 8:00	1.0311	.18351
8:00-16:00	1.1117	.33067
16:00-24:00	2.3156	.82126

With this assumption, the distribution of B is normal with mean 1.4861 and variance .04946. Thus, we estimate the probability that the average of three 24-hour test runs will exceed the EPA standard to be $\Pr(B + .033 > 1.9) = .043$.

Method III: In this method, we use only the nine 24-hour secondary measurements. We assume that these measurements form a random sample from a lognormal distribution. After taking the logarithms of these measurements, we computed the values $\bar{X} = .3107$ and $s^2 = .12845$. Therefore, for the lognormal distribution, we obtain $m = 1.4549$ and $v = .29014$.

The arithmetic mean B of three 24-hour test runs for the secondary emissions can now be represented as the average of three independent measurements from the lognormal distribution. By the Central Limit Theorem, this distribution of B will be approximately normal with mean 1.4549 and variance .09671. Thus, we estimate the probability that the average of three 24-hour test runs will exceed the EPA standard to be $\Pr(B + .033 > 1.9) = .093$.

Method IV: Our fourth method is to assume that each of the 24-hour secondary measurements has a normal distribution, rather than a lognormal distribution. We compute the values $\bar{X} = 1.459$ and $s^2 = .3045$.

The distribution of the arithmetic mean B of three 24-hour secondary emission measurements can now be represented as a normal distribution with mean 1.459 and variance .1015. Thus, we estimate the probability that the average of three 24-hour test runs will exceed the EPA standard to be $\Pr(B + .033 > 1.9) = .100$.

Method V: The method is different from all the previous methods described in this report in the sense that no specific distribution, such as lognormal or normal, is assumed for the observations. It is a distribution-free procedure. As in Method I we assume that the arithmetic mean \bar{B} of three 24-hour test runs for the secondary emissions can be represented as the average of nine independent measurements, three from each of the three 8-hour shifts.

From the nine values for each of the three shifts given in the first table of this section, we computed all 592,704 possible arithmetic means that could be formed by choosing three values from each of the shifts. To each of these means, we then added .033 to represent the primary emissions. With this method, we estimate the probability that the mean of three 24-hour tests will exceed the standard to be the proportion of these values greater than 1.9. This proportion is found to be .025. Thus, we estimate the probability that the average of three 24-hour test runs will exceed the EPA standard of 1.9 lbs/ton to be .025.

Method VI: This method is a distribution-free method similar to Method V based only on the nine 24-hour secondary emission measurements. As in Method III, the arithmetic mean \bar{B} of three 24-hour test runs can be represented as the average of three of these nine measurements. We computed all 84 possible means that could be formed in this way, added .033 representing the primary emissions to each of these means, and determined the proportion of values greater than 1.9. This proportion is found to be .095. Thus, we estimate the probability that the average of three 24-hour test runs will exceed the EPA standard of 1.9 lbs/ton to be .095.

7. Summary

For each of the four plants that we considered, we obtained several different estimates of the probability that the EPA standard will be exceeded. These estimates are summarized in the following table:

Plant	Method			
	I	II	III	IV
B	.863	.937	.899	.962
C	0	0	0	0
D	.085	.069	.076	.060

Sebree	Method					
	I	II	III	IV	V	VI
	.066	.043	.093	.100	.025	.095

We note that for each of the plants B, C and D the estimates obtained from Methods I - IV are all more-or-less of the same general magnitude. For the Sebree plant, the estimates obtained from Methods I, II and V are of the same general magnitude and smaller than the estimates obtained from Methods III, IV, and VI. The first set, Methods I, II, and V, are based on the 27 eight-hour measurements; and the second set, Methods III, IV, and VI, are based on the 9 twenty-four hour measurements. Since the estimates in the first set are based on the averaging of a larger number of eight hour measurements (assumed to be independent) than the estimates in the second set, the estimated variances for the distribution in the first set are smaller. Therefore, it is natural that the probability estimates in the first set will also be smaller. We have not attempted to choose among these estimates or to combine them in any way.

Finally, as previously mentioned, these estimates are based on very few observations and could change drastically in the light of future data.

TABLE I
ANACONDA, SEBREE PLANT EMISSION TEST
(Rept. No. 77-ALR-6)

Test Date (1977)	Test Train	Test Time (Duration)	Total F lbs/T Al					
			Primary		Secondary		Totals	
			8 hr	24 hr	8 hr	24 hr	8 hr	24 hr
3/29	a	0:00 - 8:00 (8:00)	.11		.76		.87	
		8:00 - 16:00 (8:00)	.02	.055	.77	1.39	.79	1.45
		16:00 - 24:00 (8:00)	.04		2.87		2.91	
3/29	b	0:00 - 8:00 (8:00)			.83		.94	
		8:00 - 16:00 (8:00)			.77	1.47	.79	1.53
		16:00 - 24:00 (8:00)			3.09		3.13	
3/30	a	0:00 - 8:00 (8:00)	.04		.73		.77	
		8:00 - 16:00 (8:00)	.04	.033	.63	.84	.67	.87
		16:00 - 24:00 (8:00)	.02		1.15		1.17	
3/30	b	0:00 - 8:00 (8:00)			.71		.75	
		8:00 - 16:00 (8:00)			.65	.86	.69	.89
		16:00 - 24:00 (8:00)			1.23		1.25	
3/31	a	0:00 - 8:00 (8:00)	.02		1.00		1.02	
		8:00 - 16:00 (8:00)	.02	.021	1.62	1.68	1.64	1.70
		16:00 - 24:00 (8:00)	.02		2.59		2.61	
3/31	b	0:00 - 8:00 (8:00)			1.10		1.12	
		8:00 - 16:00 (8:00)			1.70	1.78	1.72	1.80
		16:00 - 24:00 (8:00)			2.70		2.72	
4/1	a	0:00 - 8:00 (8:00)	.02		1.99		2.01	
		8:00 - 16:00 (8:00)	.01	.023	2.07	2.58	2.08	2.60
		16:00 - 24:00 (8:00)	.04		3.56		3.60	

TABLE I
ANACONDA, SEBREE PLANT EMISSION TEST
(Rept. No. 77-ALR-6)

Test Date (1977)	Test Train	Test Time (Duration)	Total F lbs/T Al					
			Primary		Secondary		Totals	
			8 hr	24 hr	8 hr	24 hr	8 hr	24 hr
4/1	b	0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00) 16:00 - 24:00 (8:00)			2.14 2.50 3.75	2.85	2.16 2.51 3.79	2.87
6/6-7	a	16:00 - 24:00 (8:00) 0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00)			3.61 .98 1.54	1.83		
6/6-7	b	16:00 - 24:00 (8:00) 0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00)			3.50 .96 1.51	1.79		
6/7-8	a	16:00 - 24:00 (8:00) 0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00)			1.64 .59 ---	.83		
6/7-8	b	16:00 - 24:00 (8:00) 0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00)			1.53 .60 .29	.80		
6/8-9	a	16:00 - 24:00 (8:00) 0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00)			1.19 1.46 .90	1.17		
6/8-9	b	16:00 - 24:00 (8:00) 0:00 - 8:00 (8:00) 8:00 - 16:00 (8:00)			1.17 1.31 .93	1.12		

TABLE I
ANACONDA, SEBREE PLANT EMISSION TEST
(Rept. No. 77-ALR-6)

Test Date (1977)	Test Train	Test Time (Duration)	Total F lbs/T Al				
			Primary		Secondary		Totals
			8 hr	24 hr	8 hr	24 hr	8 hr 24 hr
6/29-30		8:00 - 16:00 (8:00)			.84		
		16:00 - 24:00 (8:00)			1.67	1.18	
		0:00 - 8:00 (8:00)			1.00		
6/30-7/1		16:00 - 24:00 (8:00)			2.38		
		0:00 - 8:00 (8:00)			.70	1.44	
		8:00 - 16:00 (8:00)			1.08		

TABLE II
EPA PLANT C
ALCOA, WENTACREE - PREBAKE

Doc. #/page	Test Date (1972)	Test Time (Duration)	Total F lbs/T Al	
			Primary	Secondary
90/22	5/1	2:20 - 11:45 (9:25)		1.12
90/19	5/2	9:25 - 16:00 (6:35)	0.267	
90/22	5/2-3	11:20 - 8:00 (20:40)		1.37
90/19	5/3	8:43 - 15:35 (6:52)	0.168	
90/22	5/3-4	10:50 - 9:53 (23:03)		1.23
90/22	5/4-5	15:16 - 14:10 (22:54)		1.10

TABLE III
EPA PLANT D
ALCOA, BADIN - PREBAKE

<u>Doc. #/page</u>	<u>Test Date (1972)</u>	<u>Test Time (Duration)</u>	<u>Total F lbs/T Al</u>		
			<u>Primary</u>	<u>Secondary</u>	<u>Total</u>
93/22	2/29	16:20 - 20:35 (4:15)	0.612		
93/37	3/1-2	13:00 - 13:00 (24:00)		0.8615	
93/28	3/2	9:20 - 13:05 (3:45)	0.519		
93/28	3/2	15:00 - 18:40 (3:40)	0.504		
93/37	3/2-3	17:15 - 13:15 (20:00)		1.475	
93/22	3/3	7:30 - 11:20 (3:50)	0.321		
93/34	3/6	17:50 - 21:20 (3:30)	0.495		
93/34	3/7	9:00 - 12:30 (3:30)	0.381		
93/34	3/7	16:00 - 19:30 (3:30)	0.438		

TABLE IV
EPA PLANT B
REYNOLDS, LONGVIEW - HSS

Doc. #/page	Test Date (1972)	Test Time (Duration)	Total F lbs/T Al		
			Primary	Secondary	Total
92/19-A	5/12-13	13:00 - 7:25 (18:25)		1.10	
92/19-A	5/15	8:15 - 20:30 (12:15)		2.01	
92/18-A	5/15	9:15 - 13:20 (4:05)	0.410		
92/18-A	5/15	15:30 - 19:40 (4:10)	0.382		
92/19-A	5/16	7:25 - 18:20 (10:55)		2.28	
92-18-A	5/16	8:58 - 12:25 (3:27)	0.422		
92/19-A	5/17	7:35 - 15:10 (7:35)		2.85	

Morris H. DeGroot

General Information

Date of Birth: June 8, 1931
Place of Birth: Scranton, Pennsylvania
Citizenship: United States
Marital Status: Widower, two children

Degrees

B.S., 1952 Roosevelt University
M.S., 1954 University of Chicago
Ph.D., 1958 University of Chicago

Positions Held

- (1) Faculty member, Carnegie-Mellon University, 1957-present:
Professor of Mathematical Statistics, 1966-present;
Head, Department of Statistics, 1966-1972;
Associate Professor, Mathematics and Industrial Administration, 1963-1966;
Assistant Professor of Mathematics, 1957-1963.
- (2) Consultant, Western Management Science Institute, University of California at Los Angeles, 1960-1961.
- (3) Principal Investigator on research contracts and grants from Air Force Research Division, 1961-1963; Office of Ordnance Research, 1961-1964; National Science Foundation, 1962-present.
- (4) Professor, European Institute for Advanced Studies in Management, Brussels, 1971.

Honors and Professional Activities

Fellow, American Statistical Association
Fellow, Institute of Mathematical Statistics
Fellow, Royal Statistical Society
Visiting Lecturer Program in Statistics, 1967-1970, 1975-
Associate Editor, Journal of the American Statistical Association, 1970-1974
Book Review Editor, Journal of the American Statistical Association, 1971-1975
Committee on Health Effects of Nuclear Reactors, appointed by Governor of Pennsylvania, 1973
Assembly of Behavioral and Social Sciences, National Research Council, 1973-

Associate Editor, Annals of Statistics, 1974-1975
Pittsburgh Statistician of the Year, American Statistical Association,
Pittsburgh, Chapter, 1975
Committee on National Statistics, National Research Council, 1975-
Editor, Theory and Methods, Journal of the American Statistical
Association, 1976-
Council, Institute of Mathematical Statistics, 1975-
Member of Steering Committee, Study Group on Environmental Monitoring,
National Research Council, 1975-1977.

BIBLIOGRAPHY

Morris H. DeGroot

- (1) "Efficiency of gene frequency estimates for the ABO System," American Journal of Human Genetics, Vol. 8 (1956), pp. 39-43.
- (2) "The covariance structure of maximum likelihood gene frequency estimates for the MNS system," American Journal of Human Genetics, Vol. 8 (1956), pp. 229-235.
- (3) "Some aspects of the use of the sequential probability ratio test," Journal of the American Statistical Association, Vol. 53 (1958), pp. 187-199 (with Jack Nadler).
- (4) "Unbiased sequential estimation for binomial populations," Annals of Mathematical Statistics, Vol. 30 (1959), pp. 80-101.
- (5) "Simplified method of estimating the MNS gene frequencies," Annals of Human Genetics, London, Vol. 24 (1960), pp. 109-115 (with C. C. Li).
- (6) "Minimax sequential tests of some composite hypotheses," Annals of Mathematical Statistics, Vol. 31 (1960), pp. 1193-1200.
- (7) "The essential completeness of the class of generalized sequential probability ratio tests," Annals of Mathematical Statistics, Vol. 32 (1961), pp. 602-605.
- (8) "Uncertainty, information and sequential experiments," Annals of Mathematical Statistics, Vol. 33 (1962), pp. 404-419.
- (9) "Stochastic models of choice behavior," Behavioral Science, Vol. 8 (1963), pp. 47-55 (with G. M. Becker and J. Marshak).
Reprinted in Decision Making, ed. by Ward Edwards and Amos Tversky, Penguin Books, Ltd., Baltimore, Maryland, pp. 353-378 (1967).
- (10) "Some comments on the experimental measurement of utility," Behavioral Science, Vol. 8 (1963), pp. 146-149.
- (11) "Bayes estimation with convex loss," Annals of Mathematical Statistics, Vol. 34 (1963), pp. 839-846 (with M. M. Rao).
- (12) "An experimental study of some stochastic models for wagers," Behavioral Science, Vol. 8 (1963), pp. 199-202 (with G. M. Becker and J. Marschak).
- (13) "Probabilities of choices among very similar objects: An experiment to decide between two models," Behavioral Science, Vol. 8, (1963), pp. 306-311 (with G. M. Becker and J. Marschak).
- (14) "Stochastic give-and-take," Journal of Mathematical Analysis and Applications, Vol. 7 (1965), pp. 489-498 (with M. M. Rao).

- (15) "Measuring utility by a single-response sequential method," Behavioral Science, Vol. 9 (1964), pp. 226-232 (with G. M. Becker and J. Marschak).
- (16) "Optimal allocation of observations," Annals of the Institute of Statistical Mathematics, Vol. 18 (1966), pp. 13-28.
- (17) "Multidimensional information inequalities and prediction," Proceedings of the International Symposium on Multivariate Analysis, ed. by P. R. Krishnaiah, Academic Press, 1967, pp. 287-313 (with M. M. Rao).
- (18) "Correlations between similar sets of measurements," Biometrics, Vol. 22 (1966), pp. 781-790 (with C. C. Li).
- (19) "Some problems of optimal stopping," Journal of the Royal Statistical Society (B), Vol. 30 (1968), pp. 108-122.
- (20) "Optimal two-stage stratified sampling," Annals of Mathematical Statistics, Vol. 40 (1969), pp. 575-582 (with N. Starr).
- (21) "Bayesian analysis and duopoly theory," Journal of Political Economy, Vol. 78, No. 5 (1970), pp. 1168-1184 (with R. M. Cyert).

Reprinted with revisions in Studies in Bayesian Econometrics and Statistics (S. E. Fienberg and A. Zellner, eds.), North Holland, 1974, pp. 79-97.

- (22) "Multiperiod decision models with alternating choice as a solution to the duopoly problem," Quarterly Journal of Economics, Vol. 84 (1970), pp. 410-429 (with R. M. Cyert).
- (23) "Relations between Pitman efficiency and Fisher information," Sankya, Series A, Vol. 32, Part 3 (1970) pp. 319-324 (with M. Raghavachari).
- (24) "Matchmaking," Annals of Mathematical Statistics, Vol. 42 No. 2 (1971) pp. 578-593 (with P. I. Feder and P. K. Goel).
- (25) "Social preference orderings and majority rule," Econometrica, Vol. 40 (1972), pp. 147-157 (with O. A. Davis and M. J. Hinich.)
- (26) "Bayesian statistics and modern decision theory," Industrial Engineering Handbook, 3rd ed. (H. B. Maynard, ed.), McGraw-Hill (1971), Sec. 10, pp. 98-114.
- (27) "Interfirm learning and the kinked demand curve," Journal of Economic Theory, Vol. 3 (1971), pp. 272-287 (with R. M. Cyert).
- (28) "Sequential statistical decisions and optimal stopping." Behavioral Approaches to Modern Management, Vol. I: Information Systems and Decision Making (ed. by Walter Goldberg). Gothenburg Studies in Business Administration, Göteborg, Sweden (1970), pp. 323-338.

Bibliography - Morris H. DeGroot

- (29) "Statistical studies of the effect of low-level radiation from nuclear reactors on human health," "Proceedings of the Sixth Berkeley Symposium on Mathematical Statistics and Probability, University of California Press, (1972), Vol. VI, pp. 223-234.
- (30) "An Analysis of cooperation and learning in a duopoly context," American Economic Review, Vol. 63 (1973), pp. 24-37 (with R. M. Cyert).
- (31) "Doing what comes naturally: Interpreting a tail area as a posterior probability or as a likelihood ratio," Journal of the American Statistical Association, Vol. 68 (1973), pp. 966-969.
- (32) "Reaching a consensus," Journal of the American Statistical Association, Vol 69 (1974), pp. 118-121.
- (33) "Rational expectations and Bayesian analysis," Journal of Political Economy, Vol. 82 (1974), pp. 521-536 (with R. M. Cyert).
- (34) "Adaptive Utility," Adaptive Economic Models (R. H. Day and T. Groves, eds.), Academic Press, 1975, pp. 223-246 (with R. M. Cyert).
- (35) "A mean squared error approach to optimal design theory," Proceedings of the 1976 Conference on Information: Sciences and Systems, The Johns Hopkins University, 1976, pp. 217-221 (with G. T. Duncan).
- (36) "Sequential strategies in dual control problems," Theory and Decision, Vol. 8 (1977), pp. 173-192 (with R. M. Cyert).
- (37) "Statistics" to appear in Encyclopedia of Physics (R. G. Lerner and G. L. Trigg, eds.), Dowden, Hutchinson, and Ross, Inc. (with Paul Shaman).
- (38) "The matching problem for multivariate normal data" to appear in Sankhya (with P. K. Goel).
- (39) "Optimal peremptory challenges in trials by juries: a bilateral sequential process," to appear in Operations Research (with A. Roth and J. B. Kadane).
- (40) "Sequential investment decisions with Bayesian learning," to appear in Management Science (with R. M. Cyert and C. A. Holt).

Books:

Optimal Statistical Decisions, McGraw-Hill Book Co., New York, 1970. Russian translation, Mir Publishers, Moscow, 1974.

Probability and Statistics, Addison-Wesley Publishing Co., Reading, MA, 1975.

RETENTION OF FLUORIDE BY SINTERED-GLASS FILTER SUPPORTS

By William J. Mitchell and M. Rodney Midgett

Quality Assurance Branch

Environmental Monitoring and Support Laboratory

Office of Research and Development

U.S. Environmental Protection Agency

Research Triangle Park, North Carolina 27711

May 1977

SECTION 1

INTRODUCTION

In May 1975, the Quality Assurance Branch (QAB) of the Environmental Monitoring and Support Laboratory of EPA ^{3A51N} at Research Triangle Park, North Carolina, sampled for fluoride at a primary aluminum reduction plant. The purpose of the QAB testing was to establish the collection efficiency for fluoride of the EPA Method 13 sampling train when the Whatman No. 1 filter is placed between the probe and the impingers [1].

The results [2] of these tests indicated that the sintered-glass filter support that is commonly used in source sampling trains retained some of the fluoride that had passed through the filter. However, the experimental test design did not allow us to elucidate the magnitude of this retention phenomenon for a single sampling run. So, we conducted further studies at a primary aluminum plant to determine the magnitude of the fluoride retention phenomenon. In this study, the four train sampling arrangement previously developed and field tested by QAB was used. This sampling arrangement allowed four independent sampling trains to sample simultaneously and isokinetically at essentially the same point in the stack. Thus, during a sampling run all the trains sampled essentially the same pollutant concentration [3].

Six sampling runs were accomplished using the four train sampling arrangement. In each run two of the trains were assembled with the Whatman No. 1 filter located between the probe and the first impinger and the other two trains were assembled with the filter located between the third and fourth impingers. Single-point, isokinetic sampling was done in all runs, that is, no attempt was made to traverse the stack.

Table 1 summarizes the experimental design of the test, including the location of the filters in each sampling train. For all six runs, sample train integrity was maintained by taking care that the probes, impingers and control console were not interchanged among trains. Prior to the test, the calibration factors for each control console were determined using a spirometer.

Table 1. Sampling Scheme.

Sampling Run No.	Filter Support	Sampling Train Filter Location ^a			
		Train 1	Train 2	Train 3	Train 4
1	fritted glass	B	B	F	F
2	fritted glass	B	B	F	F
3	fritted glass	F	F	B	B
4	fritted glass	F	F	B	B
5	wire screen	F	F	B	B
6	wire screen	B	B	F	F

^a"F" indicates the filter was located between the probe and the first impinger.

"B" indicates the filter was located between the third and the fourth impingers.

The Whatman filters were supported on sintered-glass filter supports, except in the last two runs, when they were supported on a 20 mesh stainless steel screen designed by QAB and constructed by Scott Environmental Technology. Because the purpose was to determine the magnitude of the retention phenomenon that could occur in a sampling run, a sintered-glass filter support was replaced after it had been used in a sampling run. The filters were not heated in any of these six runs, because condensation was not a problem.

SECTION 2 SAMPLING RESULTS

The fluoride concentrations in milligrams fluoride per dry standard cubic meter (mg F/scm) determined in each run are presented in Table 2. The means for the two filter positions in each run were subjected to a comparative statistical analysis to determine if they were statistically different at the 90 percent confidence level. This statistical analysis showed that the means were not statistically different for those runs in which the Whatman filter was supported by the screen. However, the two means were statistically different for those runs in which the Whatman filters were supported on the sintered glass frit. Further, when the percent difference between the two means in a run is calculated, one observes that the amount of fluoride retained by the frit varies from run-to-run. That is, for runs 1 through 4, the mean values obtained for the filter in front location were lower than those obtained for the filter in back location as follows: run 1, 22%; run 2, 32%; run 3, 4%; and run 4, 15%. It should be noted that attempts to quantitatively recover the fluoride retained by the sintered-glass frit using a sodium hydroxide extraction were not successful.

Table 2. Sampling Results in mg F/Dry scm.

Sampling Run No.	Trains with Filter in Front of Impingers		Trains with Filter Behind Impingers	
1	0.238	0.186	0.283	0.262
2	0.148	0.120	0.155	0.237
3	0.164	0.200 ^a	0.218	0.161
4	0.154	0.183	0.184	0.212
5	0.178	0.154	0.166	0.174
6	0.191	0.194	0.196	0.188

^aFilter was dropped on floor during sample recovery

SECTION 3 CONCLUSIONS

The actual mechanism by which the fluoride is retained by the sintered-glass filter support is unknown. Two possible mechanisms that would explain this retention are: (1) small particles containing fluoride passed through the Whatman No. 1 filter (50% retention for 0.3 micron DOP particles at a 5 cm per second face velocity) and were physically filtered by the sintered-glass frit; and (2) the fluoride reacted with the glass in the filter support. However, regardless of the mechanism that caused the retention, it is apparent that a sintered-glass frit should not be placed in front of the impingers when sampling for fluoride. In addition, since the retention might be caused by a physical filtering mechanism, sintered-metal frits are also of questionable value when sampling for fluoride.

Some preliminary results from an on-going study in this laboratory indicate that a similar retention phenomenon may occur when sampling for arsenic using glass fiber filters [4]. This observation, in conjunction with the fluoride retention phenomenon, indicates that retention of sampled materials by filter supports might be a significant cause of sampling error in many sampling methods. Although stainless steel screen filter supports were found to work well in the fluoride study, the durability and suitability of these screens under other sampling conditions has not been established.

Further, a sintered-glass filter support is frequently used to sample many different sources over a short period of time. It could happen therefore, that under some sampling conditions (e.g. condensibles by EPA Method 5) materials previously retained by the frit at one source might be released at another source. For example, material collected at a source where the filter was not heated, might be thermally released at the next source if the filter was heated.

SECTION 4
REFERENCES

1. *Federal Register*, 41, 3825-3830, January 26, 1976.
2. W. J. Mitchell and M. R. Midgett, "Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride." *Atmospheric Environment*, 10, 865-872 (1976).
3. W. J. Mitchell and M. R. Midgett, *Environmental Science and Technology*, 10, 85-88 (1976).
4. J. E. Knoll, unpublished.

Investigation of EPA Method 13
For Total Fluoride Determination

by

Jerry W. Jones

September 29, 1977

INTRODUCTION

There has been much controversy as to the accuracy and precision of Method 13 "Determination of Total Fluoride Emissions From Stationary Sources" since its introduction by EPA in the October 23, 1974 Federal Register. At the request of the Analytical Task Force of the Aluminum Association, the Environmental Control Department of Revere Copper & Brass, Inc., Reduction Division, Scottsboro, Alabama agreed to participate in an evaluation of Method 13.

The evaluation is concerned with accuracy of the method or, more specifically, the collection efficiency of the method. The sources tested were (1) cross flow-packed bed wet scrubber outlets (potrooms), and (2) electrostatic precipitator outlet (carbon bake plant). The tests were performed from mid-July 1977 to mid-September 1977.

DESCRIPTION OF TEST PROGRAM

Sample Train Configuration - The EPA Method 13 sampling train (Figure 1) with filter holders in both the regular and optional locations was used. The first filter holder (A) contained a Whatman #1 filter paper (Filter #1) as required by Method 13. The second filter holder (B) contained a Gelman 0.8 μ membrane filter (Filter #2) treated with Citric Acid plus a back-up alkali impregnated Whatman #4 paper (Filter #3). The second filter holder theoretically traps any fluoride escaping the Method 13 sample with the escaping particulates captured on the membrane filter (#2) and the gaseous fluoride captured by the alkali impregnated paper (#3).

Sampling - The sampling was performed according to EPA Methods 1, 2, 3 and 13 except the minimum sample volume was not achieved on five of the tests due to the pressure drop from the second filter holder. The sampling duration was eight hours each on four potroom scrubber samples and four hours each on three electrostatic precipitator stack samples.

Analysis - The Method 13 portion of the samples (Filter #1 and impinger solution) was analyzed according to the procedure except the actual analysis was made on the Technicon Auto Analyzer. The fluorides on filters #2 and #3 were determined separately by the Auto Analyzer.

After evaluating the results of the first two tests the logical conclusion was field contamination of filters #2 and #3. However, a field blank used with tests 3, 4, 5 and 6 disproved that theory. The average lab blank for filter #2 was 0.44 mg F with a range of 0.2 to 0.8 mg F. The average field blank was 0.54 mg F with no value exceeding the maximum lab blank. The filter #3 average for the lab blank was 0.06 mg F with a range from 0.04 to 0.12 mg F. The field blanks averaged 0.07 mg F and did not exceed the maximum lab blank.

September 29, 1977

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SUBJECT: Investigation of EPA Method 13 For Total Fluoride Determination

SUMMARY OF RESULTS AND CONCLUSION

The average wet scrubber total fluoride escaping the Method 13 train was 8.4% while the average gaseous fluoride lost (Filter #3) was only 0.6%. This indicates that most of the escaping fluoride is particulate. Anderson impactor particle size tests have shown better than 80% of the particles are less than 1μ in diameter. The Whatman #1 Filter would be a poor collector of these small particles and the collection efficiency of the impingers would not be good at the low sampling flow rate.

The average electrostatic precipitator total fluoride escaping Method 13 was 0.3%. Results from prior tests indicate most of the fluoride is in the gaseous form and is captured efficiently in the impingers.

From the test data (Attachment A), it is concluded that Method 13 is an adequate method for gaseous fluorides and a biased method for particulates. However, it should be noted that the bias is on the low side and in favor of the regulated industries.

SUGGESTED EXPERIMENTAL DESIGN
FOR THE INVESTIGATION OF EPA METHOD 13

1. Sample Train Configuration: Use EPA Method 13 except an extra filter holder is placed between the third and fourth impingers. The filter holder which contains the Whatman #1 filter is placed in front of the first impinger and is designated filter #1 in the table below. The filter holder which is placed between the third and fourth impingers is designated filter #2 in the table below.

<u>Sample Set No.</u>	<u>Filter #1</u>	<u>Filter #2</u>
I	Whatman #1 with 20-mesh stainless steel filter support	0.8 um membrane filter treated with citric acid plus alkali-impregnated back-up filter (Whatman #4 or similar)
II	Whatman #1 with fritted glass filter support	Same as I above
III	0.8 um membrane filter with 20-mesh stainless steel filter support	Same as I above

2. Sources To Be Sampled: Roof vents, dry scrubber outlets, wet electrostatic precipitator outlets.
3. Analysis: Each filter is to be analyzed separately by fusion, distillation and selective ion electrode determination. Impinger contents to be analyzed by SIE. The analysis of the membrane filter which is placed in the #2 position will indicate whether particulate fluoride is passing through the train and the analysis of the alkali-impregnated filter will give an indication of the amount of gaseous fluoride which might be escaping the train.
4. Number of Samples: It is suggested that each sample set consist of at least 3 samples for each type of source sampled. A single Method 13 sampling train can be used since there is no need for simultaneous sampling. The objective is to determine how much, if any, particulate and gaseous fluorides are passing through these three variations of the Method 13 train.

NOTE: It might also be desirable to conduct simultaneous sampling with sampling train configurations II and III. This would give an indication of how much fluoride is lost in the fritted glass filter support.

Attachment A

Sampling and Analytical Data

Run #	Volume of Gas Metered (DSCF)	Gas Flow Rate (DSCFM)	Total Fluoride Method 13 (mg) Filter #1 & Impinger Solution	Total Fluoride Filter Holder B (mg)	Particulate Fluoride Filter #2 (mg)	Gaseous Fluoride Filter #3 (mg)	Percent Fluoride Escaped Method 13
1	282.01	0.59	7.5	0.78	0.70	0.08	9.4
2	186.15	0.39	17.5	0.88	0.80	0.08	4.8
3	186.40	0.39	10.0	1.55	1.50	0.05	13.4
4	115.20	0.48	117.7	0.22	0.10	0.12	0.2
5	87.08	0.36	109.7	0.32	0.20	0.18	0.3
6	71.58	0.30	99.7	0.51	0.40	0.11	0.5

(1) Filter #1 blank was 0.0 mg F on all samples.

(2) A lab blank was subtracted from test runs 1 & 2 and a field blank was subtracted from test runs 3, 4, 5 & 6.

The blank corrections were as follows:

Run #	Blank Correction (mg/F)
1	0.07
2	0.12
3	0.11
4	0.06
5	0.06
6	0.06

REVERE

COPPER AND BRASS INCORPORATED

P.O. Box 100
SCOTTSDALE, ARIZ. 85260
203-274-112

Filter Holder A equipped with Filter #1 (Whatman #1)

Filter Holder B equipped with Filter #2 (0.8 μ membrane)

and Filter #3 (Whatman #4)

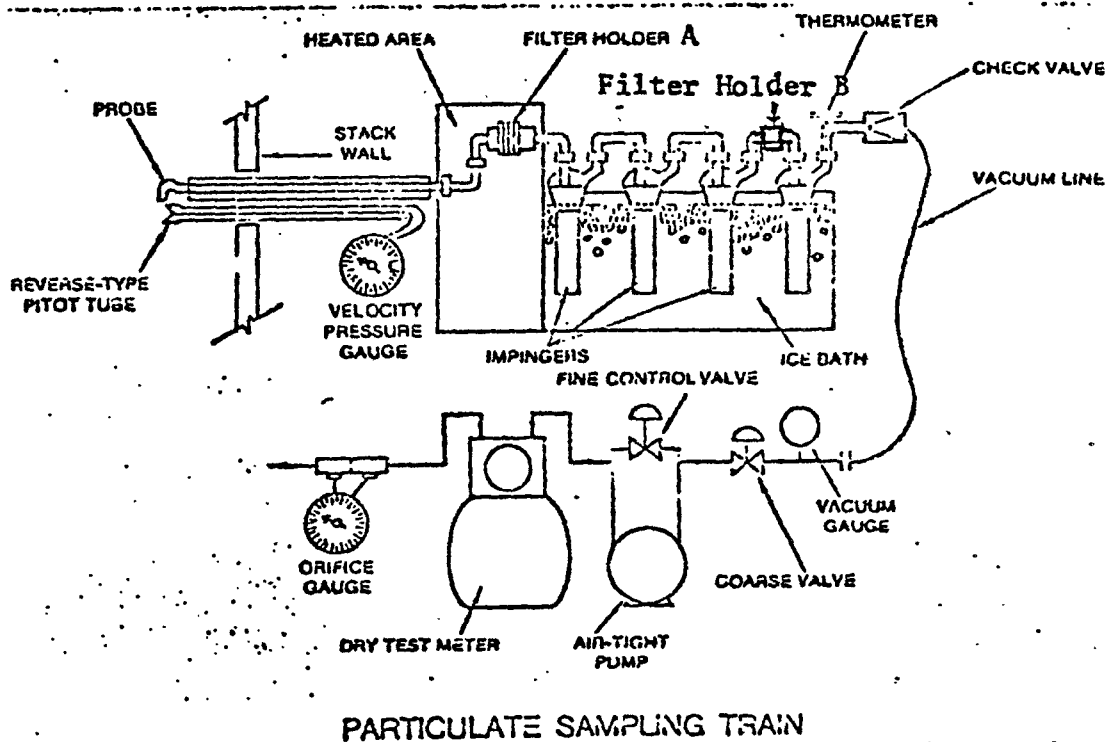


Figure 1

APPENDIX B

APR 27 1978

Dr. Patrick R. Atkins, Manager
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Aluminum Company of America
Alcoa Building
Pittsburgh, Pennsylvania 15219

Dear Dr. Atkins:

In the past few months most of the communication between EPA and Alcoa has been through attorneys. However, we have not responded to several of the points raised in your December 14, 1977, letter, for which we feel responses for the record must be made. The purpose of this letter is to respond to your comments regarding the Sebree emission test (EPA Emission Test Report No. 77-ALR-6).

We agree that the Sebree test demonstrated the variability of secondary emissions from one 24-hour period to another 24-hour period. Variability in individual test runs is precisely why compliance with all standards of performance is based on the average of three runs. We do not find it remarkable that the spread of the individual eight-hour secondary emissions measurements is more pronounced than the spread of the twenty-four-hour runs, since, as you well know, different operations occur during each shift. Thus, it is incorrect to compare the 0.29 lb F/TAP which occurred during a tapping shift with the 3.75 lb F/TAP which occurred during a carbon setting shift. None of the eight-hour measurements could be used alone in a compliance test, since they are not representative operating conditions. The minimum acceptable run time must be representative of all plant operations.

We believe that operation and maintenance can contribute to the variability of secondary emissions; for this reason, we insisted that this parameter be minimized for Phases II and III. Your statement that the Sebree Emission Test data clearly indicate that there are measurable sources of variation intrinsic to the fluoride sampling methods themselves must be placed in perspective, since the same may be said of any test method. The test results of Phases I and II show clearly that the precision of the fluoride method is within the acceptable limits for stack sampling methods in general. The emissions obtained from 2 trains sampling simultaneously varied from their average less than ± 3 percent for 6 of the 7 runs, and less than ± 5 percent for the 7th run.

The statistical analysis of the data performed by Dr. DeGroot is in substantial agreement with our analysis; i.e., the Sebree data would indicate that there is at least a 90 percent chance for a properly controlled and operated aluminum reduction plant to pass a performance test. We also agree with Dr. DeGroot that the necessarily limited number of data points makes statistical inference risky.

Your interpretation of our actions regarding copper smelters is incorrect. We did not amend the standard of performance, compliance with which is determined by the average of three six-hour runs, to provide "relief from a never-to-be exceeded standard." The standard of performance for copper smelters requires the installation and operation of a continuous monitor to measure SO₂ emissions. The standard also requires the owner or operator to report periods of excess emissions. There is no comparable requirement for primary aluminum plants because there is no continuous monitoring system available for measuring total fluoride emissions. The amendment we made to the standard for copper smelters merely changed the reporting requirement for excess emissions as measured by the continuous monitor. We did not amend the level of the standard and the requirements that apply to a copper smelter during a performance test.

You contend that "... deviations from EPA's prescribed test methods in the Sebree emission test caused the fluoride emission measurements calculated by EPA to understate the level of fluoride emissions." Two specific examples were given: (1) three propeller anemometers were used instead of two; and (2) the velocity and fluoride concentration in each eight-hour test were measured for different lengths of time. Before answering the above objections, Alcoa's statement should be clarified by adding the word "true" before "level," i.e., "... to understate the "true" level of fluoride emissions."

The use of three anemometers exceeds the requirement of Method 14, which specified that only two are needed for a roof vent of this size. (This type of variation from the reference test method is allowed under the provisions of section 60.8 of 40 CFR Part 60.) Therefore, the accuracy of the reported total flow rates should be equal to or greater than the accuracy that would have been obtained by following the Method 14 requirement exactly. Alcoa's contention that significantly higher emission rates would have resulted if two anemometers had been used is purely speculative, since no comparisons were made between the use of two and three anemometers. The Sebree data show that a substantial velocity gradient existed in the roof monitor; because of this (and in the absence of data to indicate otherwise), the use of three anemometers instead of two must be considered more representative of the actual conditions in the monitor.

During the Sebree tests, velocity was monitored for the entire 480 minutes of each 8-hour test period; therefore, the calculated volumetric flow rates are considered to be representative. Fluoride concentration, on the other hand, was measured only for the first 400 minutes of each 8-hour period. Since the majority of the activity in the potrooms occurs in the first half of each shift, fluoride emissions tend to be higher during this period. Consequently, measuring the fluoride concentration for only 400 of the 480 minutes would tend to bias the results toward the high side. Therefore, an emission rate calculated from the product of an average fluoride concentration measured over the first 400 minutes times an average volumetric flow rate measured over the entire 480 minutes would tend to be higher than the true rate, rather than "understating the secondary fluoride emission values," as Alcoa contends.

Alcoa contends that the validity of the Sebree emission test results is highly questionable because of improper initial calibration of the anemometers and backcalculation in order to rectify the erroneous anemometer readings. It is true that the velocity data from the Sebree tests were adjusted after-the-fact based upon information obtained from the anemometer manufacturer and from a series of post-test anemometer calibrations. However, these adjustments were made in order to increase the accuracy of the reported emission rates. (It should be noted that in general, the adjustments made in the Sebree data tended to increase the total flow rates and emission rates.) Alcoa's contention that industry would have no right to make similar adjustments in NSPS performance test data is unfounded. Section 60.3 provides authority for the Administrator to approve minor deviations from the reference methods; if it can be shown that more representative data will result, such deviations would be approved. Note that as a result of EPA's experience with the anemometers, Method 14 is currently being revised to include the proper calibration procedure for anemometers.

We disagree that the method of determining the level of production introduces a source of error. We considered using actual metal tapped in the calculations but decided against this in favor of using the monthly average per pot production rate, because the amount of metal tapped on any given day is not necessarily the amount of metal produced on that day. For example, it would be possible to not tap any pots in which case metal tapped would be zero, but the pots would still be producing aluminum and evolving fluorides. Of course it would be to the advantage of the source to tap a larger amount of metal during a compliance test; we understand there is some discretion in the amount of metal tapped per day and that it would be possible to "undertap" on the days preceding a test and "overtap" during the test. We thus felt that the monthly average gave a better indication of metal production than amount tapped during the test. We interpret 40 CFR 60.194(d)(1) to allow our approach, and we would allow an owner or operator to use the monthly per pot average in calculating emissions

during a compliance test. We are considering a change to 40 CFR 60.194(d)(1) to make this an explicit provision.

Good operation and maintenance of the air pollution control system is required under 40 CFR 60.11 at all times. Thus not only would we permit an owner or operator to have hoods in good repair and properly placed and to have raw materials cleaned from the pot deck, but we would require such actions during a performance test, as well as at all other times. We do not believe that such practices are beyond the possibility of any normal long-term smelter operation, and since there are no continuous monitoring requirements, observation of poor hood placement, bent hoods, sloppy material handling, etc. would be grounds for an inspector to require a performance test for an affected facility.

The only reason for requiring hand sweeping was that we observed a large amount of dust generated from the mechanical sweeper, and hand sweeping was the most expedient solution to temporarily minimize this dust. We would expect that a properly designed and functioning mechanical sweeper could be used that would not generate the dust that was observed at Sebree.

You cited two reports to support your position that EPA Method 13 consistently understates the measured level of fluoride emissions. The first report cited is entitled "Retention of Fluoride by Sintered-Glass Filter Supports," dated May, 1977, by Mitchell and Midgett. This report has no bearing on the results of the Sebree tests because at Sebree, the filter was placed behind the impingers (as allowed by Method 13) rather than in front of them. It should be noted that even if the filter had been inserted between the probe and first impinger, a stainless steel screen filter support would have been used instead of a glass frit (see the amendments to Reference Methods 13A and 13B in the November 29, 1976, Federal Register).

The second report cited is entitled "Investigation of EPA Method 13 for Total Fluoride Determination," dated September 29, 1977, by Jerry W. Jones of Revere Copper and Brass, Inc. This report is not applicable to the Sebree tests for the same reason that the first report does not apply. In addition, the findings of this study have no effect on the data base used to set the fluoride emission standard, because more efficient fiber glass mat filters (not paper filters, as used by Mr. Jones) were employed in the gathering data for the standard.

It should be noted, however, that the results obtained by Mr. Jones raise questions about the efficiency of the fluoride train in streams having significant particulate loadings. From the data provided, it is not clear what the total impact of the 13.4 percent maximum inefficiency is on the total emissions, since the majority of

the emissions are from the roof monitors and the level of emissions from the wet scrubber is about 10 times lower than from the ESP. Since a significant level of inefficiency is indicated, it is EPA's intention to revise the reference method disallowing the use of the paper filter in the front and recommending use of a more efficient glass fiber or similar filter.

As you have been informed through counsel, we are evaluating several alternatives for amending the standard which address the issue of variability. We look forward to your comments on our proposal.

Sincerely yours,

Don R. Goodwin
Director
Emission Standards and
Engineering Division

Enclosure

cc: Ron Hausmann
Donald C. Winson

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

[FRL 639-2]

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Amendments to Reference Methods 13A and 13B

On August 6, 1975 (40 FR 33151), the Environmental Protection Agency (EPA) promulgated Reference Methods 13A and 13B in Appendix A to 40 CFR Part 60. Methods 13A and 13B prescribe testing and analysis procedures for fluoride emissions from stationary sources. After promulgation of the methods, EPA continued to evaluate them and as a result has determined the need for certain amendments to improve the accuracy and precision of the methods.

Methods 13A and 13B require assembly of the fluoride sampling train so that the filter is located either between the third and fourth impingers or in an optional location between the probe and first impinger. They also specify that a fritted glass disc be used to support the filter. Since promulgation of the methods, EPA has found that when a glass frit filter support is used in the optional filter location, some of the fluoride sample is retained on the glass. Although no tests have been performed, it is believed that fluoride retention may also occur if a sintered metal frit filter support is used. However, in tests performed using a 20 mesh stainless steel screen as a filter support no fluoride retention was noted. Therefore, to eliminate the possibility of fluoride retention, sections 5.1.5 and 7.1.3 of Methods 13A and 13B are being revised to require the use of a 20 mesh stainless steel screen filter support if the filter is located between the probe and first impinger. If the filter is located in the normal position between the third and fourth impingers, the glass frit filter support may still be used.

In addition to the changes to sections 5.1.5 and 7.1.3, a few corrections are also being made. The amendments promulgated herein are effective on November 29, 1976. EPA finds that good cause exists for not publishing this action as a notice of proposed rulemaking and for making it effective immediately upon publication because:

1. The action is intended to improve the accuracy and precision of Methods 13A and 13B and does not alter the overall substantive content of the methods or the stringency of standards of performance for fluoride emissions.

2. The amended methods may be used immediately in source testing for fluoride emissions.

Dated: November 17, 1976.

JOHN QUARLES,
Acting Administrator.

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

1. Reference Method 13A is amended as follows:

(a) In section 3., the phrase "300 μ g/liter" is corrected to read "300 mg/liter" and the parenthetical phrase "(see section 7.3.6)" is corrected to read "(see section 7.3.4)".

(b) Section 5.1.5 is revised to read as follows:

5.1.5 Filter holder—If located between the probe and first impinger, borosilicate glass with a 20 mesh stainless steel screen filter support and a silicone rubber gasket; neither a glass frit filter support nor a sintered metal filter support may be used if the filter is in front of the impingers. If located between the third and fourth impingers, 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.

(c) Section 7.1.3 is amended by revising the first two sentences of the sixth paragraph to read as follows:

7.1.3 Preparation of collection train. . . .

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 first impinger if a 20 mesh stainless steel screen is used for the filter support. . . .

(d) In section 7.3.4, the reference in the first paragraph to "section 7.3.6" is corrected to read "section 7.3.5".

2. Reference Method 13B is amended as follows:

(a) In the third line of section 3, the phrase "300 μ g liter" is corrected to read "300 mg. liter".

(b) Section 5.1.5 is revised to read as follows:

5.1.5 Filter holder—If located between the probe and first impinger, borosilicate glass with a 20 mesh stainless steel screen filter support and a silicone rubber gasket; neither a glass frit filter support nor a sintered metal filter support may be used if the filter is in front of the impingers. If located between the third and fourth impingers, 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.

(c) Section 7.1.3 is amended by revising the first two sentences of the sixth paragraph to read as follows:

7.1.3 Preparation of collection train. . . .

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 if a 20 mesh stainless steel screen is used for the filter support. . . .

(d) In section 7.3.4, the reference in the first paragraph to "section 7.3.6" is corrected to read "section 7.3.5".

(Secs. 111, 114, and 301(a) Clean Air Act, as amended by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1678 and by sec. 15(c)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1657c-6, 1957c-9, and 1657g(2)))

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